

**Synthesis of novel NP₂ and NP₃ phosphine
transition metal complexes and
their application towards the catalytic
hydrogenation of levulinic acid**

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Declarations

Declaration of Originality

The work described in this thesis was carried out in the Department of Chemistry at Imperial College London, South Kensington and White City campuses, between October 2016 and December 2020. The work described is entirely my own, unless otherwise stated through cited references or other explicit acknowledgements. This thesis references small pieces of work performed during my MSci. Chemistry with a Year in Industry degree at Imperial College London (between October 2015 and March 2016), and these are explicitly acknowledged. This work has not been submitted previously for a degree at this or any other university.

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Publications

Publications directly resulting from this work are listed below:

- *Synthesis and crystallographic characterisation of a homologous series of bis-tridentate phosphine oxide NP_3O_3 Fe(II), Co(II), Ni(II) and Cu(II) complexes*

Samuel J. Page, Daisy Rogers-Simmonds, Andrew J. P. White, Philip W. Miller

Inorganica Chimica Acta, 2020, **512**, 119870

- *PNP bidentate palladium complexes for the catalytic hydrogenation of levulinic acid to γ -Valerolactone*

Samuel J. Page, Fraser Gaines, Jason Li, Felix Bennemann, Andrew J. P. White, Philip W. Miller

In preparation.

This work also contributed to the following publication:

- *Synthesis and characterisation of a range of Fe, Co, Ru and Rh triphos complexes and investigations into the catalytic hydrogenation of levulinic acid*

Uwaila Omoruyi, Samuel J. Page, Samantha Apps, Andrew J. P. White, Nicholas J. Long, Philip W. Miller

Journal of Organometallic Chemistry, 2021, **935**, 121650

Abstract

The work presented herein covers the synthesis and coordination chemistry of multidentate phosphine ligands and their application towards the homogeneous catalytic hydrogenation of biomass-derived levulinic acid (LA) to gamma-Valerolactone (GVL). Bi- and triphosphine nitrogen-centred ligands of the form $R'-N(CH_2PR_2)_2$ and $N(CH_2PR_2)_3$ (N-Triphos^R) were synthesised through phosphorus-based Mannich reactions. This modular ligand system enabled structural variations ($R = Ph, Cy, ^tBu$; $R' = Me, Bn, CH_2CH(OEt)_2$) to be prepared.

The bisphosphine ligands generated square-planar palladium complexes from $[PdCl_2(COD)]$; analogous complexes were made from N-Triphos ligands followed by oxidation of the pendant phosphine. Whilst $Me-N(CH_2PCy_2)_2$ formed a piano-stool complex with $[RuCl_2(p\text{-cymene})]_2$, N-Triphos^{Cy} generated poorly defined products. Bidentate coordination of $Me-N(CH_2PCy_2)_2$ to $[Ir(COD)Cl]_2$ was also achieved, whilst N-Triphos ligands adopted different coordination modes dependent on phosphine substituent and solvent. Reactions of $Me-N(CH_2PCy_2)_2$ and N-Triphos^{Cy} with $[Rh(COD)(MeCN)_2]BF_4$ generated highly air-sensitive complexes; further reactivity with chloroform generated a tri-chloro bridged rhodium dimer.

The complexes were tested as homogeneous catalysts for the transfer hydrogenation of LA to GVL, using formic acid (FA) as the hydrogen source. The PCy_2 -palladium complexes were the most effective. Moderate GVL yields were readily achieved in solventless conditions, however, further optimisation proved challenging. This was largely attributed to the catalysts' water insolubility promoting FA dehydration to H_2O and CO , reducing the hydrogen supply available and facilitating the formation of CO-bridged palladium dimers. Attempts to develop water-soluble catalysts gave small improvements. Using a high-pressure regime accessed quantitative LA hydrogenation to GVL with the palladium catalysts. Additionally, a $Co(BF_4)_2 \cdot 6H_2O/N\text{-Triphos}^{Ph}$ system was effective under hydrogen pressures.

A series of octahedral $N(CH_2P(O)Ph_2)_3$ complexes were formed with first-row transition metals ($M = Mn, Fe, Co, Ni, Cu$). Collectively, this work represents an advancement in the coordination chemistry and applications of nitrogen-centered phosphine and phosphine oxide ligands, demonstrating that this understudied field has high potential for future study.

List of abbreviations

$\text{\AA}$	<i>Ångstroms</i>
δ	<i>Chemical shift</i>
$^{\circ}\text{C}$	<i>Degree Celsius</i>
μ_{eff}	<i>Effective magnetic moment</i>
μ_{so}	<i>Spin-only magnetic moment</i>
χ_{D}	<i>Diamagnetic correction</i>
χ_{g}	<i>Mass magnetic susceptibility</i>
χ_{m}	<i>Molar susceptibility</i>
χ_{p}	<i>Paramagnetic molar susceptibility</i>
1,4-PDO	1,4-pentanediol
2-MTHF	2-methyltetrahydrofuran
3-HPA	3 hydroxy propionic acid
4-HVA	4-hydroxyvaleric acid
acac	Acetylacetonate
AL	Angelica lactone
AO	Atomic Orbital
Ar	Aryl
ATH	Asymmetric transfer hydrogenation
BDPPM	methylenebis[diphenyl-bis(diphenylphosphinyl)methane]
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
bipy	2,2'-Bipyridine
Bu	Butyl
c	Machine constant

COD	1,5-cyclooctadiene
Cp*	1,2,3,4,5-Pentamethylcyclopentadiene
Cy	Cyclohexyl
Cyp	Cyclopentyl
d	Doublet
DALA	δ -amino levulinic acid
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
dd	Doublet of doublets
DIPEA	N,N-Diisopropylethylamine
dippe	1,2-(bis-di-isopropylphosphino)ethane
DMI	1,3-dimethyl-2-imidazolidinone
dmmm	bis((dimethylphosphino)methyl)methylphosphine
DMSO	Dimethyl sulfoxide
DoE	Department of Energy
dpa	Dipyridylamine
DPEN	1,2-Diphenylethylenediamine
dpmp	bis[(diphenylphosphino)methyl]phenylphosphine
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppeO	[2-(diphenylphosphino)ethyl]diphenylphosphine oxide
dppf	1,1'-bis(diphenylphosphino)ferrocene
dpph	1,6-bis(diphenylphosphino)hexane
dppp	1,3-bis(diphenylphosphino)propane
dpppe	1,5-bis(diphenylphosphino)pentane
dtbpe	1,2-(bis-di-tertbutylphosphino)ethane
E	Energy

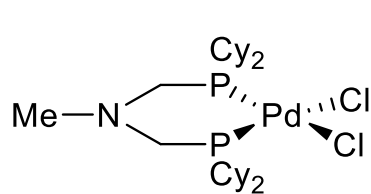
EA	Elemental Analysis
ee.	Enantiomeric excess
EL	Ethyl levulinate
Et	Ethyl
etp	bis[2-(diphenylphosphino)ethyl]phenylphosphine
FA	Formic acid
FD	Fluorescence detection
FDCA	2,5 furan dicarboxylic acid
FO	Fragment Orbital
G	Guaiacyl
GBL	γ -Butyrolactone
GVL	γ -Valerolactone
H (<i>Lignin</i>)	<i>p</i> -hydroxyphenyl
HMF	Hydroxymethylfuran
HOMO	Highest Occupied Molecular Orbital
h	Hours
IA	Itaconic acid
IPA	Isopropyl alcohol
Pr	Iso-propyl
IR	Infra-red
kg	Kilogram
L	Length
LA	Levulinic acid
LUMO	Lowest Unoccupied Molecular Orbital
M	Molar

m	Mass
<i>m</i> -	Meta
MA	Methylallyl
Me	Methyl
MeCN	Acetonitrile
MJ	Megajoules
ML	Methyl levulinate
mL	Millilitres
MO	Molecular Orbital
Mr	Molecular weight
MS	Mass spectrometry
MSA	Methylsuccinic acid
MPV	Meerwein–Ponndorf–Verley
NMR	Nuclear magnetic resonance
<i>o</i> -	Ortho
OEt	Ethoxy
OTf	Triflate
<i>p</i> -	Para
P	Pressure
PDT	Photodynamic Therapy
PEG	Polyethylene glycol
Ph	Phenyl
pKa	Logarithmic acid dissociation constant
pKb	Logarithmic base dissociation constant
P ⁿ Bu ₃	Tri- <i>n</i> -butylphosphine
P ⁿ Oct ₃	Tri- <i>n</i> -octylphosphine

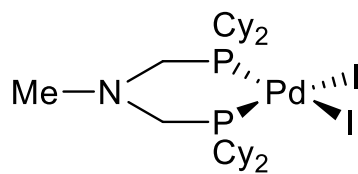
PPh ₃	Triphenylphosphine
ppm	Parts per million
Pr	Propyl
PTA	1,3,5-Triaza-7-phosphaadamantane
PTFE	Polytetrafluoroethylene
PTSA/ <i>p</i> -TsOH	<i>p</i> -toluenesulfonic acid
q	Quartet
R	Reading of magnetic balance (sample and tube)
R ₀	Reading of magnetic balance (empty tube)
RT	Room temperature
s	Singlet
S	Syringyl
SA	Succinic acid
S/C	Substrate: catalyst ratio
SEGPPOS	[(4,4'-bi-1,3-benzodioxole)-5,5'-diyl]bis[diphenylphosphine]
t	Triplet
T	Temperature
^t Bu	Tert-butyl
TH	Transfer hydrogenation
THF	Tetrahydrofuran
TOE	Tons of oil equivalent
TOF	Turnover Frequency
TON	Turnover Number
TPP	{[(phenylphosphinediyl)bis-(2,1-phenylene)]bis(methylene)}bis-(diphenylphosphine)
TPPMS	Sodium diphenylphosphinobenzene-3-sulfonate

TPPTS	Triphenylphosphine-3,3',3''-trisulfonic acid trisodium salt
ttp	bis[3-(diphenylphosphino)propyl]phenylphosphine
USDA	U.S. Department of Agriculture
wt.%	Weight percent

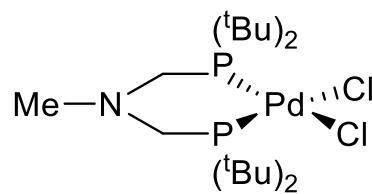
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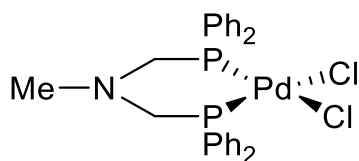
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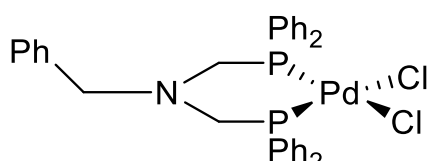
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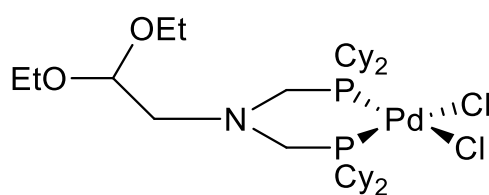
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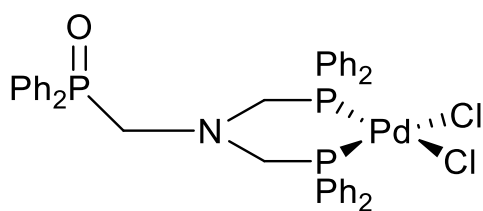
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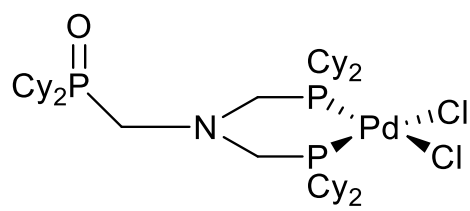
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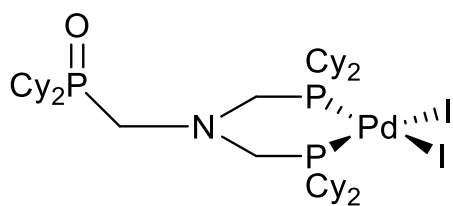
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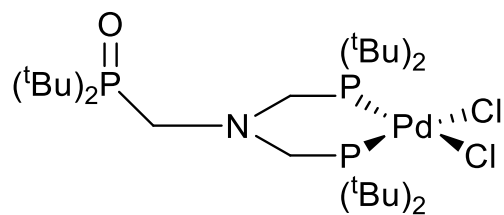
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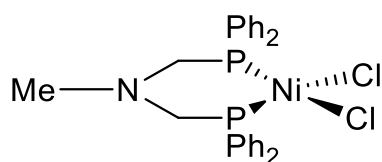
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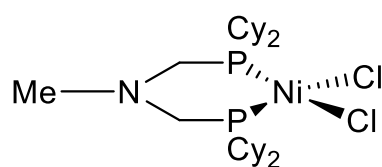
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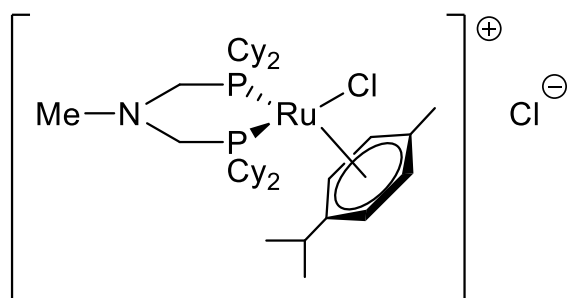
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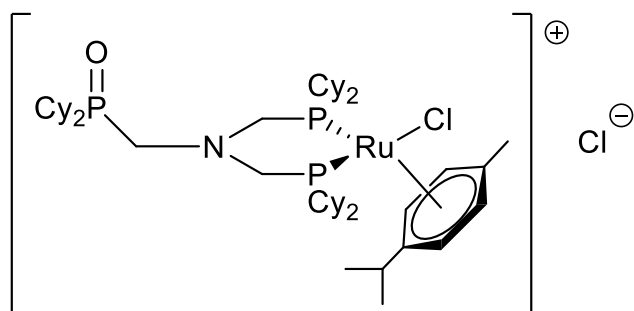
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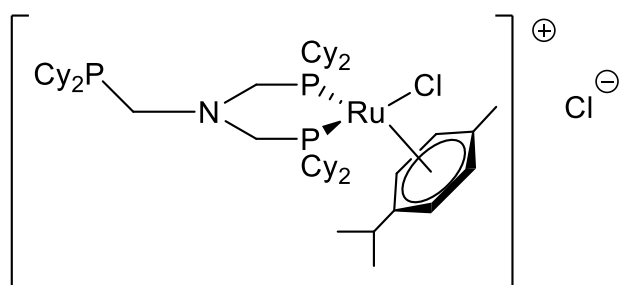
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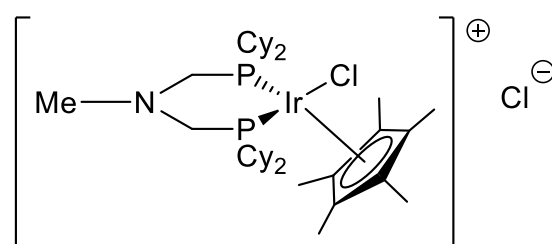
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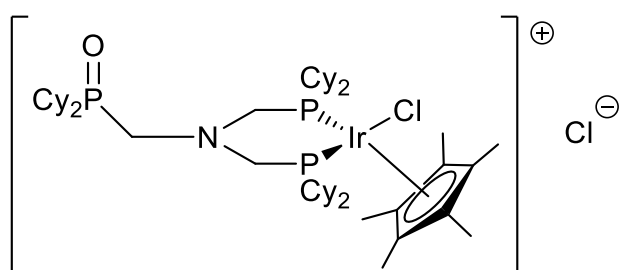
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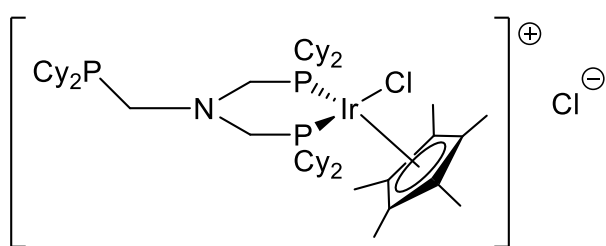
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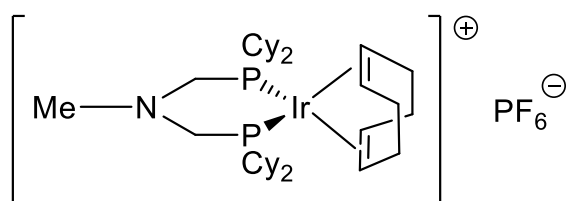
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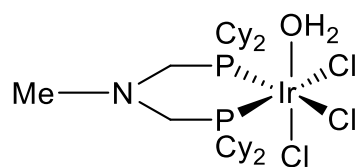
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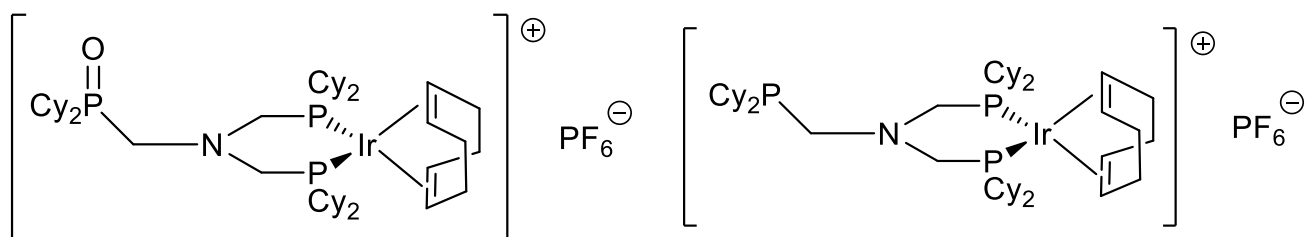
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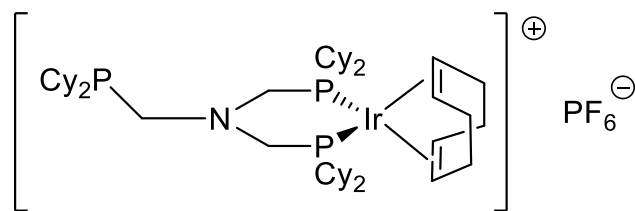
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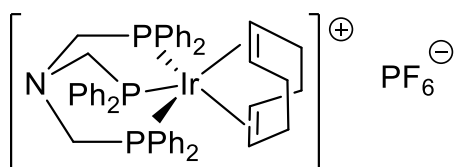
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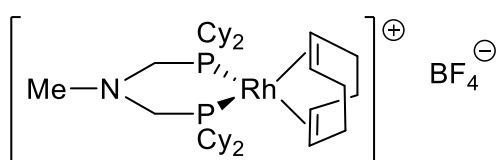
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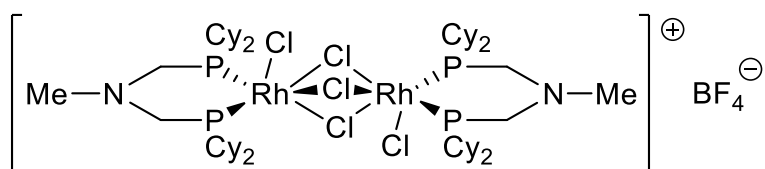
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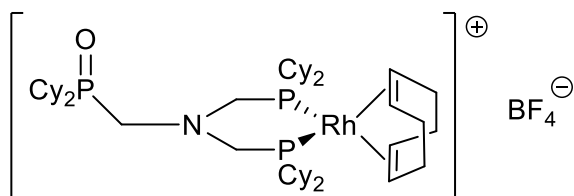
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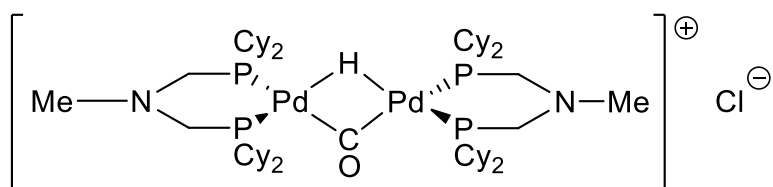
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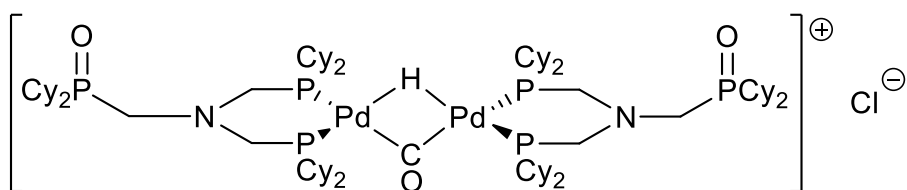
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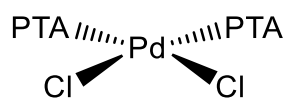
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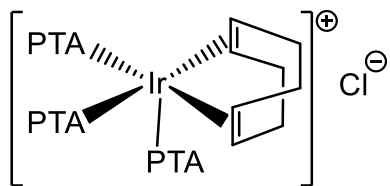
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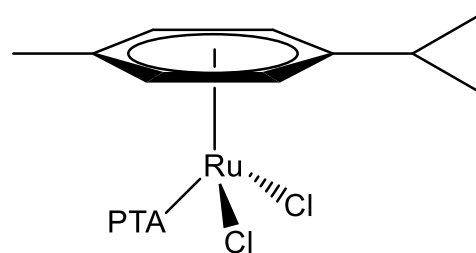
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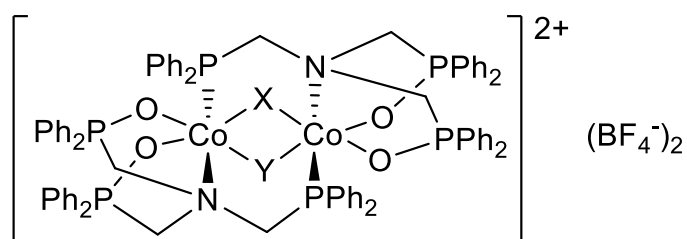
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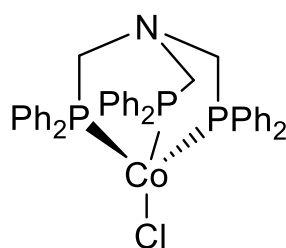
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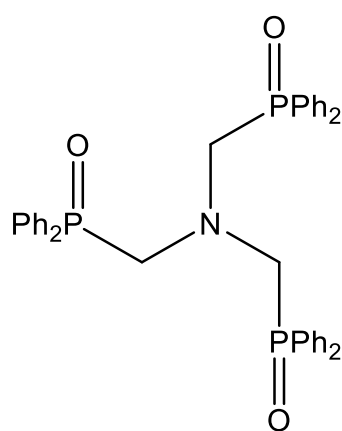
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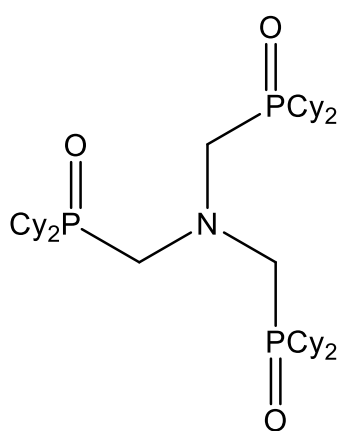
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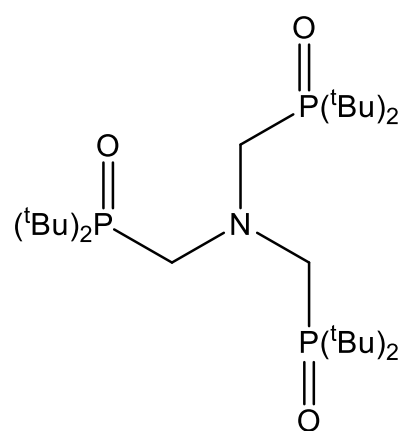
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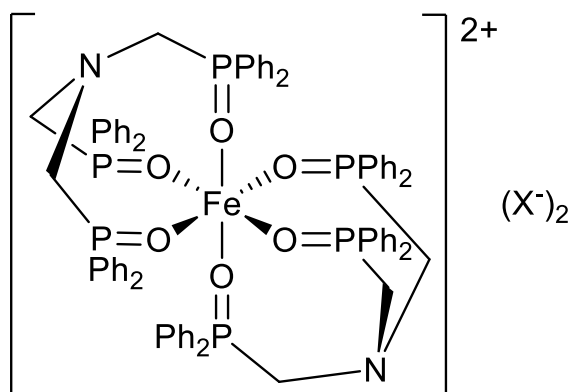
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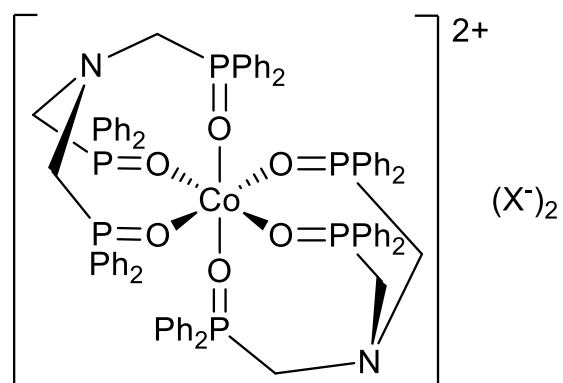
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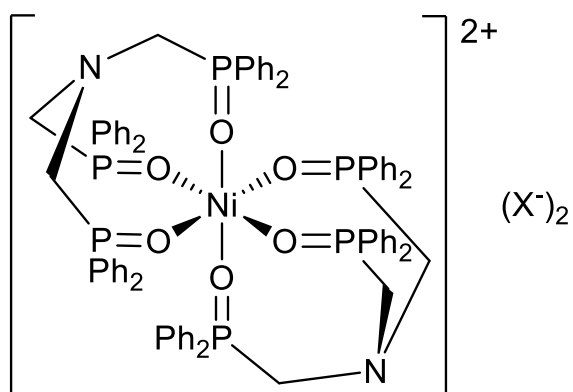
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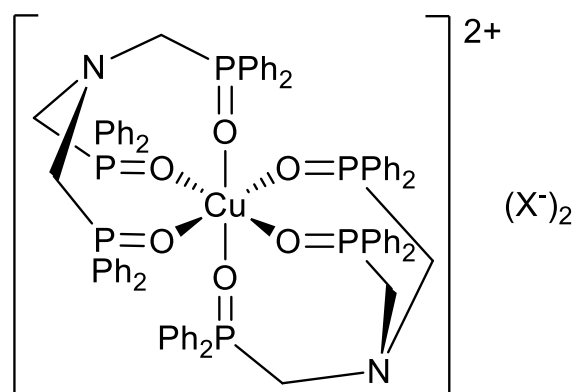
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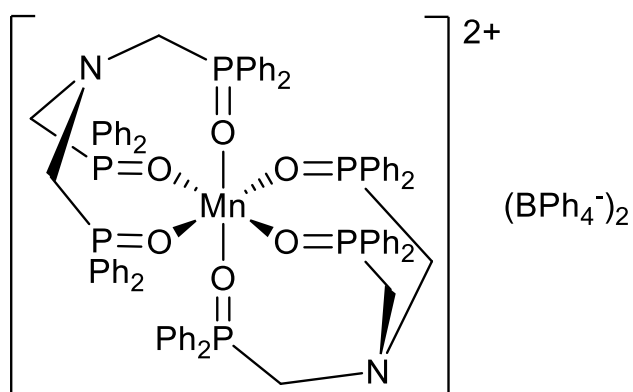
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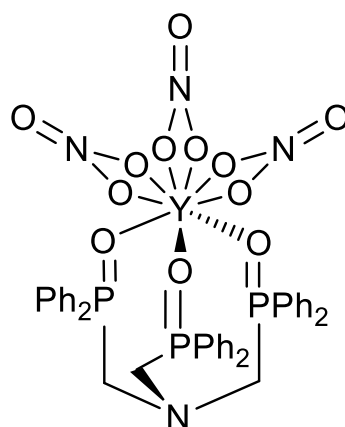
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40 (X = BPh₄), 40-A (X = BF₄)



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Chapter 1

Introduction

“Roads? Where we’re going, we don’t need roads”, *Back to the Future* (1985)

1.1 Biomass valorisation

1.1.1 The Fossil Fuel industry

Since the Industrial Revolution, the world has come to rely on the fossil fuels of coal, oil and natural gas. Fossil fuels are widely used both to generate energy, both directly and through the production of fuels, and to manufacture chemicals and materials such as plastics. The vast majority of chemicals, materials and fuels which the world uses are derived from fossil fuels. With a world population that continues to grow rapidly (from three billion in 1959 to six billion in 1999; currently 7.8 billion and predicted to reach 10 billion by 2057¹) and with increasing global development and industrialisation, the chemical and energy requirements of the world will certainly increase in coming decades.²

In 2020, almost everyone recognises that the continued exploitation of fossil fuel resources is responsible for the severe climate changes affecting our planet, with uncontrolled greenhouse gases emissions causing a global warming. The 2015 Paris Agreement called for countries to work together to limit a global temperature increase to 1.5 °C.³ In addition to the harm associated with their exploitation, fossil fuel resources are finite and non-renewable, and it is predicted that they will be exhausted within our lifetimes.⁴ The rapid depletion of fossil fuel resources runs counter to the increasing energy requirements of the world. Whilst additional fossil fuel resources continue to be identified and exploited, the quality and quantity of such resources are often tied into economic or political complexities. The 1970s saw a significant increase in global oil prices, which was considered to peak in 2011. However, the available supply and prices are hugely fluxional and dependant on political and economic factors and crises (including that of 2020).⁵ As a result, there is significant pressure from legislation and social movements to ensure that countries are taking the necessary steps to reduce their impact on the environment, including a reduction in their reliance on fossil fuels as part of a global effort.

Renewable sources of energy are becoming more and more commonplace. These include solar, tidal and wind energies. In 2019, Britain went a week without using coal for electricity generation for the first time since 1882.⁶ These non-exhaustible resources can be used without limit. Technologies are constantly improving to ensure that energies can be stored and distributed effectively where they are needed, managing daily and seasonal variations.⁷

Although renewable sources of energy are becoming well-established, the development of renewable chemicals, fuels and materials is still in its early stages. Evidently, industries are very well-established to exploit fossil fuels: petroleum's very high energy density and refinement into easy-to-transport liquid fuels are key factors for its continued use. Therefore, the introduction of renewable industries must be feasible in cost, supply and efficiency. Most scientists consider biomass to be the most viable sustainable chemical feedstock to replace or reduce the use of fossil fuels. Biomass is a renewable, and therefore sustainable, resource. Further, it is low-cost and hugely abundant across the world.

The most common route to obtain energy from biomass is through simple burning. However, there is a disparity between the energy content of biomass and that of fossil fuels (Table 1.1).⁸ Using biomass directly has a far lower energy content relative to crude oil. However, processing biomass into biofuels (such as sunflower oil) increases its energy content close to that of petrol. There are several plants/power stations in the UK using biomass to generate heating/energy for homes and businesses. Globally, biomass is the fourth largest energy resource (behind coal, oil and natural gas), contributing ~ 10 % of global primary energy. It is the largest source of renewable energy.⁹

Whilst there are concerns regarding the growing of crops directly for fuel production, competing with food production, it should be recognised that there are vast quantities of biomass available which is currently considered as waste, including agricultural waste, forestry waste and food waste. This waste generally ends up in landfill and can be considered as having “negative cost”, meaning that companies would otherwise pay for the waste to be removed.

Table 1.1. The energy content of various fossil fuel and biomass resources.⁸

Resource	Energy content
Cut grass	4 MJ/kg
Wood	15 MJ/kg
Dried wood	18 MJ/kg
Coal	25-30 MJ/kg
Crude oil	42 MJ/kg
Sunflower oil	33 MJ/L
Petrol	32-35 MJ/L

All biomass has the same chemical components (to be discussed in Section 1.1.3), therefore there is potential for the upgrading of “waste biomass”. It is estimated that of the total annual production of biomass through photosynthesis, only 3-4 % is used by humans for both food and non-food purposes.¹⁰

Therefore, biomass is a promising renewable source for the manufacture of liquid fuels, chemicals, materials and for energy production. It has been predicted that half of the world’s energy needs could be supplied by biomass by 2050; an estimated biomass potential of 1.08×10^{11} tons of oil equivalent (TOE) is approximately 10 times that of the world’s current energy need.¹¹ The US Department of Energy (DoE) and the US Department of Agriculture (USDA) have mandated that 5% of heat and power energy, 20% of liquid transportation fuel, and 25% of chemicals and materials should come from biomass by 2022.¹²

However, the use of biomass is inherently more complicated than the use of fossil fuels, owing to its increased chemical complexity. This requires extensive chemical processing to obtain the desired products. This increased complexity can also be considered as a benefit, however, by allowing a single biomass feedstock to be converted into a wider range of chemical products.

1.1.2 Lignocellulosic biomass

The term biomass in general refers to any plant or animal organic matter. Lignocellulosic biomass makes up approximately 50 % of the world’s biomass (estimated at 3×10^{11} tonnes¹³), and is the most abundant source of organic chemicals on Earth.¹⁴ There are many sources of lignocellulosic biomass. All trees, grasses and bushes are made of lignocellulose and can be classified as “Virgin biomass”. The processing of virgin biomass in industries such as agriculture and forestry generates waste materials, such as wood chippings, sawdust, and even animal waste, which can be classified as “Waste biomass”. A third classification refers to “Energy Crops”, such as sugar cane, which are grown specifically to produce biofuels. There are advantages and drawbacks to the use of each class of biomass for the development of fuels and chemicals. If a tree is cut down and used to produce biofuel, the process can only be considered carbon neutral after the time it takes for a new tree to be planted and grow. The utilisation of low-value waste biomass increases the sustainability of the process, but the chemical composition is likely to be more difficult to process. Speciality crops are designed for efficient biofuel production but might take space or resources away from food crops. However, it is estimated that the

land area devoted to growing biofuels accounts for only 0.19 % of the world's total land area, or 0.5-1.7 % of global agricultural land.⁹

1.1.3 Components of lignocellulosic biomass

Lignocellulose has three major components: cellulose, hemi-cellulose and lignin. Cellulose is generally the best-suited component as a feedstock for valorisation. Different sources of biomass can have very different proportions of each component. This means that they are more suited for particular purposes. Cellulose is generally the major component of lignocellulosic biomass and lignin is generally the minor component. Table 1.2 shows the proportions of cellulose, hemi-cellulose and lignin in a range of different types of biomass.^{15,16}

A further issue is the difficulty in separation of the three components. Nature has designed lignocellulose to physically support and provide the structure of plants as cell walls; therefore, it is not facile to break-down biomass into its individual components by conventional means. A cartoon representation of the structure of a plant cell wall is shown in Figure 1.1, showing strands of cellulose embedded in a lignin-hemicellulose matrix.¹⁷ Relatively inexpensive single-step treatment methods, such as pyrolysis, which operate at high temperatures, generally produce a complex mixture of hundreds of chemicals through destruction of the biomass.¹⁸

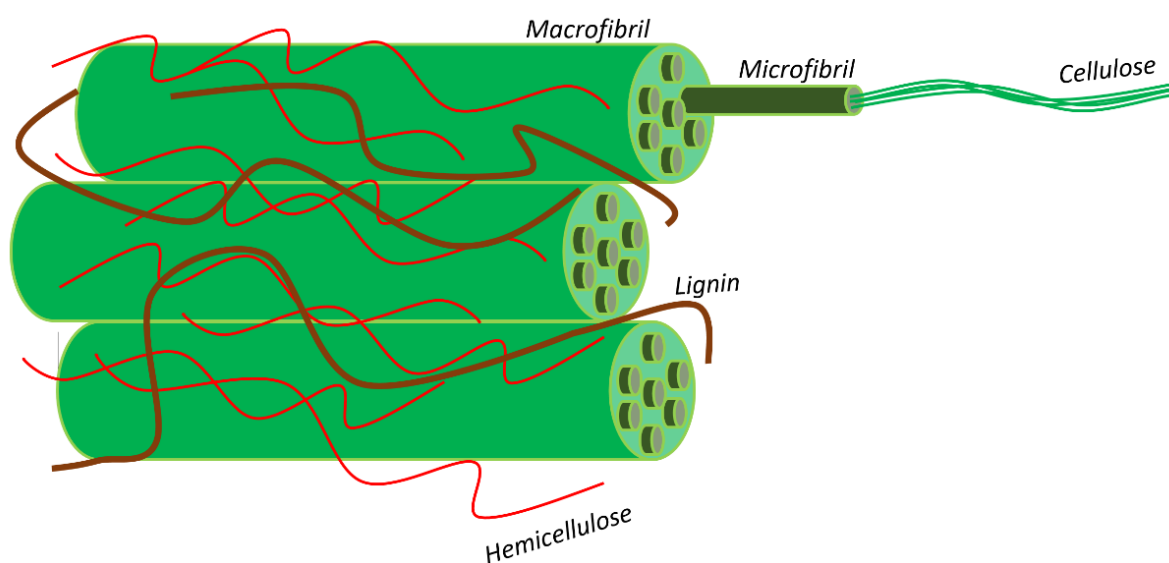


Figure 1.1. An illustration of the structure of lignocellulosic biomass.

Table 1.2. The compositions of various biomass resources.^{15,16}

Category	Lignocellulosic material	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood	Poplar	50.8-53.3	26.2-28.7	15.5-16.3
	Oak	40.4	35.9	24.1
	Eucalyptus	54.1	18.4	21.5
Softwood	Pine	42.0-50.0	24.0-27.0	20.0
	Douglas Fir	44.0	11.0	27.0
	Spruce	45.5	22.9	27.9
Grasses	Grasses	25.0-40.0	25.0-50.0	10.0-30.0
	Switchgrass	35.0-40.0	25.0-30.0	15.0-20.0
	Sweet sorghum	45	27	21
Agricultural waste	Wheat Straw	35.0-39.0	23.0-30.0	12.0-16.0
	Barley Hull	34.0	36.0	13.8-19.0
	Barley Straw	36.0-43.0	24.0-33.0	6.3-9.8
	Rice Straw	29.2-34.7	23.0-25.9	17.0-19.0
	Rice Husks	28.7-35.6	12.0-29.3	15.4-20.0
	Oat Straw	31.0-35.0	20.0-26.0	10.0-15.0
	Ray Straw	36.2-47.0	19.0-24.5	9.9-24.0
	Corn Cobs	33.7-41.2	31.9-36.0	6.1-15.9
	Corn Stalks	35.0-39.6	16.8-35.0	7.0-18.4
	Sugarcane Bagasse	25.0-45.0	28.0-32.0	15.0-25.0
	Sorghum Straw	32.0-35.0	24.0-27.0	15.0-21.0
	Nut shells	25-30	25-30	30-40
	Banana waste	13.2	14.8	14
	Bagasse	54.87	16.52	23.33
	Sponge gourd fibres	66.59	17.44	15.46
	Newspaper	40-55	25-40	18-30

It is very difficult to separate a desired chemical from these mixtures. Therefore, pre-treatment methods are generally utilised, including mechanical, chemical, physiochemical and biological methods. These modify the cellulose-hemicellulose-lignin matrix to reduce its size and open the physical structure to increase the accessibility to cellulose. Subsequent treatment methods can then more effectively isolate each component. It is beyond the scope of this thesis to survey the biomass pre-treatment methods reported; however, the efficiency and cost of these processes are crucial for the production of biofuels, bio-chemicals and biomaterials, and are the subject of intense research.^{16,19} The following sections will introduce in-turn the three main components of lignocellulosic biomass.

1.1.3.1 Cellulose

Cellulose is a highly crystalline, linear polymer composed of unbranched chains of glucose. It is the most abundant naturally occurring polymer. The repeating unit of cellulose is the disaccharide cellobiose (shown in Figure 1.2(a)), formed from the condensation of two β -glucose molecules linked by a β -(1,4) glycosidic bond. There can often be a very high degree of polymerisation, with wood cellulose reaching chains of 10,000 units and cotton cellulose reaching 15,000 units.²⁰

Cellulose forms extensive networks with chains tightly held together side-by-side through both intra- and intermolecular hydrogen bonds (shown in Figure 1.2(b)), owing to the high number of free alcohol groups present in each cellobiose unit. In plants, cellulose chains align to form microfibrils. This results in a high tensile-strength, increased further by the encapsulation of cellulose by the lignin-hemicellulose matrix in lignocellulose. The high degree of crystallinity and large molecular weight mean that cellulose is insoluble in water and most organic solvents. Additionally, it is relatively difficult to break down cellulose into its units which is necessary for upgrading cellulose into useful chemical products. Biologically, this can be done with the enzyme cellulase. Industrially, a variety of methods are used; pretreatment with dilute sulfuric acid at moderate temperatures is an effective technique to obtain high yields of glucose.^{16,20,21}

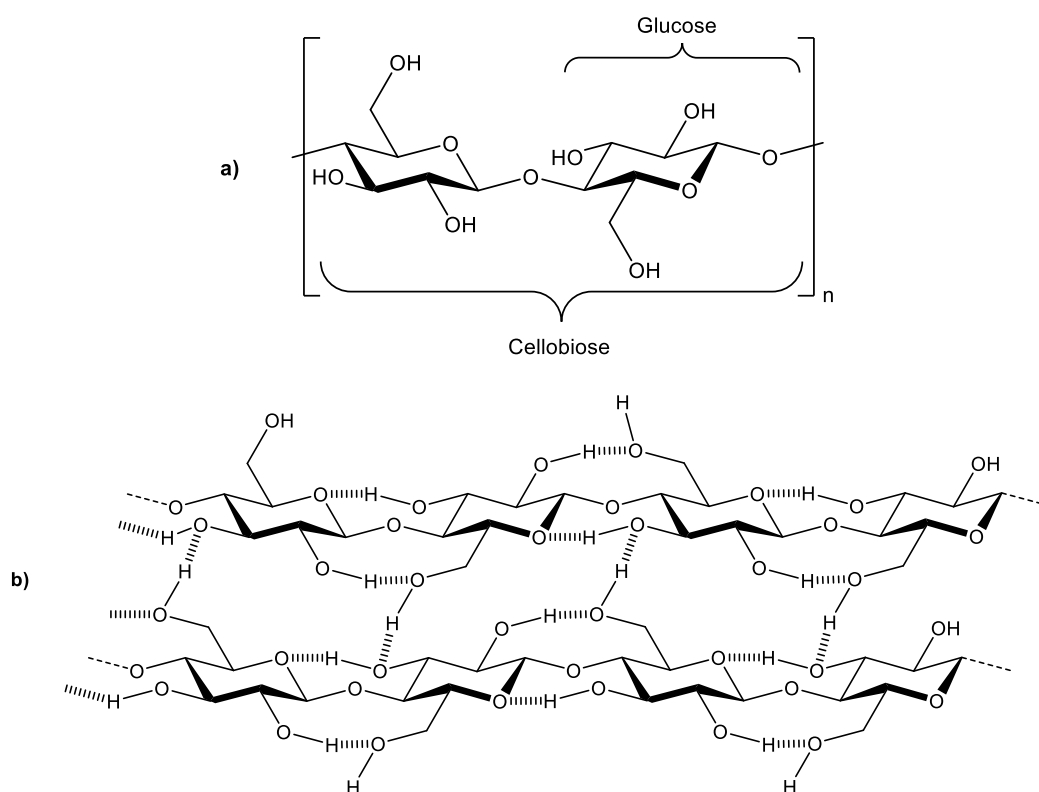


Figure 1.2. The chemical structure of cellulose: (a) the cellobiose repeating unit (b) hydrogen bonds within the cellulose network.¹⁷

1.1.3.2 Hemicellulose

Hemicellulose is the second most abundant polymer after cellulose. In stark contrast, the structure of hemicellulose is amorphous, random, and highly branched. It is composed of different C₅ and C₆ monosaccharide units; some common examples are shown in Figure 1.3(a). The units are connected by β -(1,4) glycosidic bonds (as in cellulose) to form a wide range of repeating units. Some common examples of repeating units are shown in Figure 1.3(b). Glucan, xylan and mannan are examples of repeating units with two of the same sugar connected; glucomannan is an example of a repeating unit made up of two different sugars (here glucose and mannose). The combination of these repeating units mean that hemicellulose is very heterogeneous in nature. Hemicelluloses vary in composition but are typically made up of several of these heteropolymers. Hardwood hemicelluloses are made of mostly xylans, whilst softwood hemicelluloses are made of mostly glucomannans.²²

Hemicelluloses are composed of much shorter chains than cellulose, typically just 500-3,000 monomer units. In plants, they help to provide structural strength by cross-linking the cellulose microfibrils together into macrofibrils, alongside lignin.²³ However, by themselves hemicelluloses have little strength and are easily hydrolysed, owing to their amorphous, random structure.¹⁶

1.1.3.3 Lignin

Lignin is the third most abundant organic polymer after cellulose and hemicellulose. It is a complex, three-dimensional phenolic polymer. It is extremely heterogeneous and lacks a defined primary structure. There are three major fundamental phenolic units called monolignols: *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. These differ only in their degree of methoxylation. Their structures are shown in Figure 1.4(a). Through oxidative coupling, the monolignols form the phenylpropanoid monomeric units that make up the lignin structure: *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S). Different types of biomass have different compositions of these monomeric units. Generally, hardwood lignins are composed primarily of G and S units; softwood lignins of G units; and grasses of H, G and S units. The most frequent interunit bond in lignin is a β -aryl ether linkage. A small, representative example of a fragment of a lignin polymer is shown in Figure 1.4(b), portraying the β -aryl ether linkages between S and G units.¹⁶

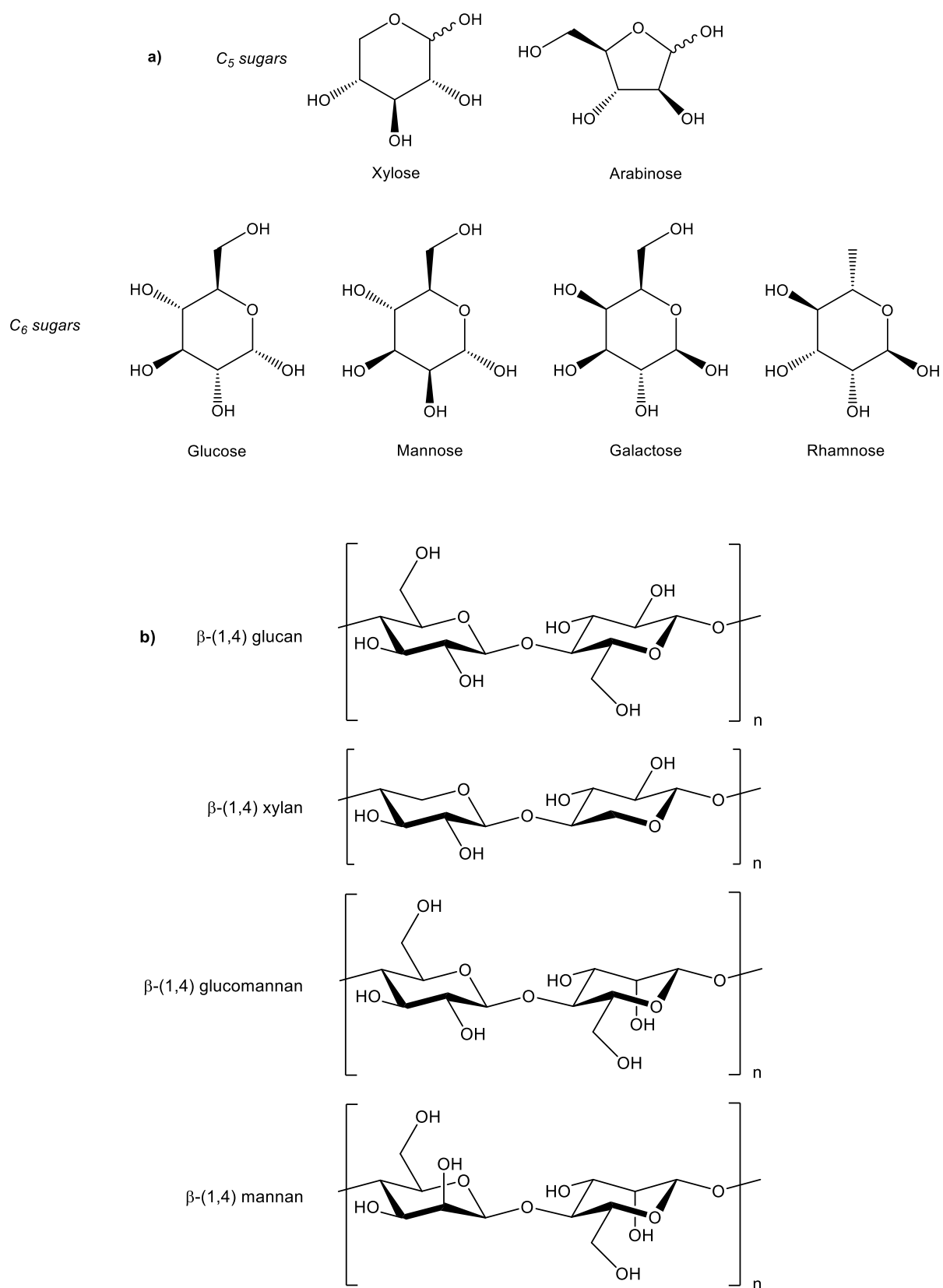


Figure 1.3. The chemical structure of hemicellulose. (a) hemicellulose mono-saccharide units (b) hemicellulose repeating units.^{16,22}

Lignin is compared to the “glue” that provides a compressive strength and stiffness to the plant. This stability results from cross-linking ether and ester linkages between cellulose, hemi-cellulose and lignin. Consequently, much of the difficulty of processing biomass is a result of the encapsulation of cellulose by lignin, and many processes study how to remove/minimise the lignin content.^{24–26}

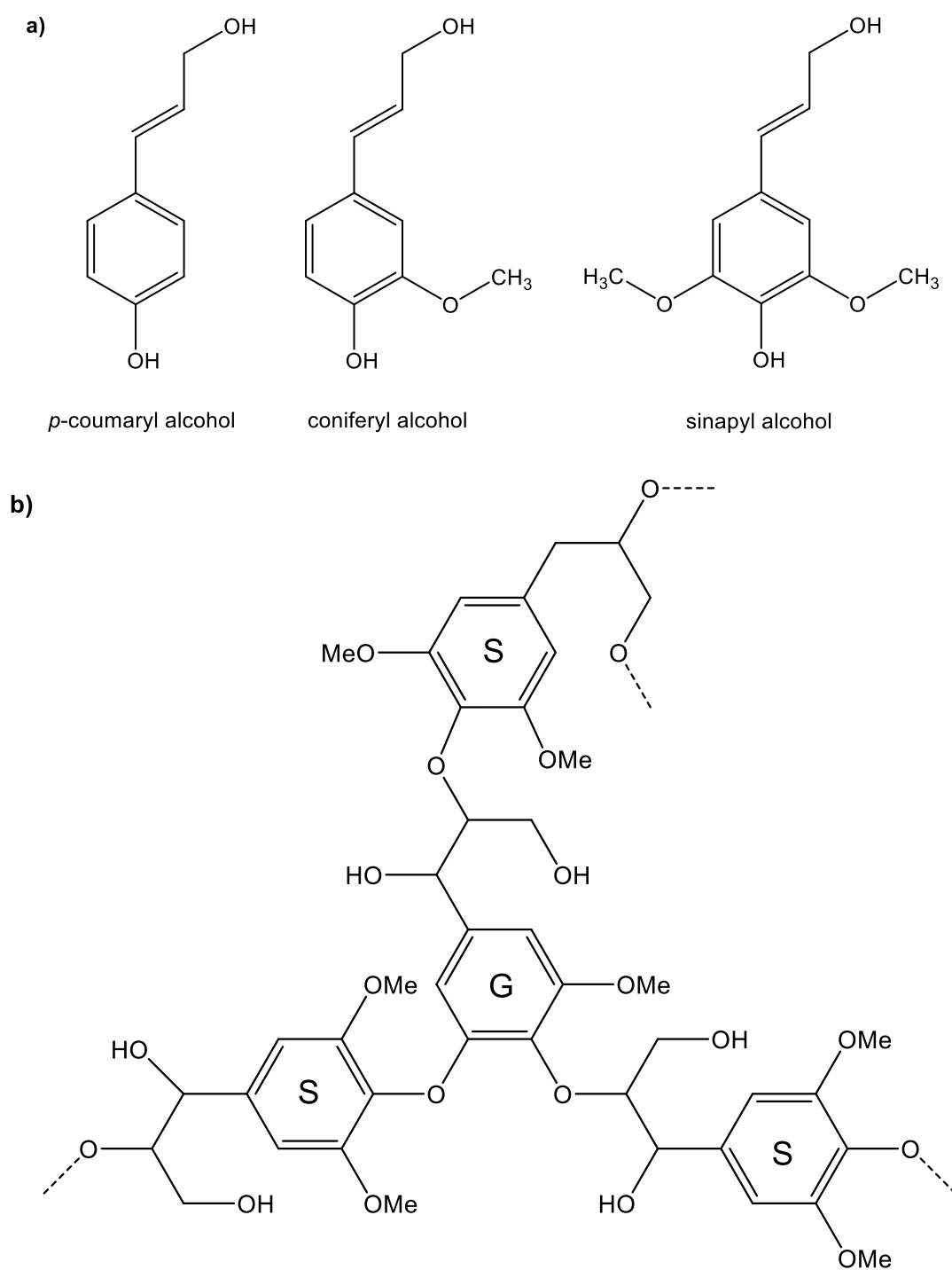


Figure 1.4. The chemical structure of lignin: (a) phenolic units (b) fragment of lignin polymer.¹⁶

1.1.4 Lignocellulosic biomass-derived platform chemicals

Aside from burning to generate energy, the chemical composition of lignocellulosic biomass offers the potential for the generation of many chemical derivatives which can be applied as fuels, materials, and across chemical industries such as pharmaceuticals and fine chemicals. If we consider crude oil as unfunctionalised hydrocarbon chains, then molecules derived from biomass have “excess functionality”, i.e., they contain a much wider range and number of functional groups, primarily oxygen-containing functional groups. This allows them to access a wider variety of chemical products but also provides difficulties. For example, their high oxygen content lowers the heat content of the products relative to fossil fuels and makes it difficult to blend them with existing fossil fuels.

Whilst the depolymerisation of cellulose yields glucose, the depolymerisation of hemicellulose yields a range of C₅ and C₆ sugars, as described in 1.1.3.2. Both glucose and the other sugars can be used to obtain platform chemicals, or building blocks, from which useful products can be obtained. Some of the most important sugar-derived platform chemicals is shown in Figure 1.5. Chemical conversions, including defunctionalisations and refunctionalisations, on each of these platform chemicals accesses a wide range of products. One of these chemicals, levulinic acid, and its conversions will be discussed in greater detail in Sections 1.2-1.5.

Lignin can also be used to access a wide range of chemical feedstocks, primarily aromatic compounds which cannot be accessed by cellulose or hemicellulose. Some of these compounds are presented in Figure 1.6. Figures 1.5 and 1.6 illustrate the range of functional groups and the variety in structures accessible from lignocellulose; this is a much wider scope than for petroleum.¹⁶

In 2004, the U.S. Department of Energy (DoE) produced a list of the “Top Value Added Chemicals from Biomass”.²⁷ These candidates were selected through study of the synthesis of each platform chemical and its derivatives, its technical complexity, market data, etc. The list is presented in full as Table 1.3. Every chemical on the list can be derived from the C₅/C₆ sugars obtained from cellulose/hemicellulose; many of them are shown in Figure 1.5. This list has shaped much of the research in this field. The list was revisited and updated in 2010.²⁸ The authors removed some candidates (fumaric, malic, aspartic, glucaric, glutamic and itaconic acids) owing to limited research activity on these candidates, and added some new candidates: ethanol, because of its importance as a key feedstock for chemical production; and furans, as technology had sufficiently improved by that point to access furans from sugar dehydration. This should illustrate that the field is dynamic and remains in its infancy.

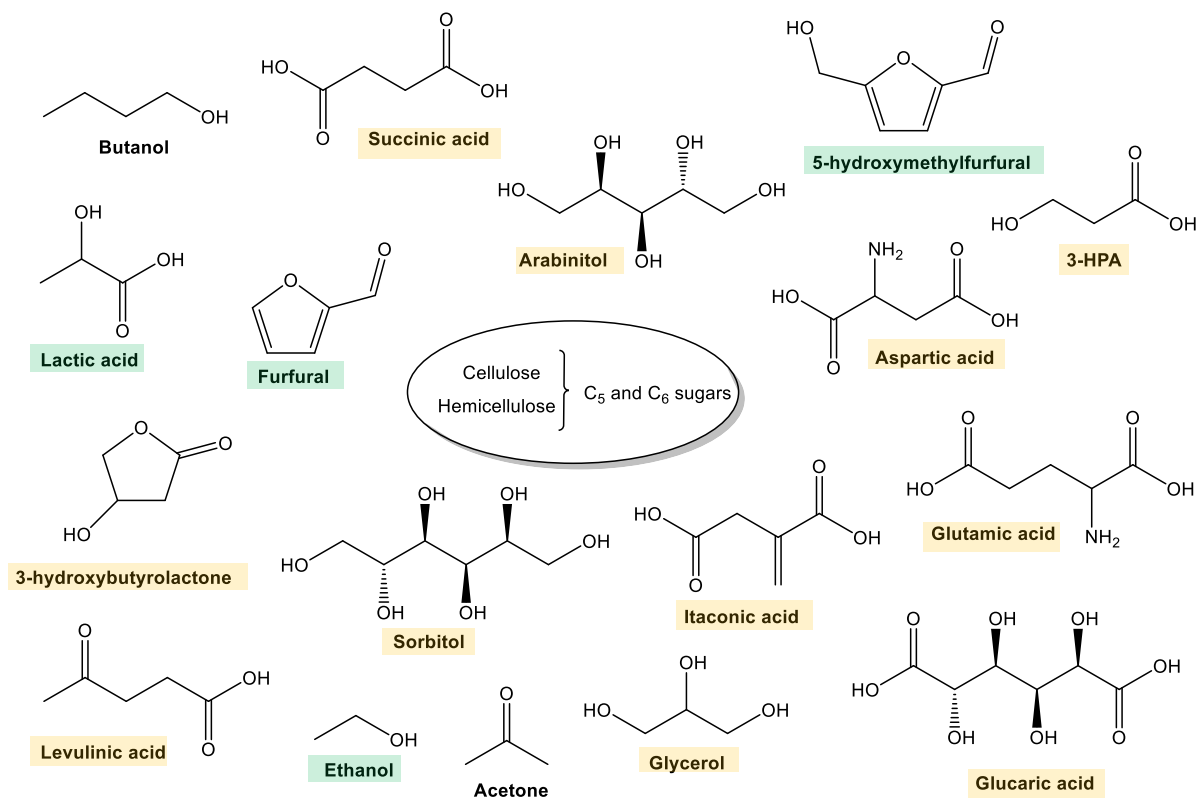


Figure 1.5. A survey of important chemicals derived from cellulose and hemicellulose.

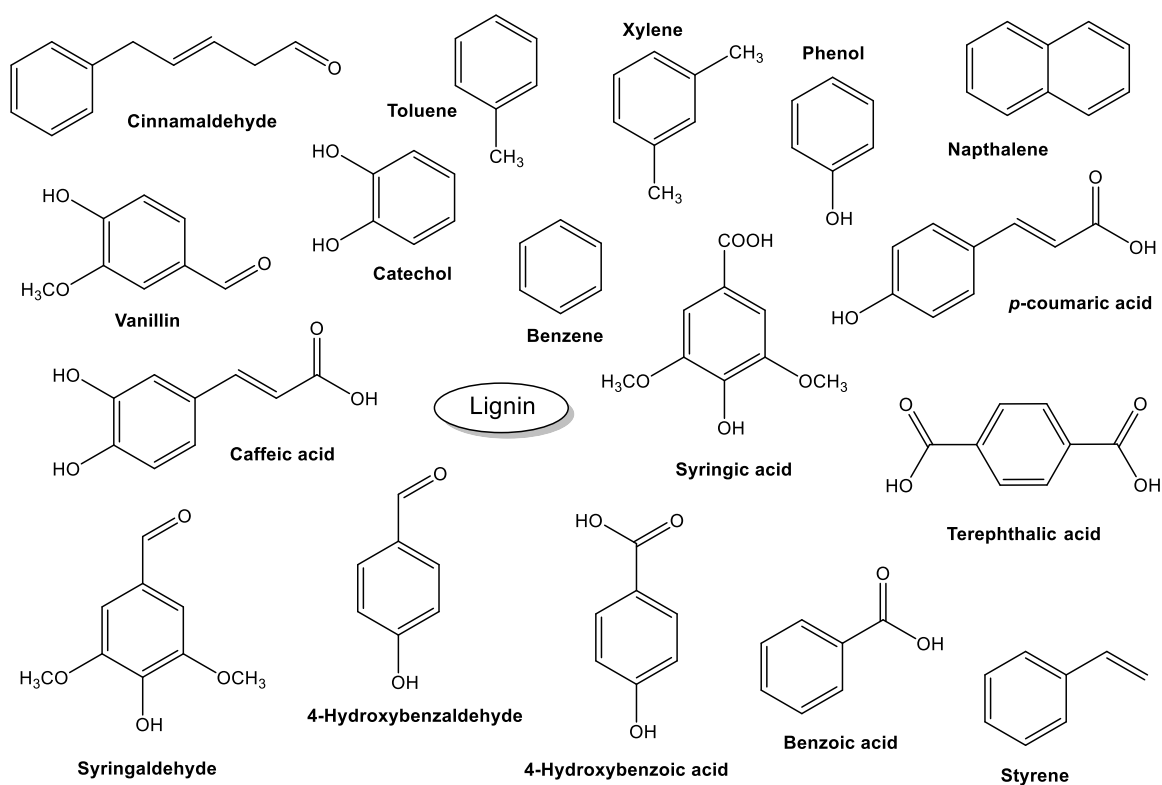


Figure 1.6. A survey of important chemicals derived from lignin.

Table 1.3. Lists of top biomass-derived platform chemicals identified in 2004 and 2010.²⁷⁻²⁸

Building block chemicals (2004)	Building block chemicals (2010)
1,4 succinic, fumaric and malic acids	Ethanol
2,5 furan dicarboxylic acid (FDCA)	Furans: Furfural, HMF, FDCA
3 hydroxy propionic acid (3-HPA)	Glycerol and derivatives
Aspartic acid	Biohydrocarbons: Isoprene, and other hydrocarbons
Glucaric acid	Lactic acid
Glutamic acid	Succinic acid
Itaconic acid	3 hydroxy propionic acid/aldehyde
Levulinic acid	Levulinic acid
3-hydroxybutyrolactone	Sorbitol
Glycerol	Xylitol
Sorbitol	
Xylitol/arabinitol	

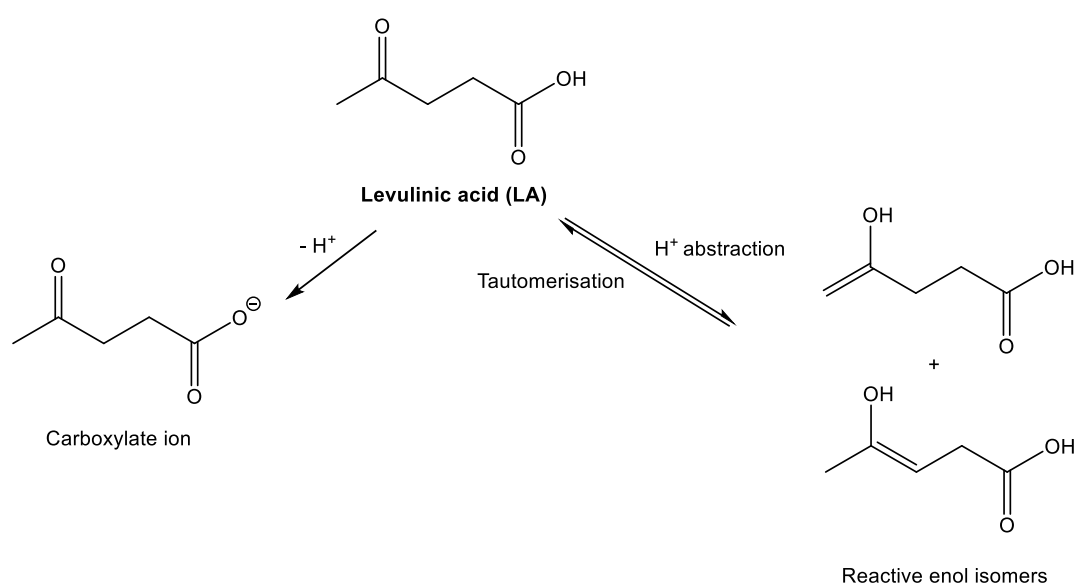
Most of the processing technologies required for biomass valorisation remain at a pre-commercial stage, in so-called “First generation biorefineries” (using food-grade resources).²⁹ However, some technologies have become well-established, such as the production of bio-ethanol from biomass, the world’s leading bio-fuel.³⁰ Some other chemicals, such as lactic acid and propionic acid, are produced from biomass sources such as corn and wheat.³¹ Most processes used in commercial production of bio-based platform chemicals/derivatives are based on microbial fermentation processes. Such microbial processes are not well-suited to many chemical products which require chemical conversion routes; these are often limited commercially by the cost of the catalysts required.³²

1.2 Levulinic acid and its hydrogenation products

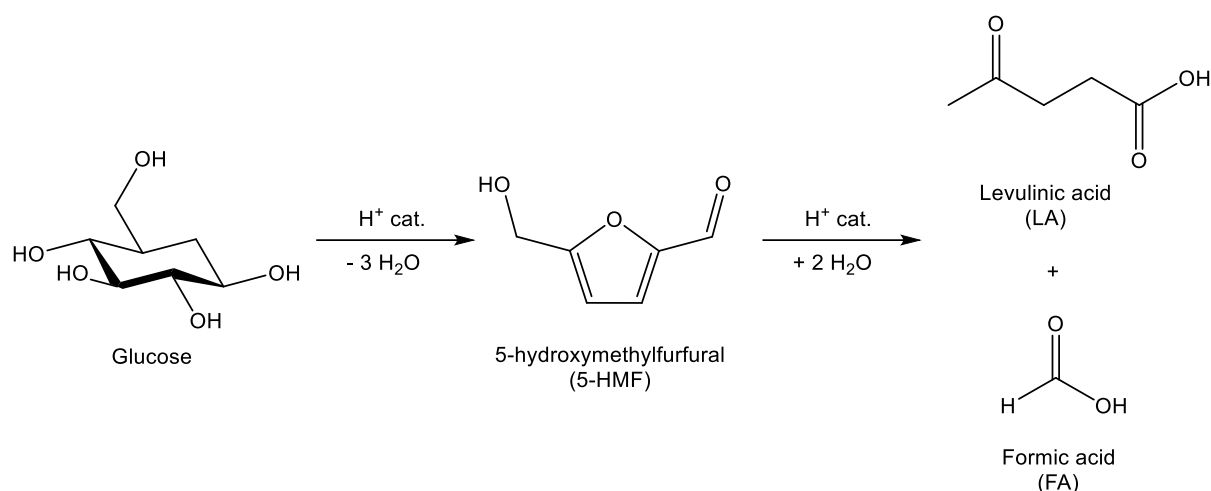
Levulinic acid (LA) was highlighted as one of the “Top Value Added Chemicals from Biomass” in the screening by the U.S. DoE in 2004.²⁷ It has continued to be the focus of much research as a biomass-derived feedstock chemical and was still considered as a “Top Building Block” chemical when the list was revisited in 2010 (unlike many of the related organic acids on the list).²⁸ Sections 1.2.1-1.2.4 will introduce LA and its hydrogenation products γ -valerolactone (GVL), 1,4-pentanediol (1,4-PDO) and 2-methyltetrahydrofuran (2-MTHF) in turn. The subsequent sections will cover the hydrogenation reactions of LA into its hydrogenation products.

1.2.1 Levulinic acid

Levulinic acid, or 4-oxopentanoic acid, is a white crystalline solid with a melting point close to room temperature. It is a five-membered carbon chain containing both carboxylic acid and ketone moieties, giving it good solubility in both water and polar organic solvents. The presence of two functional groups greatly increases the types of reactions available to LA. The ketone group is susceptible to nucleophilic attack through abstraction of an adjacent α -proton at two sites and the resulting species can tautomerise between the two reactive enol isomers. Also, a reactive carboxylate ion can be formed by ready deprotonation of the carboxylic acid proton (Scheme 1.1). This reactivity is fundamental for the catalytic transformations accessible to LA.³³



Scheme 1.1. Reactivity of levulinic acid.³³



Scheme 1.2. Synthesis of levulinic acid from glucose.³³

LA can be efficiently produced from cellulose. The initial step is an acid-catalysed dehydration of glucose forming 5-hydroxymethylfurfural (5-HMF). A second acid-catalysed hydration step yields LA, via ring cleavage, alongside equimolar amounts of formic acid (FA). The role of FA will be discussed further in Section 1.3.2. This reaction scheme is shown in Scheme 1.2. It is also possible to obtain LA from the hemicellulose-derived C₅-sugar xylose via furfural. The formation of intractable humins as undesirable side-products is also possible, which industrial processes must aim to minimise.²⁸

Industrially, a wide range of acid catalysts have been utilised for LA production. Mineral acids, such as sulfuric acid, can obtain high LA yields. However, the removal of the acids is necessary but can be complex. The industrial Biofine Process is one of the most advanced, cost-effective commercial processes, able to use very heterogeneous biomass reserves (first shredded to obtain an appropriate size) in a two-stage reactor using dilute sulfuric acid to obtain high LA yields in very short reaction times. The acid is recycled and reused.³⁴

The use of solid acid catalysts avoids the difficulty of acid separation, but their processes are characterised by low yields, long reaction times and harsh reaction conditions. This can be improved by using polymer catalysts which have better solubility, such as Amberlyst 70, which can access high yields of LA in aqueous media from both cellulose and biomass feedstocks such as corn stover.³⁵ Combinations of Brønsted and Lewis acids (such as benzenesulfonic acid and In(OTf)₃ or H₃PO₄ and AlCl₃) are also able to obtain LA from various “raw” biomass feedstocks in high yields.^{36,37}

One of the reasons why LA is considered as one of the most promising bio-derived platform chemicals is its wide range of accessible products. Some of the most important products are shown in Figure 1.7. The useful hydrogenation products γ -Valerolactone (GVL), 1,4-pentanediol (1,4-PDO) and 2-methyl-THF (2-MTHF) will be discussed in Sections 1.2.2, 1.2.3 and 1.2.4 respectively.

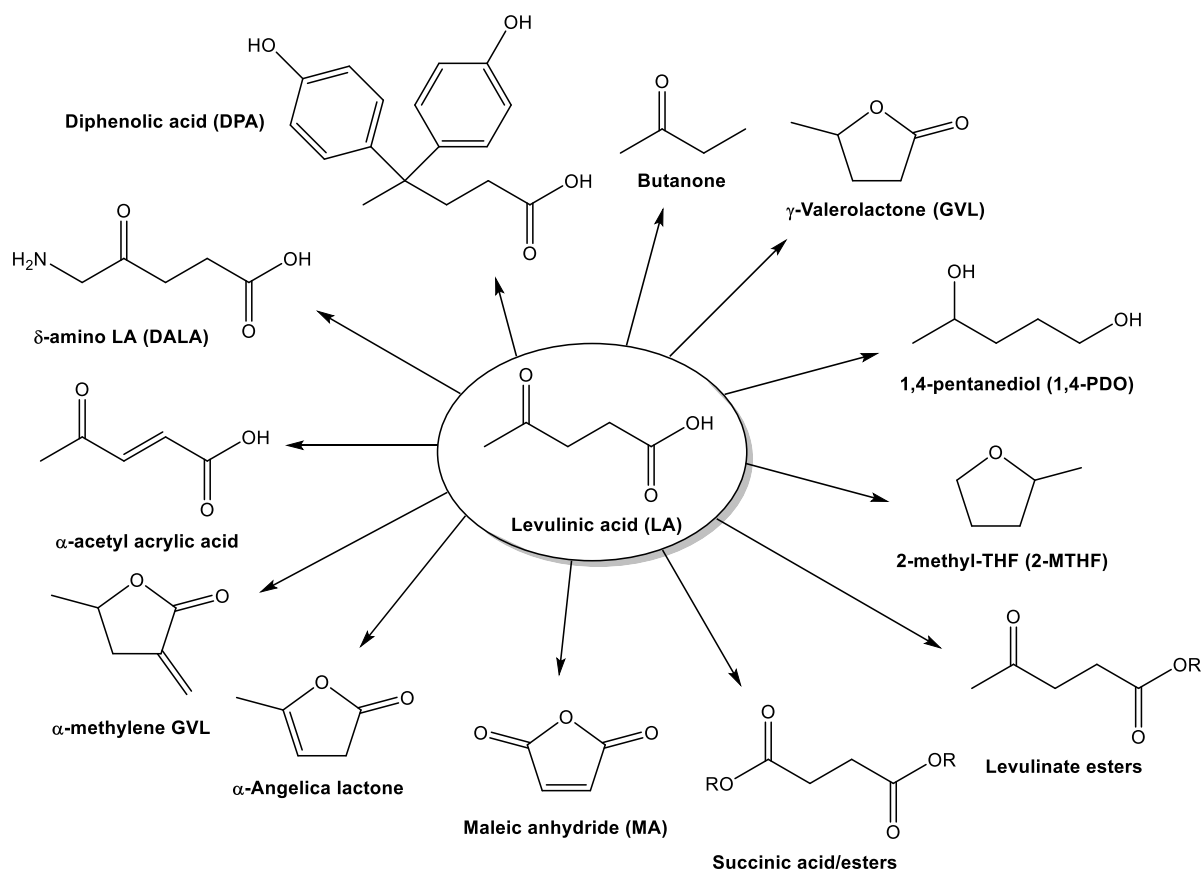


Figure 1.7. A survey of chemicals accessible from levulinic acid.³³

Those, and many of the other products, have commercial applications. For example, δ -amino levulinic acid (DALA) is used in the production of biodegradable pesticides and insecticides^{38,39}, and has also been applied as a component in photodynamic therapy (PDT)⁴⁰ and fluorescence detection (FD) in the field of oncology.⁴¹ Diphenolic acid (DPA) has found use in the production of biodegradable polymers and other materials such as fire retardants. Products derived from LA have found use in a very wide range of applications, from personal care products to electronics, batteries and drug delivery.³⁸ As such, LA can be considered as a valuable bio-based chemical feedstock with high potential.

1.2.2 γ -Valerolactone

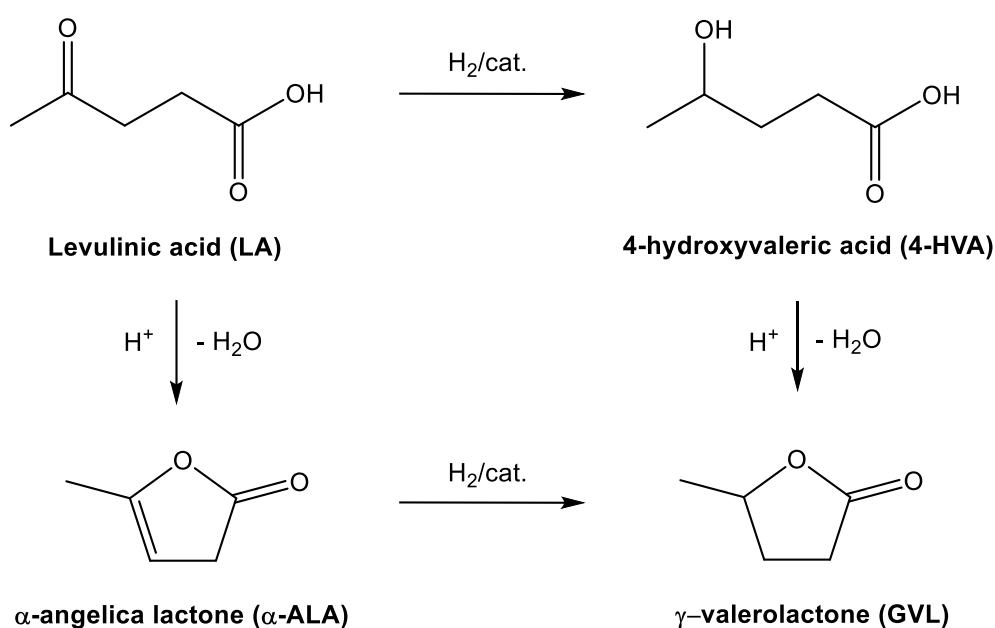
γ -Valerolactone (GVL) is the primary hydrogenation product of LA and one of the most important chemical products accessible from LA. It is a non-hazardous liquid with a high-boiling point and a pleasant smell. It is often described as having many desirable properties, such as an inertness to air

and water, water miscibility, a high flash point, a low melting-point and a low vapour pressure.^{42,43} Consequently, GVL is considered as safe for both storage and transportation in large quantities.⁴⁴

It has a range of applications as a green solvent (it provides improvements as a solvent for biomass processing), fuel additive, fine chemical intermediate, fragrance and food additive.^{45–47} Comparing mixtures of GVL and ethanol with gasoline, GVL has very similar properties to ethanol as a fuel additive.⁴⁴ GVL contains a chiral centre, although it is typically used in the racemic form. Routes to optically active GVL have been reported, which widens its potential applications to those requiring a defined chiral centre; for example as a chiral building-block in the pharmaceutical industry.⁴⁸

Scheme 1.3 shows the synthesis from LA to GVL. The conversion of LA to GVL involves a hydrogenation and a dehydration step. If LA is hydrogenated first, it forms 4-hydroxyvaleric acid (4-HVA), which ring-closes with loss of water to form GVL. Alternatively, dehydration of LA forms α -angelica lactone (α -ALA) which generates GVL upon alkene hydrogenation. The route of initial hydrogenation followed by dehydration is thermodynamically preferred and dominates kinetically at low temperatures and in the liquid phase. The alternative route is predominant in the vapour phase.^{49,50}

Whilst the dehydration step is acid-catalysed, the hydrogenation step must be achieved using a metal catalyst, alongside either molecular hydrogen or an alternative hydrogen source (e.g. formic acid).³³ A survey of the catalytic processes reported for hydrogenation of LA to GVL will be discussed in section 1.3. As GVL is a five-membered lactone, it has good stability, but can be hydrogenated further in some instances. Those hydrogenation processes will be discussed in Sections 1.4 and 1.5.

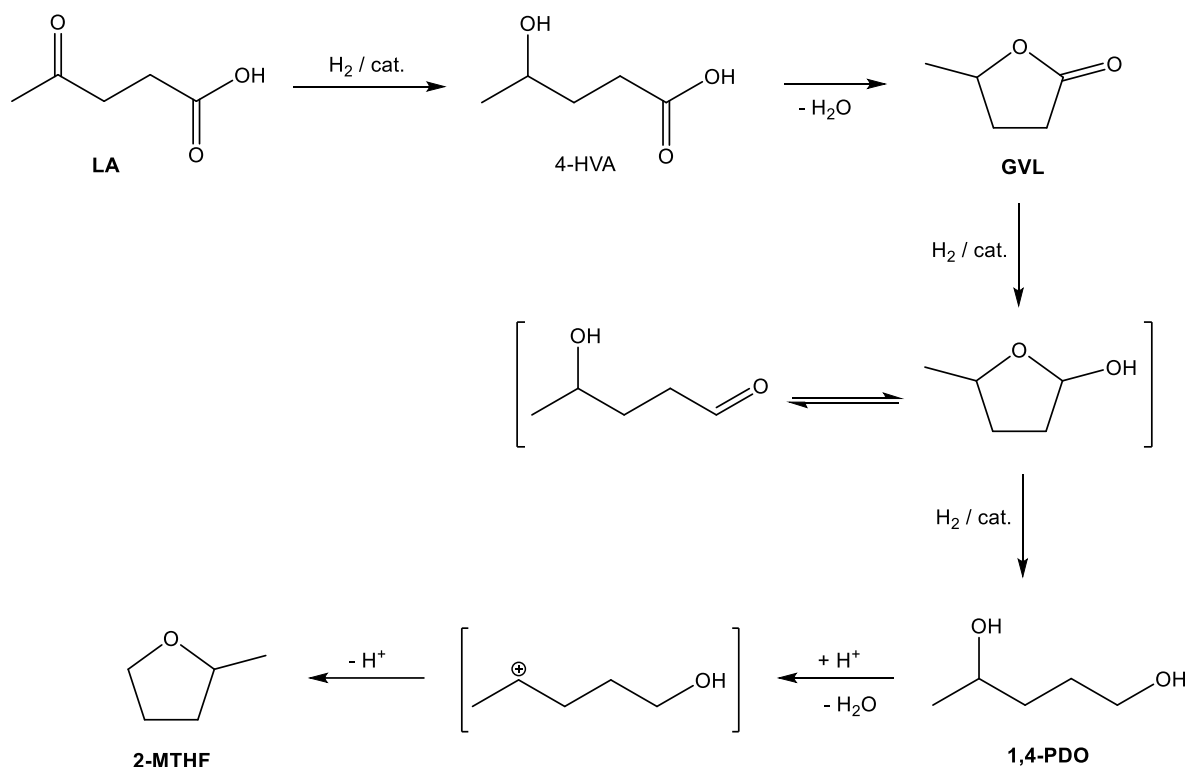


Scheme 1.3. Synthesis of γ -Valerolactone from levulinic acid.³³

1.2.3 1,4-pentanediol

1,4-pentanediol (1,4-PDO) is a non-hazardous liquid diol and a further hydrogenation product of LA. It is much more challenging to hydrogenate LA beyond GVL, because of the resistance of GVL to ring-opening. Therefore, much harsher reaction conditions are required. The ring-opening hydrogenation of GVL first produces 4-hydroxypentanal, and subsequent carbonyl reduction yields 1,4-PDO. This is shown in Scheme 1.4. Furthermore, 1,4-PDO readily undergoes dehydration to form the cyclic ether product 2-methyl-THF (2-MTHF). 2-MTHF is a 5-membered cyclic ether, offering it stability like the 5-membered lactone GVL. Indeed, one of the key roles of 1,4-PDO is as an intermediate for the synthesis of 2-MTHF. Therefore, it is a technical challenge to selectively synthesise 1,4-PDO owing to its position in the reaction scheme between the stable species GVL and 2-MTHF.³³

The main application of 1,4-PDO is in the production of biodegradable polymers including polyesters. Short chain bio-based diols are considered as important raw materials for the production of biodegradable polymers for both commodity and speciality applications. Owing to the range of polymer properties accessible, they have potential applications including hydrogels, soft-tissue engineering, drug delivery and liquid crystals.⁵¹



Scheme 1.4. Synthesis of 1,4-pentanediol and 2-methyltetrahydrofuran from levulinic acid.

1.2.4 2-methyltetrahydrofuran

2-methyl-THF (2-MTHF) has been established as the final hydrogenation product accessible from LA under forcing hydrogenation conditions. It is a highly flammable, colourless liquid. Its main applications are as a green speciality solvent and as a fuel additive.

In some cases, 2-MTHF is used as a replacement solvent for THF, owing to some of its more favourable properties. Whilst it behaves in the same manner as THF, it has a higher boiling point (80 °C versus 66 °C), allowing it to access higher reaction temperatures. Its lower melting point (-136 °C versus -108 °C) offers its potential for low-temperature processes, such as lithiations. It also has a much lower water-miscibility than THF allowing for easier organic-water phase separations. These are in addition to the “green” credentials of its sustainable feedstock and decomposition pathways; it is reported that it can be abiotically degraded by sunlight and air.^{52–54}

2-MTHF has also been identified as a promising fuel additive. Its properties make it well-suited for this application: a high energy density, low volatility, hydrophobicity, low toxicity, high specific gravity, high octane number, and resistance to polymerisation. Other related biogenic compounds, including furfural, have higher volatility and a tendency to polymerise, reducing their application as fuels.

2-MTHF has been approved by the U.S. DoE for use as a gasoline additive in “P-series” fuels.⁵⁵ These are designed as a family of renewable liquid fuels to replace gasoline and correspondingly have desirable characteristics such as a significant reduction in toxic emissions and can be as much as 70 % renewable.⁵⁶

2-MTHF can blend better with gasoline than methanol (up to 70 % 2-MTHF) and can be used in current engines without adverse effects on performance. It is also more easily integrated into a refinery distribution scheme than ethanol, as it can be blended at the refinery and transported by pipeline (ethanol must be added later to avoid phase separation from water contamination).^{2,38,57}

1.3 Hydrogenation of LA to GVL

The hydrogenation of LA into GVL is an active area of research, owing to the attractive properties and useful applications of GVL already discussed. Research interest in this field has increased dramatically within the past two decades. Of the catalysts reported for the hydrogenation of LA, the vast majority of these can access GVL, and these will be described in this Section. Owing to the

difficulty of hydrogenating beyond GVL, far fewer systems can hydrogenate LA to 1,4-PDO or 2-MTHF; these systems will be discussed in the following Sections 1.4 and 1.5 respectively.

Both homogeneous and heterogeneous catalytic systems have been reported for the hydrogenation of LA to GVL. The major advantages of heterogeneous systems are the ease of product recovery and separation from the catalyst, and catalyst recycling. These steps are highly important for the commercialisation of hydrogenation processes. Homogeneous systems, however, generally achieve higher activity and selectivity under gentler conditions. The ability to fine-tune the structure of a homogeneous catalyst, through slight modifications to the metal and ligand system, is essential in achieving the desired catalyst activity and product selectivity. It is generally more difficult to fine-tune a heterogeneous catalyst in this way. Whilst the difficulty of product separation is an issue with homogeneous catalysts, there are potential routes to facilitate this; for example, by using biphasic systems. With the use of water-soluble catalysts, aqueous media can be used and the GVL product extracted using an organic solvent. Furthermore, given the solid nature of raw biomass, homogeneous catalysis might offer an advantage in the range of biomass sources which could be used. The homogeneous catalyst in solvent media can be delivered into solid or swelled biomass in a way that is not possible with heterogeneous solid catalysts.⁴²

Whilst both heterogeneous and homogeneous catalytic systems will likely play an important role in this field, the research described in this thesis will focus on homogeneous systems. Therefore, discussion in this section will be primarily limited to the homogeneous catalytic systems reported in the literature. Reviews of heterogeneous systems are available elsewhere.⁴⁹

A further distinction will be made in the hydrogen source utilised for the hydrogenation. A typical hydrogenation reaction uses high pressures of molecular hydrogen gas (H_2). However, transfer hydrogenations are receiving more and more interest. Transfer hydrogenation reactions use an alternative hydrogen source, such as an acid or alcohol, in place of hydrogen. These reactions offer potential benefits and can be considered as operating under gentler hydrogenation conditions. This Section will first discuss the hydrogenation processes of LA to GVL using molecular hydrogen (1.3.1) before moving on to discuss the transfer hydrogenations of LA to GVL (1.3.2). It should be noted that under transfer hydrogenation conditions, it is generally not possible to hydrogenate LA to its further hydrogenation products 1,4-PDO and 2-MTHF.

Homogeneous catalysts for the hydrogenation of LA to GVL are generally based on the precious metals ruthenium, iridium and palladium, although there are some examples using earth-abundant first-row transition metals. Many of the most successful hydrogenation catalysts utilise phosphine ligands. Of these, multidentate (bi- and tridentate) phosphines are generally more effective than monodentate

phosphines. The effectiveness of the phosphine ligand is linked to its steric and electronic properties. Some applications have required chiral or water-soluble phosphine ligands. An overview of some of the phosphine ligands reported in this application is presented in Figure 1.8.

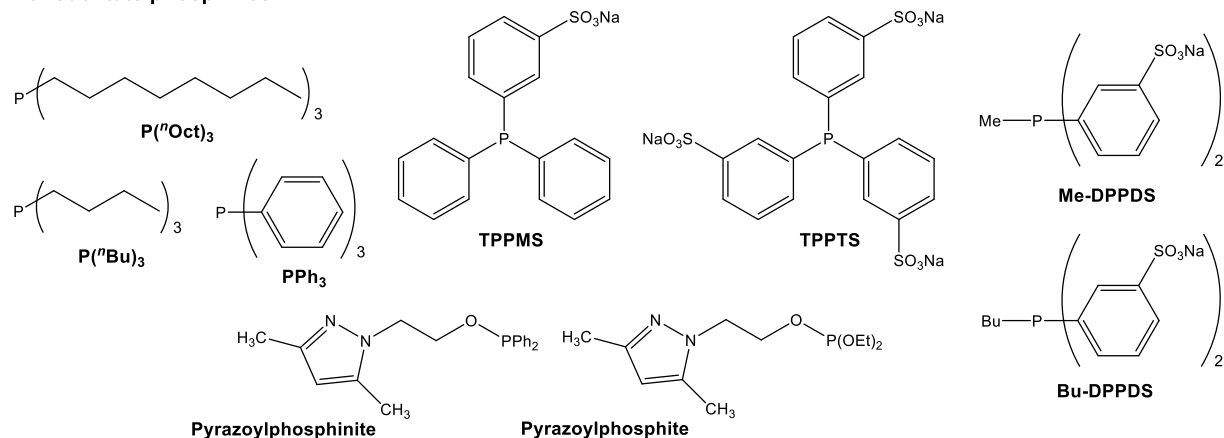
1.3.1 Hydrogenation of LA to GVL using molecular hydrogen

Most of the LA hydrogenation processes reported in the literature use pressures of H₂. From a green chemistry perspective, using H₂ is desirable for achieving a 100 % atom economy. This means that there are no undesirable by-products formed. However, whilst H₂ is produced globally on very large scales for use in processes such as ammonia production, over 90 % of H₂ gas is manufactured from fossil fuels, primarily by steam reforming of natural gas. More sustainable routes to H₂ production, including gasification of biomass and the electrolysis of water, remain in their infancy.⁵⁸ Handling and performing hydrogenation reactions using H₂ gas requires specialist equipment designed to tolerate high pressures. This introduces concerns with cost and safety.

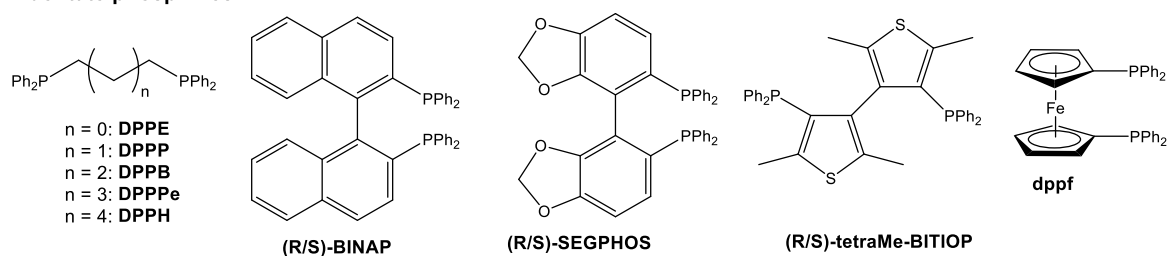
Nonetheless, using H₂ gas allows for forcing conditions to obtain high conversions of LA to GVL (or beyond GVL to further hydrogenation products). Such conditions can introduce difficulties with selectively obtaining a single product. Furthermore, the hydrogenation of LA beyond GVL can yield 2-MTHF, which is considered as hazardous for some applications. Hydrogenation conditions range from pressures of 1 – 150 bar and temperatures of 25 – 180 °C in a range of solvent systems.

The majority of homogeneous LA hydrogenation catalysts which operate under H₂ gas are based upon the precious metals ruthenium, iridium and palladium, in that order. The use of such expensive metals poses questions regarding their commercial application; however they are generally considered necessary to reach high catalyst activities. There is little precedent for using cheaper non-precious metals, but a few systems using metals such as iron and cobalt have been reported. The following Sections will look at systems using each metal in turn: ruthenium (1.3.1.1), iridium (1.3.1.2), palladium (1.3.1.3), and finally the non-precious metals (1.3.1.4). Additionally, the synthesis of optically-active GVL from LA will be briefly considered (1.3.1.1.2).

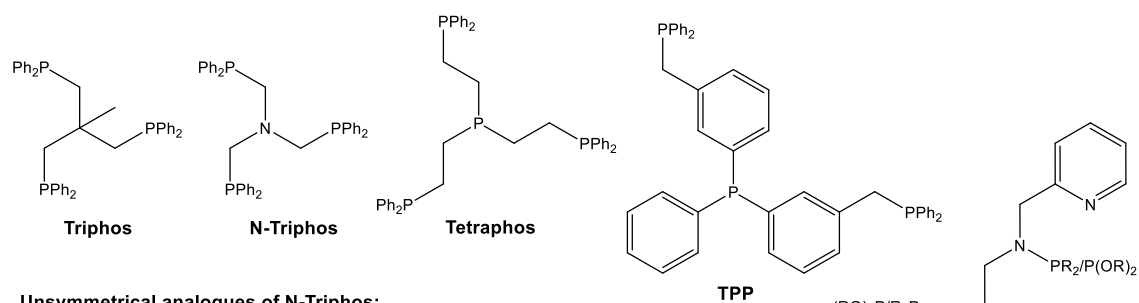
Monodentate phosphines:



Bidentate phosphines:



Multidentate phosphines:



Unsymmetrical analogues of N-Triphos:

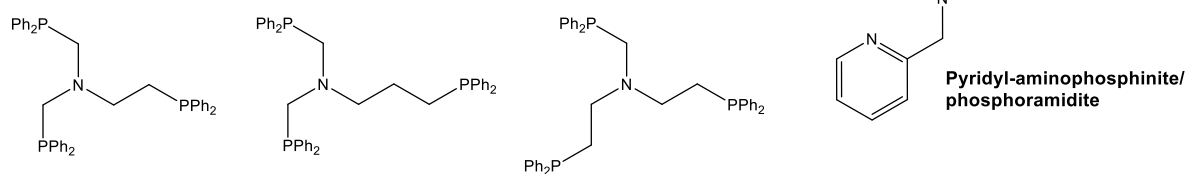


Figure 1.8. A survey of phosphine ligands utilised for the hydrogenation of levulinic acid.

1.3.1.1 Ruthenium catalysts for the hydrogenation of LA to GVL using molecular hydrogen

Most homogeneously catalysed hydrogenations of LA to GVL use ruthenium as the metal source. The ruthenium catalysts are generally prepared from a commercially available ruthenium precursor, such as $[\text{Ru}(\text{acac})_3]$ or $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$, and the vast majority use mono-, bi- or tridentate phosphine ligands (Figure 1.8). Table 1.4 provides an overview of the homogeneous Ru catalysts reported for LA hydrogenation under molecular hydrogen conditions with reaction conditions and results achieved. A chronological review of the major catalytic systems reported now follows.

In 1982 Osakada et al. reported the first quantitative hydrogenation of LA to GVL, using ruthenium complexes of triphenylphosphine (PPh_3) to hydrogenate a series of keto-acids. With $[\text{RuCl}_2(\text{PPh}_3)_3]$, a 99 % GVL yield was achieved in 24 hours at 180 °C and 12 bar H_2 (Table 1.4, Entry 1). The related catalyst $[\text{RuH}_2(\text{PPh}_3)_3]$ achieved a 58 % yield under the same conditions (Table 1.4, Entry 2). A rhodium analogue, $[\text{RhCl}(\text{PPh}_3)_3]$, gave almost zero conversion of LA to GVL. The authors suggested that it was the coordination of a carboxylate group to ruthenium which promotes the hydrogenation of the carbonyl, inducing ring closure to form the desired product.⁵⁹

More recently in 2008, Horvath et al. used in situ catalyst mixtures of $[\text{Ru}(\text{acac})_3]$ with phosphine ligands for LA hydrogenation. $[\text{Ru}(\text{acac})_3]$ and tri-*n*-butylphosphine (P^nBu_3), alongside NH_4PF_6 as additive, gave full conversion of LA to GVL in eight hours at 135 °C and 100 bar H_2 in neat conditions (Table 1.4, Entry 3). They also performed the reaction in water using the water-soluble phosphine ligand TPPTS (trisodium 3,3',3'-phosphinetriyltribenzensulfonate, Figure 1.8). An in situ mixture of $[\text{Ru}(\text{acac})_3]$ and TPPTS in water at 140 °C and 69 bar H_2 gave a 95 % GVL yield in 12 hours (Table 1.4, Entry 4).⁴²

Leitner et al. also used ruthenium catalysts made in situ from mixtures of $[\text{Ru}(\text{acac})_3]$ with the following phosphine ligands: monodentate tri-*n*-octylphosphine (P^nOct_3), bidentate DPPB (1,4-diphenylphosphinobutane) and tridentate Triphos (1,1,1-tris(diphenylphosphinomethyl)ethane). Full LA hydrogenation was achieved in each case. Using $[\text{Ru}(\text{acac})_3]$ with the monodentate P^nOct_3 ligand and additive NH_4PF_6 , they achieved > 99 % GVL yield at 160 °C and 100 bar H_2 , in neat conditions (Table 1.4, Entry 5). Increasing the temperature resulted in a mixture of GVL (56 %), 1,4-PDO and 2-MTHF.

Using the same conditions, the bidentate DPPB ligand achieved initially an 89 % GVL yield, plus 11 % 1,4-PDO (Table 1.4, Entry 6). Again, a temperature increase to 200 °C increased hydrogenation beyond GVL (39 % GVL yield). The tridentate Triphos ligand continued this trend: at 160 °C, the GVL yield was

just 8 %, and at 200 °C the GVL yield was 7 %. Changing directly from a monodentate ligand, to a bi-, and then tridentate ligand increased the conversion beyond GVL each time. This is attributed to the increased stability of the catalyst formed from the multidentate ligands inhibiting catalyst deactivation. The product distribution could be altered through addition of different acidic additives: NH_4PF_6 , *p*-TsOH, or ionic liquids. For example, using the Triphos ligand with *p*-TsOH in place of NH_4PF_6 brought the GVL yield from 8 % to 58 % (Table 1.4, Entry 7).⁶⁰

Miller et al. performed similar work using the less-studied tridentate N-Triphos^{Ph} ligand (N,N,N-tris(diphenylphosphinomethyl)amine, Figure 1.8). This is easier to synthesise than the carbon-centered Triphos ligand and can be more readily modified to include different phosphine substituents. Again, full LA conversions were achieved in all cases. Using an in situ mixture of $[\text{Ru}(\text{acac})_3]$ and N-Triphos at 150 °C and 65 bar H_2 , a 60 % GVL yield was achieved in 25 hours (Table 1.4, Entry 8). The preformed Ru catalyst $[\text{RuH}_2(\text{CO})(\text{NP}_3^{\text{Ph}})]$ was also highly active, in which the N-Triphos ligand binds in a tridentate fashion. A 95 % GVL yield was obtained with NH_4PF_6 as the additive (Table 1.4, Entry 10); with *p*-TsOH, 77 % GVL was achieved. The slightly modified catalyst $[\text{RuH}_2(\text{PPh}_3)(\text{NP}_3^{\text{Ph}})]$ gave a 68 % GVL yield, again using NH_4PF_6 (Table 1.4, Entry 11).⁶¹

Palkovits et al. took this further to survey a series of N-Triphos^{Ph} ligands – both the eponymous symmetrical N-Triphos ligand and unsymmetrical analogues with arms of different chain length (Figure 1.8). In situ mixtures of the N-Triphos ligands with different Ru precursors at 160 °C and 70 bar H_2 afforded GVL yields in the range 2-97 % in 18 hours. Surprisingly, it was found that $[\text{Ru}(\text{acac})_3]$ in the absence of phosphine ligand achieved 99 % GVL yield (Table 1.4, Entry 12). Generally, Cl or CO containing precursors ($\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$) gave higher yields of GVL relative to the other hydrogenation products, attributable to a detrimental effect of the Cl and CO coordinating groups. The highest GVL yield of 97 % was achieved using either $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ or $[\text{Ru}(\text{COD})(\text{methylallyl})_2]$ alongside the unsymmetrical N-Triphos ligand with two methylene arms and one ethylene arm (Table 1.4, Entries 13-14).⁶²

Mika et al. investigated a range of electron-donating, water-soluble sulfonated ligands of the general formula $\text{R}_n\text{P}(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})_{3-n}$ ($n = 1$ or 2 , $\text{R} = \text{Me}, \text{Pr}, \text{}^i\text{Pr}, \text{Bu}, \text{Cp}$). Using an in situ mixture of $[\text{Ru}(\text{acac})_3]$ and the phosphine ligand without additives or solvents, at 140 °C and 100 bar H_2 , the best result was achieved using the Bu-DPPDS ligand: > 99.9 % GVL yield in 1.8 hours, and a high turnover number of 6,370 (Table 1.4, Entry 15). Generally, the ligands with the electron donating alkyl substituents obtained significantly higher yields than the use of the ligand TPPTS (which lacks an alkyl substituent on its phosphine). The same yield and TON were obtained using the Bu-DPPDS ligand with a reduction

in pressure to 10 bar, in 4.5 hours (Table 1.4, Entry 16). The methyl analogue Me-DPPDS achieved GVL yields of 96.2 and 69.5 % at 100 and 10 bar respectively (Table 1.4, Entry 17).⁶³

The same group went on to study the series of chelating bidentate phosphine ligands $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1-6$) in situ with $[\text{Ru}(\text{acac})_3]$. The number of methylene spacers between the two phosphines was found to have a significant effect on the catalyst activity, owing to the size of the chelating ring formed in the resulting catalyst. The optimum ligand was DPPB (1,4-bis(diphenylphosphino)butane, $n = 4$) with a >99.9 % GVL yield in 1 hour at 140 °C and 100 bar H_2 . The GVL yields sharply dropped off with both shorter and longer carbon chains ($n=2$, 1.8 %; $n=3$, 57.5 %; $n=5$, 51.2 %; $n=6$, 25.3 %). Using DPPB, the authors found that the pressure could be reduced to 50 bar H_2 without affecting the GVL conversion (Table 1.4, Entry 18). Whilst reducing the temperature below 140 °C significantly reduced the conversions achieved, full conversion was achieved within 0.6 hours at 160 °C, giving a very high TOF of 21,233 h^{-1} (Table 1.4, Entry 19). The solvent and additive-free conditions, plus the ability to recycle the catalyst for 10 consecutive runs, were touted as strong green credentials.⁶⁴

Kuhn et al. surveyed a range of different water-soluble phosphine ligands for LA hydrogenation in the aqueous phase. TPPMS and TPPTS are shown in Figure 1.8; the remaining ligands are shown in Figure 1.9. Their system used $[\text{Ru}(\text{acac})_3]$ at 140 °C and 50 bar H_2 . With their two least-bulky ligands Tris(2-carboxyethyl) phosphine and 1,3,5-Triaza-7-phosphaadamantane (PTA), relatively low conversions of 62 and 34 % were achieved in 21 hours. Additionally, the ligands Tris(2,4-dimethyl-5-sulfophenyl) phosphine trisodium salt (TXTPS) and [2-(dicyclohexylphosphino)ethyl] trimethylammonium chloride gave conversions of 26 and 84 % in the same reaction time. However, the most successful catalysts used the sterically demanding TPPMS (3-(diphenylphosphino)benzenesulfonic acid sodium salt) and TPPTS (3,3',3''-Phosphinidynetris(benzenesulfonic acid) trisodium salt). These reached conversions of 94 and 97 % in five hours, or 100 % after 21 hours (Table 1.4, Entries 21-22). The authors believed that the bulkier ligands formed complexes with a larger free site for substrate coordination. Comparing the steric and electronic properties of the ligands, they identified that their steric bulk had a much larger effect on catalyst activity than their electronic properties. Similar to the result described by Palkovits et al.⁶², $[\text{Ru}(\text{acac})_3]$ in the absence of phosphine ligand achieved full conversion within five hours (Table 1.4, Entry 20). Owing to the discolouration and formation of solid black particles observed, they attributed this to the formation of ruthenium clusters, i.e. the system switches to heterogeneous catalysis in the absence of ligand.⁴³

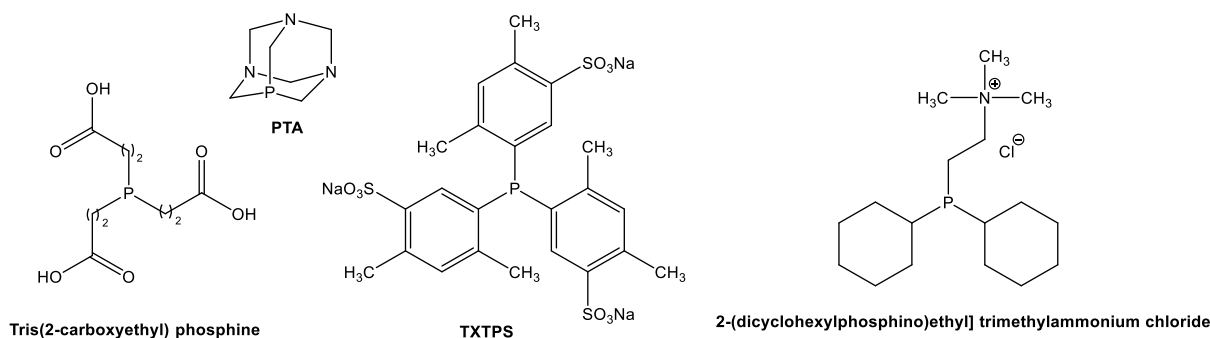


Figure 1.9. Water-soluble phosphine ligands applied by Kuhn et al.

Beller et al. performed a wide study on the effect of ligand, additive and substrate for the hydrogenation of both LA and its methyl ester methyl levulinate (ML). Initially, the most promising multidentate PPh_2 -containing ligands were (bis(2-diphenylphosphinoethyl)phenylphosphine), TPP $\{[(\text{phenylphosphinediyl})\text{bis}-(2,1\text{-phenylene})]\text{bis}(\text{methylene})\}\text{bis}-(\text{diphenylphosphine})$, and Tetraphos (tris[2-(diphenylphosphino)ethyl]phosphine). The authors identified a constructive role of the “ $\text{CH}_2\text{-PPh}_2$ ” moiety present in these ligands. The acidic additives *p*-toluenesulfonic acid (PTSA) and $\text{Sc}(\text{OTf})_3$ were the most effective, even in catalytic amounts. For ML, the highest GVL yield achieved was 95 %, after 22 hours at 140 °C and 80 bar H_2 , in solvent free conditions using PTSA additive. Under the same conditions for LA, the highest GVL yield was 73 % in 96 hours, using $\text{Sc}(\text{OTf})_3$ as the additive; a very high TON of 73,142 was achieved owing to the use of just 0.001 mol% $[\text{Ru}(\text{acac})_3]$ (Table 1.4, Entry 23).⁶⁵

Darkwa et al. studied the use of phosphite ($\text{P}(\text{OR})_3$) and phosphinite ($\text{P}(\text{OR})\text{R}_2$) ligands. Ruthenium catalysts of both pyrazolylphosphite (containing the group $-\text{O-P}(\text{OEt})_2$) and pyrazolylphosphinite (containing the group $-\text{O-PPh}_2$) ligands were prepared from $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ and cationic analogues of each were formed through reactions with both NaBARf and NaBPh₄. Testing all six catalysts at 120 °C and 20 bar H_2 in neat conditions, with KOH additive, gave LA conversions in the range of 73-100 % in 16 hours. In every case the reactions had 100 % selectivity for GVL. The cationic catalysts containing BARf anions performed better than those with BPh₄ anions, attributed to a better solubility of the more polar fluorine-containing species in LA. The most successful catalyst was the cationic complex of the pyrazolylphosphinite ligand, with BARf anion. Using this catalyst, the conditions were optimised to 110 °C and 15 bar H_2 with no reduction in conversion achieved (Table 1.4, Entry 25). The presence of KOH additive was crucial to achieve high conversions. The role of the base was considered to accelerate H_2 heterolysis and to neutralise the HCl formed during the reaction. The catalyst could be recycled three times without significant loss of activity.⁶⁶

Fischmeister et al. have studied the use of dipyridylamine (dpa) ligands in hydrogenation catalysts. Generally, their iridium catalysts have better activity. However, a dicationic ruthenium complex of dpa, [(dpa)- (*p*-cymene)RuOSO₃], formed through sulfonation with Ag₂SO₄ resulting in the coordination of a sulfonate (OSO₃⁻) anion. The complex had an unusual zwitterionic structure. 92 % conversion of LA to GVL was achieved in water at 130 °C and 5 bar H₂ over 16 hours (Table 1.4, Entry 26). Reducing the temperature to 110 °C gave only 13 % conversion. Replacing the coordinating sulfonate anion for the non-coordinating PF₆ anion had a detrimental effect on the conversion achieved with the Ru catalyst, with a maximum of 13 %.⁶⁷

Wildeman et al. achieved successful hydrogenation of LA to GVL using the ruthenium-based Shvo's catalyst. At 50 bar H₂ and 100 °C in toluene, 99 % GVL yield was achieved in 16 hours (Table 1.4, Entry 27). At 25 bar H₂, 43 % yield was achieved in five hours. However, changing toluene for isopropanol led to no GVL production.⁶⁸ The authors extended their study to use a series of Shvo-type catalysts: [2,3,4,5-Ph₄(η⁴-C₄CO)]Ru(CO)₃, {[2,3,4,5-Ph₄(η⁴-C₄CO)]₂H}Ru₂(CO)₄-(μ-H) and {[2,3,4,5-Ph₄(η⁴-C₄CO)]Ru(CO)₂]₂ (Figure 1.10). In solventless conditions at 100 °C and 50 bar H₂, the monomeric catalyst achieved a GVL yield of 63 % in five hours, whilst both dimeric catalysts achieved yields > 99 % (Table 1.4, Entries 28-29). They attributed this to a need for the monomeric catalyst to be activated by decarbonylation, whilst the dimeric species readily dissociate into monomeric species which take part in the catalytic cycle. With the monomeric catalyst, they were able to achieve near-complete conversion by optimising the conditions to 120 °C and 50 bar H₂. Whilst the dimeric species finish their reactions one hour earlier than the monomeric catalyst, the reactions are otherwise identical. It was found that catalyst recycling was possible with EL, but not with LA. This was attributed to the co-production of water from LA, considered to be destructive for the catalyst.

The authors presented a reaction mechanism which shows the positions of each catalyst (Scheme 1.5). The monomeric catalyst accesses the reaction cycle via oxidative decarbonylation. Homolytic or heterolytic dissociation of the two dimeric catalysts accesses one of two entry points into the catalytic cycle. Generally, H₂ association generates both proton and hydride moieties on the catalyst. Following LA coordination in an outer-sphere mode, the proton and hydride concertedly transfer to the ketone of LA, generating first 4-HVA and then GVL.⁶⁹

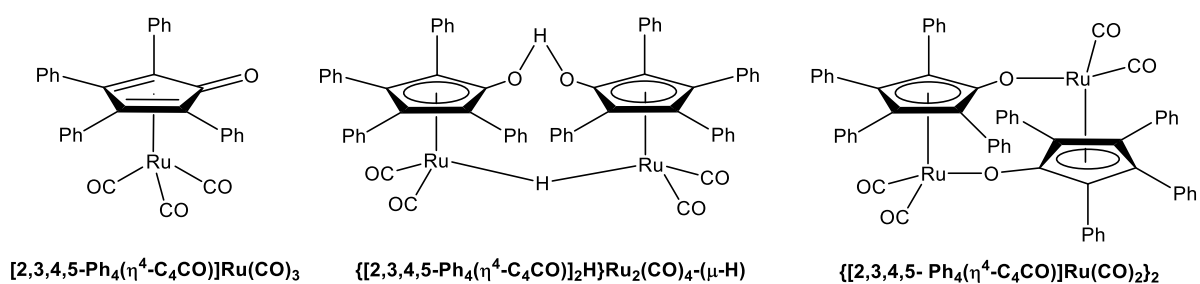
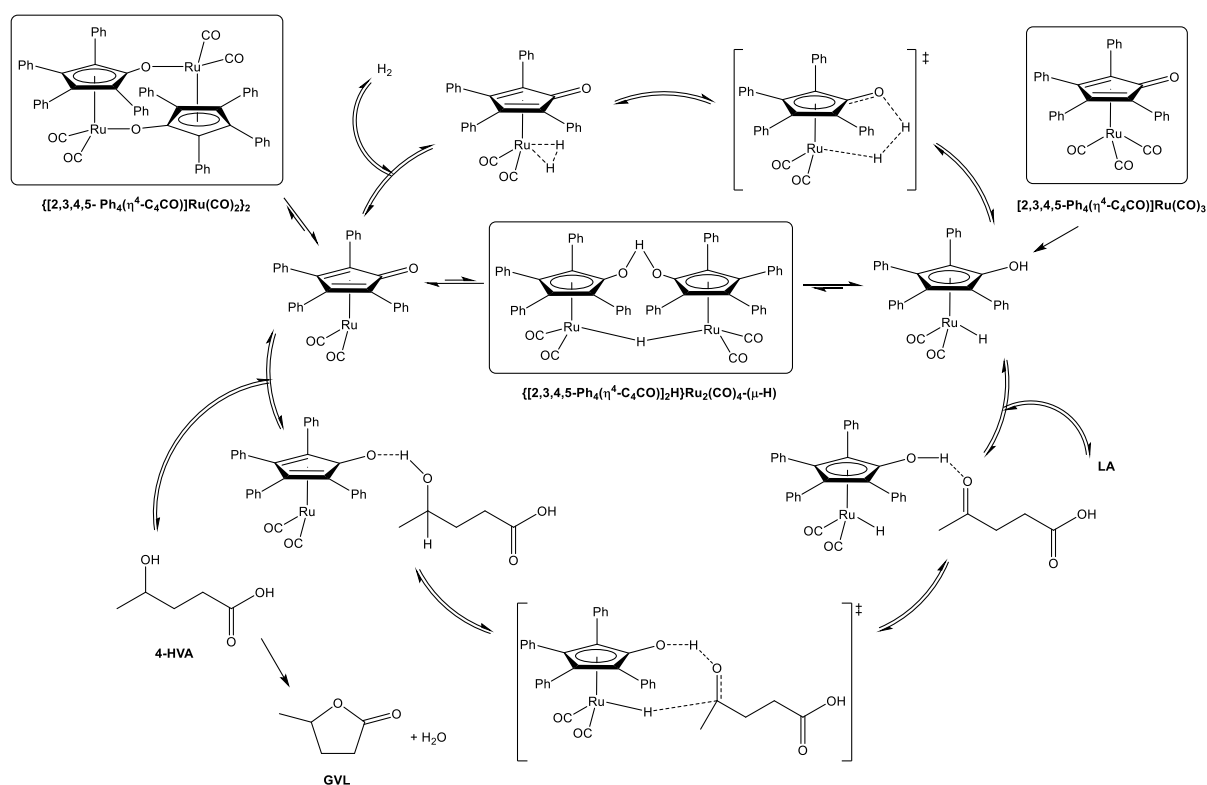


Figure 1.10. Shvo-type catalysts investigated by Wildeman et al.⁶⁹



Scheme 1.5. Catalytic cycle for LA hydrogenation with Shvo-type catalysts.⁶⁹

Table 1.4. Ruthenium catalytic systems for LA hydrogenation with molecular hydrogen gas.

Entry	Catalyst	T [°C]	P(H ₂) [bar]	S/C	Time [h]	Additives	GVL yield [%]	TON	TOF [h ⁻¹]	Ref.
1	[RuCl ₂ (PPh ₃) ₃]	180	12	181	24	-	99	180	7	59
2	[RuH ₂ (PPh ₃) ₄]	180	12	181	24	-	58	105	4	59
3	[Ru(acac) ₃]/PBU ₃	135	100	1,660	8	NH ₄ PF ₆	100	1,660	195	42
4	[Ru(acac) ₃]/TPPTS	140	69	600	12	-	95	570	48	42
5	[Ru(acac) ₃]/POct ₃	160	100	1,000	18	NH ₄ PF ₆	>99	1,000	56	60
6	[Ru(acac) ₃]/DPPB	160	100	1,000	18	NH ₄ PF ₆	89	890	49	60
7	[Ru(acac) ₃]/Triphos	160	100	1,000	18	p-TsOH	58	580	32	60
8	[Ru(acac) ₃]/N-Triphos	150	65	200	25	-	60	120	5	61
9	[Ru(H) ₂ (CO)(Triphos)]	150	65	200	25	-	85	170	7	61
10	[Ru(H) ₂ (CO)(N-Triphos)]	150	65	200	25	NH ₄ PF ₆	95	190	8	61
11	[Ru(H) ₂ (PPh ₃)(N-Triphos)]	150	65	200	25	NH ₄ PF ₆	68	136	5	61
12	[Ru(acac) ₃]	160	70	500	18	-	99	495	28	62
13	[Ru(H) ₂ (CO)(PPh ₃) ₃]/ asymm. N-Triphos	160	70	500	18	-	97	485	27	62
14	[Ru(COD)(methylallyl)]/ asymm. N-Triphos	160	70	500	18	-	97	485	27	62
15	[Ru(acac) ₃]/Bu-DPPDS	140	100	6,370	1.8	-	>99.9	6,370	3,539	63
16	[Ru(acac) ₃]/Bu-DPPDS	140	10	6,370	4.5	-	>99.9	6,370	1,416	63
17	[Ru(acac) ₃]/Me-DPPDS	140	100	6,370	1.8	-	96.2	6,128	3,404	63
18	[Ru(acac) ₃]/DPPB	140	50	12,740	1.8	-	>99.9	12,740	7,077	64
19	[Ru(acac) ₃]/DPPB	160	100	12,740	0.6	-	>99.9	12,740	21,233	64
20	[Ru(acac) ₃]	140	50	600	5	-	94	564	113	43
21	[Ru(acac) ₃]/TPPMS	140	50	600	5	-	97	582	116	43
22	[Ru(acac) ₃]/TPPTS	140	50	600	5	-	98	588	118	43
23	[Ru(acac) ₃]/Tetraphos	140	80	100,000	96	Sc(OTf) ₃	73	73,142	762	65
24	[Ru(<i>p</i> -cymene)Cl-(L1)][BARF]	120	20	1,000	16	KOH	84	840	53	66
25	[Ru(<i>p</i> -cymene)Cl(L2)][BARF]	110	15	1,000	12	KOH	100	1,000	83	66
26	[(dpa)(<i>p</i> -cymene)RuOSO ₃]	130	5	1,000	16	-	92	920	58	67
27	Shvo's catalyst	100	50	100	16	-	99	99	6	68
28	Shvo's catalyst	100	50	1,000	5	-	99.5	995	199	69
29	{[2,3,4,5-Ph ₄ (η ⁴ -C ₄ CO)]Ru(CO) ₂] ₂ }	100	50	1,000	5	-	99.1	991	198	69

1.3.1.1.1 Ruthenium catalysts for the hydrogenation of LA to optically active GVL using molecular hydrogen

The ruthenium catalysts described thus far generate racemic GVL. However, some applications require optically-pure GVL, including the food, fragrance, agricultural and pharmaceutical industries.^{70–72} A small number of homogeneous ruthenium catalysts have been developed to produce optically-pure GVL, primarily using chiral phosphine ligands. These systems will be briefly discussed in this Section, with results collated in Table 1.5.

An early example was reported by Noyori et al. in 1990, using the chiral diphosphine BINAP ligand ((2,2'-bis(diphenylphosphino)-1,1'-binaphthyl)). The catalyst containing (S)-BINAP generates the (S)-enantiomer; the catalyst containing (R)-BINAP generates the (R)-enantiomer. Generating their catalyst in situ from $\text{Ru}(\text{OCOCH}_3)_2(\text{BINAP})$ and HCl, the authors achieved a 96 % GVL yield and 99.5 % enantiomeric excess after 110 hours at 101 bar H_2 and 30 °C, from the ethyl ester of LA, ethyl levulinate (EL) (Table 1.5, Entry 1).⁷³

Sanniccolo et al. used the chiral biheteroaromatic diphosphine tetra-Me-BITOP ligand, chosen for its very electron rich nature. Using $[(\text{tetra-Me-BITOP})\text{Ru}(\text{CF}_3\text{COO})_2]$, at 100 bar H_2 and 50 °C, they achieved a 98 % ee. of GVL from EL in 76 hours (Table 1.5, Entry 2). To their initial surprise, adding 1-bromobutane resulted in a 98 % ee. after just 43 hours (Table 1.5, Entry 3). This effect was attributed to partial hydrogenolysis of the bromobutane, supplying the starting Ru complex with the acidity required to transform into a more active catalytic species.⁷⁴

Vinogradov et al. surveyed a series of Ru-BINAP catalysts for the asymmetric hydrogenation of LA and its esters. Their most active $[\text{RuCl}_2(\text{BINAP})]$ catalyst was generated in situ from the precursor $[\text{Ru}(\text{COD})(\text{methylallyl})_2]$. At 60 °C and 60–70 bar, 100 % conversion of EL was achieved in five hours (95 % GVL, 5 % γ -hydroxy ester), with a 99 % ee. (Table 1.5, Entry 4). At just 25 °C, 100 % conversion (85 % GVL, 15 % γ -hydroxy ester) and 99.5 % ee. could still be obtained over 18 hours (Table 1.5, Entry 5). With LA itself, a lower 69 % conversion was achieved (95 % GVL, 5 % γ -hydroxy ester), at 98.5 % ee. (Table 1.5, Entry 6). The authors considered that LA might be first esterified by the reaction solvent, ethanol. They also found that the conversions achieved decreased going from ethyl levulinate (100 %), to propyl levulinate (84 %), to butyl levulinate (66 %) i.e. with increasing chain length of the alkoxy fragment. This was attributed to a reduced extent of ester cyclisation proceeding with the longer chains. The incorporation of HCl was important, with a $[\text{HCl}]:[\text{Ru}]$ ratio of 10 found as the most effective. They considered that HCl was involved in activating the keto group of the coordinated substrate.⁷⁵

The same group went on to study the enantioselective hydrogenation reactions of a wider range of substrates. With RuCl_3 , BINAP and HCl, full conversion of ML was achieved in six hours at 15 bar H_2 and 65 °C to give 81 % GVL with 99.5 % ee (Table 1.5, Entry 7). Again, a $[\text{HCl}]:[\text{Ru}]$ ratio = 10 was most effective. Increasing the pressure to 60 bar gave a greater selectivity for GVL: 96 % GVL and 99 % ee. (Table 1.5, Entry 8). Increasing the temperature did not have a significant effect on conversion or product distribution. However, changing anhydrous RuCl_3 to $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ much reduced the selectivity for GVL over the γ -hydroxy ester product. Additionally, the solvent had a large effect: methanol and ethanol were highly effective, whilst aprotic solvents gave much poorer results. The authors reported that polar protic solvents facilitates the hydrolysis of H_2 coordinated to Ru, resulting in a catalytically active metal hydride intermediate.⁷⁶

The authors went on to perform in-depth kinetic studies on the $[\text{Ru}(\text{COD})(\text{methylallyl})_2\text{-BINAP-HCl}]$ system. They found that the kinetic order in both H_2 and catalyst is equal to 1, whilst the order in both substrate and HCl fell from 1 to 0 with increasing starting concentration. The mechanism was considered to involve fast and reversible heterolysis of H_2 , followed by the rate-determining step of irreversible hydride transfer to the protonated keto group of the substrate.⁷⁷

Mika et al. surveyed a range of chiral Ru catalysts for the direct asymmetric hydrogenation of LA to GVL. Using $[\text{Ru}(\text{acac})_3]$ and BINAP at 60 bar H_2 and 140 °C, 100 % conversion was achieved over 12 hours, but only at 26 % ee (Table 1.5, Entry 9). Using a propeller stirrer for more effective mixing achieved full conversion in just 2.5 hours, but the ee. remained low at 23 %. However, favourable solventless conditions were used. The addition of chiral (R,R-DPEN) ((1,2-Diphenylethylenediamine)) only brought the ee up to 26.4 %.

A range of SEGPHOS-based Ru catalysts were also trialled. These achieved conversions in the range 95-100 %, with ee values in the range of 9 – 56 % at 140 °C and 60 bar H_2 over 20 hours. The most successful was (S)- $[(\text{RuCl}(\text{SEGPHOS}))_2(\mu\text{-Cl})_3][\text{NH}_2\text{Me}_2]$, achieving 100 % conversion and 56 % ee. Subsequently, a range of variables was investigated. Higher enantioselectivities were achieved in protic solvents, with methanol the most successful. Reduction of LA to GVL with HCl in an alcohol solvent was considered to proceed through in situ formation of the corresponding alkyl ester. A minimum temperature of 140 °C was necessary. Furthermore, the Ru concentration had a large effect on the enantioselectivity achieved. At $[\text{Ru}] = 0.002 \text{ mol dm}^{-3}$, just 17 % ee was achieved; at $[\text{Ru}] = 0.016 \text{ mol dm}^{-3}$, 82 % ee was achieved (at 60 bar H_2 , 150 °C, 20 hours) (Table 1.5, Entry 10). Interestingly, using “real” biomass waste (wheat straw, rice husk, corn straw, nut and pea-pod) produced (S)-GVL from LA with 100 % conversion in 80 % ee.⁴⁸

Earlier this year, Yan, Xie et al. reported a system for asymmetric hydrogenation of γ - and δ -ketoacids to enantiomerically pure γ - and δ -lactones using an iridium catalyst system. Their chiral spiro Ir catalyst, Ir(S)-SpiroPAP, was successful for hydrogenating a wide range of ketoacids at very mild conditions (10 bar H₂, RT, with KO^tBu, for two hours). Although an 87 % yield was achieved with LA, the ee was only 56 % (Table 1.5, Entry 11).⁷⁸

Table 1.5. Ruthenium catalytic systems for enantioselective LA hydrogenation with molecular hydrogen gas.

Entry	Catalyst	T [°C]	P(H ₂) [bar]	S/C	Time [h]	Additives	GVL yield [%]	TON	TOF [h ⁻¹]	Ref.
1 ^a	[Ru(OCOCH ₃) ₂ (BINAP)]	30	101	1,015	110	HCl	96 % 99.5 % ee	974	9	⁷³
2 ^a	[(tetra-Me-BITIOP)Ru(CF ₃ COO) ₂]	50	100	500	76	-	100 % 98 % ee	500	7	⁷⁴
3	[(tetra-Me-BITIOP)Ru(CF ₃ COO) ₂]	50	100	500	43	1-bromobutane	100 % 98 % ee	500	12	⁷⁴
4 ^a	[Ru(COD)(MA) ₂]/BINAP	60	60-70	200	5	HCl	95 % 99 % ee	190	38	⁷⁵
5 ^a	[Ru(COD)(MA) ₂]/BINAP	25	60-70	200	18	HCl	85 % 99.5 % ee	170	9	⁷⁵
6	[Ru(COD)(MA) ₂]/BINAP	60	60	200	5	HCl	66 % 98.5 % ee	132	26	⁷⁵
7 ^b	RuCl ₃ /BINAP	65	15	200	6	HCl	81 % 99.5 % ee	162	27	⁷⁶
8 ^b	RuCl ₃ /BINAP	65	60	200	6	HCl	96 % 99 % ee.	192	32	⁷⁶
9	[Ru(acac) ₃]/BINAP	140	60	9,850	2.5	(R,R-DPEN)	100 % 26.4 % ee	9,850	3,940	⁴⁸
10	[(RuCl(SEGPHOS)) ₂ (μ-Cl) ₃][NH ₂ Me ₂]	150	60	438	20	-	100 % 82 % ee	438	22	⁴⁸
11	Ir(S)-SpiroPAP	25	10	1,000	2	KO ^t Bu	87 % 56 % ee	870	435	⁷⁸

^a Ethyl levulinate (EL) used as feedstock. ^b Methyl levulinate (ML) used as feedstock.

1.3.1.2 Iridium catalysts for the hydrogenation of LA to GVL using molecular hydrogen

After ruthenium, iridium is the most applied metal centre for homogeneous catalysis of LA to GVL. Key examples are collated in Table 1.6.

Zhou et al. studied iridium complexes formed in situ from $[\text{Ir}(\text{COE})_2\text{Cl}]_2$ and pincer ligands of the type PNP, PNN, NNN and PCP (Figure 1.11). Their tridentate coordination, through formation of two stable 5-membered chelating metallacycles, generated robust catalysts. The hydrogenation of LA to GVL was tested at 50 bar H_2 and 100 °C in ethanol alongside KOH. The ligands of the type PNP-1, PNN and NNN performed well, with GVL yields in the ranges of 33–99% (PNP-1), 89% (PNN) and 88–94% (NNN) in 15 hours. The other pincer ligands gave low GVL yields of <30 %. The success of the pyridine-based PNP and PNN ligands was attributed to the existence of accessible aromatisation-dearomatisation pathways. The PCP and PNP-2 type ligands lack the pyridinyl-methylene moiety considered important for this method of metal-ligand cooperation. Further, the organic substituent on the ligand was important, with $\text{R} = \text{}^t\text{Bu}$ or $\text{}^i\text{Pr}$ on PNP-1 giving the highest yields of 96 % and 99 % respectively (Table 1.6, Entries 1-2). Whilst the NNN ligands achieved high yields, iridium black formation suggested the operation of a heterogeneous system.

The PNP-1 type ligand with $\text{R} = \text{}^t\text{Bu}$ was used to optimise the process. Alcohols, principally ethanol, were the most effective solvents. Strong bases (KOH, NaOH, LiOH) were essential to achieve high yields. Reducing the temperature or pressure led to reductions in yield, but the effect was far more drastic for temperature than for pressure.

To study the effect of chloride in the reactions, which is considered to suppress catalytic activity, the authors prepared two preformed complexes of the ligand PNP-1($\text{}^t\text{Bu}$): an iridium chloride dihydride complex, $[\text{IrH}_2\text{Cl}(\text{PNP}(\text{}^t\text{Bu}_2))]$, and an iridium trihydride complex, $[\text{IrH}_3(\text{PNP}(\text{}^t\text{Bu}_2))]$. The structures of these are shown in Figure 1.12. At 50 bar H_2 and 100 °C, in ethanol with KOH and a S/C ratio of 10,000, an 82 % GVL yield was achieved with the chloride dihydride complex in 80 hours (Table 1.6, Entry 3). This was higher than the corresponding reaction using an in situ mixture at that S/C ratio. However, the trihydride complex achieved a 98 % yield in just 24 hours under the same conditions, indicating that chloride indeed has a negative effect (Table 1.6, Entry 4). After reducing the S/C ratio to 100,000, at 100 bar H_2 a 71 % yield was achieved in 48 hours, giving a very high TON of 71,000 (Table 1.6, Entry 5).⁷⁹

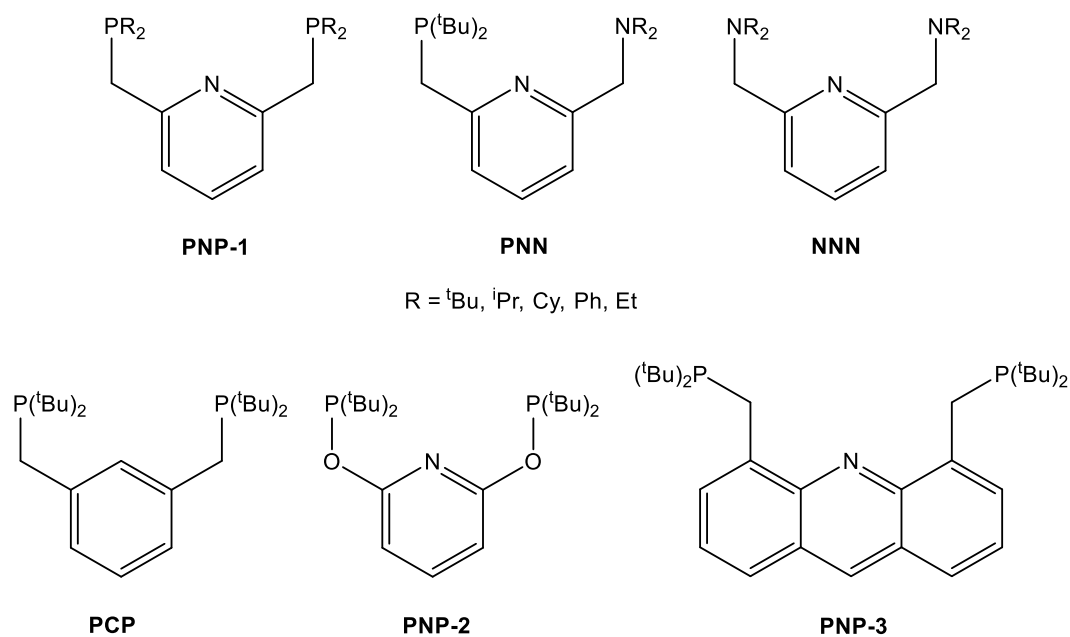


Figure 1.11. PNP, PNN, NNN and PCP pincer ligands studied by Zhou et al.⁷⁹

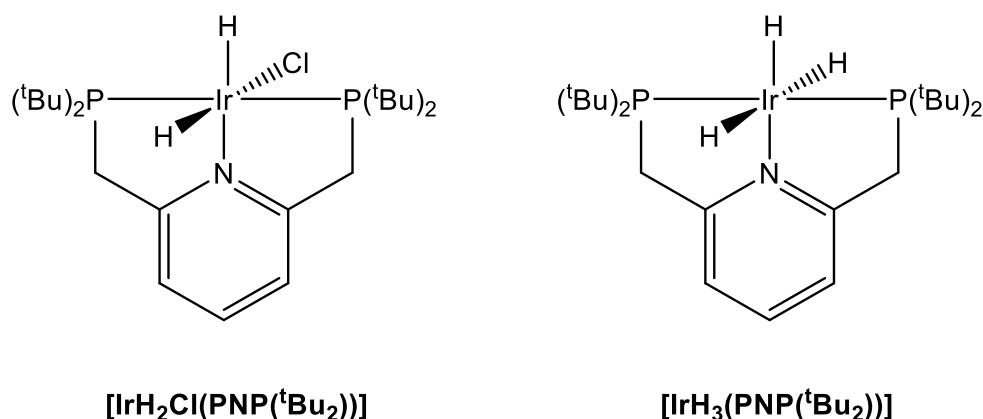


Figure 1.12. Iridium complexes of PNP-ligands studied by Zhou et al.⁷⁹

Fu et al. studied a series of water-soluble half-sandwich iridium complexes based on bidentate bipyridine ligands (Figure 1.13). They surveyed a series of substituted and unsubstituted bipyridine ligands to investigate the steric and electronic effects of different substituents ($\text{R} = \text{OMe}, \text{OH}, \text{COOH}$). At 10 bar and 120 °C in water, the iridium complex of the unsubstituted 2,2'-bipyridine ligand gave a 31 % GVL yield in four hours. Adding one or two carboxyl groups to the ligand reduced the GVL yield significantly (to a maximum of 11 %). They considered electron withdrawing groups to reduce the catalyst activity.

With 4,4'-dihydroxy-2,2'-bipyridine, the yield increased to 96 %, and with 4,4'-dimethoxy-2,2'-bipyridine, the yield reached 98 % (Table 1.6, Entry 6). Placing the same electron-donating groups in ortho-positions (6,6'-dihydroxy-2,2'-bipyridine or 6,6'-dimethoxy-2,2'-bipyridine) reduced the yields achieved, attributed to steric hindrance. Furthermore, with 6,6'-dihydroxy-2,2'-bipyridine, they considered that dehydrogenation was taking place, further reducing the GVL yield. Using the most effective catalyst (that with 4,4'-dimethoxy-2,2'-bipyridine), a reduction in catalyst loading to 0.001 mol% still achieved a 78 % GVL yield in 36 hours, giving a very high TON of 78,000 (Table 1.6, Entry 7). The catalyst could be recycled for five runs without a significant decrease in activity.⁸⁰

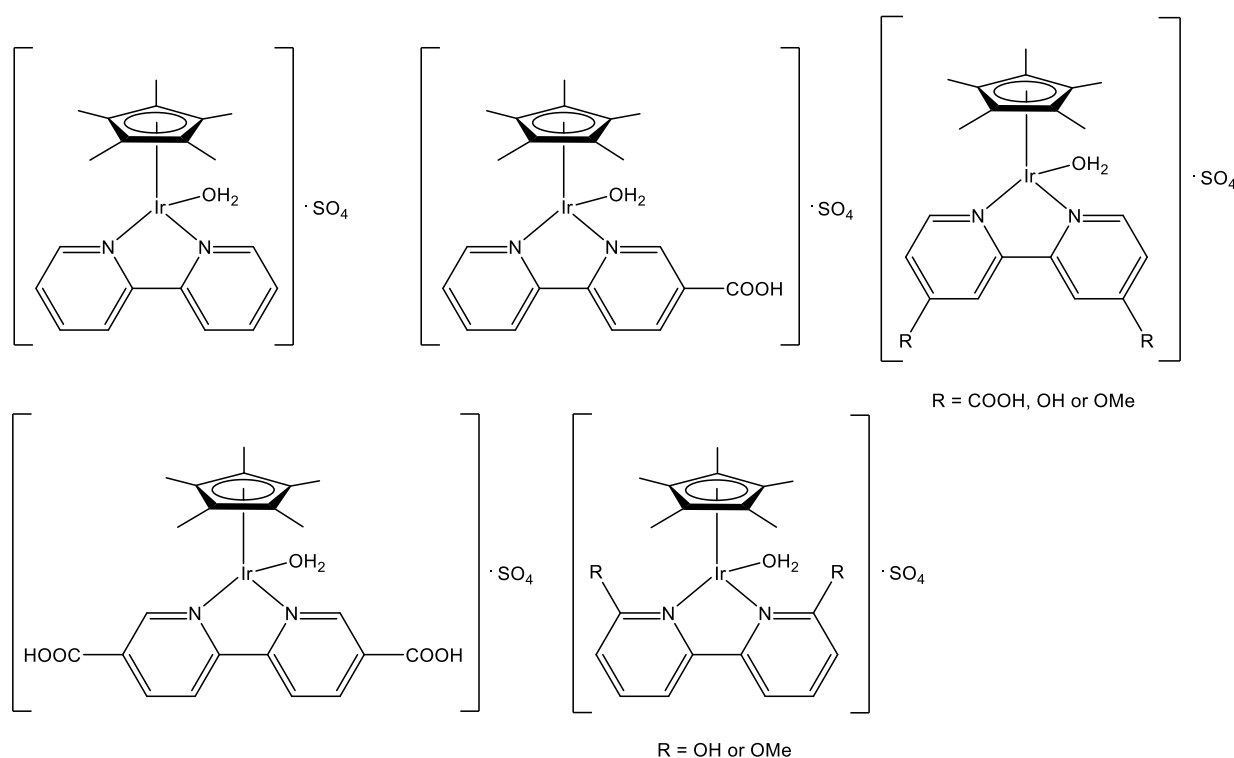
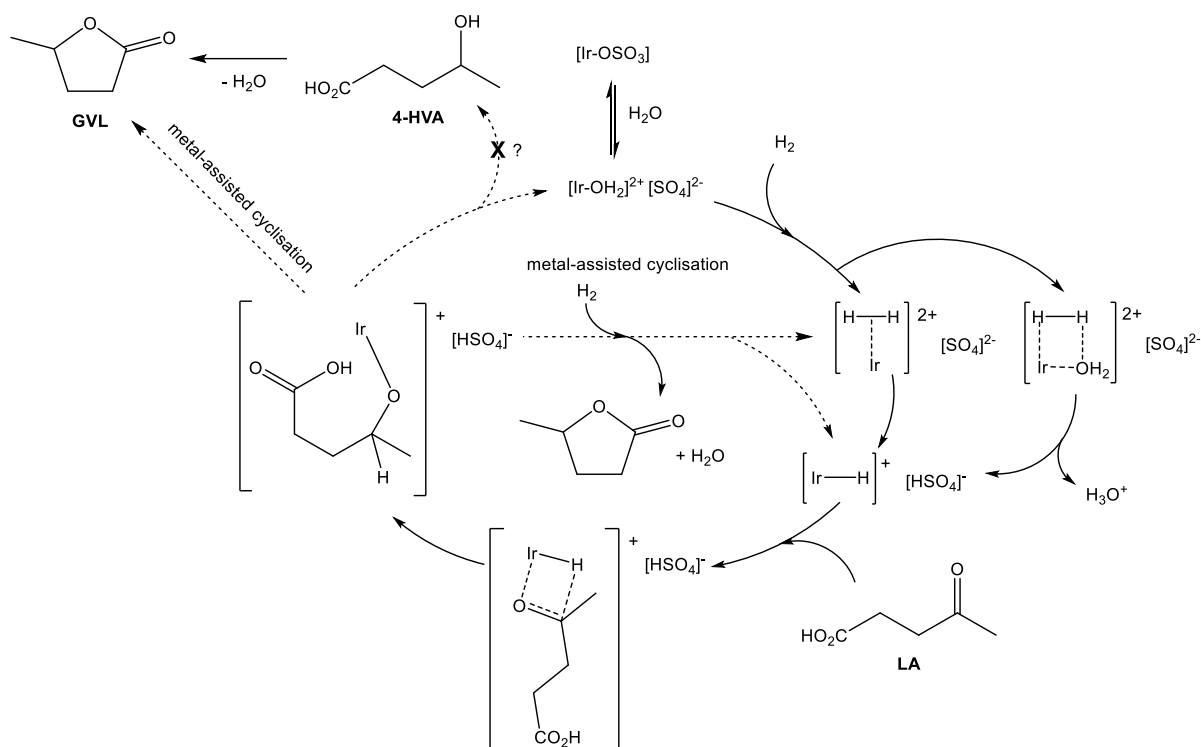


Figure 1.13. Half-sandwich iridium complexes studied by Fu et al.⁸⁰

Some work by Fischmeister et al. describing ruthenium catalysts containing dipyriddyamine (dpa) ligands was described in 1.3.1.1. Iridium catalysts from the same study were more active. Starting with complexes of the form $[\text{Cp}^*\text{Ir}(\text{dpa-R})\text{Cl}]^+\text{Cl}^-$ ($\text{R} = \text{H}$ or CH_2Ph), they intended to form dicationic versions by abstracting the chloride ligand through reaction with silver sulfate. The removal of the chloride to generate an available coordination site was considered as beneficial in terms of catalytic activity. Unexpectedly, their products were not found as dicationic aquo complexes, but rather as zwitterionic complexes with a coordinated sulfato ligand, of the form $[(\text{dpa-R})\text{Cp}^*\text{Ir}(\text{OSO}_3)]$.

The more effective catalyst was [(dpa)Cp*Ir(OSO₃)] (R = H). At 130 °C and 40 bar H₂ in water without additives, 100 % conversion was achieved in 16 hours. With reduction to 110 °C and 5 bar H₂, full conversion was still achieved, and reducing further to 2 bar H₂ still reached 90 % conversion. Reducing the catalyst loading from 0.1 mol% to 0.05 mol% achieved full conversion in 16 hours at 110 °C and 5 bar H₂ (Table 1.6, Entry 8). At 0.01 mol% loading, full conversion was achieved in 72 hours, and even at 0.0005 mol% loading, 87 % conversion was achieved in 72 hours at 130 °C (Table 1.6, Entries 9-10), giving a very high TON = 174,000. The catalyst could be recycled three times without a significant reduction in activity. The dpa analogue with R = CH₂Ph was less successful, with a maximum conversion of 30 %. Furthermore, GVL was made from glucose and fructose in 57 % and 53 % overall isolated yields respectively, at 130 °C and 5 bar H₂ in 32 hours. The relatively low yields were attributed to incomplete LA conversion and the formation of intractable humins.

The authors went on to discuss the mechanism of the hydrogenation reaction (Scheme 1.6). Generally, η^2 -H₂ complexes are considered as starting intermediates. These can generate either dihydride complexes, through homolytic cleavage, or monohydride complexes through heterolytic cleavage. In this case, monohydride species were identified. The authors suggested two possible routes to the Ir-H species. Either the η^2 -H₂ complex is deprotonated by a weak base, i.e. (SO₄)²⁻, or a σ -bond metathesis might take place with a coordinated water molecule. The latter route does not involve a base (other than H₂O). Following coordination of LA through its ketone oxygen, further hydride transfer to the electrophilic ketone carbon generates an iridium alkoxo complex. It is generally considered that protonation of this species generates 4-HVA, which subsequently generates GVL through intramolecular transesterification. However, in this study, as well as in those of others, HVA was not observed in any experiment.⁶⁶ This suggests an alternative mechanism can take place without first forming the 4-HVA intermediate; the authors suggested an intramolecular metal-assisted cyclisation involving activation of the carboxylic moiety by iridium to form GVL directly.⁶⁷



Scheme 1.6. Catalytic cycle for LA hydrogenation with $[(\text{dpa})\text{Cp}^*\text{Ir}(\text{OSO}_3)]$.⁶⁷

1.3.1.3 Palladium catalysts for the hydrogenation of LA to GVL using molecular hydrogen

Most homogeneous catalysts for the hydrogenation of LA to GVL use ruthenium or iridium. The first homogeneous system based on palladium was reported in 2015 by Garcia et al. Whilst their experiments primarily focused on transfer hydrogenations (to be discussed in Section 1.3.2.1), their catalysts were also highly active under hydrogen pressures. Their complexes used a series of alkyl/aryl biphosphine ligands of the form $\text{R}_2\text{P}(\text{CH}_2)_2\text{PR}_2$, with the most effective ligands containing bulky, strongly electron donating substituents. This was attributed to a steric effect increasing the catalyst stability and inhibiting decomposition. Strong σ -donor ligands are considered to promote the catalyst activity, as described previously.^{79,80} The most effective catalyst trialled was $[(\text{dtbpe})\text{PdCl}_2]$ (dtbpe = 1,2-(bis-di-tertbutylphosphino)ethane), achieving 100 % GVL yield after 5 hours at 5 bar H_2 and 80 °C in water (Table 1.6, Entry 11). $[(\text{dtbpe})\text{PdMe}_2]$ also achieved 100 % yield (Table 1.6, Entry 12). The next most effective catalysts, based on dippe (dippe = 1,2-(bis-di-isopropylphosphino)ethane), $[(\text{dippe})\text{PdCl}_2]$ and $[(\text{dippe})\text{PdMe}_2]$, achieved GVL yields of 72 % and 27 % respectively (Table 1.6, Entry 13). Other alkyl/aryl substituents reached a maximum yield of just 34 %. This is the only homogeneous palladium catalytic system for the hydrogenation of LA to GVL using H_2 to date.⁸¹

Table 1.6. Iridium, palladium and earth-abundant metal catalytic systems for LA hydrogenation with molecular hydrogen gas.

Entry	Catalyst	T [°C]	P(H ₂) [bar]	S/C	Time [h]	Additives	GVL yield [%]	TON	TOF [h ⁻¹]	Ref.
1	[Ir(COE) ₂ Cl] ₂ /PNP- ^t Bu	100	50	2,000	15	KOH	96	1,920	128	79
2	[Ir(COE) ₂ Cl] ₂ /PNP- ⁱ Pr	100	50	2,000	15	KOH	99	1,980	132	79
3	[IrH ₂ Cl(PNP(^t Bu) ₂)]	100	50	10,000	80	KOH	82	8,200	103	79
4	[IrH ₃ (PNP(^t Bu) ₂)]	100	50	10,000	24	KOH	98	9,800	408	79
5	[IrH ₃ (PNP(^t Bu) ₂)]	100	100	100,000	48	KOH	71	71,000	1,479	79
6	[Cp*(OH ₂)Ir(bipy-(OMe) ₂)]SO ₄	120	10	10,000	4	-	98	9,800	2,450	80
7	[Cp*(OH ₂)Ir(bipy-(OMe) ₂)]SO ₄	120	10	100,000	36	-	78	78,000	2,167	80
8	[(dpa)Cp*Ir(OSO ₃)]	110	5	2,000	16	-	100	2,000	125	67
9	[(dpa)Cp*Ir(OSO ₃)]	110	5	10,000	72	-	87	8,700	121	67
10	[(dpa)Cp*Ir(OSO ₃)]	130	5	200,000	72	-	87	174,000	2,417	67
11	[(dtbpe)PdCl ₂]	80	5	1,000	5	-	100	1,000	200	81
12	[(dtbpe)PdMe ₂]	80	5	1,000	5	-	100	1,000	200	81
13	[(dippe)PdCl ₂]	80	5	1,000	5	-	72	720	144	81
14	[Fe(CO)(H)(Br)(PNP(CH ₂ P(ⁱ Pr) ₂))]	100	50	2,000	2	KOH	90	1,800	900	82
15	[Fe(CO)(H)(Br)(PNP(NHP(ⁱ Pr) ₂))]	100	50	2,000	2	KOH	97	1,940	970	82
16	[Fe(CO)(H)(Br)(PNP(NHP(ⁱ Pr) ₂))]	100	100	50,000	12	KOH	46	23,000	1,917	82
17	Co(BF ₄) ₂ ·6H ₂ O/Tetrachos	100	1	40	24	-	95	38	2	83
18	Co(BF ₄) ₂ ·6H ₂ O/Tetrachos	100	10	40	24	-	>99	40	2	83
19	Casey's catalyst [(CO) ₂ (MeCN)]	100	60	100	20	-	>99	100	5	68
20	Casey's catalyst [(CO) ₂ (MeCN)]	100	60	1,000	20	-	57	570	29	68
21	Ni(OAc) ₂ ·4H ₂ O/DPPP	150	15	1,000	20	-	94	940	47	84
22	Ni(OAc) ₂ ·4H ₂ O/Triphos	150	1	100	20	-	98	98	5	84
23	Ni(OAc) ₂ ·4H ₂ O/Triphos	150	30	10,000	20	-	94	9,400	470	84

1.3.1.4 Non-precious metal catalysts for the hydrogenation of LA to GVL using molecular hydrogen

The utilisation of precious metals calls into question the viability of such hydrogenation processes. Their high-cost, limited supply and toxic nature is of concern and is in stark contrast to the widespread, low-cost availability of biomass resources. In the past few years, several reports of LA hydrogenation using non-precious metals have been published. There are also several examples of earth-abundant metal catalysts, principally iron, reported for LA hydrogenation to GVL under transfer hydrogenation conditions (to be discussed in Section 1.3.2.2). Under hydrogen pressure, earth-

abundant metal systems have even been found to hydrogenate LA beyond GVL to its products 1,4-PDO and 2-MTHF.⁸⁵ This will be discussed in Section 1.4. This Section will discuss some recent examples of LA hydrogenation reactions producing GVL using molecular hydrogen. The results are collated in Table 1.6.

In 2018, Song et al. reported the hydrogenation of LA using PNP-pincer iron complexes (Figure 1.14). At 100 °C and 50 bar H₂ in methanol alongside KOH, they found a strong activity dependence on the ligand structure. Their first catalyst, bearing a bis(di-isopropylphosphinomethyl)pyridine ligand, achieved a 90 % GVL yield in two hours (Table 1.6, Entry 14). Their second catalyst, with an analogous aliphatic ligand, achieved just a 27 % yield in five hours. Their third catalyst, with a 2,6-diaminopyridine scaffold, achieved 97 % yield in two hours (Table 1.6, Entry 15), whilst their final catalyst, based upon 2,6-bis(phosphinito)pyridine, showed no activity. They rationalised this by identifying that ligands with CH₂/NH spacers in the ligand can form 5-coordinate Fe-H species, which is not accessible in the ligand with O-linkers. By reducing the catalyst loading to 2 mmol%, they achieved 46 % GVL yield in 12 hours at 100 bar H₂, giving an impressive TON = 23,000 (Table 1.6, Entry 16).⁸²

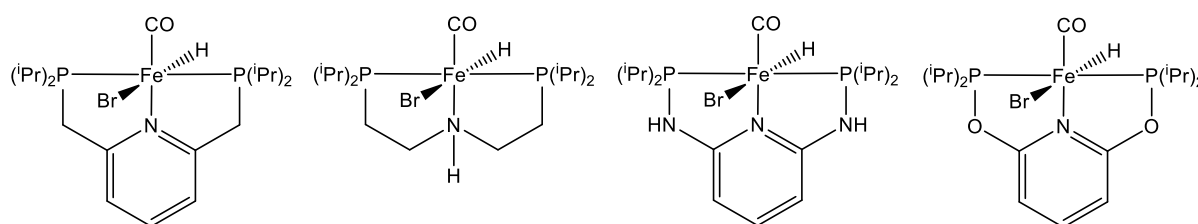


Figure 1.14. Iron complexes of PNP-ligands studied by Song et al.⁸²

Last year, Liu et al. reported a system for LA hydrogenation using Co(BF₄)₂·6H₂O and the tetradentate phosphine ligand Tetrphos. Their reactions were run at atmospheric pressure (i.e. 1 bar H₂) at 100 °C in DMI (1,3-dimethyl-2-imidazolidinone). In 24 hours, they achieved a highly impressive 97 % LA conversion and 95 % GVL yield (Table 1.6, Entry 17). Other phosphine ligands, Triphos and dppp, were also active but gave reduced conversions of 92 % and 32 % respectively, and corresponding GVL yields of just 20 % and 13 %. With Tetrphos, increasing the H₂ pressure to just 5 bar gave full LA conversion and 97 % GVL; 10 bar gave 100 % conversion and > 99 % GVL yield (Table 1.6, Entry 18).⁸³

In addition to the ruthenium-based Shvo catalysts described previously, Wildeman et al. also studied a series of iron-based catalysts based on Casey's catalyst (Figure 1.15). Casey's catalyst itself is highly air-sensitive and can be prepared from the inactive tri-carbonyl analogue. However, a more straight-

forward synthesis generates the dicarbonyl mono-acetonitrile analogue. Owing to the labile acetonitrile ligand, this can be considered as a pre-activated species which generates Casey's catalyst in situ.

With their "pre-activated" catalyst at 1 mol% loading, 60 bar H_2 and 100 °C, high yields of GVL were obtained in a range of solvents, including 2-MTHF, giving > 99 % GVL yield (Table 1.6, Entry 19). Reducing the catalyst loading to 0.1 mol% in ethanol gave a yield of 57 % and their highest TON = 570 (Table 1.6, Entry 20).⁶⁸ Trialling the same catalyst in solventless conditions (at 50 bar H_2 and 100 °C for 5 hours) gave no LA conversion. This was attributed to catalyst decomposition.⁸⁶

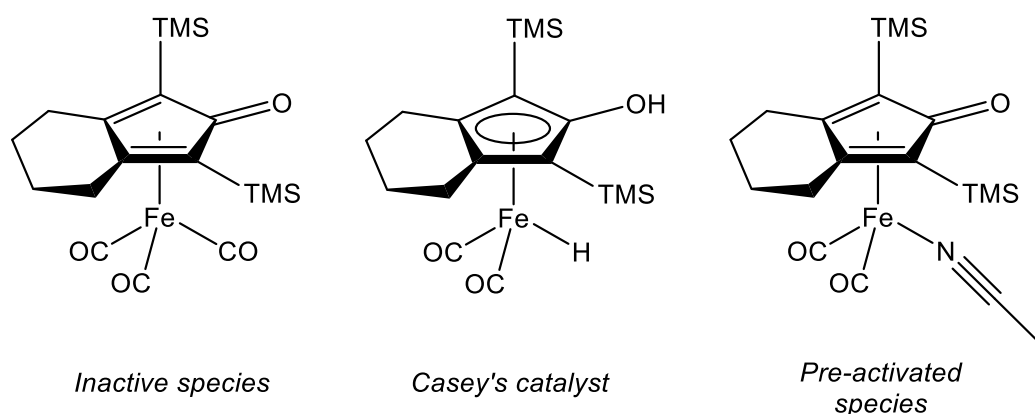


Figure 1.15. Casey's catalyst and related species studied by Wildeman et al.⁶⁸

Fu et al. recently published some very impressive results based upon a solvent-free nickel system. Their reactions used in situ mixtures of 1 mol% $Ni(OAc)_2 \cdot 4H_2O$ with a range of phosphine ligands at 1 atm pressure H_2 at 150 °C for 20 hours, without solvent/additives.

The monodentate PPh_3 ligand gave trace yields of GVL, whilst bidentate PPh_2 ligands gave GVL yields in the range of 5-37 %. Ligands forming stable 5- or 6-membered rings facilitated relatively higher activities. Bidentate PCy_2 ligands DCyPE and DCyPP were more effective, attaining GVL yields of 88 and 90 % respectively. The tridentate Triphos ligand was most successful, achieving 98 % GVL yield. It was noted that although just two of the three Triphos phosphine groups coordinated to nickel, the third arm functioned as an electron-donating group. With an increase in pressure to 30 bar H_2 , the catalyst loading was reduced to 0.01 mol% and still achieved 94 % GVL (TON = 9,400). Furthermore, the catalyst could be recycled for four runs without a significant loss in activity, given that post-treatment was performed under inert conditions. Overall, these results represent a robust catalyst based upon an inexpensive, abundant metal precursor under relatively mild and green conditions.⁸⁴

1.3.2 Transfer hydrogenation reactions of LA to GVL

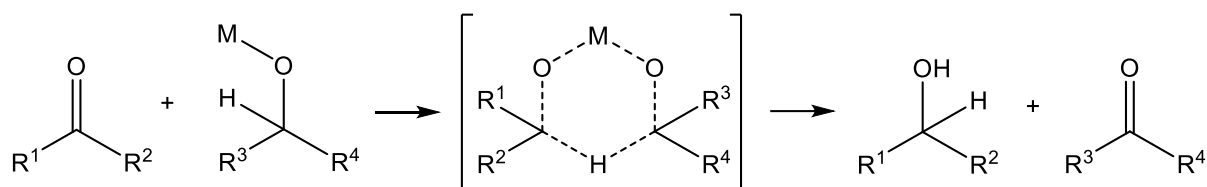
Thus far, numerous examples of highly active catalyst systems for the hydrogenation of LA to GVL have been described. However, there are difficulties and drawbacks with the use of molecular hydrogen which has led to concurrent research into transfer hydrogenation (TH) conditions for this reaction. Instead of H₂ gas, transfer hydrogenation reactions use an alternative source of hydrogen, typically an acid or an alcohol. In the case of LA, formic acid (FA) is a particularly attractive source of hydrogen, given that FA is generated alongside LA from sugars. This means that no additional hydrogen source needs to be included.

Some of the advantages of transfer hydrogenation reactions are self-evident. Avoiding high-pressures of flammable H₂ gas avoids many of the associated safety hazards. Removing the requirement for specialised equipment which can tolerate high pressures of gas also means that transfer hydrogenations are operationally simpler to perform, involve minimal costs, and are more widely accessible. It has been stated that the generation of H₂ gas primarily comes from fossil fuels; depending on the hydrogen source used, transfer hydrogenation reactions can be considered as more sustainable. The transfer hydrogen agents used are generally inexpensive, common, and easy-to-handle chemicals. Whilst transfer hydrogenation conditions are milder, perhaps making it more difficult to achieve reaction completion, this can be considered as attractive in attaining high product selectivity. Many of the catalytic systems described which operate under high-pressures generate mixtures of LA hydrogenation products through “over-hydrogenation”. Whilst the field of transfer hydrogenation reactions dates to the early-twentieth century, by 2008 there were no examples of transfer hydrogenation reactions of LA.

There are three classes of hydrogen transfer reactions: i) hydrogen migration, taking place within one molecule, ii) hydrogen disproportionation, involving transfer between identical donor and acceptor moieties, and iii) TH-dehydrogenation, involving transfer between unlike donor and acceptor moieties. The third category is the most relevant here.⁸⁷

The first TH reaction performed on carbonyl compounds was the illustrious Meerwein–Ponndorf–Verley (MPV) reduction reported in 1925. The MPV reduction converted a ketone to its corresponding alcohol, using a secondary alcohol as the hydrogen donor and an aluminium alkoxide as a promoter.⁸⁸

The homogeneous MPV reduction is considered to proceed via a direct TH through the formation of a six-membered transition state, with both the carbonyl substrate and reducing alcohol coordinated to the same metal (Scheme 1.7).⁸⁹



Scheme 1.7. The homogeneous MPV reduction.⁸⁹

The MPV reduction has been extensively applied in both academic and industrial settings; key advantages are its high chemoselectivity towards the keto moiety and its operation under mild reaction conditions.⁹⁰

The 1960s brought the first reports of TH catalysts based on transition metals, with an iridium hydride system.⁹¹ In the 1990s the key role of base was identified, whereby the TH of acetophenone by $[\text{RuCl}_2(\text{PPh}_3)_3]$ was accelerated 10^3 - 10^4 times by the addition of NaOH.⁹² The first reports of asymmetric transfer hydrogenation (ATH) come from the 1980s.⁹³⁻⁹⁵

To date, the most common metals used as TH catalysts include iridium, ruthenium and rhodium, although this has been expanded more recently to iron, palladium and osmium. A wide range of hydrogen donor sources have been utilised, including cyclohexene, cyclohexadiene, alcohols (methanol, ethanol, iso-propanol, glycerol), formic acid, hydrazine and alkanes, among others. In some cases, an organic solvent used for the reaction can also behave as the hydrogen-donor. However, aqueous systems are used frequently, owing to the advantages of water as a low cost and environmentally benign solvent in which the usual hydrogen sources have good solubility. Many TH reactions are also accelerated in aqueous media relative to organic solvents. Most TH systems also require a base, including NEt_3 , KOH, NaOH, Na_2CO_3 and HCOONa .^{96,97}

Two mechanisms are most commonly invoked for transition-metal catalysed TH reactions, which differ from the already mentioned MPV reduction. The inner-sphere mechanism involves substrate coordination. Insertion of the carbonyl substrate into an M-H bond is considered to form a new alkanoate moiety which is protonated by an incoming H source to release the hydrogenated product. The outer-sphere mechanism does not involve substrate coordination; a strongly basic ligand deprotonates the hydrogen source with simultaneous hydride transfer to the metal. Transfer of proton, from the protonated ligand, and hydride, from the metal, to the carbonyl generates the product.⁹⁰

Whilst transfer hydrogenation themselves have a long history, they have only more recently been applied for the hydrogenation of LA. The next Sections will discuss the major examples of

homogeneous systems using TH for LA hydrogenation, first with precious metal catalysts (1.3.2.1) followed by those using non-precious metals (1.3.2.2).

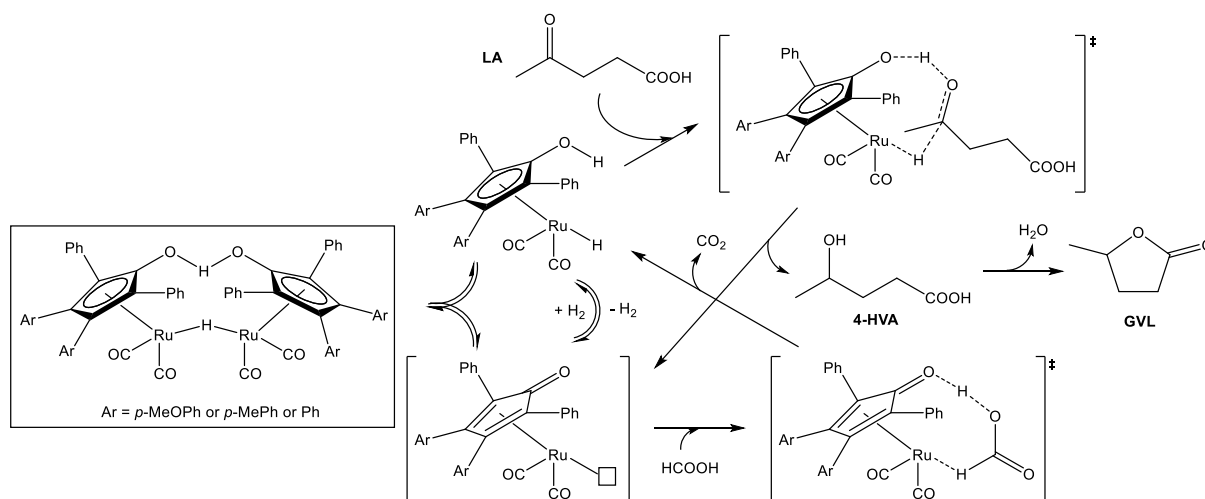
1.3.2.1 Transfer hydrogenation reactions of LA to GVL using precious metals

Table 1.7 collects the catalytic systems discussed in this section. The first study of the transfer hydrogenation of LA was reported by Horvath et al. in 2008. Using $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{bipy})(\text{H}_2\text{O})][\text{SO}_4]$ alongside sodium formate (HCOONa) and HNO_3 in water, they achieved yields of 25 % GVL, 25 % 1,4-PDO and 1 % 2-MTHF over 18 hours at 70 °C (Table 1.7, Entry 1). In this case, formic acid (FA) was generated in situ from sodium formate and HNO_3 . This represented a surprisingly active, if unselective, catalyst system operating at relatively mild conditions.⁴²

The same group went on to investigate a series of Shvo catalysts for LA transfer hydrogenation, with the general formula $\{[2,5\text{-Ph}_2\text{-3,4-(Ar)}_2(\eta^5\text{-C}_4\text{CO})]_2\text{H}\}[\text{Ru}_2(\text{CO})_4(\mu\text{-H})]$ ($\text{Ar} = p\text{-MeOPh}, p\text{-MePh}, \text{Ph}$) (Scheme 1.8). The catalyst with $\text{R} = p\text{-MeOPh}$ was found to be most effective, giving >99 % GVL yield in eight hours at 100 °C using FA (Table 1.7, Entry 2). Aqueous sodium formate in place of FA gave only 40 % GVL. No hydrogenation was observed beyond GVL. Although full conversion of LA was achieved with all three Shvo catalysts, those with the substituents $\text{R} = p\text{-MePh}$ or Ph gave much slower reactions.

Their general mechanism for transfer hydrogenation is shown in Scheme 1.8. Reversible dissociation of the starting catalyst generates two mononuclear active forms. The hydroxycyclopentadienyl ruthenium hydride has both acidic and hydride functions: it can transfer both a proton from the OH-group and a hydride to LA forming first 4-HVA, and GVL following dehydration. The second, coordinatively unsaturated form is able to activate FA, regenerating the ruthenium hydride species.⁹⁸

Guo et al. also studied a ruthenium system for LA transfer hydrogenation, investigating the effect of base and ligand on product selectivity. Initially using an in situ mixture of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and PPh_3 with FA, they surveyed a range of bases at different temperatures. At 100 °C, the maximum GVL yield was 42 % across all bases tested (Table 1.7, Entry 3). The performance of bases took the order $\text{KOH} > \text{NaOH} > \text{NEt}_3 > \text{pyridine} > \text{NH}_3 > \text{LiOH}$, i.e., a stronger base accelerated the reaction. Increasing the temperature to 150 °C saw significant improvements, with the addition of NEt_3 and pyridine reaching 94 % and 93 % GVL yields respectively in 12 hours (above those achieved with KOH and NaOH) (Table 1.7, Entries 4-5).



Scheme 1.8. Transfer hydrogenation mechanism reported by Horvath et al.⁹⁸

Increasing the temperature further to 200 °C saw further improvements, with 95 % and 93 % GVL yields in just six hours using triethylamine and pyridine respectively (Table 1.7, Entries 6-7). The authors considered that reaction of GVL with the stronger base additives reduced the yields achieved. Interestingly, although their reactions had a starting pressure of just 1 bar H₂, they found that the pressure inside the reaction reached 80 bar within 20 minutes. They attributed this to rapid FA decomposition to H₂ and CO₂, i.e., the reaction was proceeding under typical hydrogenation conditions, rather than true transfer hydrogenation. Therefore, in addition to the MPV and inner/outer-sphere TH mechanisms, it is also possible for systems to act through hydrogenation with H₂ via either M-H or M(H₂) species, either in place of or alongside TH.

They went on to test their reactions in aqueous media to improve the practicality of the reactions. At 150 °C, the same systems with NEt₃ and pyridine additives reached 90 % and 88 % GVL yields respectively, despite the water-insolubility of the PPh₃ ligand. Other hydrophobic ligands, PCy₃ and dppe, gave slightly lower yields (81 % and 80 % with pyridine), and surprisingly, the water soluble ligands TPPMS and TPPTS gave much reduced yields (54 % and 48 %, again with pyridine).⁹⁹

Section 1.3.1.2 discussed a study by Fu et al. using half-sandwich iridium complexes of substituted bipyridine ligands for the hydrogenation of LA to GVL using H₂ gas. Their most successful catalyst, [Cp*(OH₂)Ir-bipy(OMe)₂].SO₄, had electron donating OMe substituents in sterically unhindered para-positions. They went on to trial this catalyst for transfer hydrogenation in water using FA. After four hours at 120 °C, using two equivalents of FA, an excellent 99 % GVL yield was achieved (Table 1.7, Entry 8). Excess FA was required to reach the highest conversions: 1.5 equivalents of FA gave 85 %

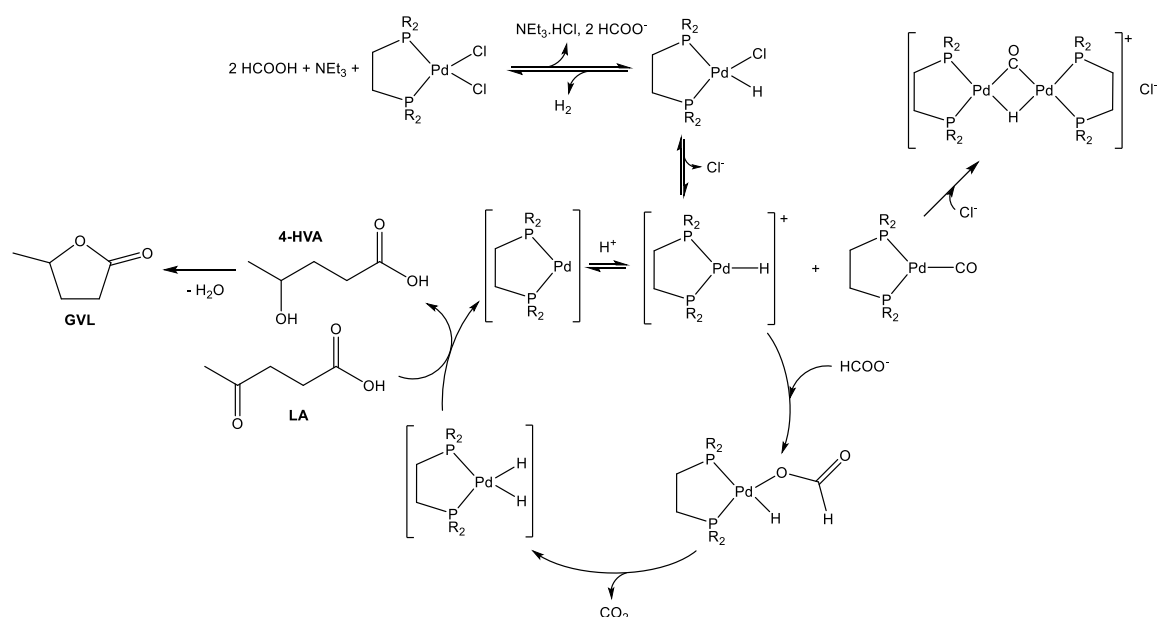
GVL and 1.2 equivalents of FA gave just 71 % (up to 76 % after 6 hours). Trialling the reaction at room temperature with two equivalents FA and an increased catalyst loading of 0.1 mol% gave 94 % GVL yield over 24 hours, an excellent result given the very mild conditions (Table 1.7, Entry 9).⁸⁰

Section 1.3.1.3 introduced some work by Garcia et al. using palladium complexes for LA hydrogenation; this work was notable for using palladium in place of ruthenium or iridium. They also investigated transfer hydrogenation conditions in water with FA as hydrogen source and triethylamine as base at 100 °C. Their palladium complexes contained diphosphine ligands of the form $R_2P(CH_2)_2PR_2$, with a general catalyst formula of $[(R_2P(CH_2)_2PR_2)PdX_2]$ ($R = ^iPr, ^tBu, Ph$; $X = Cl$ or Me). Concerning the phosphine substituents, the alkyl substituents $R = ^iPr$ and ^tBu gave highly active catalysts (reaching 100 % GVL), whilst the aryl substituent $R = Ph$ gave no activity (Table 1.7, Entries 10-13). They attributed this to both steric and electronic factors: a steric effect conferring stability to the catalyst preventing decomposition, whilst strong sigma-donating ligands promote FA decomposition.

The X substituent on the catalyst was also important; activity was significantly lower with $X = Me$ compared to $X = Cl$. The authors attributed this to catalyst decomposition by reductive elimination where $X = Me$, producing $Pd(0)$ and ethane. The use of an inert atmosphere was also important; catalyst decomposition was observed when an uncontrolled atmosphere was used. The presence of NEt_3 was essential; without a base, near-zero GVL yield was achieved. The base is considered to help remove chloride from the catalyst, essential to generate the active catalyst species. The base is also believed to accelerate FA decomposition: upon reduction of the FA loading from 2.1 equivalents to just one equivalent, full LA conversion was only achieved with an increase in base loading from 10 mol% to 33 mol%.

The authors also investigated a range of solvent systems. Omitting a solvent completely gave a maximum of 77 % GVL yield. Non-aqueous solvents 1,4-dioxane and THF gave yields of just 9 % and 3 % respectively. Therefore, full conversion was achieved only in water, which is considered to promote the decomposition of FA; in non-aqueous solvents, the authors identified the formation of an inactive form of the catalyst species. The effect of water on FA decomposition will be discussed in more detail later.

The authors presented a full mechanism for the transfer hydrogenation. Following chloride abstraction from the starting catalyst by $[HNEt_3]^+$, the main catalytic cycle involves addition of FA generating a metal-hydride-formate species, followed by fast β -hydride elimination generating a dihydride metal species. Following reaction with LA, initially 4-HVA and then GVL was produced. A separate off-cycle reaction was described, forming an inactive dimer species bridged by CO and H. The carbonyl species is considered as a by-product of FA dehydration ($FA \rightarrow H_2O + CO$), which is a possible



Scheme 1.9. Mechanism of transfer hydrogenation reported by Garcia et al.⁸¹

FA decomposition pathway in addition to the desired FA dehydrogenation ($\text{FA} \rightarrow \text{H}_2 + \text{CO}_2$). The use of aqueous solvents minimises the FA dehydration route, therefore minimising the presence of CO, minimising the presence of the carbonyl species and therefore of the inactive catalyst species. This supports the finding that their catalyst system was more active in aqueous solvents relative to non-aqueous solvents.⁸¹

Section 1.3.1.1 discussed work by Darkwa et al. using neutral ruthenium catalysts of both pyrazolylphosphite (containing the group $-\text{O}-\text{P}(\text{OEt})_2$) and pyrazolylphosphinite (containing the group $-\text{O}-\text{PPh}_2$) ligands, and cationic analogues of each with both BARF^- and BPh_4^- anions (Figure 1.16). They tried the same catalysts under solvent-free transfer hydrogenation conditions using FA as hydrogen source and KOH as base at 120 °C. The neutral complexes proved the most active, reaching 96 % LA conversion and 100 % selectivity for GVL for $\text{R}^2 = \text{ethoxy}$. The phosphinite analogue with $\text{R}^2 = \text{phenyl}$ gave 79 % conversion, but only 86 % selectivity for GVL alongside the formation of 4-HVA (Table 1.7, Entries 14-15). The cationic analogues gave lower conversions than their neutral analogues, in the range of 37-68 %. As can be seen in Figure 1.16, the cationic complexes form a stable chelate ring, preventing ready formation of the active catalyst species.

The authors identified a pressure of around 15 bar generated in their reactions, attributed to FA decomposition. Through NMR they detected the cleavage of *p*-cymene from the catalyst, suggesting that this allows for the coordination, and subsequent decomposition, of formate to the metal centre. They attributed the role of the base additive to generation of the formate ion from FA, i.e., it is the formate ion that coordinates to the metal. The base is also considered to accelerate H_2 heterolysis.⁶⁶

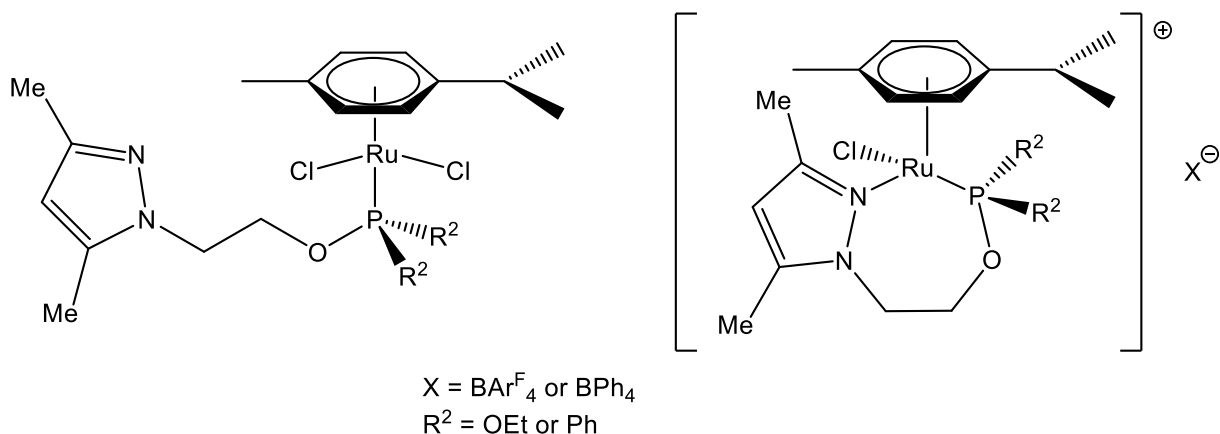


Figure 1.16. The structures of the pyrazolylphosphite and pyrazolylphosphinite catalysts used by Darkwa et al.⁶⁶

Section 1.3.1.1 also introduced the dipyridylamine (dpa) ligand system utilised by Fischmeister et al. for LA hydrogenation, with both ruthenium and iridium. Extending this to transfer hydrogenation, they first investigated ruthenium complexes with either an N-H or N-R moiety on the bridging amine (Figure 1.17 (1)). Under solvent-free conditions using FA and NEt₃, their reactions were selective for GVL. No conversion was achieved in the absence of FA or NEt₃. Their catalyst with R=H obtained a 99 % GVL yield in 16 hours at 150 °C, with two equivalents of FA and one equivalent of NEt₃ (Table 1.7, Entry 16). Reducing the temperature to 120 °C gave just a 23 % yield. Their catalyst with R=CH₂Ph achieved a slightly lower 87 % yield at 150 °C. However, their most effective catalyst contained the bulkiest substituent R = CH(CH₃)Ph, achieving 100 % conversion at 150 °C, or 99 % at 120 °C (with an increase to four equivalents FA and two equivalents NEt₃) (Table 1.7, Entries 17-18). The lack of improvement upon incorporation of an acidic N-H moiety suggested that their system was not operating under an outer-sphere mechanism involving the N-H group.

Performing the same reactions using the analogous iridium catalysts showed some surprising differences. With the iridium complexes containing the bulkiest ligands, R = CH₂Ph and R = CH(CH₃)Ph, maximum GVL yields of 64 % and 30 % were obtained. However, the catalyst with the least bulky ligand, R = H, achieved a 98 % yield at 120 °C, with four equivalents FA and two equivalents NEt₃ (Table 1.7, Entry 19). Furthermore, increasing the temperature to 150 °C reduced the GVL yield to 50 %. The authors were uncertain why the ligand steric bulk had a different effect for each system. Regarding the temperature effect, they considered that the iridium complexes might have poorer thermal stability, or that FA dehydrogenation is occurring at a higher temperature. Their most effective Ru catalyst could be recycled up to six times, and their most effective Ir catalyst could be recycled twice.¹⁰⁰

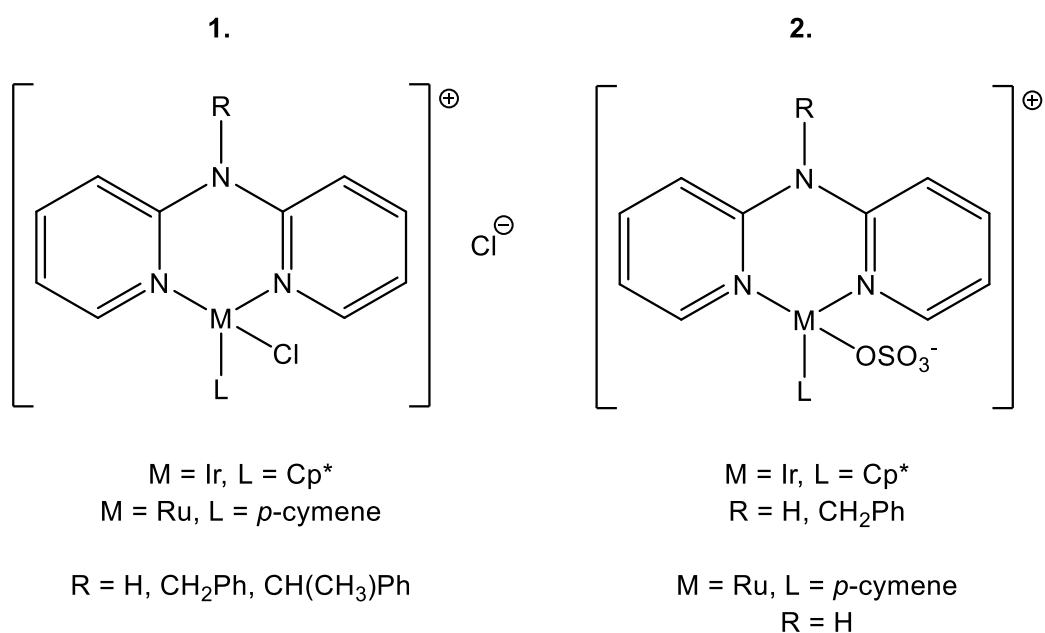


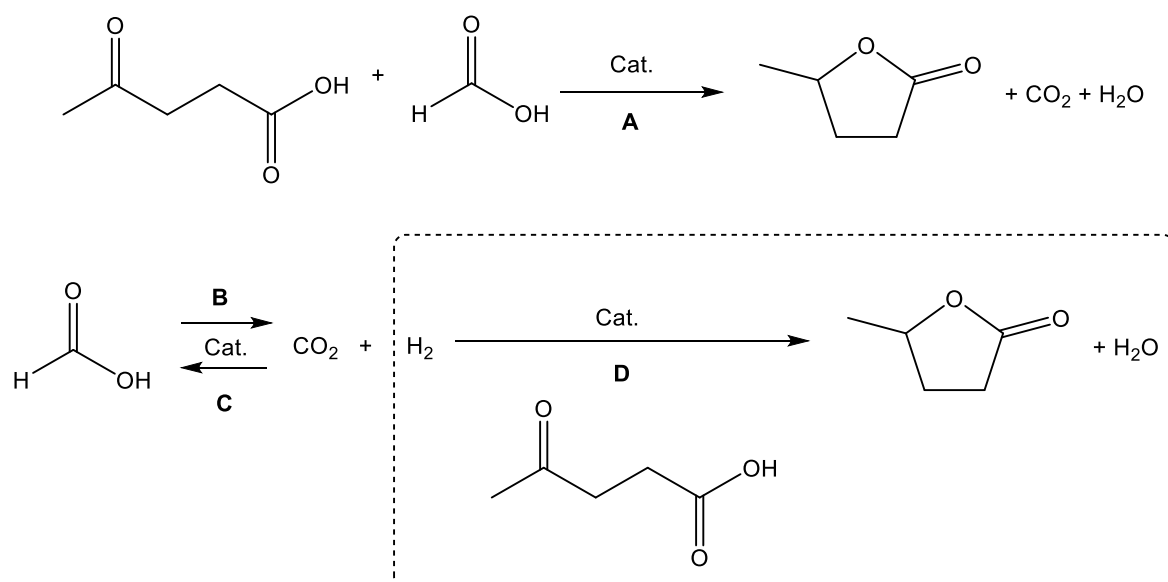
Figure 1.17. Structures of dipyriddyamine complexes reported by Fischmeister et al.^{67,100}

The same group went on to study a related series of sulfonated catalysts (Figure 1.17 (2)). The loss of the chloride ligand meant that these TH reactions could be performed without a base additive. With FA at 110 °C over 16 hours, the sulfonated ruthenium catalyst achieved < 2% conversion. However, the iridium catalysts were effective. As per the previous results, the iridium catalyst with $R = \text{CH}_2\text{Ph}$ was less effective than the catalyst with $R = \text{H}$, achieving a maximum 57 % GVL yield. The system was optimised with the Ir catalyst with $R = \text{H}$. At 110 °C, its GVL yield was 73 %, which increased to 85 % at 140 °C. The addition of NEt_3 actually had a negative effect on the conversion achieved. Changing from solventless conditions to aqueous media increased the LA conversion to 100 % (Table 1.7, Entries 20-21).

The authors wanted to investigate if their reaction was operating under true transfer hydrogenation conditions, or via a hydrogenation route from FA decomposition (as described by others after observing a large pressure rise in their reactions). In a typical hydrogenation reaction using H_2 gas, H_2 is activated to form M-H or $\text{M}(\text{H}_2)$. When FA is the hydrogen source, hydrogenation will be initiated by the generation of M-H resulting from FA dehydrogenation.

A set of possible reactions is presented in Scheme 1.10. Reaction A is the transfer hydrogenation of LA. Reactions B and D comprise the standard hydrogenation of LA, whilst C represents the reversibility of FA dehydrogenation. The authors performed a series of reactions to elucidate the reaction mechanism. In an open system, they found that the transformation of LA to GVL proceeded via a

transfer hydrogenation mechanism, despite the FA dehydrogenation. However, in a closed system, they found that the transfer hydrogenation of LA was in fact operating basically by hydrogenation. The hydrogenation of LA benefits from the easier formation of the same metal-hydride species that arises from the metal-formate species.⁶⁷



Scheme 1.10. Reactions occurring during a transfer hydrogenation process.⁶⁷

Makhubela and Oklu investigated a series of ruthenium catalysts based on Schiff base N^N pyridylimine ligands (Figure 1.18). Under solventless conditions, with FA and KOH at 150 °C, $[\text{Ru}(\text{COD})\text{Cl}_2(\text{L1})]$ achieved a maximum 96 % LA conversion in 12 hours, but with just 53 % selectivity for GVL (with the remaining selectivity for 4-HVA). The other catalysts achieved yields in the range 45–93 %, with $[\text{Ru}(p\text{-cymene})\text{Cl}(\text{L2})]\text{Cl}$ achieving the highest GVL selectivity of 66 %. When the KOH loading was reduced from one equivalent to 0.1 equivalents, the LA conversions were reduced to the range 14 – 42 %, but 100 % GVL selectivity was achieved in every case. Exchanging KOH for NEt_3 , high LA conversions (>96 %) were achieved with every catalyst, at 100 % GVL selectivity (Table 1.7, Entries 22–25). They attributed the improvement possibly due to a lack of solubility of KOH.

$[\text{Ru}(p\text{-cymene})\text{Cl}(\text{L2})]\text{Cl}$, containing an added methylene group between the imine and aromatic group was generally the least effective catalyst. The authors suggested that with an increased chain flexibility the aromatic groups could block the metal centre from substrate coordination. The catalysts could be recycled for several runs, but deactivation was observed; this was thought to be through substitution of the chloride ligands for water.

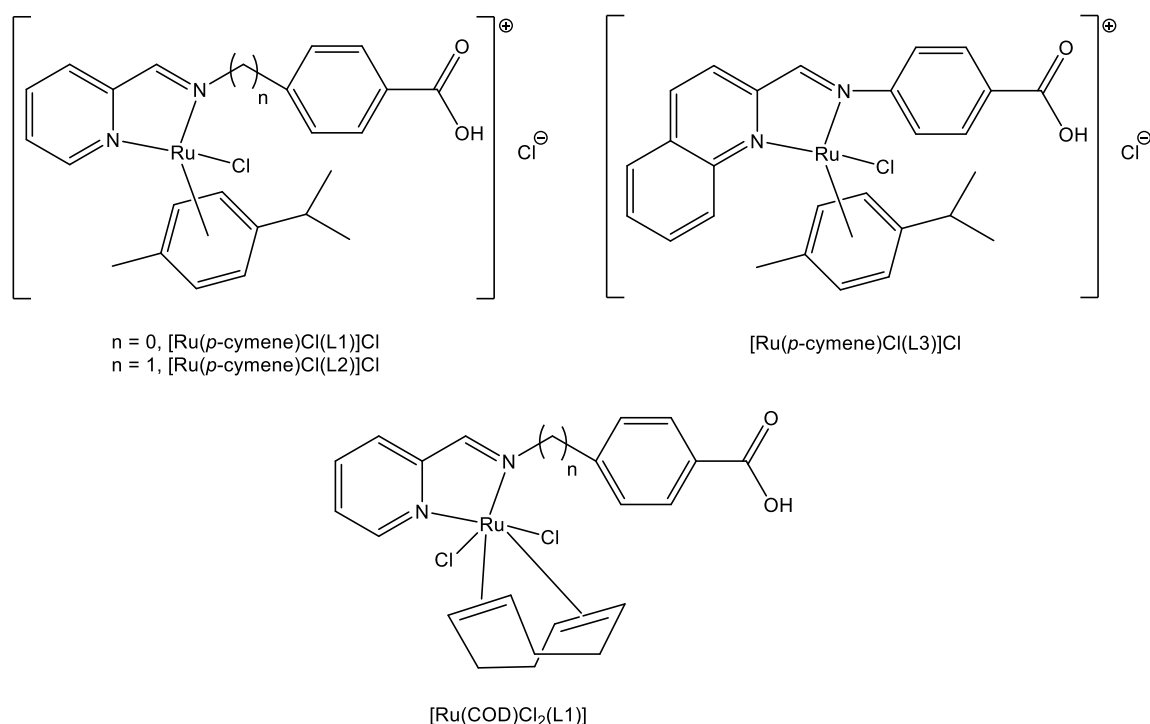


Figure 1.18. Structures of Schiff-base ruthenium complexes reported by Makhubela and Oklu.¹⁰¹

The complete formation of H_2 gas from FA was observed through NMR spectroscopy. Cleavage of the imine nitrogen-ruthenium bond was observed, probably to allow for formate coordination to the metal. A Ru-hydride species was identified. They proposed that this might originate from either metal coordination of a formate ion or by dihydrogen.¹⁰¹

Darkwa, Makhubela et al. went on to study interesting ruthenium complexes of multidentate pyridyl-phosphoramidite ($\text{R}_2\text{N-P}(\text{OR})_2$) and pyridyl-aminophosphinite ($\text{R}_2\text{N-PR}_2$) ligands of the type $\text{P}'\text{N}'\text{N}'\text{P}$. They recognised that these ligands have the potential to form homonuclear bimetallic systems with a variety of coordination modes accessible. Further, because of the direct P-N bonding they evaluated the electronic properties of the ligands as between those of phosphines and phosphinites/phosphites.

They prepared bimetallic ruthenium complexes of a series of $\text{P}'\text{N}'\text{N}'\text{P}$ ligands, both neutral complexes where the ligand binds to the ruthenium centres through Ru-P bonds only, and cationic complexes where the ligand binds to the ruthenium centres through both Ru-P and Ru-N bonds (Figure 1.19).

With their catalyst 1, alongside FA and NEt_3 , an 86 % LA conversion was achieved in 12 hours, with 95% selectivity for GVL. Increasing from one to two equivalents of FA brought the conversion up to 94 % in just eight hours (Table 1.7, Entry 26). All catalysts trialled gave at least 90 % conversion in 12 hours, with catalyst 8 achieving 100 % conversion and 97 % GVL selectivity (Table 1.7, Entry 27).

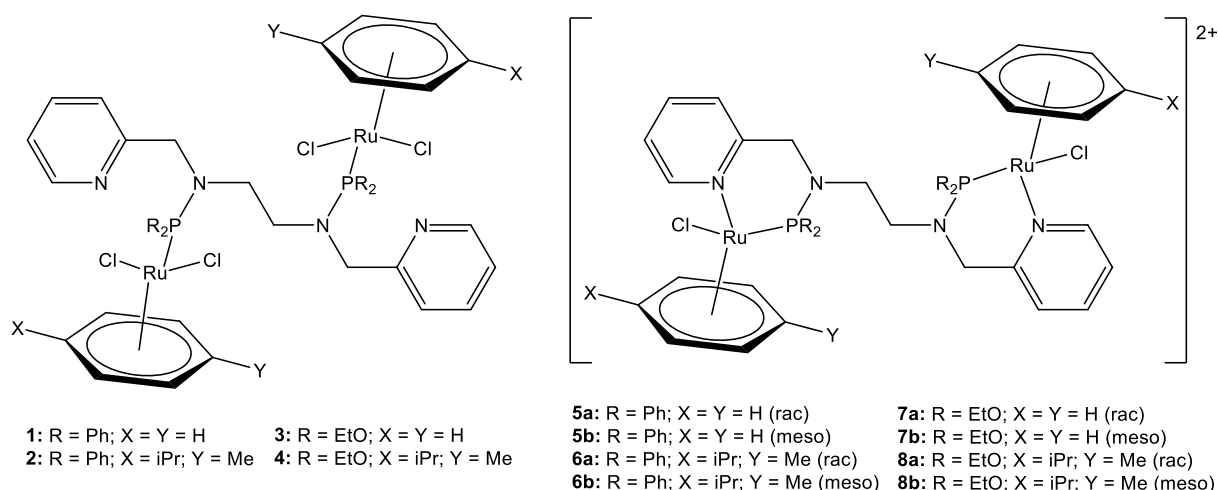


Figure 1.19. Structures of pyridyl-phosphoramidite and pyridyl-aminophosphinite complexes reported by Darkwa et al.¹⁰²

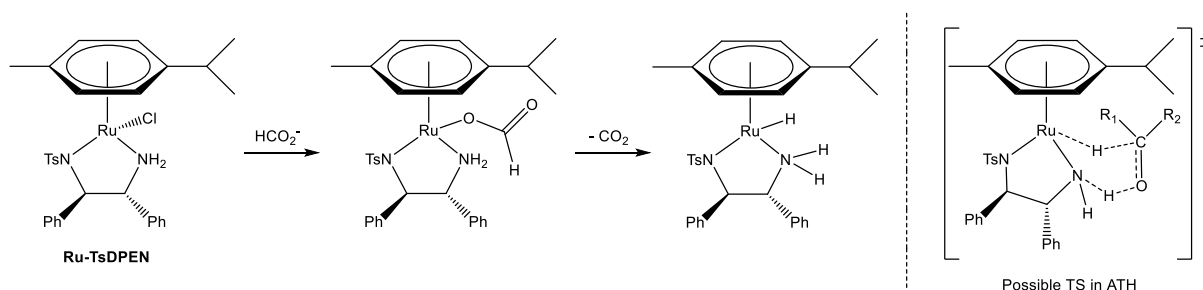
The results achieved were similar between complexes with mono- and bi-coordination of the ligands, suggesting that the configuration at the metal centre is insignificant. The authors considered that the extra stability of the chelating system might hinder ligand dissociation and therefore formation of the active species. Generally, the phosphoramidite complexes (3,4,7,8) were superior to the aminophosphinite complexes (1,2,5,6). Potentially, the electron withdrawing ethoxy moieties of the phosphoramidite ligands aid the interaction of the metal with formate ions, by making the metal centre more electrophilic. The authors credited the relatively short reaction time (eight hours) to the presence of two metal active sites in their catalyst.¹⁰²

Section 1.3.1.1 introduced some work by Wildeman et al. for the hydrogenation of LA using Shvo's catalyst. They also trialled Shvo's catalyst for the transfer hydrogenation of LA. Whilst Horvath et al. had previously trialled a series of Shvo catalysts under transfer hydrogenation conditions (discussed earlier in Section 1.3.2.1), Wildeman et al. trialled different hydrogen sources and solvents. Using FA at 100 °C for 20 hours in toluene, without additives, a 95 % GVL yield was achieved. IPA was slightly more effective than FA, achieving 99 % GVL yield in 16 hours at 80 °C (Table 1.7, Entry 28). Using IPA in toluene achieved the same yield. Whilst no 1,4-PDO or 2-MTHF were observed, trace amounts of isopropyl 4-hydroxypentanoate were seen. Their mechanism proceeds in a manner analogous to that described previously: following heterolytic dissociation of the catalyst, "outer-sphere" coordination of IPA to the catalyst transferred hydrogen in a concerted manner to provide both hydride and proton moieties on the catalyst. Through kinetic studies they identified that dilution of the catalyst system

(e.g. by increasing the equivalents of IPA) was the strongest factor in catalyst inhibition (compared to approaching depletion of IPA).⁶⁸

Recently, Bhanage et al. reported some interesting work on asymmetric transfer hydrogenation (ATH) of LA to enantiomerically-pure GVL. Whilst Section 1.3.1.1.1 discussed some catalytic systems able to produce optically active GVL under pressures of hydrogen gas, the work by Bhanage et al. represented the first ATH of LA in the presence of chiral ligands. They initially tested a series of commercially available catalysts based on chiral chelating ligands with the metals ruthenium, iridium and rhodium. Their most effective catalysts featured tosylated diamine ligands, with the most successful candidate Ru-TsDPEN. With FA and NEt₃ in methanol at RT, RuCl(*p*-cymene)[(R,R)-Ts-DPEN] achieved 99 % LA conversion in 24 hours, with a 64 % ee (Table 1.7, Entry 29). The authors presented a standard mechanism for the ATH reaction. Following deprotonation of FA, formate coordinates to the metal centre. Upon decarboxylation, an amine hydrido Ru complex is formed. The NH moiety is adequately acidic to activate the LA carbonyl, therefore both a hydride and a proton can be transferred from the catalyst to LA in a concerted manner, as shown in Scheme 1.11. The role of NEt₃ is to accept a chloride from the starting catalyst.

The authors investigated a range of variables to optimise the ee. Omitting a solvent resulted in low conversions. Potentially the increased acidity of the system hampers the active catalyst species. Raising the temperature to 30 °C gave 99 % conversion with 70 % ee. Increasing the catalyst loading to 0.01 mmol gave a 78 % ee. By changing NEt₃ for N-methylpiperidine, 98 % conversion was achieved at 93 % ee. (Table 1.7, Entry 30). Alkyl levulinate esters (R = Me, Et, ⁱPr, ^tBu) could also be hydrogenated to enantiomerically pure GVL with conversions 92-96 % and ee values of 81-85 %. Therefore, the system represents effective ATH of LA and its esters to chiral GVL under very mild reaction conditions.¹⁰³



Scheme 1.11. Mechanism for asymmetric transfer hydrogenation reported by Bhanage et al.¹⁰³

Earlier this year, Ballico, Baratta et al. surveyed a series of ruthenium complexes based on the 2,6-functionalised pyridine ligand HCNNO^{Me} (6-(4-methoxyphenyl)-2-aminomethylpyridine). HCNNO^{Me} binds to ruthenium in a C'N'N' pincer fashion, forming very robust catalysts. Several of their catalysts were active in the transfer hydrogenation of EL to GVL: $[\text{RuCl}(\text{CNNO}^{\text{Me}})(\text{PP})]$ (PP = dppb (1,4-bis(diphenylphosphino)butane) or dppf (1,1'-bis(diphenylphosphino)ferrocene) and $[\text{Ru}(\text{CNNO}^{\text{Me}})(\text{CO})(\text{PCy}_3)(\text{PPh}_3)][\text{BArF}_4]$ (Figure 1.20). Their TH reactions were run at 82 °C with IPA as the hydrogen source. With the dppb catalyst, and NaO^iPr as the base, 95 % conversion was achieved in 60 mins with 92 % selectivity to GVL. The remaining product was identified as isopropyl 4-hydroxypentanoate. Changing to the weaker base K_2CO_3 , an improved 99 % conversion and 97 % GVL selectivity were achieved in just 20 mins (Table 1.7, Entry 31). The dppf catalyst was equally successful: with K_2CO_3 , 99 % conversion and 98 % selectivity were achieved in 15 mins (Table 1.7, Entry 32). The results thus far were achieved at a S/C ratio = 1,000. The mono-carbonyl analogue was able to achieve 98 % conversion and 96 % selectivity in 30 mins, at an S/C ratio = 10,000 (Table 1.7, Entry 33) giving an impressive $\text{TOF} = 20,000 \text{ h}^{-1}$. Whilst LA itself was not trialed, this system represents a highly successful route to GVL via transfer hydrogenation in very short timescales.¹⁰⁴

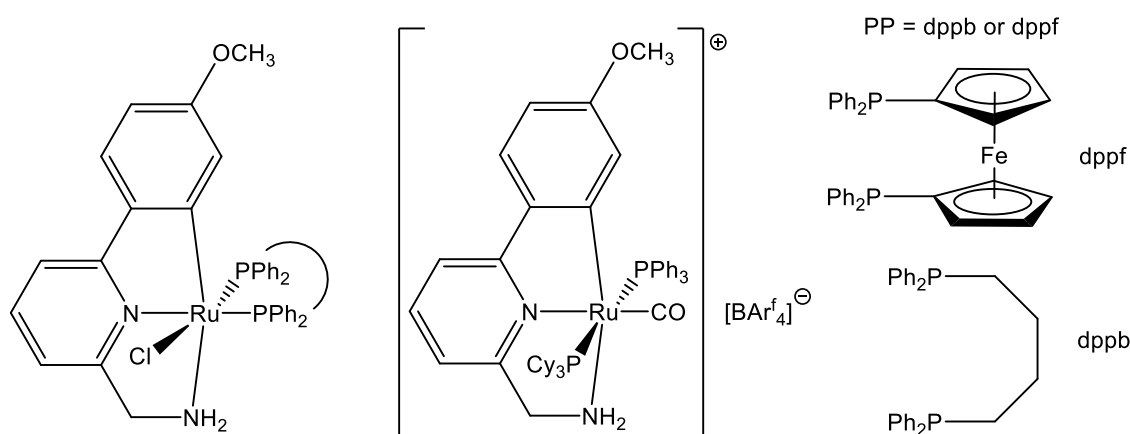


Figure 1.20. The structures of the ruthenium catalysts reported by Ballico, Baratta et al.¹⁰⁴

Table 1.7. Precious-metal catalytic systems for transfer hydrogenation of LA.

Entry	Catalyst	T [°C]	H source, equiv.	S/C	Time [h]	Additives	GVL yield [%]	TON	TOF [h ⁻¹]	Ref.
1	$[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{bipy})(\text{H}_2\text{O})][\text{SO}_4]$	70	HCOONa, 37	254	18	HNO ₃	25	64	4	42
2	Shvo's catalyst (Ar = <i>p</i> -MeOPh)	100	FA, 1.5	2,400	8	-	99.9	2,398	300	98
3	RuCl ₃ ·3H ₂ O/PPh ₃	100	FA, 1	1,000	12	KOH	42	420	35	99
4	RuCl ₃ ·3H ₂ O/PPh ₃	150	FA, 1	1,000	12	NEt ₃	94	940	78	99
5	RuCl ₃ ·3H ₂ O/PPh ₃	150	FA, 1	1,000	12	pyridine	93	930	78	99
6	RuCl ₃ ·3H ₂ O/PPh ₃	200	FA, 1	1,000	6	NEt ₃	95	950	158	99
7	RuCl ₃ ·3H ₂ O/PPh ₃	200	FA, 1	1,000	6	pyridine	93	930	155	99
8	$[\text{Cp}^*(\text{OH}_2)\text{Ir}(\text{bipy}(\text{OMe})_2)\text{SO}_4]$	120	FA, 2	10,000	4	-	99	9,900	2,475	80
9	$[\text{Cp}^*(\text{OH}_2)\text{Ir}(\text{bipy}(\text{OMe})_2)\text{SO}_4]$	25	FA, 2	1,000	24	-	94	940	39	80
10	$[(\text{dtbpe})\text{PdMe}_2]$	100	FA, 2.1	1,000	5	NEt ₃	100	1,000	200	81
11	$[(\text{dippe})\text{PdCl}_2]$	100	FA, 2.1	1,000	5	NEt ₃	100	1,000	200	81
12	$[(\text{dtbpe})\text{PdCl}_2]$	100	FA, 2.1	1,000	1	NEt ₃	100	1,000	1,000	81
13	$[(\text{dtbpe})\text{PdCl}_2]$	100	FA, 2.1	3,000	1	NEt ₃	70	2,100	2,100	81
14	$[\text{Ru}(\textit{p}\text{-cymene})\text{Cl}(\text{L1})]$	120	FA, 1	1,000	16	KOH	96	960	60	66
15	$[\text{Ru}(\textit{p}\text{-cymene})\text{Cl}(\text{L2})]$	120	FA, 1	1,000	16	KOH	68	680	43	66
16	$[(\text{dpa})(\textit{p}\text{-cymene})\text{RuCl}]\text{Cl}$	150	FA, 2	1,000	16	NEt ₃	99	990	62	100
17	$[(\text{mbdpa})(\textit{p}\text{-cymene})\text{RuCl}]\text{Cl}$	150	FA, 2	1,000	16	NEt ₃	100	1,000	63	100
18	$[(\text{mbdpa})(\textit{p}\text{-cymene})\text{RuCl}]\text{Cl}$	150	FA, 2	2,000	16	NEt ₃	99	1,980	124	100
19	$[(\text{dpa})\text{Cp}^*\text{IrCl}]\text{Cl}$	120	FA, 4	1,000	16	NEt ₃	98	980	62	100
20	$[(\text{dpa})\text{Cp}^*\text{Ir}(\text{OSO}_3)]$	110	FA, 2	1,000	16	(H ₂ O)	100	1,000	63	67
21	$[(\text{dpa})\text{Cp}^*\text{Ir}(\text{OSO}_3)]$	110	FA, 2	2,000	24	(H ₂ O)	100	2,000	83	67
22	$[\text{Ru}(\textit{p}\text{-cymene})\text{Cl}(\text{L1})]\text{Cl}$	150	FA, 1	1,000	12	NEt ₃	96	960	80	101
23	$[\text{Ru}(\textit{p}\text{-cymene})\text{Cl}(\text{L2})]\text{Cl}$	150	FA, 1	1,000	12	NEt ₃	96	960	80	101
24	$[\text{Ru}(\textit{p}\text{-cymene})\text{Cl}(\text{L3})]\text{Cl}$	150	FA, 1	1,000	12	NEt ₃	97	970	81	101
25	$[\text{Ru}(\text{COD})\text{Cl}_2(\text{L1})]$	150	FA, 1	1,000	12	NEt ₃	97	970	81	101
26	$[(\text{Ru}(\text{benzene})\text{Cl}_2)_2\text{L1}]$	120	FA, 2	1,000	8	NEt ₃	89	890	111	102
27	$[(\text{Ru}(\textit{p}\text{-cymene})\text{Cl})_2\text{L2}]_2\text{BPh}_4$	120	FA, 2	1,000	8	NEt ₃	97	970	121	102
28	Shvo's catalyst	80	IPA, 25	100	16	-	99	99	6	68
29	$\text{RuCl}(\textit{p}\text{-cymene})[\text{Ts-DPEN}]$	25	FA	100	24	NEt ₃	99, 64 % ee	99	4	103

30	RuCl(<i>p</i> -cymene)[Ts-DPEN]	30	FA	100	16	N-methylpiperidine	98, 93 % ee	98	6	¹⁰³
31^a	[RuCl(CNNO ^{Me})(dppb)]	82	IPA	1,000	0.33	K ₂ CO ₃	96	960	2,909	¹⁰⁴
32^a	[RuCl(CNNO ^{Me})(dppf)]	82	IPA	1,000	0.25	K ₂ CO ₃	97	970	3,880	¹⁰⁴
33^a	[Ru(CNNO ^{Me})(CO)(PCy ₃)(PPh ₃)] [BARf ₄]	82	IPA	10,000	0.50	K ₂ CO ₃	94	9,400	18,800	¹⁰⁴

^a Ethyl levulinate (EL) used as feedstock.

1.3.2.2 Transfer hydrogenation reactions of LA to GVL using non-precious metals

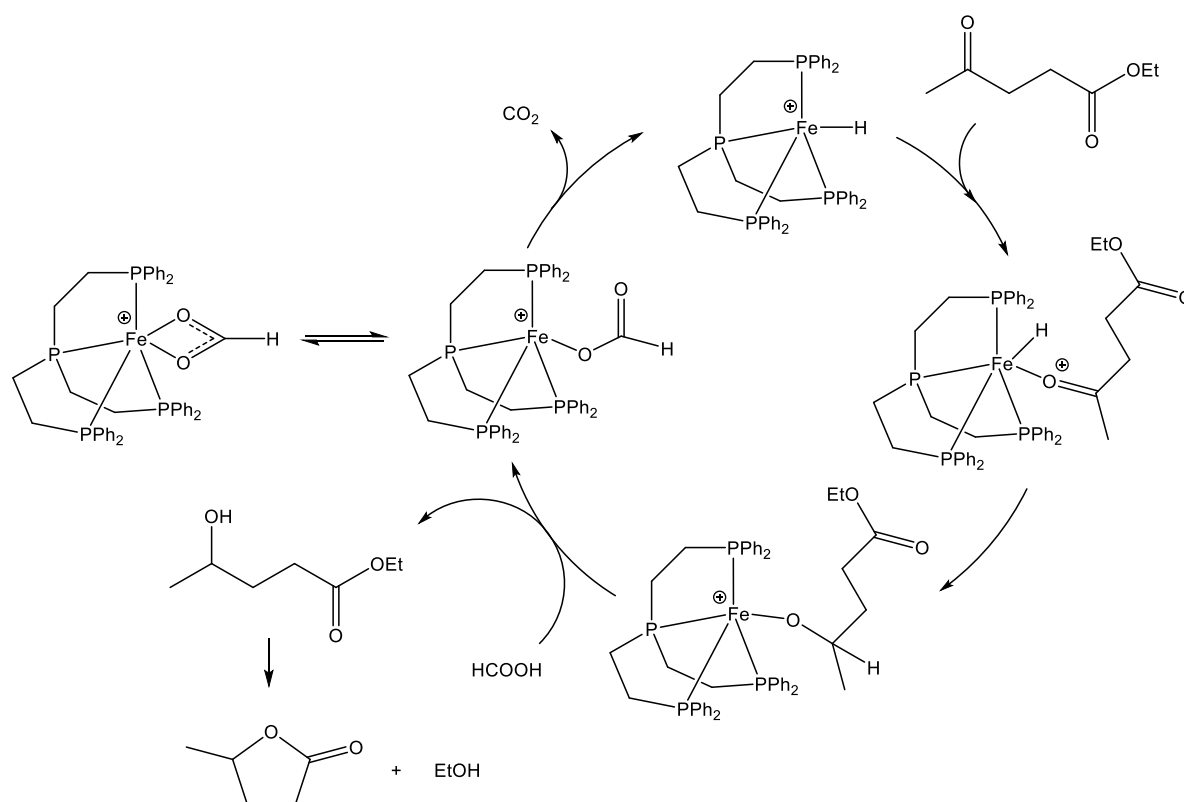
There are also several examples of transfer hydrogenation reactions of LA that are based upon non-precious metals. These results are collected in Table 1.8.

Fu et al. became interested in the use of iron catalysts for GVL production via transfer hydrogenation, owing to the potential sustainability of such a process across feedstock source, hydrogen source and catalyst. This followed some theoretical studies that indicated iron catalysts would be feasible for such reactions.¹⁰⁵ In fact, the work by Fu et al. represented the first iron-catalysed hydrogenation of ketones with FA.¹⁰⁶

Their system trialled a series of iron sources alongside the multidentate Tetrachos ligand. Chloride containing iron precursors achieved no activity; the authors attributed this to poisoning of the catalyst, an effect which had been reported previously. Iron(II) triflate (Fe(CF₃SO₃)₂) was found to be most effective, attributed to the weakly coordinating nature of the triflate anion. Furthermore, a temperature of 140 °C was necessary to achieve high GVL yields. The polar solvents DMA and DMSO produced no GVL, whilst ethers, principally 1,4-dioxane, were the most effective. Although with LA as the substrate no conversion was achieved, ethyl levulinate (EL) was an excellent substrate for GVL production. Using (Fe(CF₃SO₃)₂) and Tetrachos, with FA in 1,4-dioxane at 140 °C, > 99 % conversion was achieved in 24 hours (Table 1.8, Entry 1). Methyl levulinate (ML) was also an effective feedstock, obtaining 90 % GVL yield. Other multi- and monodentate ligands – including Triphos, dppe, dppb, BINAP and PPh₃ – resulted in <10 % conversions. Curiously, the addition of triethylamine, even in catalytic amounts, reduced the GVL yield almost to zero. Hence, their reactions were performed without any base or additive. Interestingly, replacing iron for Co/Pd/Ru/Ir gave no conversion and the reaction did not proceed under pressures of H₂ in the absence of FA. This suggests that the reaction was genuinely proceeding by transfer hydrogenation, rather than as a result of H₂ production from FA. They identified the active species as the Fe–H intermediate generated after dehydrogenation of FA.

The mechanism presented by the authors is shown in Scheme 1.12. The triflate anion is readily displaced by the formate anion, and following isomerisation and dehydrogenation generates a Fe-H species. After coordination of EL (which might be considered to compete with any strongly coordinating anions present), the carbonyl is reduced by the Fe-H moiety and after protonation generates the product. The cycle restarts by coordination of a formate anion.¹⁰⁶

The group went on to study further iron-based systems for the hydrogenation of EL to GVL. They initially trialed the iron-centered Casey's catalyst (Figure 1.21). This gave a GVL yield of just 4 %. An activated form of the catalyst was generated through treatment with acid and base, recognising a need for both acidic and hydridic hydrogens on the catalyst. They tested a series of the "activated" catalysts with R = SiMe₃, SiMe₂^tBu and SiMe₂Et. From EL in isopropanol (as solvent and hydrogen source) at 75 °C, a 42 % GVL yield was achieved in 16 hours using the least bulky catalyst (R = SiMe₃) (Table 1.8, Entry 2). The catalysts with bulkier ligands gave just 10 % and 7 % GVL yields.



Scheme 1.12. Mechanism of transfer hydrogenation of ethyl levulinate presented by Fu et al.¹⁰⁶

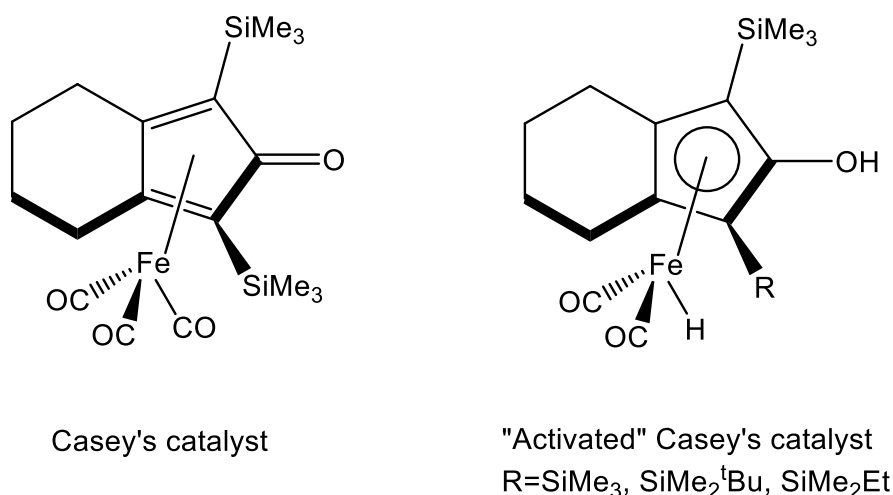


Figure 1.21. The structures of Casey's catalyst and an activated form described by Fu et al.¹⁰⁷

Their system was optimised with the least bulky catalyst. Increasing the temperature to 100 °C brought the GVL yield to 71 %. Higher temperatures gave much reduced yields, attributed to catalyst decomposition. With the addition of bases, further improvements were found, with NaHCO₃ as the most effective, facilitating a 95 % GVL yield (Table 1.8, Entry 3). The more typical TH base NEt₃ reduced the yield to 64 %. Both ML and butyl levulinate (BL) could be used as feedstocks, giving 91 % and 92 % GVL yields respectively. Finally, a range of hydrogen sources were tested. Surprisingly, FA led to just 12 % yield. Generally secondary alcohols were more effective than primary alcohols, with IPA the most effective. Additionally, 10 bar H₂ gas gave just 33 % yield, suggesting that the reactions are proceeding primarily through transfer hydrogenation via a Fe-H intermediate, rather than as a result of IPA decomposing to H₂.¹⁰⁷

It should be noted that the iron systems mentioned thus far use alkyl levulinates as feedstocks rather than LA itself. There is debate over which starting material is preferred. Whilst some claim that alkyl levulinate esters are easier to prepare and isolate than LA, the generation of the esters from lignocellulose has some drawbacks. Whilst LA is prepared from lignocellulose in water and produces FA in a 1:1 ratio, the production of esters uses alcohol solvents (leading to the generation of volatile alkyl ethers and alkenes) and does not produce FA. LA and its alkyl levulinate esters can be produced in the same yield range.

Burtoloso and Metzker investigated the transfer hydrogenation of LA to GVL using FA in water using a range of Fe(0) carbonyl compounds. These are inexpensive, commercially available, and straightforward to prepare. [Fe₃(CO)₁₂] was the most effective iron catalyst, achieving 92 % GVL yield in 15

hours using imidazole as the base at 180 °C (Table 1.8, Entry 4). Pyridine was also an effective base, achieving 87 % yield (Table 1.8, Entry 5). Omitting the base entirely gave a yield of just 12 %.

Interestingly, some conversion was achieved in the absence of $[\text{Fe}_3(\text{CO})_{12}]$: imidazole and pyridine achieved yields of 31 % and 16 % respectively. They considered that hydrogenation was able to take place because of thermal decomposition of FA to H_2 at high temperatures. However, with neither Fe nor base, <5 % yield was achieved. The base was considered necessary even in the absence of metal catalyst, because the conjugate base of FA, formate, is a better hydrogen donor than FA itself.

The authors found that after 10 hours at 180 °C, the GVL yield remained < 10 %. Only after 12 hours did the yield grow, reaching a maximum at 15 hours. The long induction time indicated that $[\text{Fe}_3(\text{CO})_{12}]$ needed to be converted into a more active species prior to LA hydrogenation. At the end of the reaction, no $[\text{Fe}_3(\text{CO})_{12}]$ was recovered; instead the only Fe species was Fe_2O_3 . The authors postulated that their reaction might involve the generation of iron nanoparticles/clusters and operate under a heterogeneous regime.¹⁰⁸

Section 1.3.1.4 introduced some work by Wildeman et al. using a series of Casey's catalyst analogues for LA hydrogenation. Their most active catalyst was a dicarbonyl mono-acetonitrile analogue, achieving quantitative conversions of LA to GVL. Unfortunately, the same catalyst was much less active under transfer hydrogenation conditions. With IPA as both donor and solvent at 80 °C, just 14 % conversion was achieved in 20 hours. Changing the solvent to toluene increased the conversion to 38 %, but an increase in temperature to 100 °C gave just 5 % yield. After studying the kinetic profiles, the authors identified catalyst deactivation after four hours. The catalyst lifetime was not affected by the catalyst loading. Hence, the authors were unable to optimise the system any further with their iron catalyst.⁶⁸

Table 1.8. Non-precious metal catalytic systems for transfer hydrogenation of LA.

Entry	Catalyst	T [°C]	H source, equiv.	S/C	Time [h]	Additives	GVL yield [%]	TON	TOF [h ⁻¹]	Ref.
1 ^a	$[\text{Fe}(\text{CF}_3\text{SO}_3)_2]/\text{Tetrachos}$	140	FA, 2	10	24	-	99	10	-	106
2 ^a	Casey's catalyst (R = SiMe ₃)	75	IPA	100	16	-	42	42	3	107
3 ^a	Casey's catalyst (R = SiMe ₃)	100	IPA	100	19	NaHCO ₃	95	95	5	107
4	$[\text{Fe}_3(\text{CO})_{12}]$	180	FA, 4	25	15	Imidazole	92	23	2	108
5	$[\text{Fe}_3(\text{CO})_{12}]$	180	FA, 4	25	15	Pyridine	87	22	2	108
6	Casey's catalyst [[CO] ₂ (MeCN)]	80	IPA, 25	25	20	-	38	10	1	68

^a Ethyl levulinate (EL) used as feedstock.

1.4 Hydrogenation of LA to 1,4-PDO

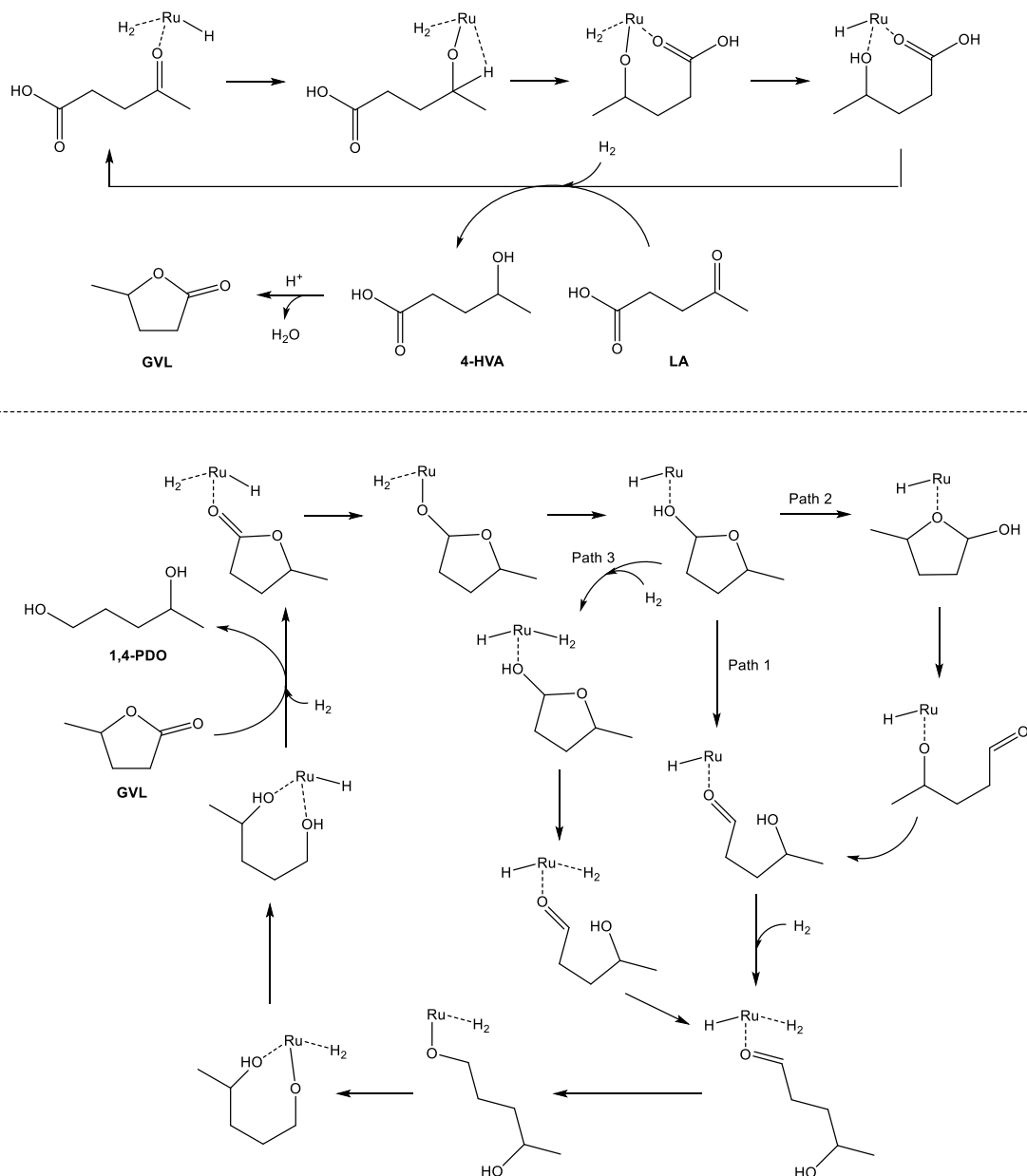
1,4-PDO was introduced in Section 1.2.3 as a further hydrogenation product of LA. Owing to the difficulty of hydrogenating beyond GVL, and the readiness of 1,4-PDO to dehydrate to form 2-MTHF, relatively few homogeneous catalytic systems have been able to successfully catalyse the hydrogenation of LA to 1,4-PDO. A survey of some of the most important systems follows. Key results are collated in Table 1.9.

A variety of Ru systems were trialled by Horvath et al. under both molecular hydrogen and transfer hydrogenation conditions. Using an in situ mixture of $[\text{Ru}(\text{acac})_3]$ and PBU_3 in neat conditions at 83 bar H_2 and 200 °C, they achieved full conversion of LA to 63 % 1,4-PDO, and 37 % GVL, over approximately 42 hours (Table 1.9, Entry 1). Under transfer hydrogenation conditions, both the conversion and selectivity for 1,4-PDO were reduced. Using the preformed catalyst $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{bipy})(\text{H}_2\text{O})][\text{SO}_4]$ in water, alongside sodium formate as hydrogen source and HNO_3 to adjust the pH, 25 % 1,4-PDO and 25 % GVL were produced from LA after 18 hours at 70 °C.⁴²

Leitner et al. surveyed a range of catalytic systems to study the effect of different variables on the LA reaction network. Alongside $[\text{Ru}(\text{acac})_3]$, they tested a series of ligands (P^nOct_3 , dppb, Triphos) to study their influence on the stereoelectronic properties of the catalyst; acidic ionic liquid additives to study their effect on the reactivity/stability of the active catalyst species; and acid additives (NH_4PF_6 , *p*-TsOH) to study the effect of acid strength. Full LA conversion was achieved in every case. The best selectivity for 1,4-PDO was achieved with $[\text{Ru}(\text{acac})_3]$ and Triphos at 100 bar H_2 and 160 °C, without additives: 95 % 1,4-PDO yield in 18 hours (Table 1.9, Entry 2). Different additives changed the selectivity completely: adding NH_4PF_6 or ionic liquids favoured 2-MTHF (by aiding 1,4-PDO dehydration), *p*-TsOH favoured GVL (although 1,4-PDO dehydration was aided, the overall hydrogenation activity was reduced). With P^nOct_3 and dppb ligands, the maximum 1,4-PDO yields were 30 % and 11 % respectively, with GVL as the major product. Again, this shows that using the multidentate Triphos ligand generates a more active catalyst. An organometallic compound identified as $[\text{Ru}(\text{Triphos})(\text{CO})(\text{H})_2]$ was isolated from the reaction mixtures.⁶⁰

The authors went on to study their system further. Compared to the 95 % 1,4-PDO yield achieved with an in situ mixture of $[\text{Ru}(\text{acac})_3]$ and Triphos, the preformed complex $[\text{Ru}(\text{Triphos})(\text{CO})(\text{H})_2]$ achieved a reduced 73 % 1,4-PDO yield (Table 1.9, Entry 3). They considered $[\text{Ru}(\text{Triphos})(\text{CO})(\text{H})_2]$ as a resting state which needs protonation to generate the active $[\text{Ru}(\text{Triphos})\text{H}]^+$ species. Interestingly, using GVL as the substrate, a 76 % 1,4-PDO was achieved with the in situ catalyst mixture; the pre-formed catalyst achieved just 3 % 1,4-PDO yield.

The authors studied the reaction mechanism further computationally. The reaction networks for both hydrogenation of LA to GVL, and for GVL to 1,4-PDO, are shown in Scheme 1.13. They both begin with the catalytically active unit $[\text{Ru}(\text{Triphos})\text{H}]^+$. They found that from $[\text{Ru}(\text{Triphos})\text{H}]^+$, hydride transfer from Ru-H inserting into the carbonyl/carboxyl carbon of the substrate (the rate-determining step) was followed by protonation of the resulting Ru-O moiety via sigma-bond metathesis from a coordinated H_2 molecule, regenerating the active unit.¹⁰⁹



Scheme 1.13. Reaction networks for hydrogenation of LA to GVL and 1,4-PDO reported by Leitner et al.¹⁰⁹

The authors went on to study the hydrogenation reactions of a wide range of carboxylic and carbonic acid derivatives, using $[\text{Ru}(\text{Triphos})(\text{TMM})]$ (TMM = Trimethylenemethane) as the catalyst prepared from $[\text{Ru}(\text{COD})(\text{methylallyl})_2]$. It proved to be excellent for LA hydrogenation to 1,4-PDO, giving a 99 % yield (and 99 % selectivity) in 16 hours at 140 °C and 50 bar H_2 in dioxane without additives (Table 1.9, Entry 4). The same near-quantitative 1,4-PDO yield was achieved from both methyl levulinate (ML) and GVL. They also identified deactivation pathways generating the inactive catalyst species $[\text{Ru}(\text{Triphos})(\text{CO})(\text{H})_2]$ (previously mentioned by Leitner et al.), resulting from substrate-dependent carbonylation, and $[\text{Ru}(\text{Triphos})(\mu\text{-H})_2]$. Where necessary, these could be suppressed by the addition of catalytic amounts of acids.¹¹⁰

Zhou et al. studied the hydrogenations of a range of carboxylic esters and lactones using ruthenium complexes of tetradentate PNNN or PNNP bipyridine ligands (Figure 1.22). The catalysts were prepared from $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$. At 50 bar and 25 °C in THF with NaOMe base additive, GVL was converted to 98 % 1,4-PDO in four hours with Ru-PNNN-1 ($\text{R}^1 = \text{tBu}$, $\text{R}^2 = \text{NEt}_2$) (Table 1.9, Entry 5). At the same conditions, Ru-PNNN-2 ($\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{NEt}_2$) achieved a 96 % 1,4-PDO yield in seven hours (Table 1.9, Entry 6), whilst Ru-PNNP ($\text{R}^1 = \text{tBu}$, $\text{R}^2 = \text{P}(\text{tBu})_2$) achieved just a 30 % yield in 14 hours. The authors recognised the need for the hemilabile NEt_2 group to achieve high activity. Their mechanism showed that after the formation of a dihydride complex under basic conditions, the dissociation of the hemilabile NEt_2 group provided a vacant site for substrate coordination to the metal; the chelate ring was more resistant to opening with a phosphine substituent in its place.

A range of solvents facilitated high 1,4-PDO yields, with 2-MTHF, diethyl ether, toluene, isopropanol (giving 99 % yield), and neat conditions, achieving yields ≥ 78 %. Using ethanol and methanol gave much reduced yields, and whilst KO^tBu was an effective base, inorganic bases NaOH and Na_2CO_3 gave no conversion. Reducing the pressure to 10 bar gave 95 % yield in 16 hours. Even at 0.001 mol% catalyst loading, 50 % yield was achieved at 50 bar in 64 hours with a TON = 50,000; at 100 bar, a 91 % yield was achieved in 48 hours, giving a TON = 91,000 (Table 1.9, Entry 7). Additionally, starting from ML, a 95 % 1,4-PDO yield was achieved after 16 hours at the standard conditions.¹¹¹

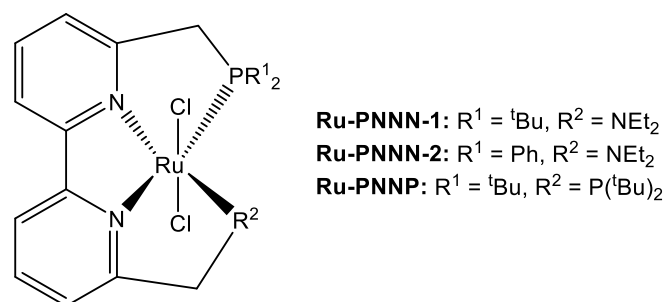


Figure 1.22. Structure of the ruthenium bipyridine complexes reported by Zhou et al.¹¹¹

Miller et al. studied the hydrogenation of LA using ruthenium complexes of the tridentate Triphos and N-Triphos ligands. An in situ system of $[\text{Ru}(\text{acac})_3]$ and Triphos ligand at 65 bar H_2 and 150 °C in THF, gave an 83 % yield of 1,4-PDO alongside 9 % GVL in 25 hours (Table 1.9, Entry 8). Using instead the N-Triphos ligand gave just a 37 % 1,4-PDO yield, alongside 60 % GVL and 2 % 2-MTHF.

The preformed dihydride catalyst $[\text{RuH}_2(\text{CO})(\text{N-Triphos}^{\text{Ph}})]$ gave just a 36 % yield of 1,4-PDO, alongside 53 % GVL. However, changing to the catalyst $[\text{RuH}_2(\text{PPh}_3)(\text{N-Triphos}^{\text{Ph}})]$ made a great difference, giving a 99 % yield of 1,4-PDO (Table 1.9, Entry 9). This was attributed to the greater lability of the PPh_3 ligand relative to CO, facilitating LA hydrogenation more readily by the formation of $[\text{RuH}_2(\text{N-Triphos}^{\text{Ph}})]^+$. Surprisingly, modifying the N-Triphos substituents from phenyl to cyclopentyl, generating the catalyst $[\text{RuH}_2(\text{PPh}_3)(\text{N-Triphos}^{\text{Cyp}})]$, gave just 1 % 1,4-PDO yield. The use of the bulky and electron-donating cyclopentyl substituents was expected to give improvements; it was unclear if the reduction was attributable to the increased steric bulk around the metal hindering substrate coordination, or due to the increased electron rich nature of the metal centre. LA could be further transformed beyond 1,4-PDO to 2-MTHF under acidic conditions; this will be discussed in Section 1.5.⁶¹

Some work by Palkovits et al. was described earlier in Section 1.3.1.1 for LA hydrogenation to GVL. However, some of their systems also showed good conversion of LA to 1,4-PDO. They surveyed a range of Ru precursors alongside unsymmetrical N-Triphos ligands, most of which gave a higher selectivity for GVL; however $\text{RuH}_2(\text{PPh}_3)_4$ and the unsymmetrical N-Triphos ligand containing two methylene arms and one ethylene arm gave a 98 % 1,4-PDO yield in 18 hours at 70 bar H_2 and 160 °C in THF. $[\text{RuH}_2(\text{PPh}_3)_4]$ was considered to have the greatest activity for LA hydrogenation owing to its lack of CO or Cl substituents. Switching $[\text{RuH}_2(\text{PPh}_3)_4]$ for $[\text{RuCOD}(\text{methylallyl})_2]$ or $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ swings the reaction from a 98 % 1,4-PDO yield to a 97 % GVL yield (Table 1.9, Entry 10).⁶²

Recently, Elsevier, de Bruin et al. studied a cobalt-based system for the hydrogenation of ester and carboxylic substrates, including LA. They recognised that the use of first-row transition metals is largely unprecedented for this reaction, attributed to the weaker metal-ligand bonds formed with first-row transition metals relative to later transition-metals. These weaker bonds facilitate ligand protonation and subsequent dissociation, generating vacant coordination sites that can lead to over-coordination by the coordinated carboxylate conjugate base, and catalyst deactivation.

They generated a catalyst in situ from $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and the tridentate carbon-centered Triphos ligand. They achieved no activity using mono- or bidentate ligands. From LA, >99 % conversion was achieved over 22 hours, at 80 bar H_2 and 100 °C in THF. The yields of 1,4-PDO and 2-MTHF were 47 % and 14 % respectively (Table 1.9, Entry 11). A high 10 mol% catalyst loading was required, although

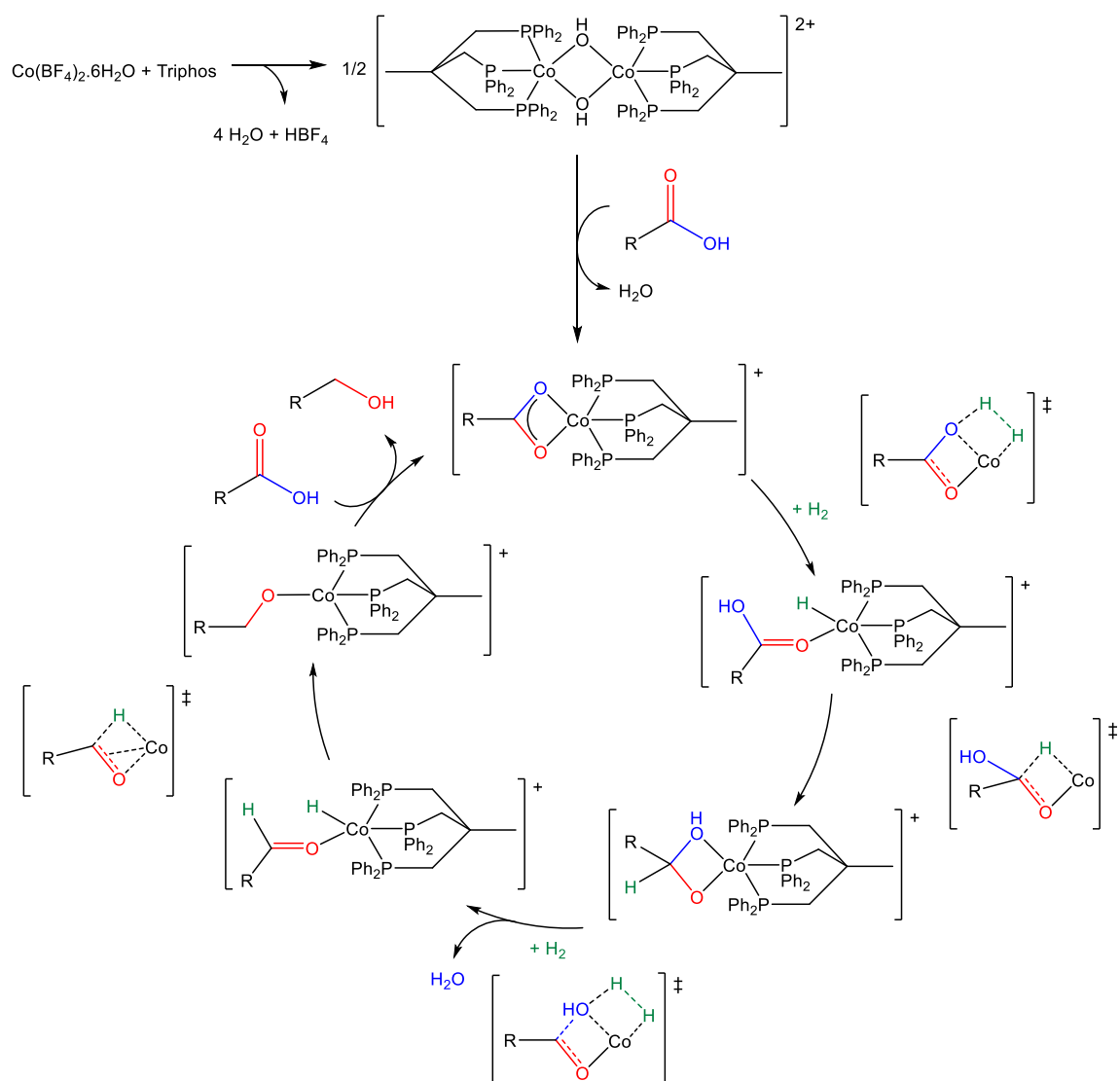
this is more acceptable for a cobalt-based system. Starting from GVL, 98 % conversion was achieved, with slightly higher 1,4-PDO and 2-MTHF yields of 63 % and 25 % respectively.

The authors presented a mechanism with calculated transition states (Scheme 1.14). Their mechanism begins with the spontaneous formation of $[\text{Co}_2(\mu\text{-OH})_2(\text{Triphos})_2](\text{BF}_4)_2$ from $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and Triphos. This is split by substitution of the OH ligands for carboxyl groups, forming the active catalyst species $[\text{Co}(\text{Triphos})(\text{OOCR})](\text{BF}_4)$. Following heterolytic hydrogen splitting over the Co-O bond and migratory insertion of the hydride into the carbonyl carbon, a second heterolytic hydrogen splitting generates $[\text{Co}(\text{Triphos})(\text{H})(\text{aldehyde})](\text{BF}_4)$. Hydride migration from the metal centre to the substrate, followed by proton transfer from an incoming substrate, generates the alcohol product and regenerates the active catalyst species.

Although the TONs and product yields are moderate, and the Triphos ligand has limitations (in cost, ease of synthesis and structural versatility), this work represented an important finding that earth-abundant metals like cobalt could hydrogenate carboxylic acids like LA beyond GVL.⁸⁵

Table 1.9. Catalytic systems for hydrogenation of LA to 1,4-PDO.

Entry	Catalyst	T [°C]	P(H ₂) [bar]	S/C	Time [h]	Additives	1,4-PDO yield [%]	TON	TOF [h ⁻¹]	Ref.
1	$[\text{Ru}(\text{acac})_3]/\text{PBU}_3$	200	83	417	42	-	63	263	6	42
2	$[\text{Ru}(\text{acac})_3]/\text{Triphos}$	160	100	1,000	18	-	95	950	53	60
3	$[\text{Ru}(\text{Triphos})(\text{CO})(\text{H})_2]$	160	100	1,000	18	-	73	730	41	109
4	$[\text{Ru}(\text{Triphos})(\text{TMM})]$	140	50	50	16	-	98	49	3	110
5	Ru-PNNN-1	25	50	1,000	4	NaOMe	99	990	248	111
6	Ru-PNNN-2	25	50	1,000	7	NaOMe	96	960	137	111
7	Ru-PNNN-1	25	100	100,000	48	NaOMe	91	91,000	1,896	111
8	$[\text{Ru}(\text{acac})_3]/\text{Triphos}$	150	65	200	25	-	83	166	7	61
9	$[\text{RuH}_2(\text{PPh}_3)(\text{N-Triphos}^{\text{Ph}})]$	150	65	200	25	-	99	198	8	61
10	$[\text{RuH}_2(\text{PPh}_3)_4]$	160	70	200	18	-	98	196	11	62
11	$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}/\text{Triphos}$	100	80	10	22	-	47	5	-	85



Scheme 1.14. Catalytic cycle for hydrogenation of carboxylic acids, as reported by Elsevier, de Bruin et al.⁸⁵

1.5 Hydrogenation of LA to 2-MTHF

2-MTHF was introduced previously as an LA hydrogenation product with useful applications as a green solvent and fuel additive. It is formed after the acid-catalysed dehydration of 1,4-PDO. The formation of 2-MTHF requires hydrogenation beyond the stable GVL, necessitating highly active catalytic systems and forcing reaction conditions. Furthermore, product selectivity becomes difficult to control. For these reasons, there are few homogeneous catalysts that can selectively achieve high yields of 2-MTHF from LA. The most important systems will be discussed in this Section and are summarised in Table 1.10.

Section 1.4 introduced a system reported by Horvath et al., for the hydrogenation of LA to 1,4-PDO using an in situ mixture of $[\text{Ru}(\text{acac})_3]$ and PBU_3 . A similar system ($[\text{Ru}(\text{acac})_3]$ and PBU_3 at 83 bar H_2 and 200 °C over 46 hours), with the addition of NH_4PF_6 , achieved quantitative conversion of LA to 2-MTHF after initially forming 1,4-PDO (Table 1.10, Entry 1). This illustrates that the dehydration of 1,4-PDO to 2-MTHF is acid catalysed and can be completely turned on or off, with the addition or omission of an acidic additive. The same system (at 76 bar, over 60 hours) achieved 72 % conversion of GVL to 2-MTHF.⁴²

Previous sections discussed a system reported by Leitner et al. surveying the use of $[\text{Ru}(\text{acac})_3]$ alongside different ligands (P^nOct_3 , dppb, Triphos) and acidic additives (NH_4PF_6 , *p*-TsOH, ionic liquids), with reference to the production of GVL and 1,4-PDO. Their system was also able to reach high yields of 2-MTHF. The general conditions used 100 bar H_2 over 18 hours and achieved full LA conversion in every case. With the monodentate ligand P^nOct_3 and the bidentate ligand dppb, maximum 2-MTHF yields of 3 % and 51 % were achieved with NH_4PF_6 at 200 °C. The tridentate Triphos ligand was required for high 2-MTHF yields. Without any acidic additive 0 % 2-MTHF was produced. With the Triphos ligand and NH_4PF_6 additive, 59 % 2-MTHF was produced at 200 °C (Table 1.10, Entry 2). The stronger acid *p*-TsOH gave a reduced 39 % 2-MTHF yield at 160 °C: although all the 1,4-PDO made was converted to 2-MTHF, the overall hydrogenation activity was lower and GVL was the major product. However, with the addition of the acidic ionic liquid 1-butyl-2-(4-sulfobutyl)imidazolium-*p*-toluenesulfonate (aIL), an 87 % yield of 2-MTHF was achieved, which increased to 92 % with the addition of both aIL and NH_4PF_6 (at 160 °C) (Table 1.10, Entries 3-4). The same system achieved a 92 % 2-MTHF yield in just five hours at 200 °C and 50 bar H_2 . The system could be recycled for four consecutive runs without significant catalyst deactivation.⁶⁰

The authors went on to compare the in situ mixture of $[\text{Ru}(\text{acac})_3]$ and Triphos against the preformed catalyst $[\text{Ru}(\text{Triphos})(\text{CO})(\text{H})_2]$. Under conditions of 100 bar H_2 and 160 °C, with the acidic ionic liquid additive N-butyl-N'-(4-sulfobutyl)imidazolium *p*-toluenesulfonate, both the in situ mixture and the preformed catalyst were highly active for the hydrogenation of GVL, achieving 2-MTHF yields of 95 % and 96 % respectively (Table 1.10, Entries 5-6). This is in stark contrast to the hydrogenations performed without an acidic additive in which the preformed catalyst showed almost no activity. Therefore, the involvement of the acidic additive is crucial. This might be attributed to acid-catalysed ring-opening of GVL to form a more active substrate. Alternatively, considering $[\text{Ru}(\text{Triphos})(\text{CO})(\text{H})_2]$ as a “resting state” and $[\text{Ru}(\text{Triphos})\text{H}]^+$ as the active species, the acidic additive might aid conversion of the resting state into the active species by protonation, in place of or in addition to protonation by LA itself.¹⁰⁹

Section 1.4 also introduced some work by Miller et al. for the hydrogenation of LA to 1,4-PDO using ruthenium systems of the tridentate Triphos and N-Triphos ligands. They went on to study the effect of incorporating acidic additives to generate 2-MTHF. Under the general conditions of 150 °C and 65 bar H₂ in THF over 25 hours, full LA conversion was achieved in all cases. An in situ mixture of [Ru(acac)₃] and Triphos, with NH₄PF₆, generated just 2 % 2-MTHF. The same system with N-Triphos also generated only 5 % 2-MTHF. However, switching NH₄PF₆ for HN(Tf)₂ led to a much improved 45 % 2-MTHF yield (Table 1.10, Entry 7).

Trialling the three preformed catalysts [RuH₂(CO)(Triphos^{Ph})], [RuH₂(CO)(N-Triphos^{Ph})] and [RuH₂(PPh₃)(N-Triphos^{Ph})] gave < 1 % 2-MTHF yields in every case when NH₄PF₆ or *p*-TsOH was used as the acid additive with GVL as the major product. However, [RuH₂(PPh₃)(N-Triphos^{Ph})] in the presence of HN(Tf)₂ gave an excellent 87 % yield of 2-MTHF, meaning that LA is effectively hydrogenated beyond GVL and readily converted from 1,4-PDO to 2-MTHF under the acidic conditions (Table 1.10, Entry 8).

The negative effect of acids NH₄PF₆ and *p*-TsOH was attributed to a deactivating interaction of the additive with the catalyst. Upon release of H⁺, the generated conjugate bases of NH₄PF₆ and *p*-TsOH, NH₃ and *p*-TsO⁻ respectively, are coordinating species and may be considered to compete with the substrate for metal coordination, deactivating the metal. Hence, the use of these acidic additives drastically reduces the catalyst activity. However, the acidic additive HN(Tf)₂ generates a highly non-coordinating conjugate base which does not compete with substrate binding. Therefore, the catalyst remains highly active for the hydrogenation of LA through to 1,4-PDO, whilst the acidity provided by HN(Tf)₂ allows for the ready dehydration of 1,4-PDO to 2-MTHF. The catalyst containing the labile PPh₃ ligand is most efficient for similar reasons: decoordination of the PPh₃ ligand generates a vacant coordination site accessible to the substrate.⁶¹

Table 1.10. Catalytic systems for hydrogenation of LA to 2-MTHF.

Entry	Catalyst	T [°C]	P(H ₂) [bar]	S/C	Time [h]	Additives	2-MTHF yield [%]	TON	TOF [h ⁻¹]	Ref.
1	[Ru(acac) ₃]/PBu ₃	200	83	402	46	NH ₄ PF ₆	100	402	9	42
2	[Ru(acac) ₃]/Triphos	200	100	1,000	18	NH ₄ PF ₆	59	590	33	60
3	[Ru(acac) ₃]/Triphos	160	100	1,000	18	aIL	87	870	48	60
4	[Ru(acac) ₃]/Triphos	160	100	1,000	18	aIL + NH ₄ PF ₆	92	920	51	60
5 ^a	[Ru(acac) ₃]/Triphos	160	100	1,000	18	aIL	95	950	53	109
6 ^a	[Ru(Triphos)(CO)(H) ₂]	160	100	1,000	18	aIL	96	960	53	109
7	[Ru(acac) ₃]/N-Triphos	150	65	200	25	HN(Tf) ₂	45	90	4	61
8	[RuH ₂ (PPh ₃)(N-Triphos ^{Ph})]	150	65	200	25	HN(Tf) ₂	87	174	7	61

^a GVL used as feedstock.

1.6 Summary and outlook

This chapter began by considering the chemical and energy industries in the world today, particularly with respect to the production of liquid fuels, chemicals and materials. These industries rely upon fossil fuels as a resource. However, owing to their rapid depletion and detrimental involvement in climate change, it is becoming increasingly necessary to develop more sustainable routes to the fuels and chemicals which our world relies on. Most scientists consider biomass to be the most promising alternative feedstock, as it is hugely abundant, renewable and low-cost. Lignocellulosic biomass has three main components: cellulose, hemicellulose and lignin. From cellulose in particular, a wide range of important chemical feedstocks can be derived. A major difference between feedstocks derived from biomass compared to those derived from fossil fuels is their excess functionality. Whilst this introduces complexities to their processes, it allows for a much wider range of target molecules from a single chemical feedstock. This is exemplified by levulinic acid, a 1,4-ketoacid derived from cellulose. Levulinic acid has been identified as one of the most promising biogenic substrates. Its two reactive functional groups allow it to access a wide range of target products. Of particular interest are the hydrogenation products of LA: γ -Valerolactone, 1,4-pentanediol and 2-methyltetrahydrofuran. These products have many useful applications.

The hydrogenation of LA requires effective catalytic systems. Whilst both heterogeneous and homogeneous systems have been reported for this application, discussion in this chapter has focused on homogeneous catalysts. These systems almost exclusively use the precious metals ruthenium, iridium and palladium, however several systems based on the non-precious metals iron and cobalt have been reported in recent years. Most reported systems can hydrogenate LA to GVL. Far fewer systems are sufficiently active for hydrogenation beyond GVL to 1,4-PDO or 2-MTHF.

Whilst a mixture of in situ and preformed catalysts have been utilised, many of the systems use phosphine ligands. In particular, a number of multidentate and chelating phosphine ligands have been found to generate robust and active metal catalysts for LA hydrogenation. The steric and electronic effects of these ligands must be carefully tailored. Key examples are the tridentate Triphos ligand, and its nitrogen-centered analogue N-Triphos. Whilst the N-Triphos ligand offers the potential for greater structural versatility, it is very understudied relative to Triphos itself.

In this chapter, discussion of hydrogenation reactions was separated into those utilising pressures of molecular hydrogen and those using an alternative hydrogen source. The latter reactions are classed as transfer hydrogenation reactions and have several advantages over high-pressure reactions. As such, an increasing number of catalytic systems for the transfer hydrogenation of LA have been

reported in the past decade. Again, these generally use ruthenium and iridium as the metal source, often alongside phosphine ligands.

For the development of truly sustainable systems for chemical production, all these factors must be considered. In addition to the sustainable chemical feedstock, of which LA is a key example, the catalyst should aim to avoid or reduce a requirement for expensive precious metals; the ligand system itself should be inexpensive, straight-forward to handle and simple to tailor; and the hydrogenation conditions should be as uncomplicated, safe, and “green” as possible, whilst providing highly selective and active systems. In this context, the work described in this thesis aims to expand the knowledge in this field. Understanding that multidentate phosphine ligands are effective for use in hydrogenation catalysts, the family of N-Triphos and related ligands has been applied. Attempts to widen the choice of metal beyond ruthenium and iridium to less-studied metals have been investigated, and whilst research into transfer hydrogenations is becoming increasingly active, the field remains understudied relative to high-pressure hydrogenations. Therefore, the work presented in this thesis aims to expand the insight into the effectiveness of LA hydrogenation systems, with the view that these processes could be a sustainable route to the LA hydrogenation products which can substitute or replace products derived from fossil fuels.

1.7 Aims and Thesis outline

This chapter has highlighted several important considerations required for the development of catalytic systems for LA hydrogenation. Whilst several references were made to the use of multidentate phosphine ligands, study of the nitrogen-centred N-Triphos ligands remains limited relative to their carbon-centred analogues and analogues with other apical atoms (e.g. boron, silicon).¹¹² This is despite their greater structural versatility and ease of synthesis, compared to the carbon-centred analogues. Our group has investigated the N-Triphos ligand family extensively in recent years, especially in relation to LA hydrogenation processes, however there are large areas unexplored. This includes an expanded study into the involvement of different functional groups or substituents. Furthermore, their coordination chemistry has been studied with a relatively limited set of metals. This chapter highlighted a narrow set of metals which have found applications as homogeneous catalysts for LA hydrogenation: ruthenium, iridium, palladium, as well as iron and cobalt.

This thesis aims to investigate the synthesis and coordination chemistry of a series of both bidentate and tridentate nitrogen-centred phosphine ligands, targeting the development of effective catalysts

for the hydrogenation of LA to GVL, primarily under transfer hydrogenation conditions. The synthesis of both symmetrical and unsymmetrical phosphine ligands, and phosphine oxide ligands, and their coordination to second and third-row transition metals (ruthenium, rhodium, palladium, and iridium) and first-row transition metals (manganese, iron, cobalt, nickel and copper) will be described. Two major aspects of the complexes studied will be emphasised. Firstly, the coordination chemistry of the ligands, aided by crystallography in most cases; and second, the application of the complexes for the hydrogenation of LA to GVL.

Chapter 2 will provide a more detailed introduction to phosphine ligands, with a discussion of their bonding and stereo-electronic properties. The chapter will describe the synthesis of symmetrical N-Triphos ligands, and attempted syntheses of unsymmetrical mixed N-Triphos ligands. It will also describe the syntheses of nitrogen-bridged bisphosphine ligands. **Chapter 3** will discuss the reactivity of the bi- and triphosphine ligands with a series of transition metals (palladium, ruthenium, iridium, rhodium and nickel). The synthesis, characterisation and coordination chemistry of the complexes will be described. It will be seen that changes to both the ligand structure and the choice of metal precursor affect the structures and properties of the complexes generated. **Chapter 4** will describe the application of the complexes described in Chapter 3 as homogeneous catalysts for the hydrogenation of LA to GVL. Principally utilising transfer hydrogenation conditions, the efficacy of the different catalysts will be evaluated in different systems with a wide investigation of reaction variables. Some preliminary results obtained under high-pressure conditions will also be discussed. **Chapter 5** will discuss the coordination chemistry of N-Triphos ligands with first-row transition metals. It will be seen that the coordination of their phosphine oxide analogues allowed for the generation of interesting complexes with manganese, iron, cobalt, nickel and copper. **Chapter 6** will summarise the main findings of this research and identify areas for future investigation. **Chapter 7** provides the experimental details for all syntheses and experiments performed.

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Chapter 2

Phosphine ligands

“I will take the Ring to Mordor, though I do not know the way”, *Lord of the Rings: Fellowship of the Ring* (2001)

2.1 Introduction to phosphines

Phosphine ligands are ubiquitous in coordination chemistry. Whilst phosphine itself refers to PH_3 (also known as phosphane), phosphine ligands can be summarised as $\text{PR}_n\text{H}_{3-n}$, with $n=1-3$ referring to primary, secondary and tertiary phosphines respectively. The tertiary phosphines of the general formula PR_3 (R = alkyl or aryl) are the most relevant class to this work. Chapter 1 introduced many metal-based catalytic systems using a range of phosphine ligands: from the most simple, symmetrical PR_3 ligands such as triphenylphosphine (PPh_3), to those including two, three or four coordinating phosphine moieties, sometimes in addition to other coordinating P, N or C moieties. Phosphine ligands can be chiral, essential for some applications. Phosphines have found applications as ligands in a wide range of different systems; examples from just this year include ethylene oligomerisation, cross-couplings, aminations, arylations, hydrogenations and hydrations.¹⁻⁸

Metal phosphine complexes have some universal characteristics. The phosphine generally adopts a pyramidal structure upon coordination; they are compatible with metals in a variety of oxidation states; and their complexes tend to have good solubility in organic solvents. Owing to their nature as L-type (2e^-) ligands, they do not affect the formal charge of a metal complex. They are generally considered as spectator ligands and are not directly involved in reactions, other than their coordination or dissociation from a metal centre. Rather, their steric and electronic properties tailor the catalyst for its purpose by modifying its reactivity.

The first metal-phosphine complexes, reported in 1870 by Cahours and Gal, were cis- and trans- $[\text{PtCl}_2(\text{PEt}_3)_2]$. There are now numerous prominent examples including Wilkinson's catalyst $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ ⁹, the ruthenium-centred Grubb's catalysts¹⁰ and the widely-used Pd-catalysed cross-coupling catalyst $[\text{Pd}(\text{PPh}_3)_4]$ (Figure 2.1).¹¹

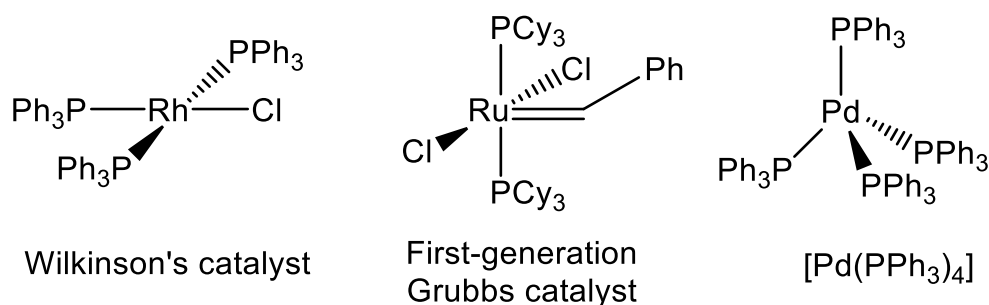


Figure 2.1. Structures of prominent metal-phosphine complexes.

2.1.1 Bonding in phosphines

The bonding in phosphines can be described in several ways. Using standard VSEPR theory, phosphorus has five valence electrons and these can be distributed in a PR_3 ligand through the formation of three P-R bonds and one lone pair of electrons. The resulting tetrahedral geometry, with a position taken by the lone pair, results in a pyramidal arrangement with a bond angle slightly less than that for a tetrahedron (107° v. 109°). Table 2.1 shows some representative bond angles for simple PR_3 ligands. For PPh_3 and $\text{P}(\text{tBu})_3$, the bond angles of 103.0 and 109.9 respectively correspond well to this simple picture. The wider bond angle observed for $\text{P}(\text{tBu})_3$ can be attributed to a steric requirement to position the bulky tert-butyl groups further apart from each other. However, ligands like PMe_3 with an angle of 98.6° , and particularly PH_3 with an angle of 93.4° , show considerable deviations with bond angles closer to 90° .¹²

A standard tetrahedral arrangement results from sp^3 hybridisation of the bonding orbitals. A bond angle of less than 109° and closer to 90° suggests a reduced involvement of the s orbital and an increased involvement of the p orbitals which lie at 90° to each other. This suggests that in PH_3 , relative to NH_3 with a bond angle of 106.7° , the s orbitals are less accessible. This is supported by the radial maxima of the relative s and p orbitals: the 2s and 2p orbitals of nitrogen have similar radial maxima, whilst the 3p orbitals of phosphorus have significantly larger radial maxima than the 3s orbital. Therefore, in NH_3 there is a greater degree of sp^3 hybridisation than in PH_3 and a correspondingly wider bond angle. The larger angles observed for PPh_3 and $\text{P}(\text{tBu})_3$ can be considered as a steric effect, where the bulkier substituents necessitate more space between groups. Furthermore, going from PH_3 to PF_3 also results in an increased bond angle. This can be attributed to the greater electronegativity of fluorine, pulling electron density away from the phosphorus.

Table 2.1. Bond angles for a series of different ligands.¹²

Phosphine	Bond angle ($^\circ$)
PH_3	93.4
PF_3	97.8
PMe_3	98.6
PPh_3	103.0
$\text{P}(\text{tBu})_3$	109.9
NH_3	106.7

The bonding in phosphine ligands can also be described by molecular orbital (MO) theory. In MO theory, electrons are distributed across all atoms in a molecule. Molecular orbitals are formed by linear combinations of atomic orbitals, with orbitals interfering constructively or destructively to form bonding or antibonding orbitals respectively. Atomic orbitals will only overlap with each other if they are of the same symmetry function, and if they are sufficiently close in energy. Constructing molecular orbital diagrams for polyatomic molecules, such as PR_3 , is more complicated than those for similar diatomic molecules. Taking PH_3 as the simplest phosphine ligand, its point group is C_{3v} . The molecule can be divided into two fragments: P and H_3 . The three atomic orbitals from the H_3 fragment – 3 x 1s orbitals – are used to generate three fragment orbitals. One of these has a_1 symmetry and is nondegenerate. The two remaining fragment orbitals have e symmetry, meaning that they are doubly degenerate (of the same energy). For P, the orbitals involved are 3s and 2p orbitals. The 3s orbital has a_1 symmetry, as does $3p_z$, whilst $2p_x$ and $2p_y$ are doubly degenerate with e symmetry. Accordingly, the H_3 fragment orbitals with e symmetry can interact with the P orbitals with e symmetry, and the H_3 fragment orbital with a_1 symmetry can interact with the P orbitals with a_1 symmetry.

A qualitative MO diagram for PH_3 is shown in Figure 2.2. Although the respective positions of orbitals are merely illustrative, some details can be drawn. The H_3 a_1 fragment orbital overlaps with the phosphorus 3s a_1 AO, and the H_3 e orbitals overlap with the phosphorus $3p_x$ and $3p_y$ orbitals of e symmetry. This leaves the remaining phosphorus $3p_z$ orbital of a_1 symmetry, which can be considered as non-bonding, or to have a small interaction with the H_3 a_1 FO (in which case it can still be considered as non-bonding, via a bonding component from P and anti-bonding component from H_3). The two electrons in the $2a_1$ MO can be considered as the lone pair of electrons on the phosphorus. As this is the HOMO, this rationalises why phosphine ligands are generally good Lewis bases and readily donate the lone pair of electrons. The LUMO is an anti-bonding orbital, explaining the poor acidic properties of phosphines. VSEPR suggested that the angles close to 90° in PH_3 originated from the use of orthogonal p orbitals, unlike the sp^3 hybridisation of NH_3 . The MO diagram shows that most electrons in bonding orbitals result from p orbitals; whilst there are s orbitals contributing to the bonding $1a_1$ MO, they also contribute a non-bonding component to $2a_1$. Hence, there is a reduced contribution of the s-orbitals, indicating why PH_3 bond angle is so distinct from that expected from a sp^3 hybridisation.

The relative energies of the MOs will be heavily influenced by the substituents on the phosphine ligand, making the bonding picture much more complicated. Phosphorus and hydrogen themselves have very similar electronegativities (2.19 v. 2.20). However, nitrogen and hydrogen have a significant electronegativity difference (3.04 v. 2.20). Therefore, electrons will be held more tightly to nitrogen than to phosphorus. Therefore, from a MO perspective, there should be greater interaction of the H_3 fragment with nitrogen, leading to an increased s-involvement in the MOs. The relative energy of the

lone pair, sitting in the HOMO of PR_3 , and the LUMO will be determined by the relative positions of the phosphorus orbitals and those of the substituents. More electron withdrawing substituents which make the ligand less basic will reduce the energy of the HOMO and reduce the energy of the LUMO. More electron donating substituents which make the ligand more basic will increase the energy of the HOMO and increase the energy of the LUMO.

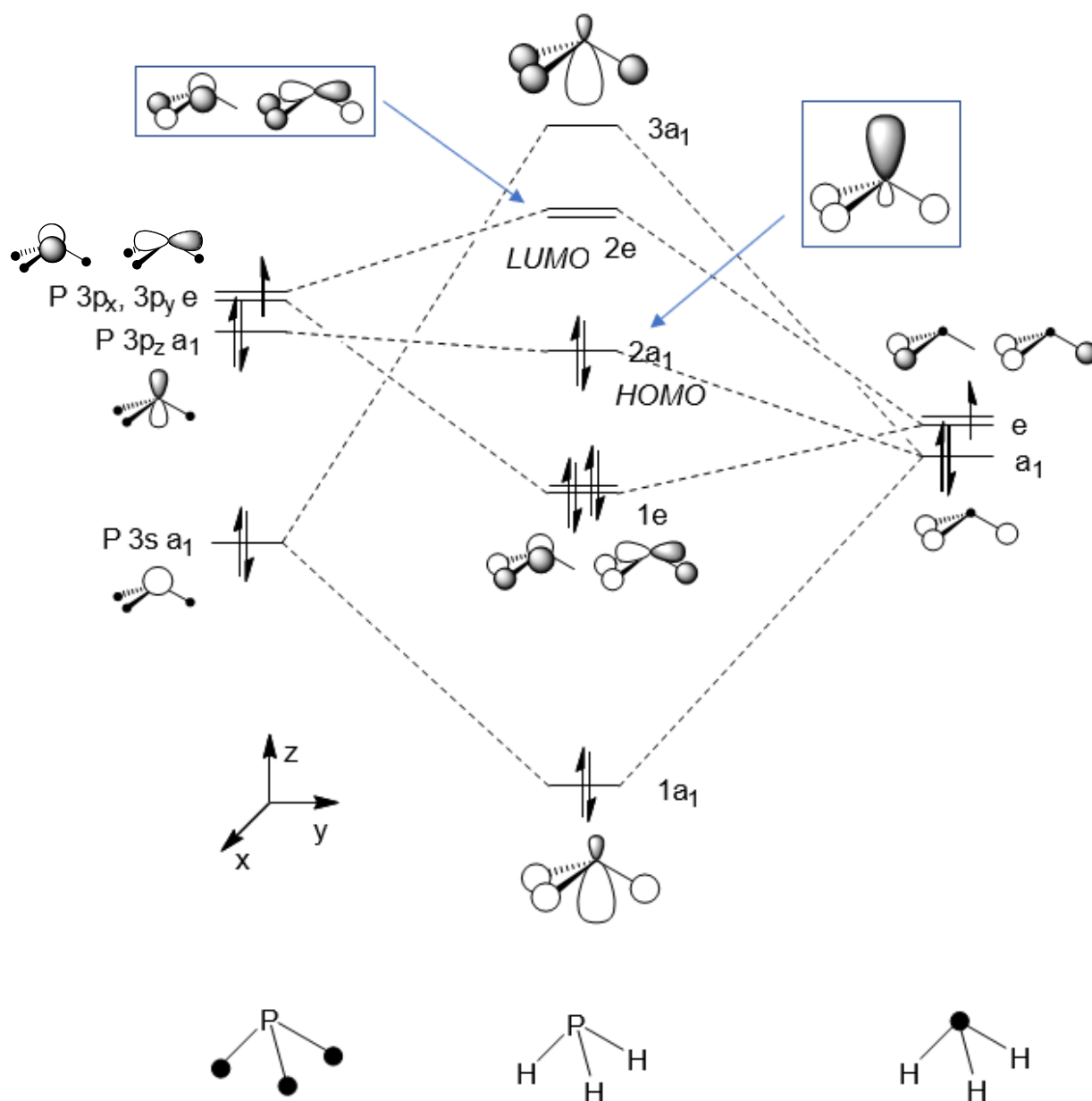


Figure 2.2. Illustrative molecular orbital diagram for PH_3 .

2.1.2 Steric and electronic parameters of phosphines

The bonding of a phosphine to a metal centre has strong similarities to metal-carbonyl bonding. Phosphines can act as both σ -donors and π -acceptors. σ -donation originates from the donation of a hybrid lone pair of electrons on the phosphorus into a vacant d orbital on the metal, forming a σ -bond from ligand to metal. The ligand can also act as a π -acceptor by accepting electrons from a filled metal d-orbital into a mixture of an empty phosphorus d orbital and the σ^* of the P-C bond, forming a π -bond from metal to ligand. This is illustrated in Figure 2.3. Historically, there has been some debate regarding which phosphorus orbitals behave as π -acceptors, with some favouring the empty 3d-orbitals on phosphorus and some favouring the P-C σ^* orbitals. Consequently, the nature of the organic R substituent on the phosphine has a strong effect on the relative donor-acceptor strength of the ligand. Ligands with strongly electron-donating substituents (electron-rich phosphines) will behave as stronger σ -donors and weaker π -acceptors. Ligands with more strongly electron-withdrawing substituents (electron-poor phosphines) will behave as stronger π -acceptors and weaker σ -donors. These effects are generally evaluated by the Lewis basicity of the phosphine. Accordingly, phosphine ligands can be ordered by their basicity; for example, $\text{PCy}_3 > \text{PEt}_3 > \text{PMe}_3 > \text{PPh}_3 > \text{P(OMe)}_3 > \text{P(OPh)}_3 > \text{PCl}_3 > \text{PF}_3$.¹³ Some representative examples of pKa values for the conjugate acids of phosphine ligands are shown in Table 2.2.¹⁴

Phosphines with electron-donating substituents have higher basicity and are stronger σ -donors, and phosphines with electron-withdrawing substituents have lower basicity and are stronger π -acceptors. Generally, phosphines with alkyl substituents are more basic than those with aryl substituents.

Table 2.2. Collection of pKa values for the conjugate acid $[\text{HPR}_3]^+$ of different phosphine ligands.¹⁴

Phosphine ligand	pKa
PCy_3	9.70
PEt_3	8.69
PMe_3	8.65
P^iBu_3	8.43
PPh_3	2.73

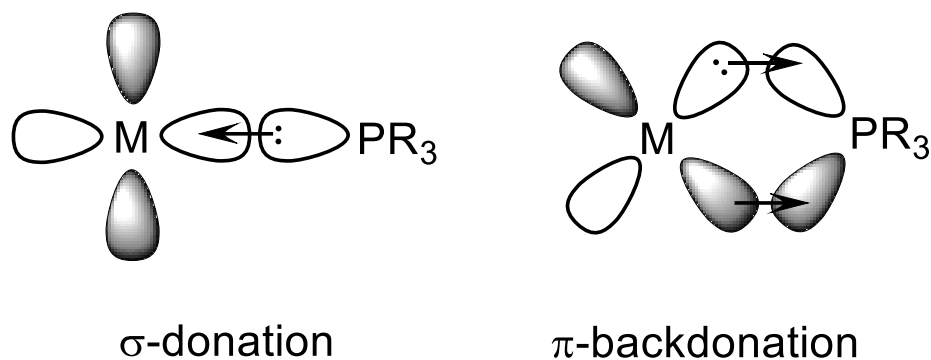


Figure 2.3. An illustration of metal-phosphine bonding.

The strength of a metal-phosphine bond is not just dependent on the relative donor-acceptor strength of the ligand. Electron-rich phosphines will form stronger bonds with more electron-poor metal centres, whilst electron-poor phosphines will form stronger bonds with electron-rich metals. This can be related by the Hard Soft Acid Base theory, where “soft” bases form stronger bonds with “soft” acids and vice versa. Generally, phosphine ligands can be considered as soft bases owing to the relatively low electronegativity, large atomic radius and high polarizability of phosphorus. Therefore they tend to form stronger bonds with soft acids. This includes row two or three transition metals in low oxidation states.

Another way of measuring the donor-acceptor strength of a phosphine ligand is called the Tolman Electronic Parameter. This method uses complexes of the formula $[\text{Ni}(\text{CO})_3\text{L}]$, where L is the ligand under study. Through IR spectroscopy, the A1 stretching frequency of the CO ligand is measured. The CO stretching frequency is affected by the electronic properties of the ligand, and the two factors can be related to one another. Take a phosphine ligand with strongly electron donating substituents (e.g. PEt_3). The stronger electron-donation of the phosphine ligand results in a greater electron density on the metal centre, resulting in greater backbonding into the C-O π^* orbitals. This weakens the C-O bond and lowers the stretching frequency of the C-O bond, whilst strengthening the M-C bond. A phosphine ligand with less electron donating substituents (e.g. PPh_3) results in a lower electron density at the metal centre and reduced backbonding to the C-O π^* orbital. This means the CO bond is relatively strong with a correspondingly higher stretching frequency. Some representative examples of the CO stretching frequency in complexes with different phosphine ligands are presented in Table 2.3.¹⁵

Resultingly, the π -acidity of phosphine ligands can be ranked in the order: $\text{PR}_3 < \text{PAR}_3 < \text{P}(\text{OR})_3 < \text{P}(\text{OAr})_3 < \text{PF}_3$, with electron-withdrawing substituents enhancing the degree of back-donation from M to P.¹⁶

Table 2.3. Collection of CO stretching frequencies for $[\text{Ni}(\text{CO})_3\text{L}]$ complexes of different phosphine ligands.¹⁵

Phosphine ligand, L	ν (cm^{-1}) for $[\text{Ni}(\text{CO})_3\text{L}]$
$\text{P}(\text{tBu})_3$	2056.1
PCy_3	2056.4
$\text{P}(\text{iPr})_3$	2059.2
PEt_3	2061.7
PMe_3	2064.1
PPh_3	2068.9
$\text{P}(\text{OEt})_3$	2076.3
$\text{P}(\text{OMe})_3$	2079.5
PF_3	2110.8

Allen and Taylor also studied the donor properties of a series of heteroarylphosphine ligands in a series of selenium and platinum complexes. Through ^{31}P NMR spectroscopy, they investigated the effect of the phosphine substituent on the $^1\text{J}(^{77}\text{Se}-^{31}\text{P})$ or $^1\text{J}(^{195}\text{Pt}-^{31}\text{P})$ coupling constant. Their results are collated in Table 2.4 ((2-furyl) = $\text{C}_4\text{H}_3\text{O}$, 2-thienyl = $\text{C}_4\text{H}_3\text{S}$). It was found that the more electron-withdrawing the substituents, the greater the magnitude of the coupling constant. Phosphines with more electron-donating substituents, or bulkier groups, led to smaller coupling constants. This was rationalised by considering that the coupling constant depends on the degree of occupation by the lone pair of the phosphorus 3s orbital, i.e. the magnitude of the coupling constant depends on the probability of finding the bonding electrons at the nuclei.¹⁷ Electron-withdrawing substituents increase the s-character of the lone pair, resulting in a larger coupling constant. Electron-donating substituents reduce the s character of the lone pair, reducing the size of the coupling constant.¹⁸

Table 2.4. Collection of $^1\text{J}(^{77}\text{Se}-^{31}\text{P})$ and $^1\text{J}(^{195}\text{Pt}-^{31}\text{P})$ values for different phosphine ligands.¹⁸

Phosphine ligand	$^1\text{J}(^{77}\text{Se}-^{31}\text{P})$ (Hz)	$^1\text{J}(^{195}\text{Pt}-^{31}\text{P})$ (Hz)
PPh_3	732	3,678
$\text{PPh}_2(2\text{-thienyl})$	743	3,685
$\text{PPh}(2\text{-thienyl})_2$	752	3,699
$\text{PPh}_2(2\text{-furyl})$	754	3,665
$\text{PPh}(2\text{-furyl})_2$	774	3,698

Table 2.5. Collected data of percentage s character of lone pair donor orbital on different phosphine ligands.¹⁹

Phosphine ligand	Percentage s character (%)
PF ₃	68
P(OMe) ₃	51
PMe ₃	36
PMe ₂ Ph	28
PEt ₃	27

As an example, the percentage of s character was calculated for a series of [CoL(TPP)] complexes (Table 2.5). The phosphine ligands with electron-withdrawing groups had significantly higher percentages of s character. The more electronegative groups use a larger fraction of the available phosphorus 3p orbitals in bonding, meaning that the lone pair donor orbital is left with a larger percentage of 3s character. This is considered to have an effect on M-P bond length, with a larger percentage of s character corresponding to a shorter M-P bond length.¹⁹

Other work by Tolman investigated substitution reactions of Ni(0) complexes with a series of phosphine ligands. By measuring the intensities of free or bound ligand by ³¹P NMR spectroscopy, a relative stability series was generated. This series did not correlate with the electronic properties of the ligands, suggesting a steric effect was important, whereby displacement of CO from Ni(CO)₄ by phosphine ligands decreased as the size of the phosphine ligand increased. (Exceptions were found with chelating phosphines which enabled the formation of significantly stronger complexes). Furthermore, phosphine complexes with bulkier phosphine ligands were found to dissociate more extensively in solution.²⁰

Evidently the steric bulk of a ligand can have a strong influence on the reactivity and properties of a catalyst, in addition to the electronic effects. Bulky ligands which introduce a high degree of strain into a complex might dissociate more readily to minimise the strain and provide a vacant site for substrate coordination. If bulky ligands cannot readily dissociate, they might make it more difficult for substrates to approach the metal centre, inhibiting associative processes. A sterically bulky ligand might increase the stability of a complex by inhibiting decomposition pathways. Beyond this, the size of the ligand(s) will have an impact on the coordination numbers and geometries accessible. Bulkier ligands result in larger angles between substituents, localising more p character in the phosphorus lone pair and increasing the M-P bond length.²¹

Although it is possible to model the steric effects of ligands in several ways, a classic approach for phosphine ligands is Tolman's cone angle method. This assesses the extent of steric crowding around a ligand. The M-P bond is set as the vertex with the other atoms sitting at the perimeter of an approximated cone. The cone is defined by the maximum possible distance of the atoms from their van der Waals radii. After setting the M-P distance as 228 ppm ($2.28 \text{ \AA}$), the cone angle is determined by a space-filling model. A schematic of this method is shown in Figure 2.4. Less bulky ligands have a smaller cone angle, and larger ligands have a wider cone angle owing to steric repulsion between the substituents. Bulky ligands favour dissociation processes. Table 2.6 presents the Tolman cone angles for a series of common PR_3 ligands. It is also possible, but more complex, to calculate cone angles for unsymmetrical phosphine ligands.

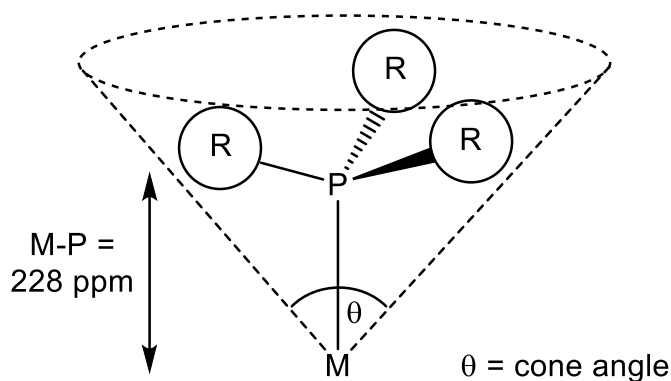


Figure 2.4. Illustration of the Tolman's cone angle method.

Table 2.6. Values of Tolman cone angle for different phosphine ligands.¹³

Ligand	Tolman cone angle (°)
PH_3	87
PF_3	104
P(OMe)_3	107
P(OEt)_3	109
PMe_3	118
PCl_3	125
P(OPh)_3	127
PEt_3	132
PPh_3	145
PCy_3	169
P^tBu_3	182
P(o-tolyl)_3	193

2.2 Tridentate phosphine ligands

In Chapter 1 several tridentate phosphine ligands involved in homogeneous catalysis were introduced. They offer several potential advantages, as well as drawbacks, over mono- or bi-dentate phosphine ligands. Metal coordination through multiple sites generates stable, well-defined metal complexes with high kinetic and thermal stability, attributed to the chelate effect. Whilst this allows for catalysts which can tolerate extreme reaction conditions and avoid decomposition, there is the potential for excessively stable, coordinatively saturated complexes which are unsuitable for catalysis. However, this can also allow for slower, more controlled reactions. Most phosphine ligands behave as spectator ligands, hence the ligand system must be chosen carefully to incorporate available sites at the metal centre for substrate coordination. This is facilitated by the well-defined coordination modes adopted by most tridentate phosphine ligands. This can help with increased control over product selectivity. The incorporation of multiple phosphine moieties in a metal complex can increase the basicity or nucleophilicity at the metal centre, affected by the stereo-electronic properties of the phosphine ligand. Most tridentate phosphine ligand scaffolds can be modified in multiple different ways, increasing their structural versatility relative to monodentate phosphines. They are known to form stable complexes with a wide range of metal centres (typically mid- to late-transition metals) in a range of oxidation states and geometries, including monomeric and dimeric structures.

Despite these factors, tridentate phosphines have received less attention than their mono- or bi-dentate analogues. Tetradentate and hexadentate phosphine ligands are also known, but their steric rigidity remains a difficulty. Tridentate phosphine ligands can be divided into two main groups: linear; and branched, or tripodal, triphosphine ligands. Other classes, such as cyclic, macrocyclic and ferrocenyl polyphosphines exist, but these lie outside the scope of this thesis.^{22,23}

2.2.1 Linear tridentate phosphine ligands

Many linear tridentate phosphine ligands are known, containing three coordinating phosphine moieties along a linear carbon chain, typically with phosphine groups at either end and a third group at the centre. Common examples of linear triphosphine ligands are $[(\text{Ph}_2\text{PCH}_2)_2\text{PPh}]$, bis[(diphenylphosphino)methyl]phenylphosphine (dpmp), $[(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}]$, bis[2-(diphenylphosphino)ethyl]phenylphosphine (etp) and

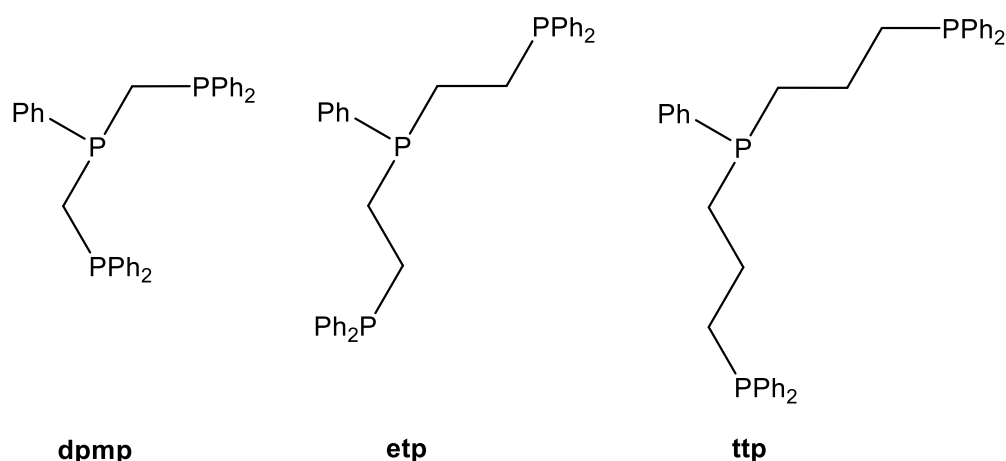


Figure 2.5. The structures of dpmp, etp and ttp ligands.

$[(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2)_2\text{PPh}]$, bis[3-(diphenylphosphino)propyl]phenylphosphine (ttp) (Figure 2.5). Whilst their coordination modes vary according to the ligand substituents and the coordination sphere, a key factor for linear triphosphines is the length of the backbone. It is more facile for longer, more flexible ligands to act in a tridentate manner. However, with three phosphine groups in a chain it is possible to access any combination of mono-, bi- or tri-ligate, and mono-, bi- or tri-metallic structures. They can form a range of geometries including tetrahedral, trigonal bipyramidal, square pyramidal and octahedral.²⁴

The etp ligand has been found to adopt all possible coordination modes, depending upon the choice of metal and co-ligands (Figure 2.6). Table 2.7 shows the metals with which etp formed each coordination mode. It can be seen that the triligate monometallic mode is the most common coordination mode.²⁵

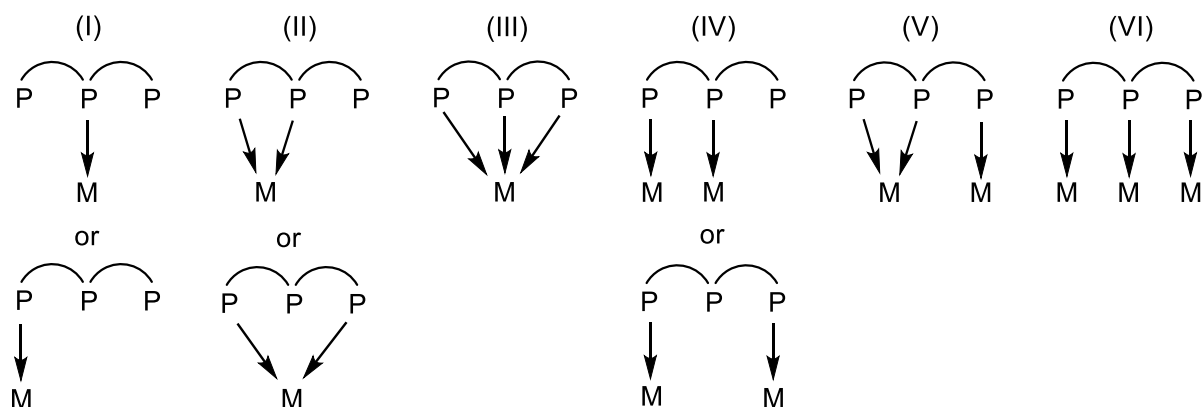


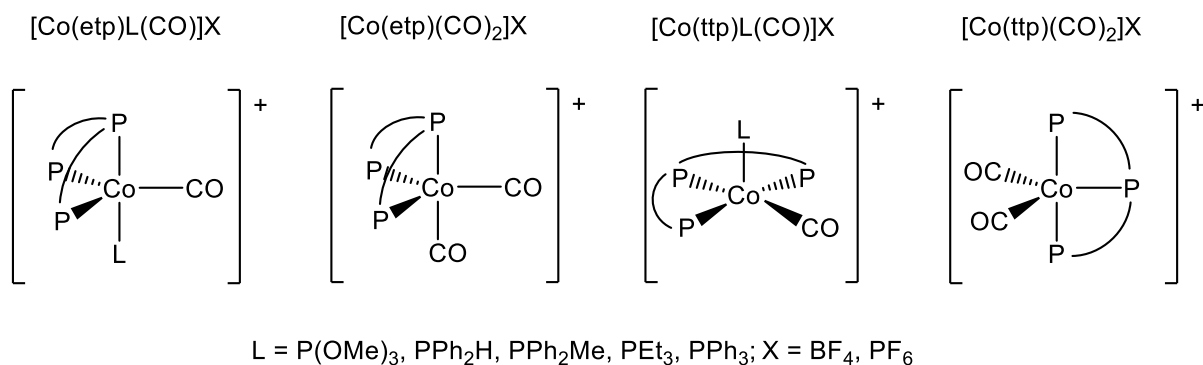
Figure 2.6. Illustration of coordination modes accessible to etp ligands.²⁵

Table 2.7. Summary of the coordination modes adopted by etp ligands with different metals.²⁵

Coordination mode of etp	Metal
Monoligate monometallic (I)	Fe
Biligate monometallic (II)	Os, Cr, Mo, Mn
Triligate monometallic (III)	Ni, Pd, Pt, Co, Rh, Ir, Cr, Mo, W, Mn, Mo, Fe
Biligate bimetallic (IV)	Fe
Triligate bimetallic (V)	Mn
Triligate trimetallic (VI)	Mo

King et al. went on to study the coordination of etp-type ligands where one or both of the terminal PPh₂ groups was exchanged for PMe₂, and/or the central P-Ph was exchanged for P-Me. In the ligands containing PMe₂ groups, there was always full coordination of the PMe₂ groups. This was attributed to the high basicity and small steric bulk of the PMe₂ groups relative to PPh₂.²⁶

A later study investigated the different geometries adopted by etp and ttp ligands in a series of cobalt complexes of the general formulae [Co(triphosphine)L(CO)]X and [Co(triphosphine)(CO)₂]X where L = P(OMe)₃, PPh₂H, PPh₂Me, PEt₃ or PPh₃, and X = BF₄ or PF₆. The geometries of these complexes are shown in Figure 2.7. Whilst the complexes of the longer ttp ligand could adopt either square-pyramidal or trigonal bipyramidal geometries, the shorter etp ligand adopted exclusively, stereochemically rigid, trigonal bipyramidal geometries. In the complexes of the longer ttp ligand, the increased chain length allows for less steric repulsion between the phosphine groups, permitting structures where all phosphines lie in the same plane. The shorter etp ligand forms 5-membered chelate rings with a smaller “chelate bite” angle. Consequently, the central phosphine must either approach the metal more closely to be able to adopt a square-pyramidal geometry (unfavoured owing to steric hindrance) or adopt a trigonal-bipyramidal geometry allowing for the smaller bite angle.²⁷

**Figure 2.7.** Geometries of [Co(triphosphine)L(CO)]X and [Co(triphosphine)(CO)₂]X complexes.²⁷

Balch et al. studied complexes of the shorter dpmp ligand, where each phosphine is separated by a single carbon. Two different coordination modes were found. With palladium, the two terminal phosphines bound to a single metal centre, leaving the central phosphine uncoordinated. Owing to the even smaller “bite angle” of the shorter dpmp ligand, it is not possible to coordinate all three phosphines to a single metal centre. However, the uncoordinated central phosphine can bind to a second metal centre to form bimetallic complexes. Examples of these are shown in Figure 2.8 (a) and (b). An alternative coordination mode of dpmp is triligation across three metal centres. An example with rhodium is shown in Figure 2.8 (c), where two dpmp ligands bind across three rhodium centres in a trimetallic complex.²⁸

The authors went on to study bis((dimethylphosphino)methyl)methylphosphine (dmmm), the methylated analogue of dpmp. Considering the increased basicity and reduced steric bulk of the ligand, they considered that they could access complexes with higher coordination and therefore more electron-rich metal centres. With dmmm, they formed a surprisingly crowded rhodium dimer, where two dmmm ligands bind across two rhodium centres, each in a triligate mode (Figure 2.8 (d)).²⁹

The examples discussed in this section demonstrate that small modifications to the phosphine ligand, through substituent or chain length, and changes to the metal centre and co-ligands, can have a drastic impact on the geometries and coordination modes attained.

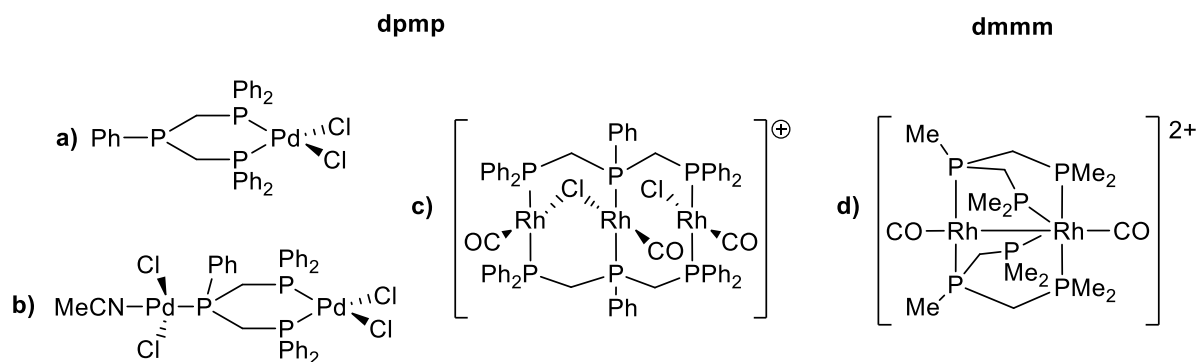


Figure 2.8. Structures of complexes formed with dpmp and dmmm ligands.^{28,29}

2.2.2 Branched tridentate (tripodal) phosphine ligands

A limitation with linear triphosphine ligands is the difficulty of arranging three phosphines bound in a single chain around a single metal centre. Whilst this can be modified through changing the chain length or the phosphine substituent, this limits the types of complexes that can be accessed. Branched triphosphine ligands have three phosphine groups on separate chains connected to a central point. They tend to adopt a tripodal structure around a metal centre, forming well-defined, tridentate coordination modes. The tridentate coordination around a single metal centre generates robust, stable complexes.

A wide number of these tripodal phosphine ligands are known. Some early examples include tris(2-diphenylphosphinoethyl)phosphine, $[(C_6H_5)_2PCH_2CH_2]_3P$,³⁰ tris(o-diphenylphosphinophenyl)phosphine,³¹ tris(diphenylphosphino)methane³² and tris[3-(dimethylphosphino)propyl] phosphine (Figure 2.9).³³

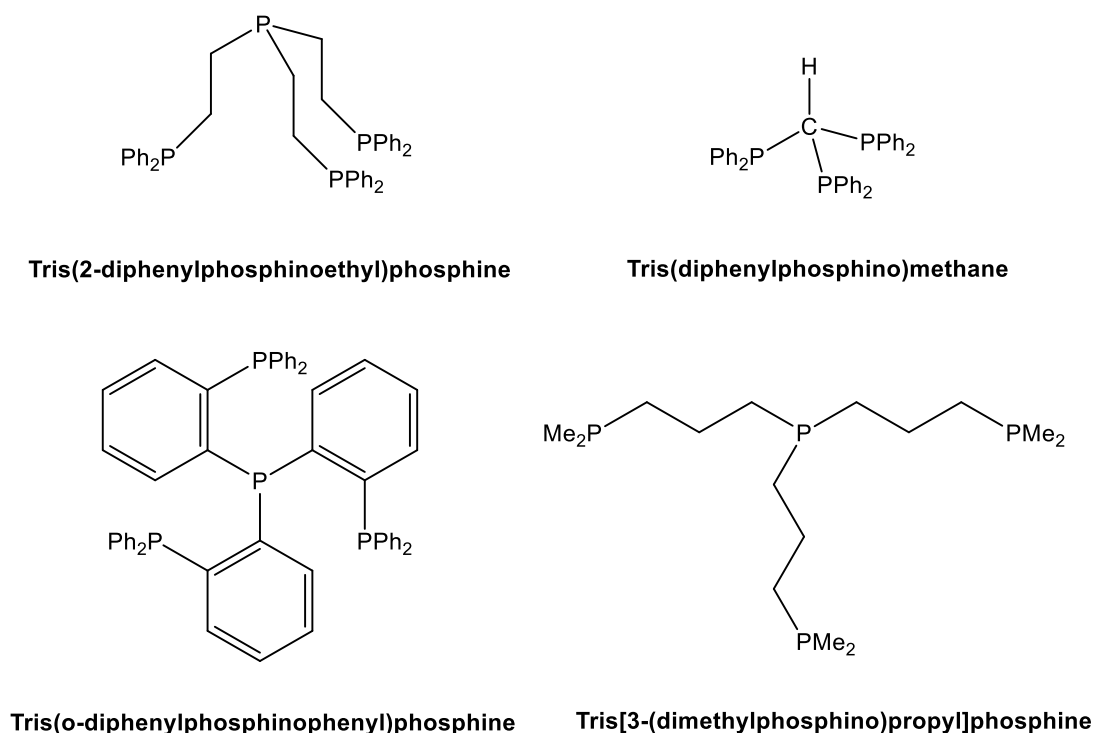


Figure 2.9. Structures of prominent tripodal phosphine ligands.^{30–33}

The most prolific tripodal phosphine ligands belong to the Triphos family with the general formula $R'C(CH_2PR_2)_3$. 1,1,1-tris(diphenylphosphinomethyl)ethane, generally referred to simply as Triphos ($R = Ph$, $R' = Me$), has three PPh_2 arms connected to an apical carbon atom with a methyl substituent. The eponymous Triphos ligand was first reported in 1962 and has gone on to be included in over 900 publications.³⁴ Several of the catalytic systems described in Chapter 1 used Triphos ligands.

Triphos ligands generally bind to a metal through triligation in a facial coordination mode. Common geometries are square-pyramidal, trigonal-bipyramidal and octahedral, generating several free cis-positions for other ligands.³⁵ Figure 2.10 shows some representative examples of these common geometries obtained with Triphos.^{36,37} Bidentate coordination modes of Triphos are generally accessible only when the coordination sphere prevents facial coordination.³⁸

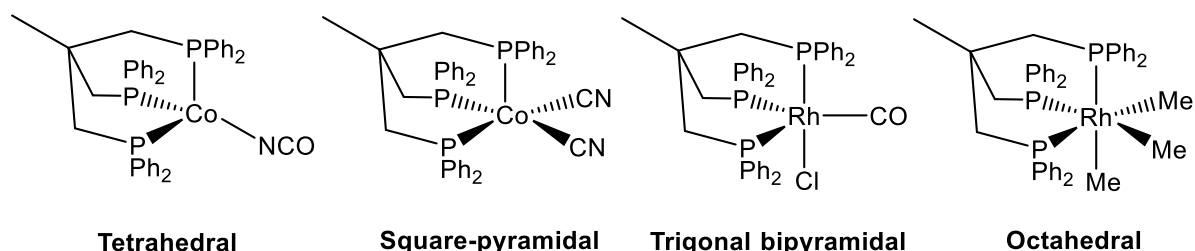


Figure 2.10. Geometries adopted by complexes of Triphos ligand.^{36,37}

The structure of the Triphos ligand can be modified in several ways: the apical atom itself, the chain length of the phosphine arms, the nature of the coordinating groups, and the ancillary arm. This includes unsymmetrical Triphos ligands where not every coordinating arm is identical. Some of the most interesting Triphos analogues are those which replace the apical carbon atom for a different element. This can alter the stereoelectronic properties of the ligand significantly and can introduce a formal charge to the ligand or provide a potential for the apical atom to be involved in metal-coordination. Ligands of the form $R'B(CH_2PR_2)_3$, $R'Si(CH_2PR_2)_3$, $R'Sn(CH_2PR_2)_3$, $N(CH_2PR_2)_3$ and $P(CH_2PR_2)_3$, with apical atom = B, Si, Sn, N or P are known, although they are much less studied than the carbon-centered Triphos. Of these, the vast majority are boron analogues, with a number of different phosphine substituents across a wide range of metal centres.²²

The first nitrogen-centered Triphos analogues were first reported in 1981 by Märkl, of the formula $N(CH_2PRR')_3$ ($R=R'=Ph$; $R=Ph$, $R'=C_{10}H_7$; $R=Ph$, $R'=Me$). In each case, tridentate coordination to molybdenum was obtained, resulting in the formation of octahedral tricarbonyl complexes (Figure 2.11, (a)).³⁹

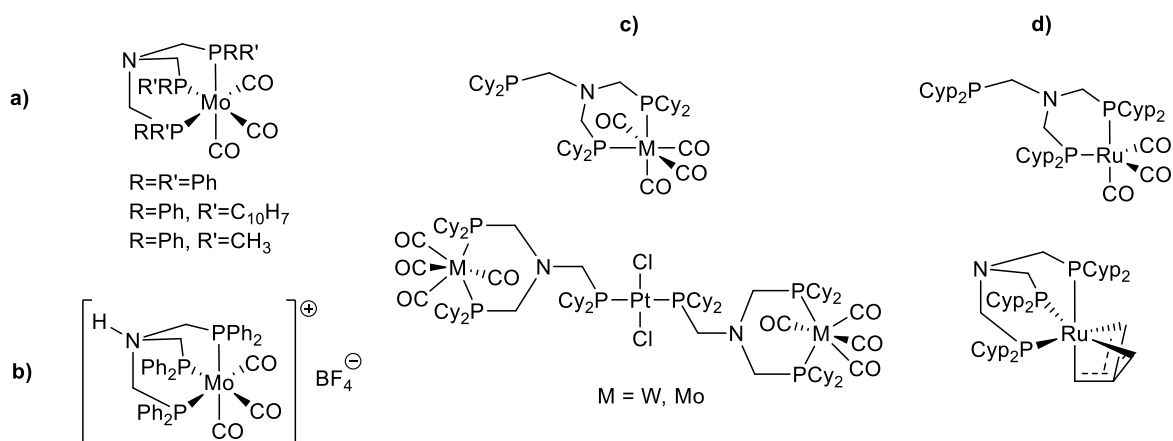


Figure 2.11. Structures of complexes formed with N-Triphos ligands.^{39,40,43,45}

Presently, the most prolific N-Triphos ligand is N(CH₂PPh₂)₃, commonly referred to as N-Triphos^{Ph}, or simply N-Triphos. Catalyst systems using N-Triphos ligands were also introduced in Chapter 1. The presence of the central nitrogen atom suggests a potential for metal interaction. Whilst formal bonds between the nitrogen centre of N-Triphos and a metal centre have not been observed in complexes of N-Triphos, some early studies of N-Triphos complexes found that there were in fact interactions between the apical nitrogen and the metal, meaning that the apical atom cannot be considered completely “innocent”. These were determined through comparisons between the spectral data for molybdenum complexes of N-Triphos^{Ph} where the nitrogen of the N-Triphos ligand was either unprotonated or protonated through reaction with HBF₄ (Figure 2.11, (b)). Nonetheless, the short methylene spacers in N-Triphos ligands and the resulting small “bite angles” generally preclude the formation of formal M-N bonds.⁴⁰ N-Triphos analogues with longer spacer groups in their chains are able to use the apical nitrogen atom for coordination.⁴¹ Furthermore, the phosphorus-centered analogue, P(CH₂PPh₂)₃, has formed Mn complexes in which the central phosphorus atom coordinates to the metal centre alongside the terminal phosphine groups.⁴²

N-Triphos ligands do not coordinate exclusively through tridentate coordination modes. For example, N-Triphos^{Cy} (Cy = cyclohexyl) coordinates to Mo and W in a bidentate fashion, with the third phosphine arm uncoordinated. This was attributed to the increased steric bulk of the cyclohexyl substituent, with insufficient space around the metal centre for three PCy₂ groups. The pendant phosphine arm allowed for the formation of hetero bi- and tri- metallic complexes with Au, Pt and Ag (Figure 2.11, (c)).⁴³ Furthermore, changes to the reaction conditions can access different coordination modes. Whilst the sterically bulky N-Triphos^{DPP} (DPP = 2,5-diphenyl) ligand tends to adopt a bidentate coordination mode

with ruthenium, a higher temperature and longer reaction time allowed for triligation to be obtained.⁴⁴

Furthermore, ruthenium complexes of N-Triphos^{Cyp} (Cyp = cyclopentyl) featured different coordination modes depending on the oxidation state of the metal. With Ru(II) tridentate coordination was achieved, whilst exclusively bidentate coordination was obtained with Ru(0) (Figure 2.11, (d)). This was attributed to the increased electron-donating ability of the PCyp₂ groups. On the already electron-rich Ru(0) centre, tridentate coordination is disfavoured as this would increase Ru electron density both through coordination of an extra PCyp₂ moiety and a strengthened N-Ru interaction.⁴⁵

Therefore, whilst coordination of N-Triphos ligands is typically straight-forward, there are many variations accessible. Pleasingly, the synthesis of N-Triphos ligands allows for the ready modification of their structure in several ways, meaning that their coordination modes and geometries can be carefully tailored.

2.3 Synthesis of triphosphine ligands

There are several synthetic strategies which have been used to synthesise triphosphine ligands. The original synthesis of Triphos was through reaction of Ph₂PNa with CH₃C(CH₂Cl)₃. Ph₂PNa itself can be made from either triphenylphosphine or diphenylphosphine. Whilst the use of triphenylphosphine avoids the air-sensitive diphenylphosphine, it resulted in lower yields (50 % v. 73 %) and a product of lower purity. The synthesis of Triphos itself involved an eight hour reflux, followed by separations and washings, distillation and crystallisations. This route is shown in Figure 2.12 (a).³⁴

However, the method of obtaining polyphosphines via reaction of an alkali metal dialkylphosphide and a polyhalide was difficult to extend to other ligands. Either an appropriate polyhalide was unavailable or it was difficult to achieve reaction completion. Even with Triphos itself, the reaction between Ph₂PNa and CH₃C(CH₂Cl)₃ can be complicated. If there is insufficient Ph₂PNa, and not all of the halides are replaced for phosphines, a phosphetanium ion is formed in place of the desired Triphos ligand (Figure 2.12 (a)).

Some other early work synthesised several polyphosphine ligands in high yields through the base-catalysed addition of P-H bonds across the C=C bonds of vinylphosphines. For example, the linear triphosphine ligand etp could be synthesised from either phenylphosphine and diphenylvinylphosphine, or from diphenylphosphine and phenyldivinylphosphine, in the presence of tert-butoxide or phenyllithium respectively (Figure 2.12 (b)). The vinylphosphine precursors are more

readily available than the polyhalides, and the C=C bonds are considered to be sufficiently activated by the neighbouring phosphorus atom for facile addition of the P-H bond.³⁰

The original synthesis of N-Triphos ligands was through the reaction of diaryl or alkyl-aryl hydroxymethylphosphines with excess ammonia, in moderate to high yields (61-94 %) (Figure 2.12, (c)). The diaryl hydroxymethylphosphine was formed from the diarylphosphine with paraformaldehyde. The alkyl-aryl hydroxymethylphosphines were formed from the phenyl(bishydroxymethyl)phosphine via its phosphonium hydroxide.³⁹ Later, an alternative route to N-Triphos^{Ph} was reported using LiPPh₂ and N(CH₂Cl)₃ (Figure 2.12 (d)). LiPPh₂ was made in situ from Ph₂PH and lithium.⁴⁰

More recently, N-Triphos ligands have been synthesised from air-stable diaryl/dialkyl hydroxymethyl phosphonium chlorides (Figure 2.12 (e)), avoiding the difficulties of handling air-sensitive diaryl/alkylphosphines. The phosphonium chlorides themselves are prepared from their corresponding secondary phosphine with formaldehyde and concentrated HCl. This route was first described by Kemmitt et al. in 1993, who formed the diphenyl and dicyclohexyl phosphonium chlorides in quantitative yields.⁴⁶ To synthesise the N-Triphos ligands, the phosphonium chloride is deprotonated in situ with excess triethylamine to form the corresponding hydroxymethylphosphine, which undergoes a phosphorus-based Mannich condensation reaction with NH₄Cl to form the N-Triphos ligand. These routes are well established for the formation of a range of phosphine ligands.^{47,48} Generally, the N-Triphos ligands are isolated in high yields through precipitation of a white solid after several hours of reflux.⁴³ Ammonia, NH₃, is often used in place of ammonium chloride.⁴⁹

The phosphine substituent on the N-Triphos ligand is tailored through the choice of the starting diaryl/dialkyl phosphine, of which a wide range are available. Whilst NH₃ is used to generate the tridentate N-Triphos ligand, amines with alternative substituents can be used to generate nitrogen-centred phosphine ligands with fewer coordinating arms. Therefore, the synthetic route to N-Triphos can be readily modified by the straight-forward substitution of different phosphines and amines.

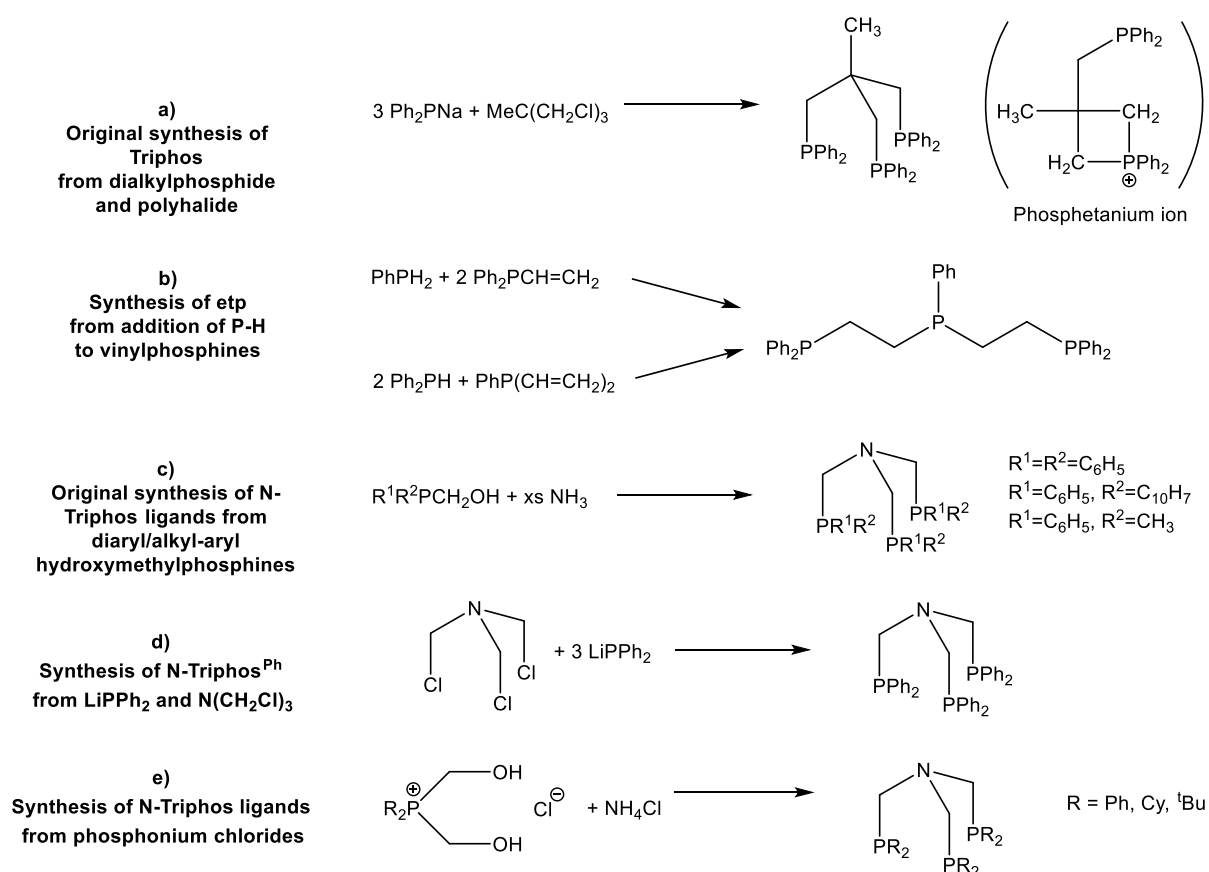


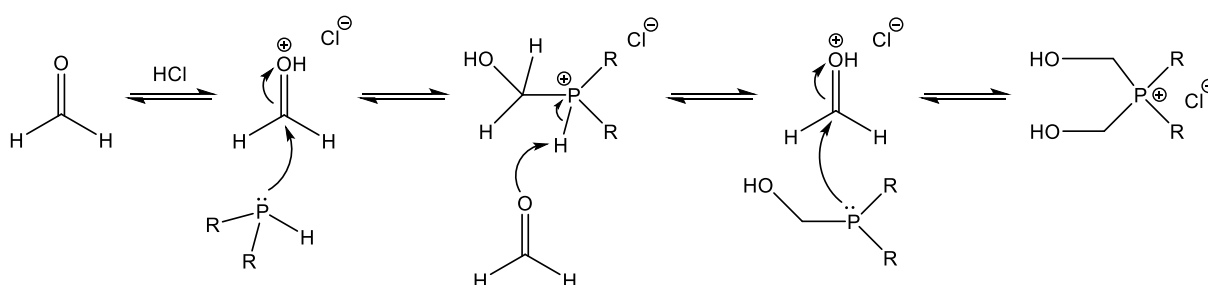
Figure 2.12. Synthetic routes towards triphosphine ligands.^{30,34,39,40,46}

The general mechanism for the formation of a dialkyl/aryl hydroxymethylphosphonium chloride from a dialkyl/aryl phosphine is shown in Scheme 2.1. Through attack of the phosphine on formaldehyde, after loss of H⁺ the dialkyl/diaryl hydroxymethylphosphine is produced. The hydroxymethylphosphine is the species involved in the synthesis of N-Triphos ligands. However, attack of the hydroxymethylphosphine on a second equivalent of formaldehyde generates the phosphonium chloride which can be prepared on large scales in high yields and requires no air protection. Hence, it is convenient to prepare large batches of the phosphonium chloride for use as a reagent to synthesise N-Triphos ligands, regenerating the hydroxymethylphosphine in situ. The requirement for two equivalents of formaldehyde and hydrochloric acid is evident.

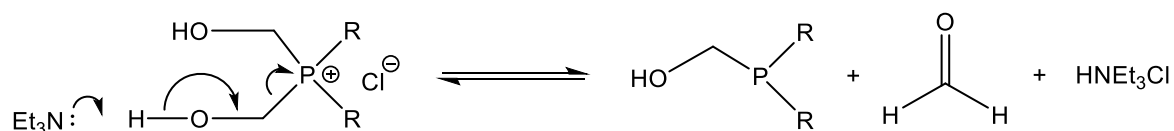
The first step in the synthesis of N-Triphos from a hydroxymethylphosphonium chloride involves the addition of excess triethylamine, which serves to produce the corresponding hydroxymethylphosphine (Scheme 2.2). The subsequent production of the phosphine ligand is commonly described as a phosphorus-based Mannich reaction. The classic Mannich reaction involves a reaction between an amine and formaldehyde to form an iminium ion, which is attacked by a

nucleophilic substrate to form a so-called Mannich base. A general scheme for the “classic” Mannich reaction is shown in Scheme 2.3.⁵⁰

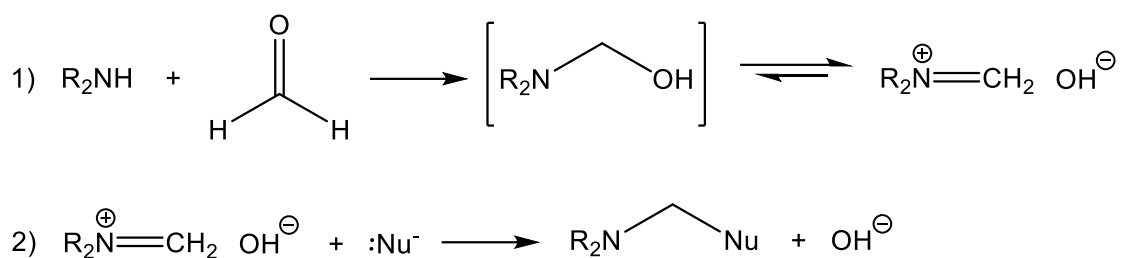
There has been some disagreement in the literature over the exact mechanism for the phosphorus-based Mannich reaction. One school of thought postulates that the hydroxymethylphosphine intermediate decomposes to form a phosphine, which then behaves as the nucleophile in attacking an iminium ion formed from an amine and formaldehyde in the standard manner.⁵¹ However, more recently it has been suggested that the hydroxymethylphosphine instead generates a methylenephosphonium ion, the phosphorus analogue of the iminium ion. The amine substrate then acts as the nucleophile to generate the product. This general mechanism is shown in Scheme 2.4, with a mechanism for the formation of N-Tripos^{Ph} shown in Scheme 2.5. From diphenylhydroxymethylphosphine, the diphenylmethylenephosphonium ion can be formed by hydroxide elimination. This ion is susceptible to nucleophilic attack by NH₃ and following elimination of water generates the “one-armed” analogue of N-Tripos. Given that the correct stoichiometry is used (three equivalents of phosphonium chloride to one equivalent of NH₃), the amine can go on to attack two further diphenylmethylenephosphonium ions to form N-Tripos^{Ph}. The reaction is pushed to completion by the elimination of three equivalents of water and ligand precipitation.⁵⁰



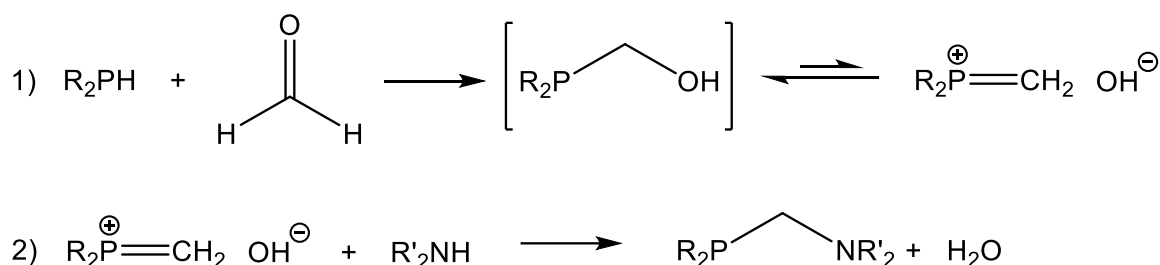
Scheme 2.1. Synthesis of a dialkyl/aryl hydroxymethylphosphonium chloride from a dialkyl/aryl phosphine.



Scheme 2.2. Deprotonation of a phosphonium chloride to generate a hydroxymethylphosphine.

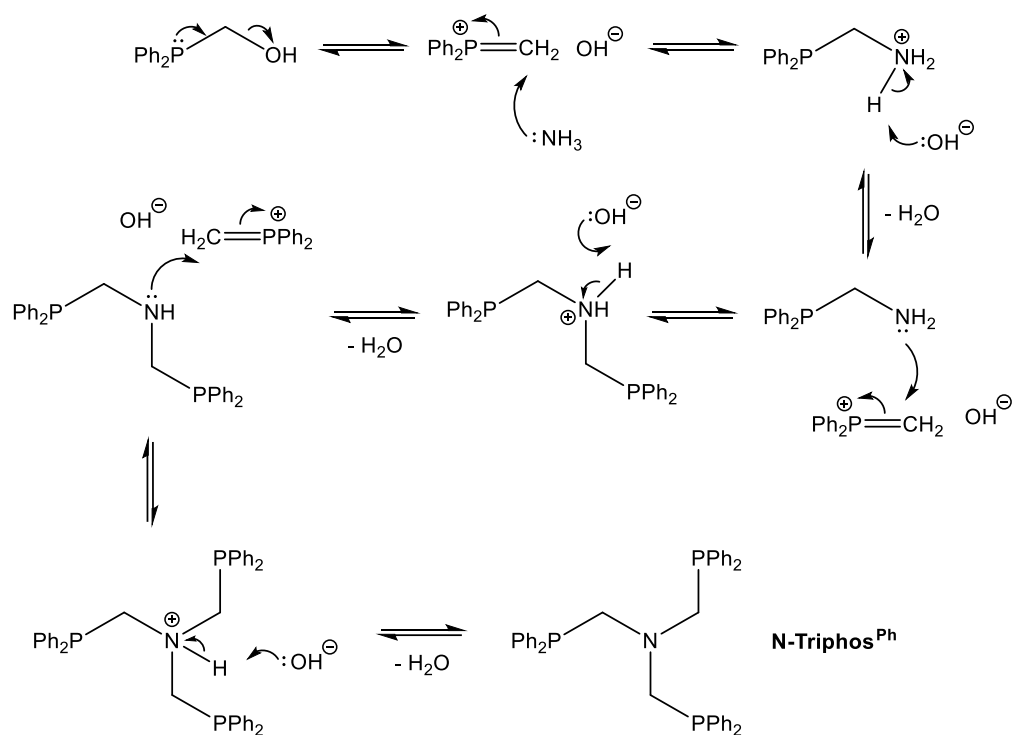


Scheme 2.3. Reaction scheme of the “classic” Mannich reaction.⁵⁰

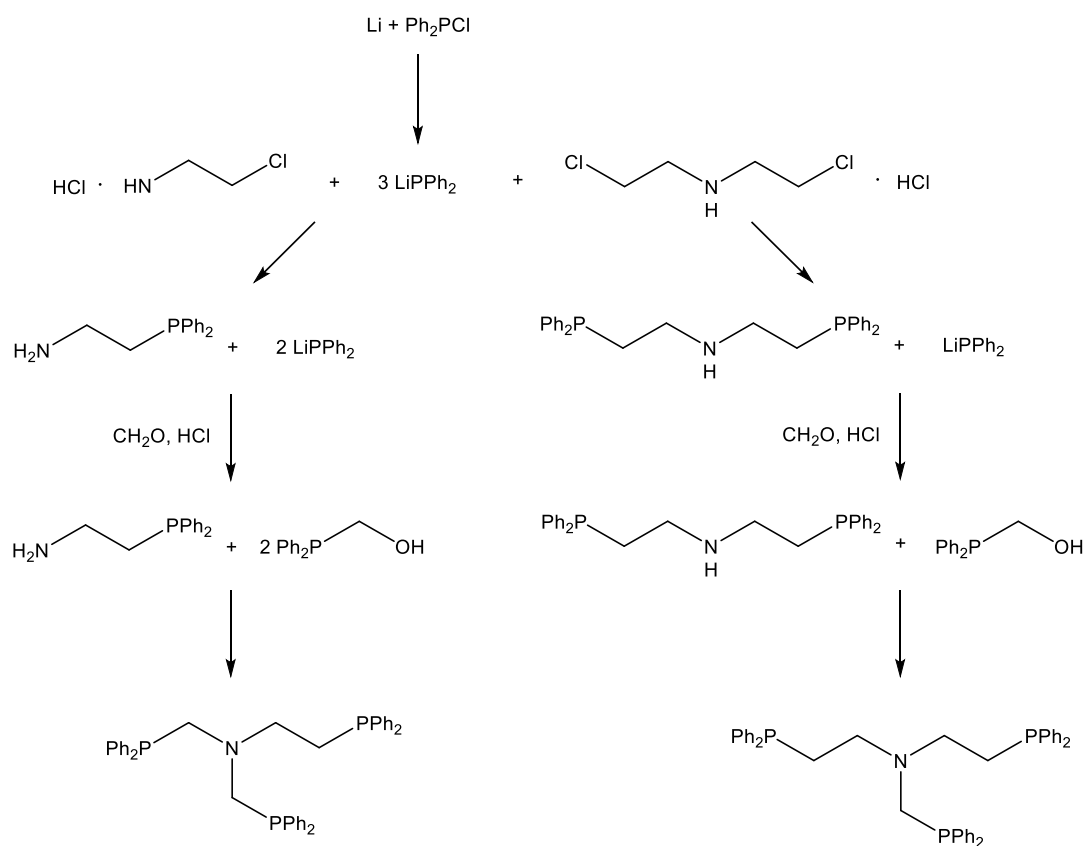


Scheme 2.4. Reaction scheme of the “phosphorus-based” Mannich reaction.⁵⁰

Unsymmetrical N-Triphos ligands can be formed through similar routes. Some recent examples reported by Palkovits et al. contain PPh₂ arms of unequal chain length. They made their phosphonium chloride from reaction of lithium and chlorodiphenylphosphine, forming initially lithium diphenylphosphide, and following addition of formaldehyde and hydrochloric acid, bis(hydroxymethyl)diphenylphosphonium chloride. To generate their unsymmetrical N-Triphos ligands, the reactions were reordered somewhat from that for N-Triphos itself. Taking the example with two methylene arms and one ethylene arm, to three equivalents of lithium diphenylphosphide was first added one equivalent of 2-chloroethylamine, generating one equivalent of Ph₂P(CH₂)₂NH₂. The remaining two equivalents of lithium diphenylphosphide were converted into the hydroxymethylphosphine (via addition of formaldehyde, hydrochloric acid, and subsequently sodium carbonate), providing the two methylene arms for the ligand product. An analogous reaction was performed with bis(2-chloroethyl)amine hydrochloride to form the N-Triphos ligand containing two ethylene arms and one methylene arm. These reactions are shown in Scheme 2.6.⁵²



Scheme 2.5. Synthetic route of N-Triphos from hydroxymethylphosphine and ammonia.



Scheme 2.6. Synthesis of "unsymmetrical" N-Triphos ligands.⁵²

2.3.1 Synthesis of symmetrical N-Triphos ligands

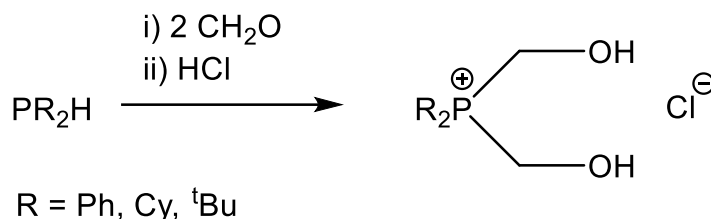
The general synthetic routes to generate N-Triphos ligands were introduced in the previous section. Whilst N-Triphos ligands can be synthesised directly from their corresponding dialkyl/diaryl phosphine, in this work N-Triphos ligands were always prepared from the corresponding bis(hydroxymethyl)dialkyl/aryl phosphonium chloride. There are several advantages to this.

Dialkyl/aryl phosphines are liquids which catch fire spontaneously upon exposure to air. Therefore, their storage and handling must be performed with care. Commercial dialkyl/aryl phosphines are supplied in either nitrogen-sealed bottles or glass ampoules. Whilst phosphines supplied in nitrogen-sealed bottles can be stored if sufficient care is taken not to introduce air into the bottle, once a glass ampule is snapped open, the contents must be immediately transferred to a secondary container under an inert atmosphere. Generally, the liquid phosphine was frozen in liquid nitrogen, then the neck of the ampoule was snapped open and the whole bottle was transferred to a Schlenk tube under nitrogen. After the phosphine melted it was transferred to the reaction vessel. Owing to the risks involved, dialkyl/aryl phosphines were handled as infrequently as possible. The phosphonium chlorides are entirely air-stable for indefinite periods of time and were typically prepared on multigram scales. From the phosphonium chloride, N-Triphos ligands can be made in a facile manner without any special safety concerns. The syntheses were performed under an inert atmosphere to avoid oxidation of the N-Triphos ligand.

2.3.1.1. Syntheses of bis(hydroxymethyl)dialkyl/aryl phosphonium chlorides from R_2PH

Syntheses of bis(hydroxymethyl)dialkyl/aryl phosphonium chlorides were performed with R = phenyl, cyclohexyl and tert-butyl, adapting the general procedures described previously (Scheme 2.7). All syntheses were performed with the strict exclusion of air.⁴⁶

Bis(hydroxymethyl)diphenylphosphonium chloride was synthesised from diphenylphosphine on a 10 g scale. The reaction involves addition of excess formaldehyde solution (37 wt.%) to diphenylphosphine without an additional solvent. The reaction mixture was initially stirred for 30 minutes at room temperature before addition of hydrochloric acid solution (2M). After one hour, solvent reduction under reduced pressure yielded a product which was collected as a white crystalline solid in 96 % yield after washing with diethyl ether and drying in vacuo.



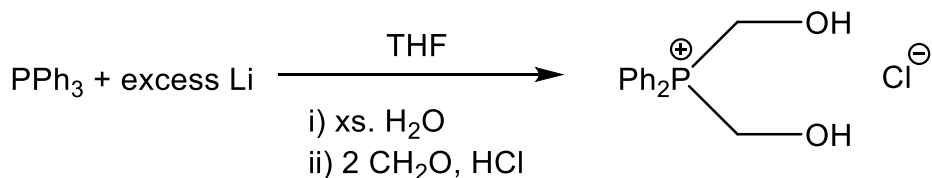
Scheme 2.7. General synthesis of bis(hydroxymethyl)dialkyl/aryl phosphonium chlorides from dialkyl/aryl phosphines.

Bis(hydroxymethyl)dicyclohexylphosphonium chloride was made through an analogous route from dicyclohexylphosphine, Cy₂PH (5 g). After the addition of formaldehyde solution, a white emulsion formed with slight warming. After stirring for 30 minutes at room temperature, hydrochloric acid solution was added. After some fuming, a white solid precipitated immediately. The solid product was isolated by vacuum filtration and recrystallized from isopropanol. The product was collected as a white crystalline solid in very high yield (92 %). The reaction was also performed on a much larger scale using 25 g Cy₂PH to form the product in near quantitative yield (97 %).

Bis(hydroxymethyl)diterbutylphosphonium chloride was also made following an analogous route. However, diterbutylphosphine, (^tBu)₂PH, is significantly more expensive than diphenylphosphine and is more reactive with air. Therefore, the synthesis of the analogous phosphonium chloride was performed initially on a small 1 g scale. Whilst the synthesis proceeded in a similar manner to those described above, the product yield was lower (57 %). Later, the reaction was scaled-up to 5 g (^tBu)₂PH which increased the product yield to 72 %. The success of all reactions was readily determined through ³¹P{¹H} NMR spectroscopy.

2.3.1.2 Synthesis of bis(hydroxymethyl)diphenylphosphonium chloride from PPh₃ and Li

Whilst the syntheses of phosphonium chlorides from their dialkyl/aryl phosphine are high-yielding and facile, there remains the safety issues of the dialkyl/aryl phosphine. Additionally, the dialkyl/aryl phosphines are less readily available and significantly more expensive than their corresponding trialkyl/aryl phosphine. For example, on Sigma Aldrich, PPh₃ can be purchased at 4 pence per gram, whilst PPh₂H costs ~£5 per gram (*retrieved: 22/12/20). Furthermore, trialkyl/aryl phosphines are generally solids which require minimal air protection.



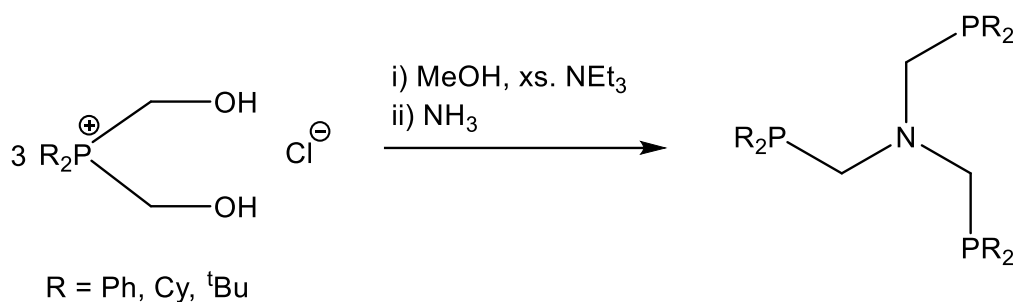
Scheme 2.8. Synthesis of bis(hydroxymethyl)diphenyl phosphonium chloride from triphenylphosphine and lithium.

As such, a modified synthesis of bis(hydroxymethyl)diphenylphosphonium chloride was performed using triphenylphosphine and lithium. Whilst lithium is very water-reactive and releases flammable gases upon contact with water, this is relatively easy to control by using dried glassware and dried solvents. The formation of HPPH₂ from PPh₃ and lithium is well-established, and here this was adapted for the direct formation of the phosphonium chloride without isolation of HPPH₂.^{53–55}

The reaction scheme used is shown in Scheme 2.8. The synthesis used a scale of 5 g PPh₃ with four equivalents of lithium pellets. After slow addition of dry THF, the mixture became dark red in colour within a short time through the formation of LiPPh₂. The mixture was stirred overnight at RT. Solid, undissolved lithium was present for the entire duration. Through ³¹P{¹H} NMR spectroscopy, conversion to LiPPh₂ was observed (δ = -15 ppm). To generate HPPH₂, water was added slowly with cooling. Gas evolution was observed from the lithium chunks. After one hour of stirring at RT, full conversion to PPh₂H was observed by {¹H} NMR spectroscopy (δ = -41 ppm). After addition of formaldehyde and excess hydrochloric acid, full conversion to the phosphonium chloride product was determined after a further one hour (δ = 14 ppm). A solid was obtained by solvent reduction and vacuum filtration, and after recrystallization from methanol the product was collected as a white crystalline powder in high yield (89 %), with its identity confirmed by ¹H and ³¹P{¹H} NMR spectroscopy. The reaction was also performed on a larger scale from 10g PPh₃, producing the product in equally high yield (88 %).

As such, this represents a convenient, high-yielding route to bis(hydroxymethyl)diphenylphosphonium chloride avoiding the use of diphenylphosphine. It is uncertain if this route could be expanded to further aryl analogues. Alkyl analogues might be expected to suffer from deprotonation.

2.3.1.3 Syntheses of N-Triphos ligands



Scheme 2.9. General synthesis of N-Triphos ligands from bis(hydroxymethyl)dialkyl/aryl phosphonium chlorides.

The general synthesis of N-Triphos ligands from their corresponding bis(hydroxymethyl)dialkyl/aryl phosphonium chloride has already been introduced. The syntheses of the N-Triphos ligands with $R =$ phenyl, cyclohexyl and tert-butyl were performed, adapting the general procedures. All syntheses were performed under inert conditions to avoid oxidation of the phosphine groups to phosphine oxides. N-Triphos^{Ph} has good air-stability in the solid form for extended period of times but is susceptible to oxidation in solution. N-Triphos^{Cy} and N-Triphos^{tBu} have poorer air stability and were stored under protection from air to avoid oxidation.⁴³

Following dissolution of bis(hydroxymethyl)diphenylphosphonium chloride in methanol, excess triethylamine was added and the reaction stirred at RT to convert the phosphonium chloride into the hydroxymethylphosphine intermediate. Then, 1/3 equivalents of ammonia (2M solution in methanol) was added and the reaction mixture was heated to reflux for two hours. During this time, the solid product precipitated from the reaction mixture, and after cooling to RT was isolated by cannula filtration, washed with methanol and dried in vacuo. The N-Triphos^{Ph} ligand was collected as a white solid in high yield (78 %) with its identity confirmed by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy.

N-Triphos^{Cy} was synthesised in an analogous manner from bis(dicyclohexyl)diphenylphosphonium chloride. Product isolation and purification were undertaken with strict exclusion of air to avoid oxidation of the ligand product. After drying in vacuo, the solid product was taken into a glovebox for long-term storage. N-Triphos^{Cy} was also synthesised in high yield (92 %) with its identity confirmed by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy.

The synthesis of N-Triphos^{tBu} was more difficult than for the phenyl or cyclohexyl analogues. The product did not precipitate from the reaction mixture as per the other ligands, even over extended times. Several aliquots were taken from the reaction mixture for $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, which showed a mixture of signals each time.

Table 2.8. Collected $^{31}\text{P}\{^1\text{H}\}$ NMR data for dialkyl/aryl phosphines, bis(hydroxymethyl)dialkyl/aryl phosphonium chlorides and N-Triphos ligands (R = Ph, Cy, ^tBu).

$^{31}\text{P}\{^1\text{H}\}$ NMR Chemical shift of phosphorus moiety, δ (ppm in CDCl_3)	R = Ph	R = Cy	R = ^tBu
Dialkyl/aryl phosphine	-40.5	-27.5*	+20.6
Bis(hydroxymethyl)dialkyl/aryl phosphonium chloride	+13.4	+28.3	+35.1
N-Triphos ligand	-28.9	-17.0	+12.5

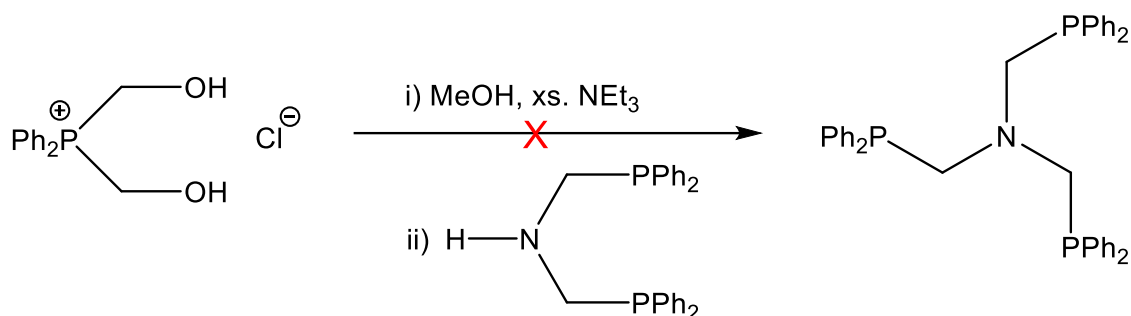
*Literature value in C_6D_6 ⁵⁶

The presence of significant signals attributable to the hydroxymethylphosphine intermediate indicated that without product precipitation the reaction lacked a driving force towards completion. This is attributed to the increased solubility of N-Triphos ^{^tBu} in methanol relative to N-Triphos^{Ph} and N-Triphos^{Cy}. After reducing the volume of solvent to $\sim$ one-third, a white solid precipitated and was isolated in the usual way. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy confirmed the identity of the product as N-Triphos ^{^tBu} and showed that the ligand can be stored without air protection for two hours without any oxidation (given that the NMR sample is prepared under inert conditions). However, preparing an NMR sample without air protection showed complete degradation of the product, indicating poor air-stability in solution. The product yield of 34 % was significantly lower than for N-Triphos^{Ph} and N-Triphos^{Cy}.

Table 2.8 collects the $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts of the dialkyl/aryl phosphines, bis(hydroxymethyl)dialkyl/aryl phosphonium chlorides and N-Triphos ligands, with R = Ph, Cy, ^tBu . The N-Triphos ligands have $^{31}\text{P}\{^1\text{H}\}$ NMR shifts close to their corresponding dialkyl/aryl phosphine, whilst the chemical shifts of the phosphonium chlorides are shifted significantly downfield.

An alternative synthesis of N-Triphos^{Ph} was attempted, using N,N-bis(diphenylphosphinomethyl)amine in place of ammonia (Scheme 2.10). The initial attempt was performed on an NMR scale in deuterated methanol with a J Young tap. Full conversion of the phosphonium chloride to the hydroxymethylphosphine intermediate was observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Upon introduction of N,N-bis(diphenylphosphinomethyl)amine in THF, a solid precipitated, but by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy signals for both the hydroxymethylphosphine intermediate and N,N-bis(diphenylphosphinomethyl)amine indicated that no reaction had occurred. No reaction progress was observed even after heating for two days. Considering that the reaction might be limited by solubility and stoichiometry issues on the NMR scale, the reaction was scaled up. No precipitation was observed, and NMR spectroscopy showed no reaction progress. After heating overnight, solvent removal caused precipitation of a white solid which was washed with methanol. Then, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed a single peak at -28.9 ppm which might be attributable to

either N,N-bis(diphenylphosphinomethyl)amine or N-Triphos^{Ph}. No signal was observed for the hydroxymethylphosphine intermediate. ¹H NMR spectroscopy and mass spectrometry were inconclusive in distinguishing the product identity. Nonetheless, the incomplete reaction observed suggests that N,N-bis(diphenylphosphinomethyl)amine is an ineffective nucleophile for this reaction. Generally, secondary amines are considered more basic, and therefore more nucleophilic, than NH₃. However, in this case the amine is sterically hindered which might inhibit nucleophilic attack on the hydroxymethylphosphine. Given that N,N-bis(diphenylphosphinomethyl)amine is one of the final intermediates involved in synthesising N-Triphos^{Ph} from NH₃, however, this is a surprising result.



Scheme 2.10. Attempted synthesis of N-Triphos^{Ph} using N,N-bis(diphenylphosphinomethyl)amine.

2.3.2 Synthesis of unsymmetrical N-Triphos ligands

As has been described, the syntheses of symmetrical N-Triphos ligands are relatively straight-forward and can access a wide range of different phosphine substituents. Beyond the N-Triphos ligands synthesised in this work, there are further examples reported in the literature with isopropyl, cyclopentyl or difluorophenyl substituents. Changing the phosphine substituent inevitably affects the stereoelectronic parameters of the ligand; for example, in the literature the Tolman cone angles for N-Triphos^{Ph} and N-Triphos^{Cy} have been reported as 134 and 149 ° respectively.⁵⁷

There is motivation for introducing asymmetry into an N-Triphos ligand. This might allow for new coordination modes or geometries to be accessed. Whilst symmetrical N-Triphos ligands tend to form robust complexes through tridentate coordination, this can inhibit the reactivity of the complex as a catalyst. Different coordinating arms incorporated into an N-Triphos ligand, each with different binding properties, might allow for some arms to coordinate more strongly to a metal centre, whilst other, more labile, arms could create vacant coordination sites for substrate molecules. Some unsymmetrical N-Triphos ligands have already been introduced.⁵²

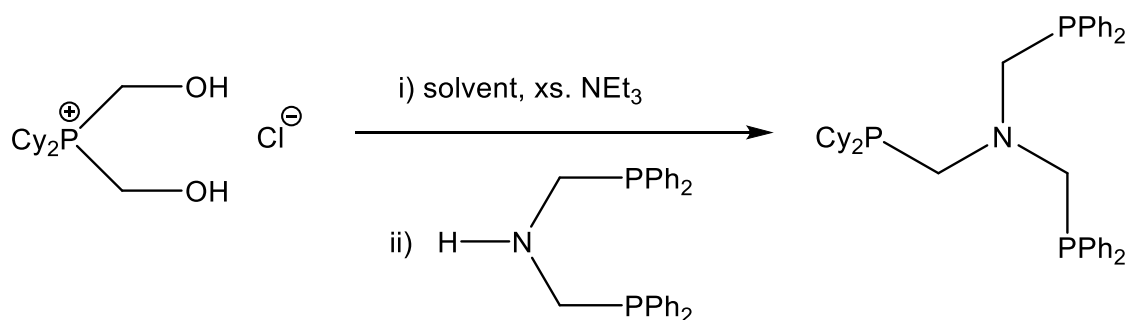
In this work, two targets were investigated. Firstly, N-Triphos ligands of the form $N(\text{CH}_2\text{PR}_2)(\text{CH}_2\text{PR}'_2)_2$ where $R/R' = \text{phenyl or cyclohexyl}$. PPh_2 groups are less bulky and less electron-donating than PCy_2 groups, hence the incorporation of both phosphines in a single N-Triphos ligand would give the ligand interesting stereo-electronic properties. Secondly, N-Triphos ligands of the form $N(\text{CH}_2\text{PPh}_2)(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$ were investigated. Phosphine oxide moieties have significantly different binding character to phosphines, hence a ligand with both phosphine and phosphine oxide moieties would be expected to have properties distinct from typical N-Triphos ligands. The synthesis and coordination chemistry of phosphine oxide ligands will be the focus of Chapter 5.

2.3.2.1 Attempted synthesis of unsymmetrical N-Triphos ligand

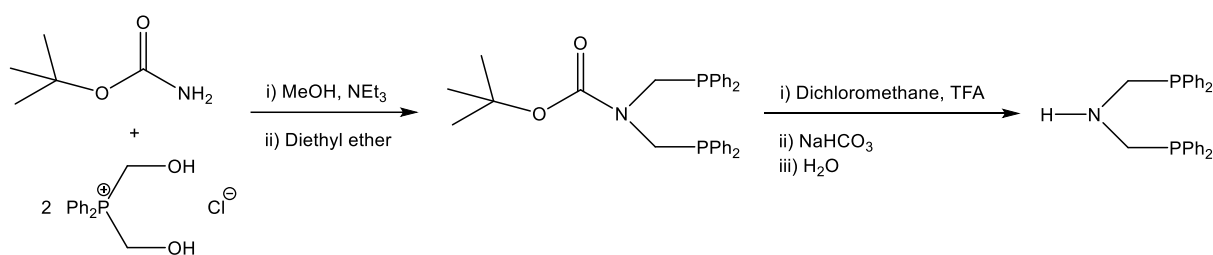
$N(\text{CH}_2\text{PCy}_2)(\text{CH}_2\text{PPh}_2)_2$

$\text{N-Triphos}^{\text{Ph}}$ binds to metals almost exclusively in a tridentate fashion, whilst $\text{N-Triphos}^{\text{Cy}}$ tends to bind through only two of its phosphines, owing to the increased steric bulk of the PCy_2 moiety. Therefore, a ligand with two PPh_2 and PCy_2 arms might be expected to bind in a tridentate fashion, but with an increased lability of the PCy_2 arm. The target ligand $N(\text{CH}_2\text{PCy}_2)(\text{CH}_2\text{PPh}_2)_2$ is unreported in the literature.

A scheme to the target ligand was devised using bis(dicyclohexyl)phosphonium chloride and N,N-bis(diphenylphosphinomethyl)amine, $\text{HN}(\text{CH}_2\text{PPh}_2)_2$ (Scheme 2.11). The synthesis of N,N-bis(diphenylphosphinomethyl)amine has been reported previously and was reproduced successfully.⁵⁸ It involves a reaction between tert-butyl carbamate and bis(diphenyl)phosphonium chloride to form initially N,N-bis(diphenylphosphinomethyl)-tertbutylcarbamate, generating $\text{HN}(\text{CH}_2\text{PPh}_2)_2$ upon treatment with TFA and NaHCO_3 (Scheme 2.12). The product identity was confirmed by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy ($\delta = -30$ ppm).



Scheme 2.11. Attempted synthetic route towards $N(\text{CH}_2\text{PCy}_2)(\text{CH}_2\text{PPh}_2)_2$.



Scheme 2.12. Synthesis of N,N-bis(diphenylphosphinomethyl)amine.⁵⁸

$\text{HN}(\text{CH}_2\text{PPh}_2)_2$ has poor solubility in methanol, therefore THF was selected as a solvent in which both reagents had good solubility. The reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy in which a mixture of signals were observed, some of which may be attributable to the desired ligand product. In dichloromethane and acetonitrile, poor conversion of the phosphonium chloride to the hydroxymethylphosphine intermediate was observed. This step happens readily in methanol. Therefore, the conversion of the phosphonium chloride to its hydroxymethylphosphine was performed in methanol, and subsequently a solution of $\text{HN}(\text{CH}_2\text{PPh}_2)_2$ in THF was introduced. The major $^{31}\text{P}\{^1\text{H}\}$ NMR signals showed that the starting materials were persisting; however several new signals were observed in the expected product regions around -17 ppm for PCy_2 and -29 ppm for PPh_2 . The multiple signals in each region, and their relative intensities, suggested the formation of several N-Triphos ligands with different combinations of PCy_2 and PPh_2 arms (Figure 2.13). A representative $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is shown in Figure 2.14. This might be attributed to “ligand scrambling”, with arms detaching and reattaching. A solid product did not precipitate, which would help to drive the reaction forward to completion. Potentially a small amount of N-Triphos ligand formed, remained in solution and was in equilibrium with its scrambled analogues. Even if the reaction progressed further from the reagents, it would not be facile to separate the different ligands.

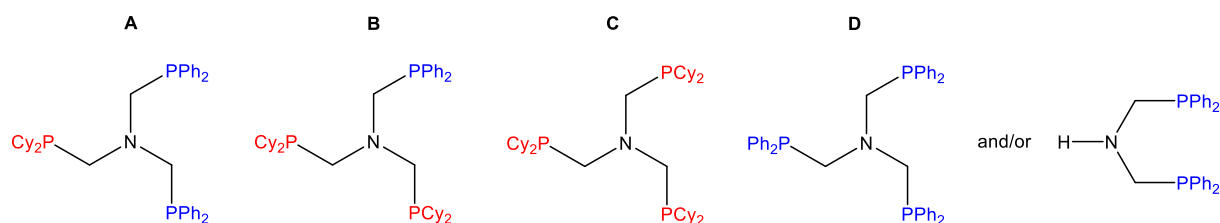


Figure 2.13. Structures of “ligand-scrambled” N-Triphos products.

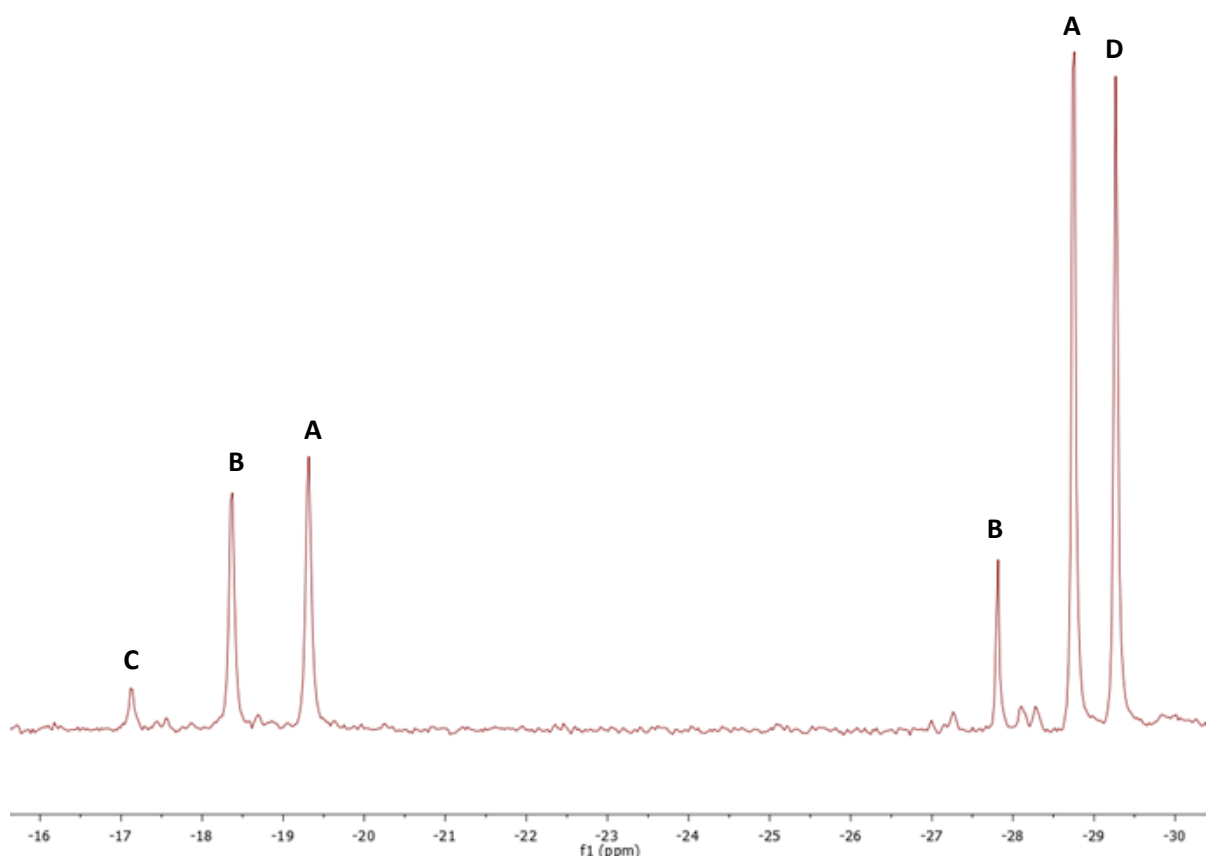


Figure 2.14. Expanded $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum indicating the presence of “scrambled” N-Triphos ligands.

Repeating the reaction at a higher temperature in 1-butanol achieved full solubility of both reagents and some increased conversion of the reagents was observed. A solid product precipitated from the reaction mixture after cooling to RT, and after washing with 1-butanol, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed signals only attributable to the desired ligand product, and not to the other “scrambled” ligands. An expanded $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is shown in Figure 2.15. However, the overall reaction progress remained very poor, indicating that this is not a feasible route to the desired unsymmetrical N-Triphos ligand.

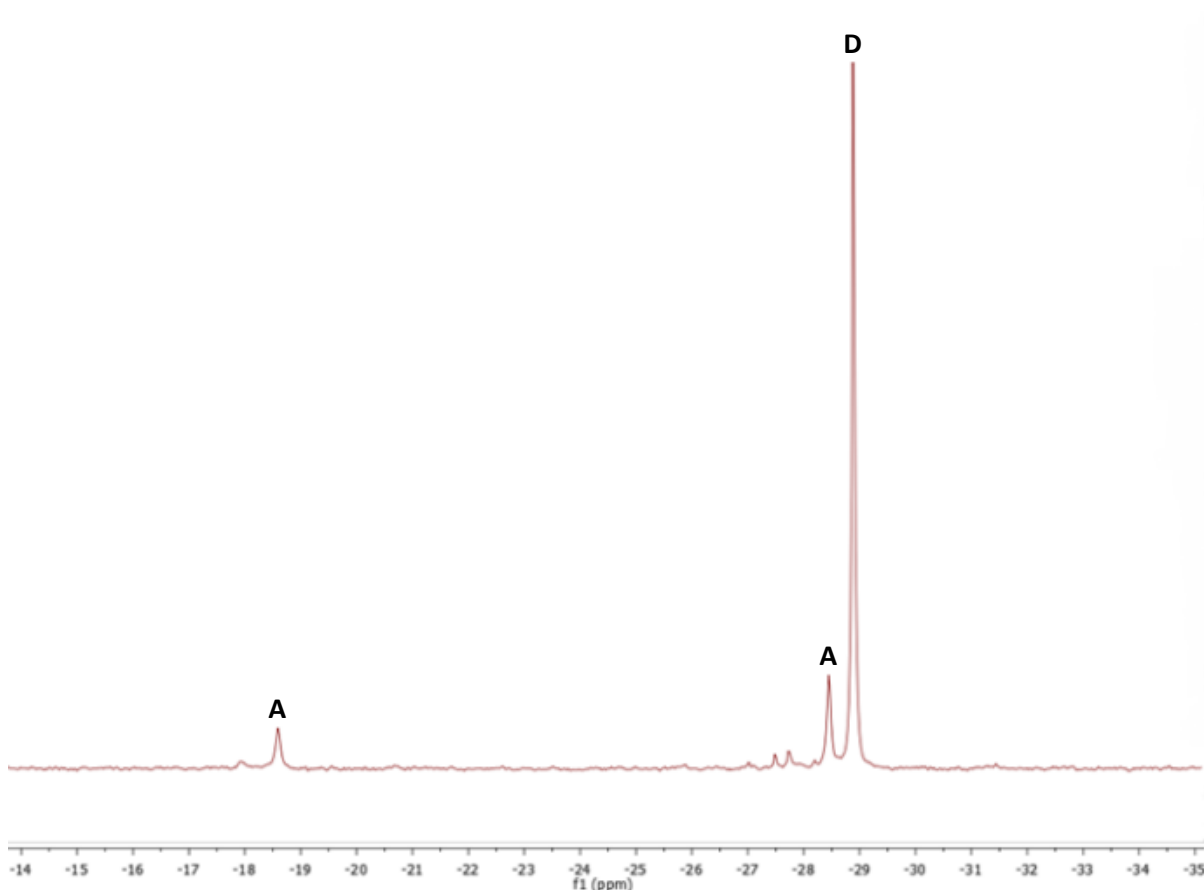
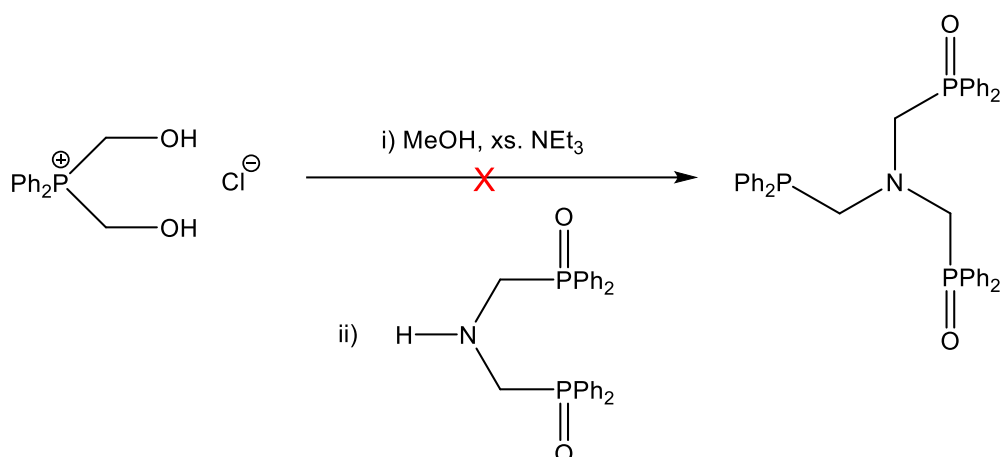


Figure 2.15. Expanded $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum from attempted synthesis of $\text{N}(\text{CH}_2\text{PCy}_2)(\text{CH}_2\text{PPh}_2)_2$.

2.3.2.2 Attempted synthesis of unsymmetrical N-Triphos ligand $\text{N}(\text{CH}_2\text{PPh}_2)(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$

The next target ligand was $\text{N}(\text{CH}_2\text{PPh}_2)(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$, containing two phosphine oxide groups and a single phosphine group. Again, this target is unreported in the literature. According to HSAB theory, phosphine oxides are harder bases than phosphines and therefore generally bind better to “hard” metal centres. Therefore, the inclusion of both phosphine and phosphine oxide moieties in a single ligand might be a route to the formation of heterometallic complexes or to complexes where the coordinating arms are of unequal stability/lability.

A similar route was attempted to that described in the previous section. $\text{HN}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$ was easily obtained through oxidation of $\text{HN}(\text{CH}_2\text{PPh}_2)_2$ with hydrogen peroxide (30 wt.% in H_2O) in THF within one hour. Its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a large shift from -30 ppm for $\text{HN}(\text{CH}_2\text{PPh}_2)_2$ to +30 ppm for $\text{HN}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$.

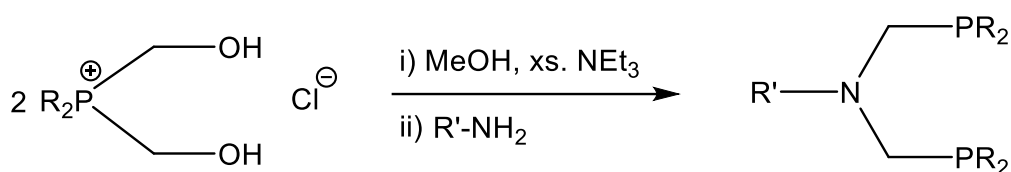


Scheme 2.13. Attempted synthetic route towards $\text{N}(\text{CH}_2\text{PPh}_2)(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$.

However, attempts at synthesising the mixed ligand $\text{N}(\text{CH}_2\text{PPh}_2)(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$ were less successful (Scheme 2.13). Again, the reactions were monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The desired product was expected to have two distinct signals at around +30 ppm and -30 ppm. The first attempts showed no reaction progress beyond the hydroxymethylphosphine intermediate and $\text{HN}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$, with no signals observed for an N-Triphos PPh_2 group. Even changing the reaction solvent from methanol to acetonitrile or DMSO to access higher temperatures did not promote the reaction. It is suspected that the phosphine oxide moieties of $\text{HN}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$ reduce the nucleophilicity of the nitrogen atom further, thus inhibiting its attack on the hydroxymethylphosphine.

2.4 Synthesis of nitrogen-bridged bisphosphine ligands

Owing to the difficulties in synthesising unsymmetrical N-Triphos ligands, attention turned to a slightly different family of ligands. The formation of bidentate nitrogen-centered ligands, which contain an alkyl/aryl substituent on the amine in place of a third phosphine arm, still allows for the ligand properties to be fine-tuned. The phosphine substituent can be tailored by the choice of bis(hydroxymethyl)dialkyl/aryl phosphonium chloride precursor, and the amine substituent by the choice of starting amine. A general reaction scheme is shown in Scheme 2.14. It involves the standard conversion of a bis(hydroxymethyl)dialkyl/aryl phosphonium chloride into its hydroxymethylphosphine intermediate with excess triethylamine. In place of ammonia, a primary amine was added to form the bisphosphine ligand. The stoichiometry is altered so that there are two phosphines available per amine.



R = Ph, R' = Me, Bn

R = Cy, R' = Me, CH₂CH(OEt)₂

R = ^tBu, R' = Me, Bn

Scheme 2.14. General synthetic route of nitrogen-bridged bisphosphine ligands.

The previous section considered that the syntheses of unsymmetrical N-Triphos ligands might have been unsuccessful because the nucleophilic attack of HN(CH₂PPh₂)₂ or HN(CH₂P(O)Ph₂)₂ is inhibited by the steric bulk around the amine and/or the presence of electron withdrawing PO moieties. These issues are largely avoided with the use of primary amines with alkyl substituents. Generally, primary amines have higher basicity than ammonia, unless the substituent contains electron-withdrawing moieties or the amine is involved in hybridisation. Table 2.9 collects some representative values of pK_a for the conjugate acids of different amines.⁵⁹ Furthermore, primary amines largely avoid any steric issues which might reduce their ability to act as a nucleophile.

Further motivation for the investigation into bidentate PNP-type ligands was some work reported by Garcia et al. for LA hydrogenation using palladium complexes of R₂P(CH₂)₂PR₂-type ligands (Chapter 1).⁶⁰ The bidentate PNP ligands introduced here would be expected to form similar complexes through coordination of both phosphines to a metal centre. However, the ligand properties could be modified through introduction of the nitrogen linker.

Table 2.9. Collection of pK_a values for the conjugate acids of different amines.⁵⁹

Amine	pK _a
Ammonia	9.2
Benzylamine	9.3
Tert-butylamine	10.5
Methylamine	10.6
Ethylamine	10.6
Cyclohexylamine	10.6

Furthermore, the nitrogen-based system allows for more facile modification of the ligand through choice of primary amine or phosphine substituent. Of the catalysts reported by Garcia et al., those using ligands with isopropyl and tert-butyl substituents were the most active. This was in line with the PNP pincer-type ligand system found by Zhou et al., with $^i\text{Pr} > ^t\text{Bu} > \text{Cy} > \text{Ph}$. This was attributed to both a steric effect preventing catalyst decomposition and an activating effect of strongly electron-donating substituents.⁶¹ Others, including Serindag and Varnali, have also investigated palladium complexes of nitrogen-bridged bisphosphine ligands.^{62,63}

There are some difficulties with synthesising the bidentate PNP ligands: generally, they do not precipitate from their reaction mixture, and they can take a form between a solid/liquid/oil making their handling more difficult. A small series of ligands was synthesised, and their structures are shown in Figure 2.16.

First the synthesis of $\text{Me-N}(\text{CH}_2\text{PPh}_2)_2$ was performed, starting from bis(hydroxymethyl)diphenylphosphonium chloride and methylamine. This synthesis has been previously described in the literature, using a solvent mixture of methanol and water.^{63,64} After the addition of triethylamine to form the hydroxymethylphosphine intermediate, methylamine solution was added and the mixture heated to reflux. After two hours $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed reaction completion ($\delta = -27.4$ ppm). After cooling to RT, dichloromethane was added and the organic layer was dried over MgSO_4 . After removing the solvent in vacuo, a white oil formed. The ligand identity was confirmed by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy. The previously reported ligand $\text{Bn-N}(\text{CH}_2\text{PPh}_2)_2$ was also formed in an analogous way from benzylamine adapting a literature preparation.⁶⁵ This ligand was prepared by MSci. student Jason Li (JL) under supervision.

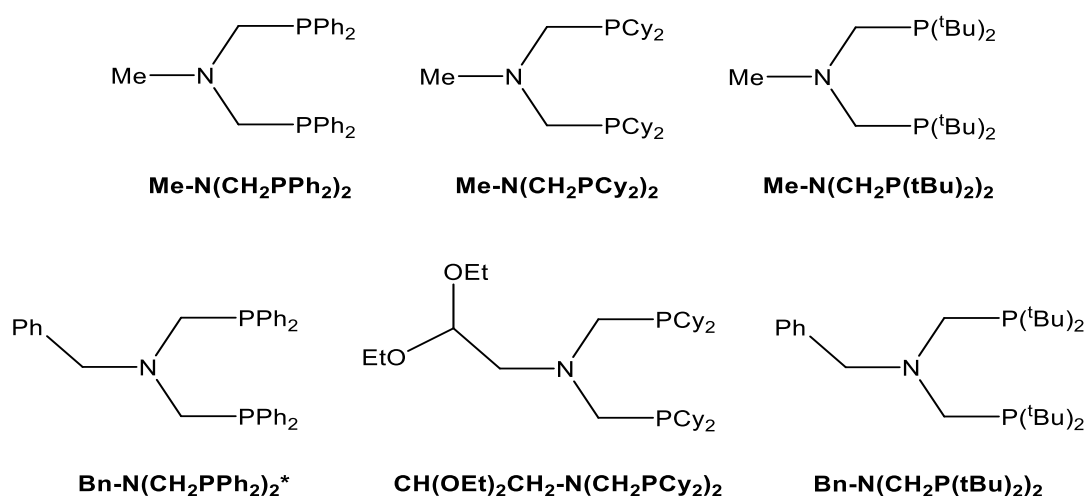


Figure 2.16. Summary of the nitrogen-bridged bisphosphine ligands studied.

*Synthesised by JL under supervision.

The synthesis of $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ was also modified from a literature procedure.⁶⁴ The synthesis starts from bis(hydroxymethyl)dicyclohexylphosphonium chloride, and the hydroxymethylphosphine intermediate was formed in the usual way by addition of triethylamine in methanol. After addition of methylamine solution (33 wt.% in methanol), the reaction was heated under reflux overnight. $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed that the desired ligand product had formed ($\delta = -17$ ppm). However, no solid had precipitated. Upon solvent reduction, a white oil formed. With cooling to -78°C , and addition of methanol for washings, the oil precipitated as a white solid. After drying in vacuo, the ligand was collected as a free-flowing white powder in high 91 % yield, but generally the yields were somewhat lower (33 – 78 %) than for the corresponding N-Triphos^{Cy} ligand, owing to the less facile product isolation. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy matched those of literature. The ligand was stored in a glovebox to avoid oxidation.

A similar reaction was attempted for the synthesis of $\text{Me-N}(\text{CH}_2\text{P}^t\text{Bu})_2$. No reference to this ligand can be found in the literature. Starting from bis(hydroxymethyl)di-tertbutylphosphonium chloride, after addition of methylamine solution the reaction was heated under reflux overnight. The reaction was again monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. A mixture of signals were observed throughout the reaction. A signal at 14 ppm was attributed to the desired product $\text{Me-N}(\text{CH}_2\text{P}^t\text{Bu})_2$, close to the N-Triphos^{tBu} signal at 12 ppm. However, additional major signals at 20 ppm and 44 ppm were observed, attributable to the hydroxymethylphosphine intermediate and a phosphine oxide species. Whilst the reactions were performed using standard Schlenk line techniques, these results indicated that the P^tBu_2 moiety is much more susceptible to oxidation than the PCy_2 and PPh_2 analogues. There was no improvement to the reaction progress with additional time, heating or addition of extra MeNH_2 . No solid product precipitated from the reaction mixture, even after cooling in ice. After solvent reduction in vacuo, a white solid precipitated which was washed with methanol and dried further in vacuo. The solid product obtained was mostly pure by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, with very small impurity signals, but was isolated in a tiny yield (< 10 %). This was attributed to the increased solubility of the product ligand in methanol.

The reaction was repeated in a sealed Schlenk tube, to allow for heating above the boiling point for an extended period of three days. Overall reaction progress towards the ligand product was improved, however NMR spectra continued to show oxidised signals. An initial product was isolated in 65 % yield. Although the desired product has decent solubility in methanol, it had been found to be successful for removing other impurities. After recrystallization from methanol, a white solid was isolated in 44% yield, with $^{31}\text{P}\{^1\text{H}\}$ NMR spectra which were cleaner than before but still showed impurity signals at 20 and 44 ppm.

Concerned that the overall reaction progress might be limited by incorrect stoichiometry, MeNH₂ solution was substituted for MeNH₂.HCl, which could be weighed as a solid with greater accuracy. However, this gave no improvement. It was hoped that precipitating the ligand as a borane adduct might help to drive the reaction forwards. With addition of borane-THF solution to the reaction mixture, ³¹P{¹H} NMR spectra showed no change from the previous spectra, indicating no coordination of borane to the ligand. ¹¹B NMR spectroscopy suggested the formation of a borane adduct, with borane preferentially coordinating to the solvent rather than to the ligand.

To circumvent this, alternative solvent systems were sought. THF as the solvent alone was unsuitable, as the phosphonium chloride did not dissolve. Acetonitrile was selected as a polar solvent with a relatively weak Lewis basicity to minimise borane coordination. However, the phosphonium chloride was also insoluble in acetonitrile. A combination of THF/acetonitrile, however, was a more successful solvent system (without the addition of borane-THF). Much greater reaction progress was observed by ³¹P{¹H} NMR spectroscopy, with very small intermediate signals. After ceasing the reaction, a white solid formed; as this showed no ³¹P{¹H} NMR signals, it was attributed to triethylammonium chloride (HNEt₃Cl). After separating this by cannula filtration, the reaction mixture showed one signal at 14 ppm, with small oxide signals. After removing solvent in vacuo, a solid product was collected but showed degradation, probably resulting from the reaction work-up.

Using a Schlenk tube fitted with a J Young tap provided some advantages. The product solution was separated from precipitated HNEt₃Cl by decanting the mixture into a second Schlenk tube with a Young's tap fitting, in which the solvent was directly removed in vacuo. This allowed for the isolation of a solid product which showed only very small oxide signals in its NMR spectra. It was found easiest to use this solid directly for metal complexation reactions (to be discussed in Chapter 3), which avoided the potential for oxidation/degradation of the ligand through handling and storage. In most cases, any impurities remaining with the ligand remained in solution or were lost in purification of the resulting metal complex.

When the Me-N(CH₂P(^tBu)₂)₂ ligand was not used directly, it was isolated in 61 % yield in a glovebox. However, the actual yield was likely significantly higher, as both the transfer of the reaction mixture from HNEt₃Cl and extracting the solid product from the thin-necked Schlenk tube involved product loss.

The ligand Bn-N(CH₂P(^tBu)₂)₂ (Bn = benzyl, -CH₂Ph) has been previously reported in the literature.⁶⁶ Attempts to produce Bn-N(CH₂P(^tBu)₂)₂ by the usual route from bis(hydroxymethyl)di-tertbutylphosphonium chloride and benzylamine were performed. Adapting the reaction to use methanol as the solvent showed similar observations to those described for Me-N(CH₂P(^tBu)₂)₂: a

mixture of $^{31}\text{P}\{^1\text{H}\}$ NMR signals attributable to product (14 ppm), hydroxymethylphosphine intermediate (20 ppm) and downfield signal(s) attributed to oxide species. Subsequently, the reaction was trialled using a solvent mixture of methanol, water and toluene, as per literature. Again a mixture of $^{31}\text{P}\{^1\text{H}\}$ NMR signals was observed, but after solid isolation and washing with methanol, the major $^{31}\text{P}\{^1\text{H}\}$ NMR signal at 13.0 ppm matched that of literature.

Then the reaction was trialled using an acetonitrile/THF solvent mixture, which was effective for $\text{Me-N}(\text{CH}_2\text{P}(\text{tBu})_2)_2$. The reaction was cleaner through $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, with signals only observed at $\delta = 12.9$ ppm (product) and $\delta = 35.3$ ppm, attributed to the original phosphonium chloride. No signals were observed for the hydroxymethylphosphine intermediate or additional oxide species. Addition of further NEt_3 to promote the reaction did not help. With addition of extra benzylamine, the reaction was observed to shift heavily towards the hydroxymethylphosphine intermediate, resulting in the loss of the desired ligand product. It appeared as if benzylamine was reacting with the ligand to reform the intermediate species.

In an attempt to generate water-soluble complexes, the unreported diethoxy ligand $\text{CH}(\text{OEt})_2\text{CH}_2\text{-N}(\text{CH}_2\text{PCy}_2)_2$ was synthesised from bis(hydroxymethyl)dicyclohexylphosphonium chloride and 2,2-diethoxyethylamine in methanol. Whilst $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showed several signals, the major signal at $\delta = -17.4$ ppm matched the expected ligand product. After heating under reflux overnight, the mixture was cooled to RT and solvent was removed almost to completion. The white, oily residue which was isolated formed a white solid upon cooling to -78°C . However, at RT the product remained as an oily residue. Owing to the air-sensitive nature of the ligand and the difficulty of handling the ligand as an oil, it was decided to take the ligand forward for complexation to palladium without fully isolating the product (to be discussed in Chapter 3).

2.5 Summary and outlook

This Chapter introduced the family of N-Triphos ligands. Whilst they have found applications in several areas, including in the formation of catalysts for the hydrogenation of LA, they are relatively unexplored, especially compared to the carbon-centred Triphos ligand. In addition to the general features of phosphine ligands, N-Triphos ligands are highlighted for their tridentate, facial coordination to metals resulting in the formation of robust metal complexes. However, variations in the choice of phosphine substituent, metal centre, and reaction conditions can lead to more unusual coordination modes and geometries.

Straight-forward routes to symmetrical N-Triphos ligands are well-established in the literature, typically using a bis(hydroxymethyl)dialkyl/aryl phosphonium chloride as a precursor. Commonly, the air-stable phosphonium chlorides are generated from their corresponding dialkyl/diaryl phosphine, although a preferred route to the formation of bis(hydroxymethyl)diphenylphosphonium chloride from triphenylphosphine and lithium has been developed.

A number of unsymmetrical N-Triphos ligands have been reported in the literature, because the modification of the phosphine arms results in changes to the stereo-electronic properties, and therefore behaviour, of the ligand. Attempts to synthesise the unsymmetrical ligands $\text{N}(\text{CH}_2\text{PCy}_2)(\text{CH}_2\text{PPh}_2)_2$ and $\text{N}(\text{CH}_2\text{PPh}_2)(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$ were complicated by incomplete reaction progress and/or a mixture of product formation. It therefore appears that $\text{HN}(\text{CH}_2\text{PPh}_2)_2$ and $\text{HN}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$ are ineffective nucleophiles and cannot replace NH_3 directly. Therefore, the syntheses of these mixed ligands cannot benefit from the facile synthetic routes to symmetrical N-Triphos ligands.

A series of bidentate nitrogen-bridged phosphine ligands were synthesised. Although they lose the tridentate nature of N-Triphos ligands, they retain the structural versatility allowing for modifications at the phosphine or amine sites. However, the ligands do not readily precipitate from their reaction mixtures, and sometimes they take the form of an oil at ambient temperatures. The $\text{P}(\text{tBu})_2$ ligands are the most difficult to synthesise, although an acetonitrile/THF solvent system was found effective for the synthesis of $\text{Me-N}(\text{CH}_2\text{P}(\text{tBu})_2)_2$. The air sensitive nature of the $\text{P}(\text{tBu})_2$ and PCy_2 ligands means that utmost care must be taken in product isolation, purification and storage. In some cases, it was found more effective to react the ligands directly without significant work-up, making their complexes which are much easier to isolate and purify.

Whilst this chapter has highlighted that the family of N-Triphos ligands offer significant benefits in their ease of synthesis, low-cost syntheses, and structural versatility (as compared to the carbon-centred Triphos), it has been seen that certain variations of N-Triphos are significantly more difficult to prepare. If we return to the motivation to develop sustainable, efficient catalysts for the hydrogenation of biogenic acids, then the ligands play a key role in such systems. Therefore, they should be facile to prepare, straight-forward to handle and cost-effective, in addition to demonstrating good activity and selectivity. From the point of view of applying these systems to a purpose, it is of value to focus on the ligands which will be suitable for the intended purpose.

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Chapter 3

Transition-metal phosphine complexes

“I’ve seen things you people wouldn’t believe... All those moments will be lost in time, like tears in rain”, *Blade Runner* (1982)

3.1 Introduction

Chapter 1 introduced numerous catalyst systems for the hydrogenation of LA to GVL, 1,4-PDO and 2-MTHF. Many of those catalysts used phosphine ligands and generally multidentate phosphine ligands were the most successful. The homogeneous catalysts predominantly used ruthenium, with some examples of iridium and a single example of palladium. If the motivation is to develop catalysts which are effective for the upgrading of biomass-derived feedstocks, then the overall sustainability of the system must be considered. This includes the choice of metal applied as a catalyst. A key motivation for the development of chemical and fuel syntheses from biomass is to replace the established routes based upon fossil fuels, a finite and diminishing resource. Precious metals – including ruthenium, iridium and palladium – have a low natural abundance. In fact, these metals have some of the very lowest abundances in the Earth’s crust: ruthenium and iridium at just 0.001 ppm, and palladium at 0.015 ppm (Table 3.1).¹

In 2019, the European Chemical Society produced some resources to highlight the relative scarcity or abundance of each element.² Ruthenium, iridium and palladium are considered as “at rising threat from increased use”. Furthermore, the total palladium production worldwide in 2017 was just 212 tons (Table 3.2). Additionally, production is limited to just a handful of countries, with Russia, South Africa, Canada, USA and Zimbabwe producing over 90 % of the world’s palladium between them. This uneven global distribution raises concerns over the sustainability of such metals for their future global use. Consequently, palladium is often recycled; scrapped catalytic converters are a major source of recycled palladium. The wide-ranging applications of palladium – from catalytic converters, fuel cells, electronics and medicine – ensure that the metal is in high-demand.³

Table 3.1. Natural abundance of different metals in the Earth’s crust.¹

Element	Natural abundance in Earth’s crust (ppm)
Iron	56,300
Nickel	84
Copper	60
Cobalt	25
Palladium	0.015
Ruthenium	0.001
Iridium	0.001
Rhodium	0.001

Table 3.2. Palladium production per country in 2017.³

Country	Palladium production in tons, 2017
1. Russia	81 (38 %)
2. South Africa	78 (37 %)
3. Canada	19 (9 %)
4. USA	13 (6 %)
5. Zimbabwe	12 (6 %)
6. Others	8.4 (4 %)
Total	211.4

Figure 3.1 displays the prices of some precious metals between 2016 and 2021. Whilst there is some volatility in their prices, the trends are for increasing cost over time. This is likely to continue with increasing demand and diminishing supply.^{4–12}

The factors of cost and abundance of the precious metals cannot be ignored. However, their excellent catalytic activity cannot be understated either. Whilst so-called earth abundant metals – such as the first-row transition metals iron, cobalt, nickel and copper – are significantly more abundant and inexpensive compared to the precious metals, they can still be considered as at-risk owing to their high usage in applications such as smartphones. From this group, only iron, the fourth-most abundant element on Earth, can truly be considered as at no risk.

Catalytic systems cannot simply exchange a precious metal for a more abundant metal with no change in activity. The incorporation of earth abundant metals into catalysts remains a huge technical change, and this remains the case for the specific application of LA hydrogenation. Therefore, the use of precious metals in this field remains important at present and moving forward. Therefore, it is essential that catalysts based on these metals are as effective and efficient as possible. Only when the catalysts are sufficiently cost-effective and widely applicable to industrial processes will they be utilised on the major scale which will be necessary in future. Therefore, research and development into the optimisation of catalysts in this field remains hugely active.

An important way to tailor the properties of a homogeneous catalyst is through its ligand system. Multidentate phosphine ligands have been highlighted for their formation of robust, well-defined metal complexes. Figure 3.3 collects some examples of multidentate phosphine-catalysts applied for LA hydrogenation, with both carbon and nitrogen centred ligands. Whilst many of the catalytic systems described in Chapter 1 used in situ mixtures of a metal precursor and ligand(s), the formation of defined metal complexes allows for closer study of the coordination chemistry and geometry of those complexes. These factors are hugely important in determining the properties of a catalyst.

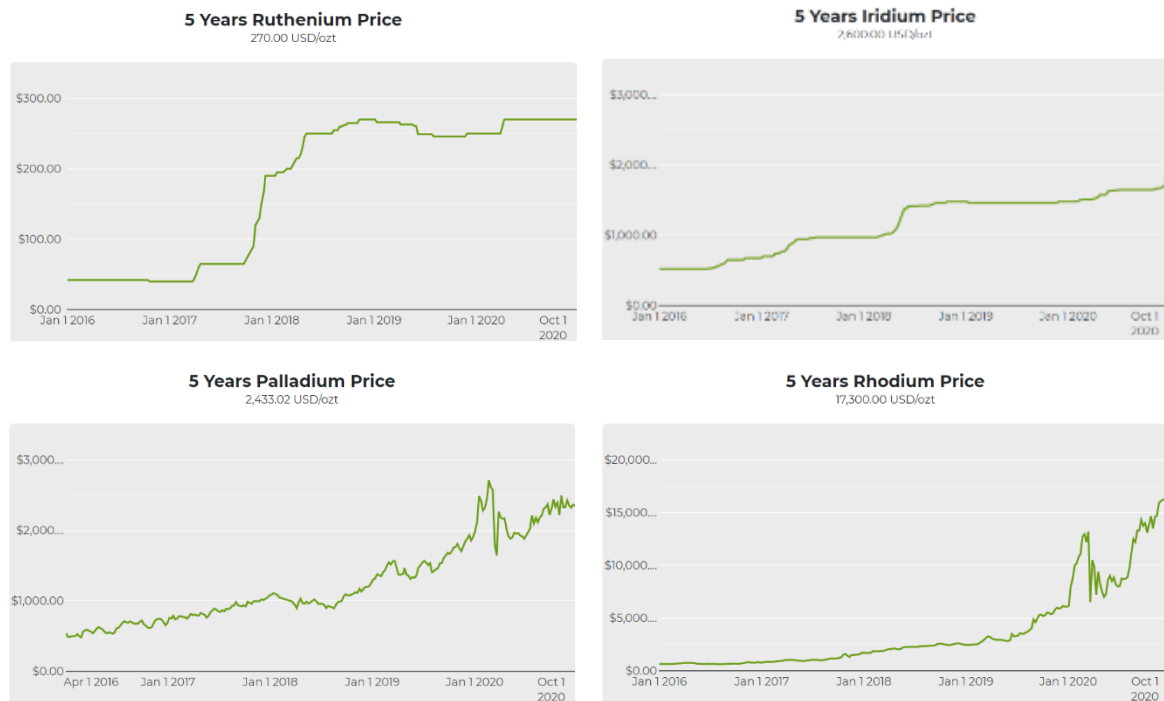


Figure 3.1. Graphs displaying the cost of the metals ruthenium, iridium, palladium and rhodium across 2016-2021.⁹⁻¹²

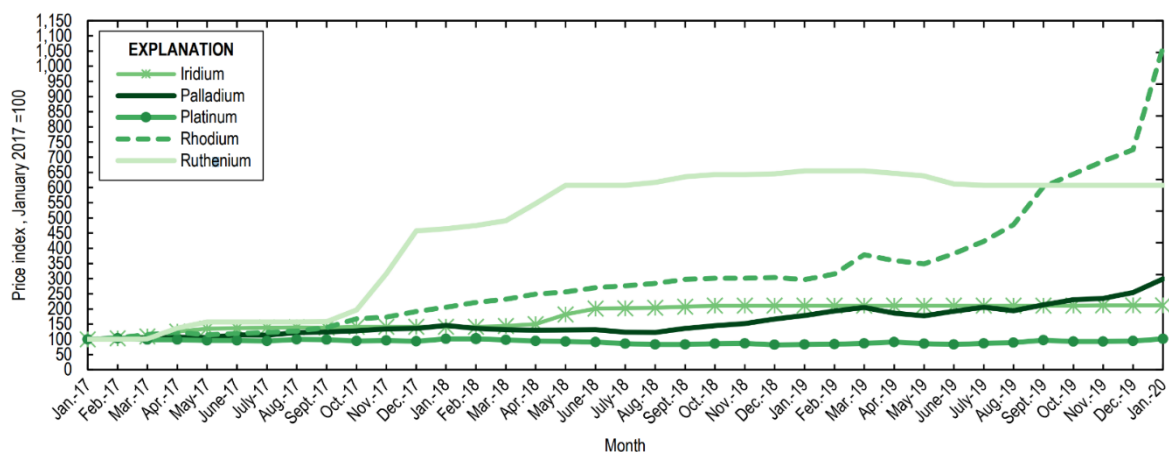


Figure 3.2. Prices of precious-metals from January 2017-January 2020.⁸

This Chapter will discuss the coordination chemistry of the bi- and triphosphine ligands introduced in Chapter 2. The focus will be on complexes with palladium, which is under-explored in this field. Complexes of other platinum-group metals ruthenium, iridium and rhodium will also be discussed. The coordination chemistry of platinum-group metals with phosphine ligands show similar trends. Discussions will focus on the coordination chemistry of the ligands and the geometries of their metal complexes. This Chapter will also briefly discuss the use of earth abundant metals; Chapter 5 will centre on the coordination chemistry of phosphine and phosphine oxide ligands with first-row transition metals.

The key properties of metal catalysts include their activity and selectivity. However, as for the ligands themselves, the catalysts should be straight-forward to prepare, well-defined and show good stability if they are to be applied industrially. Furthermore, their cost-effectiveness can be affected by factors such as the choice of metal precursor. Therefore, this Chapter will also highlight any complexities or difficulties in the preparation or use of the complexes which would have a factor in their potential application.

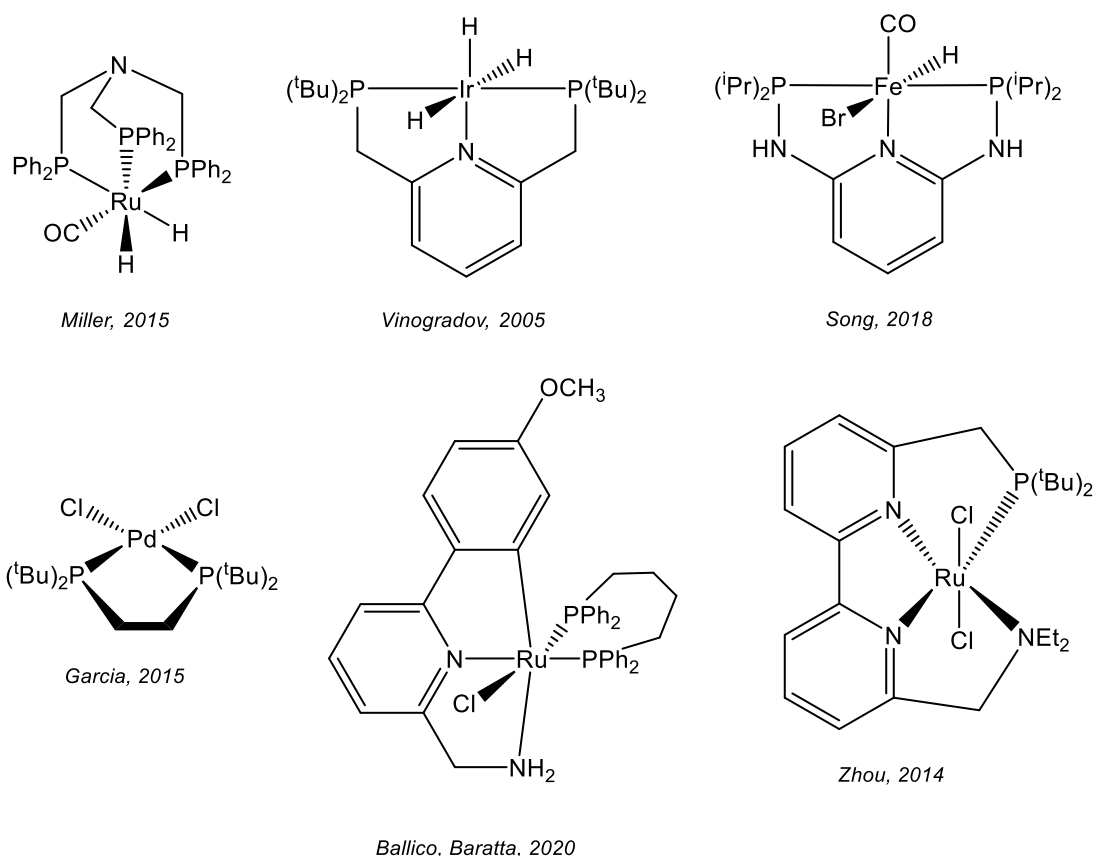


Figure 3.3. Examples of catalysts using multidentate phosphine ligands.^{13–18}

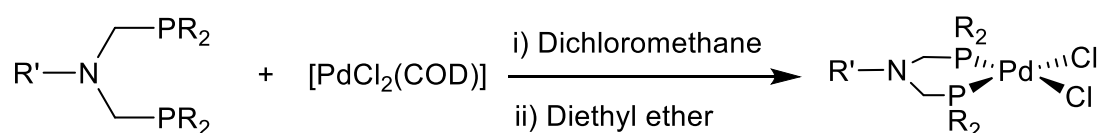
3.2 Coordination of multidentate phosphine ligands to Group 10 metals

This Section will begin by discussing the coordination chemistry of nitrogen-bridged bisphosphine ligands with palladium (3.2.1), before moving onto the coordination of triphosphine N-Triphos ligands with palladium (3.2.2). Section 3.2.3 will discuss the coordination chemistry of nitrogen-bridged bisphosphine ligands with nickel.

3.2.1 Complexes of nitrogen-bridged bisphosphine ligands with palladium

Palladium complexes of the nitrogen-bridged phosphine ligands were prepared through reactions of each ligand with $[\text{PdCl}_2(\text{COD})]$ in a 1:1 ratio. $[\text{PdCl}_2(\text{COD})]$ [dichloro(1,5-cyclooctadiene)palladium(II)] is a commonly used palladium precursor. Direct reactions using PdCl_2 can suffer from its poor solubility in many organic solvents, whilst $[\text{PdCl}_2(\text{COD})]$ has good solubility across many common solvents. It was prepared in straight-forward reactions between PdCl_2 and excess COD in a mixture of ethanol and HCl solution. COD is readily displaced from $[\text{PdCl}_2(\text{COD})]$ to generate dichloro-palladium complexes.

The general scheme for the reactions between nitrogen-bridged phosphine ligands of the general formula $\text{R}'\text{-N}(\text{CH}_2\text{PR}_2)_2$ and $[\text{PdCl}_2(\text{COD})]$ is shown in Scheme 3.1. The reactions were strictly protected from air, owing to the air-sensitivity of the phosphine ligand, particularly in solution. Dichloromethane was chosen as solvent, owing to the full solubility of both ligand and $[\text{PdCl}_2(\text{COD})]$ at room temperature (RT). The reactions were generally complete within one hour of stirring at RT, indicated by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. With the addition of diethyl ether and vigorous stirring, a solid product precipitated from the reaction mixture.



$\text{R} = \text{Cy}$, $\text{R}' = \text{Me}$ (**1**), $\text{CH}_2\text{CH}(\text{OEt})_2$ (**6**)

$\text{R} = \text{tBu}$, $\text{R}' = \text{Me}$ (**3**)

$\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$ (**4**), Bn (**5**)

Scheme 3.1. General scheme for reaction of nitrogen-bridged bisphosphine ligands with $[\text{PdCl}_2(\text{COD})]$.

The air-stable products were isolated by filtration and after washing with additional diethyl ether and drying in vacuo, were collected as free-flowing pale-coloured powders in high yields. The resulting palladium complexes were stored without any protection from air, with no degradation observed at ambient conditions.

The reaction between Me-N(CH₂PCy₂)₂ and [PdCl₂(COD)] produced a beige-coloured solid product in 93 % yield. A single ³¹P{¹H} NMR signal at 30.2 ppm indicated full coordination of the phosphine arms. Crystals suitable for X-ray diffraction were grown from vapour diffusion dichloromethane/diethyl ether and confirmed the expected bidentate complex [Me-N(CH₂PCy₂)₂PdCl₂] (**1**). The complex was previously modelled as part of a wider DFT study by Varnali et al.¹⁹ Two separate crystal structures were obtained for **1**, which were identical except for the presence/absence of a solvated dichloromethane molecule. The crystal structures show the expected square-planar geometry of the complex (Figure 3.4), as anticipated for a d⁸ Pd(II) complex with a 16-electron configuration.

The bond angles around the palladium centre show some deviation from a perfect 90 ° angle between each coordinating atom (Table 3.3). The angle between the two phosphorus atoms is ~ 5 ° wider than the angle between the two Cl atoms. This might be attributed to a steric effect, whereby the PCy₂ centres position themselves slightly further apart to relieve steric crowding. The structure of **1** was further confirmed by mass spectrometry, albeit as a DMSO adduct owing to instrument contamination ([M-Cl]⁺ + DMSO calc. m/z = 669.2375, found m/z = 669.2357). [A low-resolution mass spectrum was obtained without DMSO, [M+Cl]⁺ calc. m/z = 592.2, found m/z = 592.0].

Table 3.3. Collected bond angles and bond lengths for complexes **1**, **3** and **4**.

[Me-N(CH ₂ PCy ₂) ₂ PdCl ₂] (1)			[Me-N(CH ₂ P(^t Bu) ₂) ₂ PdCl ₂] (3)		[Me-N(CH ₂ PPh ₂) ₂ PdCl ₂] (4)	
Bond	Angle (°)	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
P(5)-Pd(1)-P(3)	95.36(4)	95.08(2)	P(3)-Pd(1)-P(5)	97.04(5)	P(3)-Pd(1)-P(3)#1	92.25(4)
P(5)-Pd(1)-Cl(1)	86.94(4)	87.04(2)	P(5)-Pd(1)-Cl(2)	88.20(6)	P(3)#1-Pd(1)-Cl(1)#1	87.99(2)
P(3)-Pd(1)-Cl(2)	88.39(3)	87.73(2)	P(3)-Pd(1)-Cl(1)	90.81(6)	P(3)-Pd(1)-Cl(1)	87.99(2)
Cl(1)-Pd(1)-Cl(2)	89.26(4)	90.26(2)	Cl(2)-Pd(1)-Cl(1)	85.24(6)	Cl(1)#1-Pd(1)-Cl(1)	91.60(3)
	Length (Å)	Length (Å)		Length (Å)		Length (Å)
Pd(1)-P(5)	2.2385(11)	2.2483(6)	Pd(1)-P(5)	2.2931(16)	Pd(1)-P(3)	2.2341(7)
Pd(1)-P(3)	2.2493(9)	2.2503(6)	Pd(1)-P(3)	2.2893(15)	Pd(1)-P(3)#	2.2341(7)

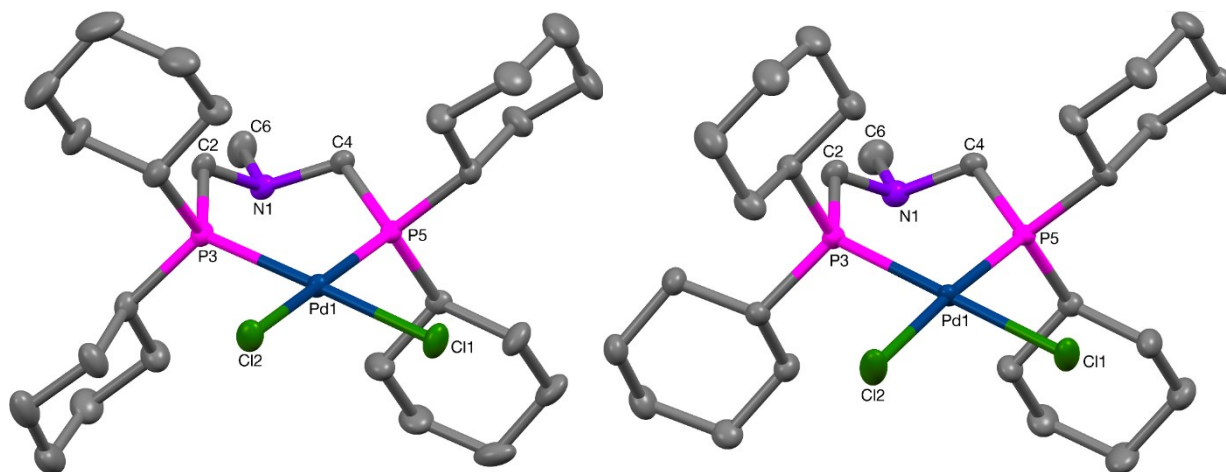


Figure 3.4. Crystal structures of $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{PdCl}_2]$ (**1**), dichloromethane solvate (left) and unsolvated (right). Hydrogen atoms and solvent molecules omitted for clarity.

The novel iodo-analogue, $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{PdI}_2]$ (**2**), was synthesised from a reaction between $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ and $(\text{TBA})_2[\text{Pd}_2\text{I}_6]$. $(\text{TBA})_2[\text{Pd}_2\text{I}_6]$ was provided by the Wilton-Ely group as a recovery product from spent exhaust gas catalysts. The product **2** readily precipitated from the reaction mixture in acetone and was isolated in 64 % yield. $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed a singlet at 24.5 ppm, slightly upfield of the signal observed for the chloride analogue **1**. Additionally, small doublets at 21.9 and 32.9 ppm were observed, likely resulting from small impurities in the palladium precursor. Mass spectrometry identified the product as the expected $[\text{M-I}+\text{CH}_3\text{CN}]^+$ species at $m/z = 725.1862$ (calc. $m/z = 725.1842$). Crystals were grown from dichloromethane and diethyl ether and identified a square-planar structure with iodides in place of chlorides (Figure 3.5). Both the P-Pd-P ($94.32(5)^\circ$) and I-Pd-I ($87.400(16)^\circ$) bond angles around the palladium centre in **2** were slightly narrower than for the chloride analogue **1**.

The tert-butyl analogue, $[\text{Me-N}(\text{CH}_2\text{P}(\text{tBu})_2)_2\text{PdCl}_2]$ (**3**), was slightly more difficult to prepare. Whilst $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction mixture showed a major signal at 37.8 ppm, several other signals were observed. A solid product was isolated in a similar way, albeit in a lower yield (62 %). The product was collected as a gummy orange solid which was difficult to handle, even after recrystallization. With extended drying in vacuo, a free-flowing pale-yellow powder was obtained. The product showed a single $^{31}\text{P}\{^1\text{H}\}$ NMR signal at 37.8 ppm, alongside a minor oxide signal at 44 ppm.

Crystallisations of **3** were successful, again using a vapour diffusion technique from dichloromethane/diethyl ether. The resulting crystal structure, found as a DCM solvate, shows the expected structure and square-planar geometry (Figure 3.5). Important bond angles and bond lengths

are collated in Table 3.3. The difference in the angles between the two coordinated phosphine atoms ($97.04(5)^\circ$) and the two chlorides ($85.24(6)^\circ$) is even more pronounced than for **1**. This reflects an increased deviation from idealised square-planar geometry, attributed to the increased steric bulk of the $P(tBu)_2$ substituents. Furthermore, there is a small but statistically significant ($0.3\text{--}0.4\text{ \AA}$) increase in P-Pd bond length for **3** compared to **1**, presumably also to accommodate for the increased steric bulk of the $P(tBu)_2$ substituents. The structure of **3** was further confirmed by mass spectrometry, again found as $[M-Cl]^+$ (calc. $m/z = 490.1598$, found $m/z = 490.1597$).

Alongside this work, an MSci. student in the Miller group, Jason Li, synthesised the PPh_2 -analogues $[Me-N(CH_2PPh_2)_2PdCl_2]$ (**4**) and $[PhCH_2-N(CH_2PPh_2)_2PdCl_2]$ (**5**) in high yields (88 % and 75 % respectively) from methylamine and benzylamine respectively, following the standard method. The synthesis of **4** was previously reported by Serindag et al.^{19,20} Crystals of **4** and **5** suitable for X-ray crystallography were grown from diffusion of diethyl ether into dichloromethane solutions. The crystal structures show the expected square-planar geometry (Figure 3.6). Important bond angles and bond lengths for **4** are collated in Table 3.3. Comparing the bond angles for **4** in the same way as for the cyclohexyl and tert-butyl analogues **1** and **3** reveals a very small difference ($< 1^\circ$) between the P-Pd-P bond angle and the Cl-Pd-Cl bond angle, showing much less distortion from a standard square-planar geometry. This fits with the reduced steric bulk of the PPh_2 substituents, showing that the P-Pd-P bond angle increases with increasing steric bulk of the substituent ($tBu > Cy > Ph$). There is no further reduction of Pd-P bond length for **4** compared to **1**.

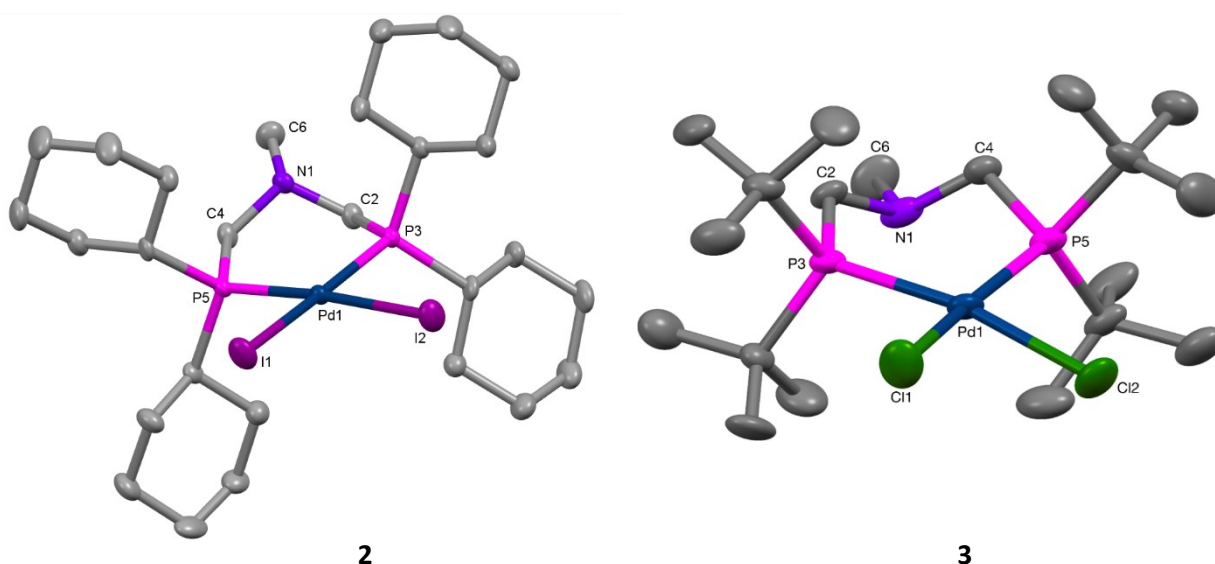


Figure 3.5. Crystal structures of $[Me-N(CH_2PCy_2)_2PdI_2]$ (**2**) (left) and $[Me-N(CH_2P(tBu)_2)_2PdCl_2]$ (**3**) (right). Hydrogen atoms and solvent molecules omitted for clarity.

Table 3.4. collates the important bond angles and bond lengths of both **4** and **5**. In changing the substituent on the amine from methyl to benzyl, there is a small change in the angles around the palladium centre. There is around a 2 ° increase in the P-Pd-P bond angle, with an increase in Cl-Pd-Cl bond angle of <1 °. This might be to minimise steric interactions with the benzyl substituent on the amine. There is however no statistically significant difference between the Pd-P bond lengths between **4** and **5**. This indicates that the amine substituent has no effect on the metal-phosphine bonding, as would be expected owing to its distance from the metal centre.

Table 3.4. Comparison of bond angles and bond lengths for [Me-N(CH₂PPh₂)₂PdCl₂] (**4**) and [PhCH₂-N(CH₂PPh₂)₂PdCl₂] (**5**).

[Me-N(CH ₂ PPh ₂) ₂ PdCl ₂] (4)		[PhCH ₂ -N(CH ₂ PPh ₂) ₂ PdCl ₂] (5)	
Bond	Angle (°)	Bond	Angle (°)
P(3)-Pd(1)-P(3A)	92.25(4)	P(3)-Pd(1)-P(5)	94.61(6)
P(3A)-Pd(1)-Cl(1A)	87.99(2)	P(3)-Pd(1)-Cl(2)	87.11(6)
P(3)-Pd(1)-Cl(1)	87.99(2)	P(5)-Pd(1)-Cl(1)	86.10(6)
Cl(1A)-Pd(1)-Cl(1)	91.60(3)	Cl(2)-Pd(1)-Cl(1)	92.49(6)
	Length (Å)		Length (Å)
Pd(1)-P(3)	2.2341(7)	Pd(1)-P(3)	2.2405(17)
Pd(1)-P(3A)	2.2341(7)	Pd(1)-P(5)	2.2422(17)

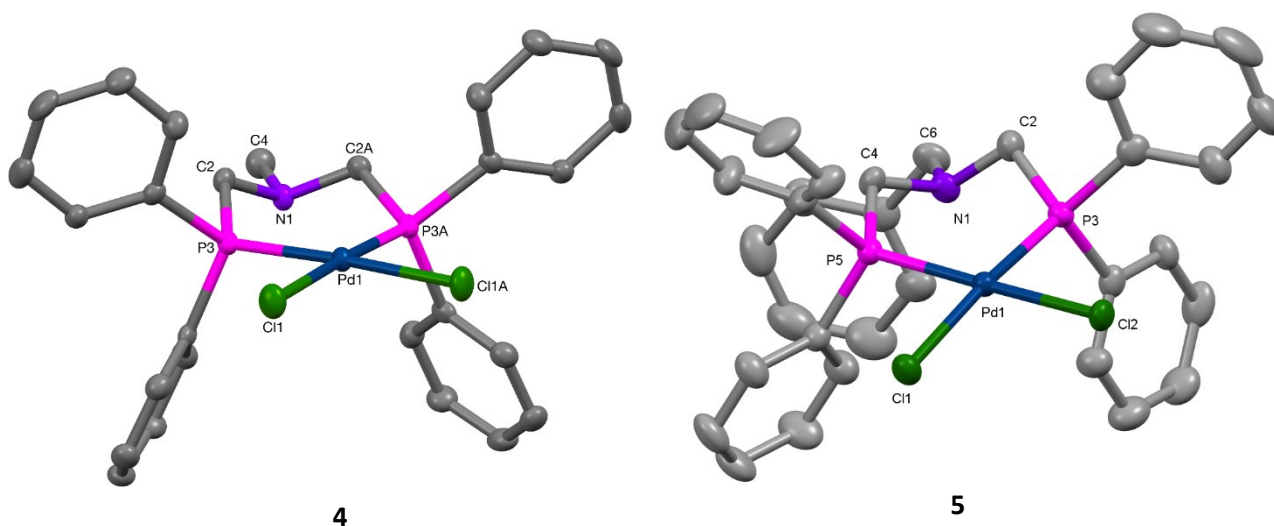


Figure 3.6. Crystal structures of [Me-N(CH₂PPh₂)₂PdCl₂] (**4**) (left) and [PhCH₂-N(CH₂PPh₂)₂PdCl₂] (**5**) (right). Hydrogen atoms and solvent molecules omitted for clarity.

Table 3.5. Collected $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts for bisphosphine ligands and their palladium complexes.

Compound	$^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift, δ (ppm, in CDCl_3)	Shift upon complexation
$\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$	-16.7	-
$\text{Me-N}(\text{CH}_2\text{P}^t\text{Bu})_2$	14.1	-
$\text{Me-N}(\text{CH}_2\text{PPh}_2)_2$	-27.5	-
$\text{PhCH}_2\text{-N}(\text{CH}_2\text{PPh}_2)_2$	-29.2	-
$\text{C}(\text{OEt})_2\text{HCH}_2\text{-N}(\text{CH}_2\text{PCy}_2)_2$	-17.3	-
$[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{PdCl}_2]$ (1)	30.2	+46.9 ppm
$[\text{Me-N}(\text{CH}_2\text{P}^t\text{Bu})_2\text{PdCl}_2]$ (3)	37.8	+23.7 ppm
$[\text{Me-N}(\text{CH}_2\text{PPh}_2)_2\text{PdCl}_2]$ (4)	7.97	+35.5 ppm
$[\text{PhCH}_2\text{-N}(\text{CH}_2\text{PPh}_2)_2\text{PdCl}_2]$ (5)	8.49	+37.7 ppm
$[\text{C}(\text{OEt})_2\text{HCH}_2\text{-N}(\text{CH}_2\text{PCy}_2)_2\text{PdCl}_2]$ (6)	28.4	+45.7 ppm

Table 3.5. collects the $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts for each of the bisphosphine ligands and their corresponding dichloro-palladium complexes **1** and **3-6**. It is interesting to compare how complexation of each ligand affects their $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift. The free PPh_2 ligands $\text{Me-N}(\text{CH}_2\text{PPh}_2)_2$ and $\text{PhCH}_2\text{-N}(\text{CH}_2\text{PPh}_2)_2$ have the most upfield chemical shifts of -27.5 and -29.2 ppm respectively. The PCy_2 ligand $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ also shows a pronounced upfield chemical shift of -16.7 ppm. The P^tBu_2 ligand $\text{Me-N}(\text{CH}_2\text{P}^t\text{Bu})_2$ shows a downfield chemical shift of +14.1 ppm. All the ligands are shifted significantly downfield upon coordination to palladium. The magnitude of change in chemical shift upon metal coordination follows the order $\text{Cy} > \text{Ph} > ^t\text{Bu}$. The similarity in this difference for the two PPh_2 ligands again shows that the amine substituent has little effect upon the metal-phosphine bonding.

The series of palladium complexes described thus far have good solubility in common polar organic solvents, such as chloroform, dichloromethane and acetonitrile. However, they have no water solubility. Whilst the substituent on the amine is considered to have little effect on the behaviour of the metal centre, it was considered as a route to obtain improved solubility in water (the importance of this will be discussed further in Chapter 4).

Chapter 2 described the synthesis of the ligand $\text{C}(\text{OEt})_2\text{HCH}_2\text{-N}(\text{CH}_2\text{PCy}_2)_2$ from bis(hydroxymethyl)dicyclohexylphosphonium chloride and 2,2-diethoxyethylamine. It was hoped that the incorporation of the diethoxy substituent at the amine position would increase the water solubility of the resulting palladium complex, whilst having a minimal effect on the properties of the palladium centre itself.

The diethoxy ligand was synthesised as an oil showing minor $^{31}\text{P}\{^1\text{H}\}$ NMR impurity signals. Owing to its air-sensitivity, it was not fully isolated prior to reaction with $[\text{PdCl}_2(\text{COD})]$. Pleasingly, $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction mixture showed a main signal at 28.1 ppm attributed to the desired palladium complex, alongside a small signal at 11.2 ppm carried forward from the ligand. The product was isolated as a pale-yellow powder in the standard manner with a single $^{31}\text{P}\{^1\text{H}\}$ NMR signal at 28.4 ppm in 57 % yield. The $^{31}\text{P}\{^1\text{H}\}$ NMR signal is very close to that observed for **1**, with a similar change in chemical shift from the free ligand. Again, this suggests that the amine substituent has little effect on the palladium centre. Whilst the product was not readily soluble in water, some solubility could be achieved with sonication and heating. The identity of $[\text{C}(\text{OEt})_2\text{HCH}_2\text{-N}(\text{CH}_2\text{PCy}_2)_2\text{PdCl}_2]$ (**6**) was confirmed by mass spectrometry, found as $[\text{M-Cl+MeCN}]^+$ (calc. $m/z = 735.3166$, found $m/z = 735.3181$).

Vapour-diffusion crystallisations from acetonitrile/diethyl ether yielded crystals suitable for X-ray crystallography. Crystallography confirmed the expected square-planar geometry of **6**, with the structure containing two independent complexes (Figure 3.7). The bond angles around the palladium centre were in the expected range (85.29(5)-96.13(5) °), as were the Pd-P bond lengths (2.2450(13)-2.2549(14) Å).

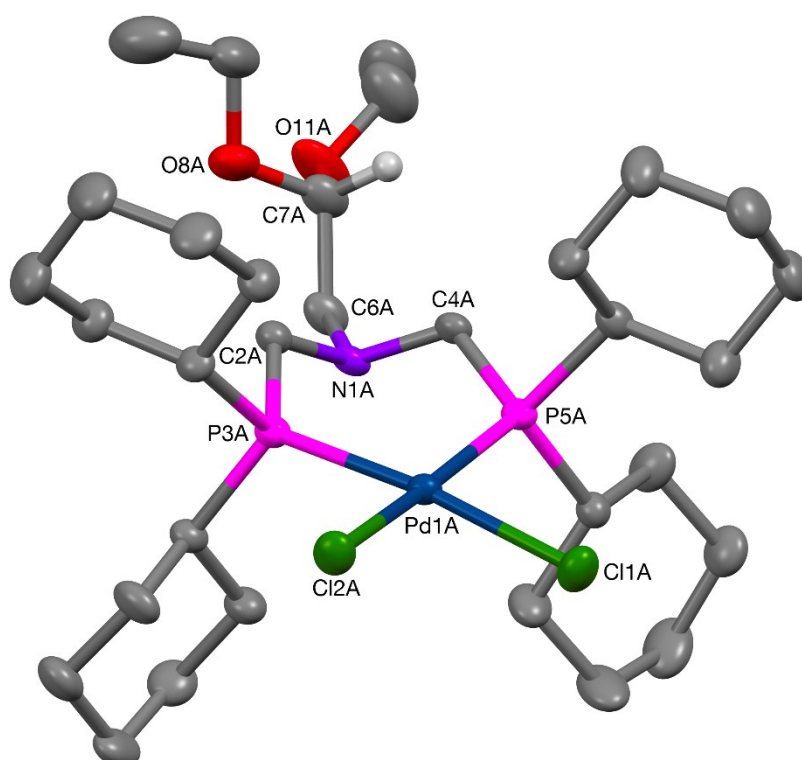
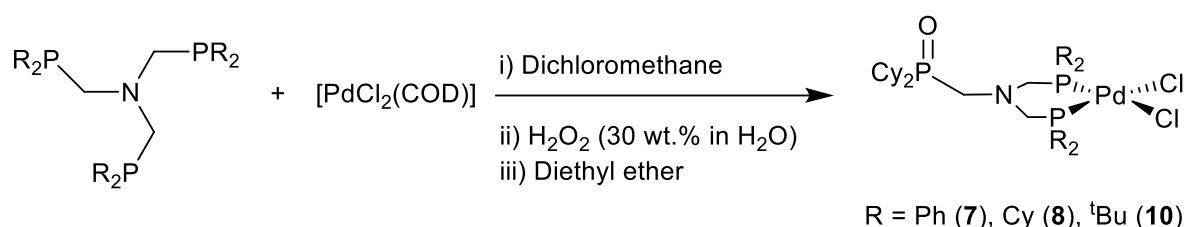


Figure 3.7. Crystal structure of $[\text{C}(\text{OEt})_2\text{HCH}_2\text{-N}(\text{CH}_2\text{PCy}_2)_2\text{PdCl}_2]$ (**6**) (one of two independent complexes). Hydrogen atoms and solvent molecules omitted for clarity.

3.2.2 Complexes of N-Triphos ligands with palladium

Whilst the coordination of nitrogen-bridged bisphosphine ligands to palladium as described in the previous section is straight-forward, these ligands have proved more difficult to isolate and purify compared to their N-Triphos analogues. Therefore, it was considered that the N-Triphos ligands themselves could be reacted with $[\text{PdCl}_2(\text{COD})]$. If two of the three arms coordinated to palladium, as expected, then a pendant PR_2 arm would remain. Tridentate coordination would likely be prohibited for steric and electronic reasons. The pendant third arm might be suitable for further modification, or coordination to other metal centres. It might also be a suitable method for achieving water solubility, for example by converting the phosphine into a water-soluble moiety.



Scheme 3.2. General reaction scheme for reaction of N-Triphos ligands with $[\text{PdCl}_2(\text{COD})]$.

The synthetic route for the palladium complexes described in Section 3.2.1. was adapted for the coordination of N-Triphos ligands. A general reaction scheme for the complexation of N-Triphos ligands to palladium is shown in Scheme 3.2. Two of the three phosphine arms were observed to coordinate to the palladium centre within a short time by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The chemical shift of the third, uncoordinated phosphine arm remained unchanged from that of the free ligand. Upon addition of hydrogen peroxide solution (30 wt.% in water), there was clean oxidation of the uncoordinated phosphine arm to a phosphine oxide, without any effect on the coordinated phosphines. Upon addition of diethyl ether, the air-stable palladium complexes precipitated from the reaction mixture and were isolated in high yields. Without addition of hydrogen peroxide, the uncoordinated phosphine arm would be expected to slowly oxidise over time without protection from air.

The coordination of N-Triphos^{Ph} to palladium proceeded as described above. The reactions were again performed under an inert atmosphere. After addition of a solution of N-Triphos^{Ph} in dichloromethane to a solution of $[\text{PdCl}_2(\text{COD})]$ in dichloromethane, the mixture was stirred at RT. Within a short time

(20 minutes), $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed two signals at 9 ppm (P-Pd) and -31 ppm (PPh_2) in a 2:1 ratio. Following the addition of one equivalent of hydrogen peroxide, within 10 minutes $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed two signals at 9 ppm (P-Pd) and at 27 ppm (P(O)Ph_2) in a 2:1 ratio, indicating full oxidation of the pendant phosphine arm. Addition of diethyl ether resulted in the precipitation of a solid product, which was isolated by cannula filtration, washed with diethyl ether and dried in vacuo. The product was collected as a free-flowing pale-yellow powder in 59 % yield. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the solid product showed two signals at 27.0 ppm and 8.9 ppm in the expected ratio. Mass spectrometry confirmed the product identity of $[\text{P(O)Ph}_2\text{CH}_2\text{-N(CH}_2\text{PPh}_2)_2\text{PdCl}_2]$ (**7**), found as $[\text{M-Cl+MeCN}]^+$ (calc. m/z = 809.0975, found m/z = 809.1007). The product was soluble in the standard polar organic solvents but had no water solubility.

Crystals of **7** suitable for X-ray crystallography formed in situ from the reaction mixture filtrate (a combination of dichloromethane and diethyl ether). The determined crystal structure matched the expected product and was found as two independent complexes (Figure 3.8). Table 3.6 collects key bond angles and bond lengths of **7**. There is a significant difference in the angles around the palladium centre between the two independent complexes of **7**. In complex **7-A**, the P-Pd-P bond angle is $93.80(3)^\circ$, whilst for complex **7-B**, the P-Pd-P bond angle is just $89.14(3)^\circ$. Nonetheless, these values represent a relatively small deviation from standard square-planar geometry, and in-line with that observed for the palladium complexes of the bisphosphine PPh_2 ligands. The Pd-P bond lengths are also unchanged from those found for the bisphosphine complexes, indicating that the pendant arm has little effect on the palladium centre.

Complexation of N-Triphos^{Cy} to $[\text{PdCl}_2(\text{COD})]$ proceeded in an analogous manner. Initially, two $^{31}\text{P}\{^1\text{H}\}$ NMR signals were observed at 29.7 ppm (Pd-P) and -17.4 ppm (PCy_2) in a 2:1 ratio. After addition of hydrogen peroxide, the free PCy_2 signal was replaced by a P(O)Cy_2 signal at 46.7 ppm. The product was collected as a free-flowing yellow powder in 60 % yield. The product identity of $[\text{P(O)Cy}_2\text{CH}_2\text{-N(CH}_2\text{PCy}_2)_2\text{PdCl}_2]$ (**8**) was further confirmed by mass spectrometry, found as $[\text{M-Cl+MeCN}]^+$ (calc. m/z = 845.3816, found m/z = 845.3830).

Vapour diffusion crystallisations from dichloromethane/diethyl ether yielded crystals of **8** suitable for X-ray crystallography. The structure is shown in Figure 3.8, with key bond angles and bond lengths collected in Table 3.6. Following the same trend as for the bisphosphine ligands, the bulkier PCy_2 groups resulted in a slight widening of the P-Pd-P bond angle (of $\sim 1\text{-}5^\circ$) relative to the PPh_2 analogue, and a small ($< 0.1 \text{ \AA}$) but statistically significant lengthening of the P-Pd bond angle.

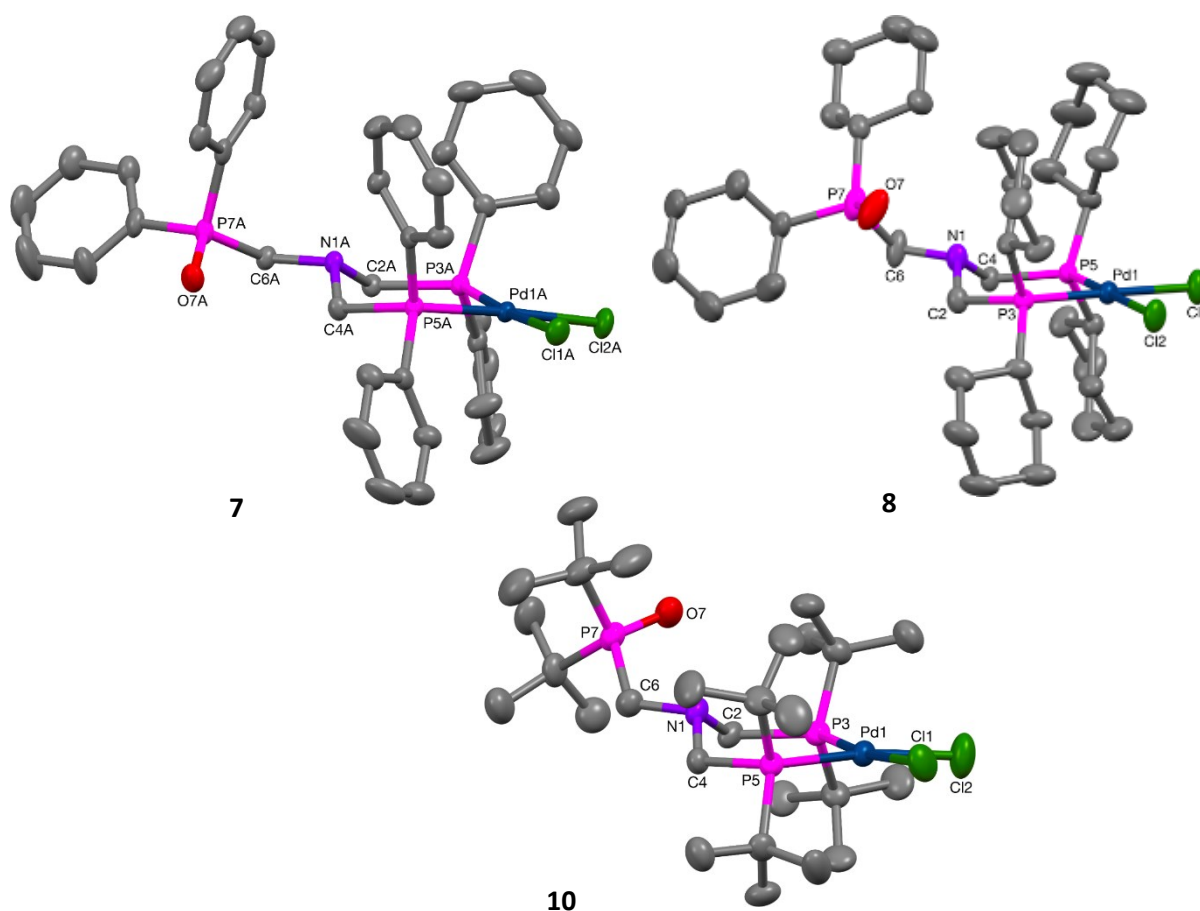


Figure 3.8. Crystal structures of $[P(O)Ph_2CH_2-N(CH_2PPh_2)_2PdCl_2]$ (**7**) (showing one of two independent molecules), $[P(O)Cy_2CH_2-N(CH_2PCy_2)_2PdCl_2]$ (**8**) and $[P(O)(tBu)_2CH_2-N(CH_2P(tBu)_2)_2PdCl_2]$ (**10**). Hydrogen atoms and solvent molecules omitted for clarity.

An analogous reaction was attempted between N-Trip^{Cy} and $(TBA)_2[Pd_2I_6]$ to form the iodo-analogue to **8**. Upon mixing N-Trip^{Cy} and $(TBA)_2[Pd_2I_6]$ in acetone, the resulting orange mixture was analysed by $^{31}P\{^1H\}$ NMR spectroscopy after a short time, and showed a main signal at 23.8 ppm, indicating ligand coordination. After addition of hydrogen peroxide, a precipitate could not be obtained by addition of diethyl ether. With full solvent removal in vacuo, an orange-coloured solid was collected. However, the solid showed many $^{31}P\{^1H\}$ NMR signals. Whilst signals at 22.9 and 49.1 ppm matched the expected species, the signal intensity suggested significant over-oxidation had occurred. After recrystallization from dichloromethane and diethyl ether, $^{31}P\{^1H\}$ NMR showed the product signals at 23.1 and 46.6 ppm in a 2:1 ratio, with removal of the major oxide signal. However, numerous additional signals remained. Single crystals for X-ray crystallography were grown by vapour diffusion of diethyl ether into dichloromethane solutions; however, the collected data could not be solved.

Table 3.6. Collection of bond angles and bond lengths for complexes **7**, **8** and **10**.

[P(O)Ph ₂ CH ₂ -N(CH ₂ PPh ₂) ₂ PdCl ₂] (7)		[P(O)Cy ₂ CH ₂ -N(CH ₂ PCy ₂) ₂ PdCl ₂] (8)		[P(O)(^t Bu) ₂ CH ₂ -N(CH ₂ P(^t Bu) ₂) ₂ PdCl ₂] (10)	
Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
P(3A)-Pd(1A)-P(5A)	93.80(3)	P(3)-Pd(1)-P(5)	94.84(5)	P(3)-Pd(1)-P(5)	96.57(5)
P(3A)-Pd(1A)-Cl(2A)	88.61(3)	P(3)-Pd(1)-Cl(2)	88.13(5)	P(3)-Pd(1)-Cl(2)	90.35(5)
P(5A)-Pd(1A)-Cl(1A)	87.09(3)	P(5)-Pd(1)-Cl(1)	85.33(5)	P(5)-Pd(1)-Cl(1)	89.14(5)
Cl(1A)-Pd(1A)-Cl(2A)	90.72(3)	Cl(1)-Pd(1)-Cl(2)	91.67(5)	Cl(1)-Pd(1)-Cl(2)	84.58(6)
P(3B)-Pd(1B)-P(5B)	89.14(3)				
P(3B)-Pd(1B)-Cl(2B)	93.48(3)				
P(5B)-Pd(1B)-Cl(1B)	86.41(3)				
Cl(1B)-Pd(1B)-Cl(2B)	91.18(3)				
	Length (Å)		Length (Å)		Length (Å)
Pd(1A)-P(3A)	2.2358(8)	Pd(1)-P(3)	2.2447(13)	Pd(1)-P(3)	2.2884(12)
Pd(1A)-P(5A)	2.2291(8)	Pd(1)-P(5)	2.2519(13)	Pd(1)-P(5)	2.2970(14)
O(7A)-P(7A)	1.493(2)	O(7)-P(7)	1.489(4)	O(7)-P(7)	1.495(5)
Pd(1B)-P(3B)	2.2358(8)				
Pd(1B)-P(5B)	2.2356(9)				
O(7B)-P(7B)	1.488(2)				

Mass spectrometry found product signals for [P(O)Cy₂CH₂-N(CH₂PCy₂)₂PdI₂] (**9**) as [M+H]⁺ (found m/z = 1024.2061, calc. m/z = 1024.2029) and [M+Na+CH₃CN]⁺ (found m/z = 1087.2144, calc. m/z = 1087.2144); however, the product signals were of very low intensity. Owing to the low yield and purity of the collected products, no further analysis was possible. The results suggest that the iodo-complex is surprisingly sensitive to degradation.

Complexation of N-Triphos^{tBu} to [PdCl₂(COD)] was also performed using the same method. The initial ³¹P{¹H} NMR signals at 36.9 ppm (Pd-P) and 11.8 ppm (P(^tBu)₂) were replaced by signals at 36.9 ppm (Pd-P) and 59.2 ppm (P(O)(^tBu)₂) after addition of hydrogen peroxide. Surprisingly, addition of diethyl ether to the reaction mixture gave no solid precipitation. Instead, solvent was removed to dryness in vacuo, leading to the formation of a yellow solid product. Initially, the product was sticky, but after washing with diethyl ether and drying further in vacuo, a free-flowing pale yellow powder was collected in just 22 % yield. Mass spectrometry confirmed the product identity of [P(O)(^tBu)₂CH₂-N(CH₂P(^tBu)₂)₂PdCl₂] (**10**), found as [M-Cl]⁺ (calc. m/z = 648.2611, found m/z = 648.2626).

Again, vapour diffusion crystallisations from dichloromethane/diethyl ether yielded crystals of **10** suitable for X-ray crystallography. The square-planar geometry is as expected. The structure of **10** is shown in Figure 3.8, with key bond angles and bond lengths collected in Table 3.6. The P-Pd-P bond

angle is over 1 ° wider than for the PPh₂ analogue, and the Pd-P bond lengths ~ 0.03 Å longer. Again, the same trends are observed, whereby increasing steric bulk ^tBu > Cy > Ph results in wider P-Pd-P bond angles and lengthened Pd-P bond lengths, presumably to minimise steric interactions. In all three palladium complexes of N-Triphos ligands, **7**, **8** and **10**, a puckering effect can be observed with the nitrogen atom sitting above the plane of the palladium centre.

The NMR chemical shifts between the three N-Triphos complexes **7**, **8** and **10** can also be compared (Table 3.7). The free N-Triphos^{Ph} ligand has initially the most upfield ³¹P{¹H} NMR chemical shift of -28.9 ppm. Upon coordination to palladium, the signal moves to +8.9 ppm, a change of 37.8 ppm; upon oxidation, the signal moves to +27.0 ppm, a change of 55.9 ppm. This demonstrates that oxidation has a larger effect on the value of the ³¹P{¹H} NMR shift than metal coordination, as would be expected from the strong deshielding effect of the highly electronegative oxygen atom. The same observations hold for N-Triphos^{Cy}, however the effects of coordination and oxidation have larger effects on the chemical shift than for N-Triphos^{Ph}. For N-Triphos^{tBu}, whilst oxidation has a larger effect than coordination on the chemical shift, the overall effects are smaller than for both N-Triphos^{Ph} and N-Triphos^{Cy}.

Table 3.7. Collected ³¹P{¹H} NMR chemical shifts for N-Triphos ligands upon coordination to palladium and oxidation.

³¹ P{ ¹ H} NMR Chemical shift of phosphorus moiety, δ (ppm in CDCl ₃)	-PPh ₂	-PCy ₂	-P(^t Bu) ₂
Free N-Triphos ligand	-28.9	-17.0	+12.5
Coordinated to Pd	+8.9	+29.7	+36.9
Pendant arm (unoxidised)	-31.0	-17.4	+11.8
Pendant arm (oxidised)	+27.0	+46.7	+59.2
Change to chemical shift upon coordination	+37.8	+46.7	+24.4
Change to chemical shift upon oxidation	+55.9	+63.7	+46.7

3.2.3 Complexes of nitrogen-bridged bisphosphine ligands with nickel

It has been established that multidentate phosphine ligands form well-defined complexes with palladium by adopting bidentate coordination modes in stable square planar Pd(II) d^8 complexes. To study this further, complexes of the nitrogen-bridged bisphosphine ligands were also prepared from nickel.

Nickel(II) centres are expected to adopt square-planar complexes for the same electronic reasons as palladium(II). However, owing to their smaller size they can be considered as “hard” metal centres, which will affect their interactions with phosphine ligands. The commercially available complex $[\text{NiCl}_2(\text{PPh}_3)_2]$ was selected as an appropriate precursor. It was prepared in a straight-forward reaction between NiCl_2 and PPh_3 in high yield (78 %).²¹ The reaction mixture must be kept above RT until after filtering, to avoid contamination by PPh_3 . $[\text{NiCl}_2(\text{PPh}_3)_2]$ is readily soluble in common organic solvents and the PPh_3 ligands are readily displaced.

However, there are some complexities with $[\text{NiCl}_2(\text{PPh}_3)_2]$. There are two possible isomers which co-exist: a blue, tetrahedral isomer and a red, square-planar isomer (Figure 3.9). As 16 electron complexes, the tetrahedral form is paramagnetic, whilst the square-planar form is diamagnetic. Whilst it is generally energetically favourable for four-coordinate d^8 complexes to adopt a square-planar geometry, sterics is an important consideration for $[\text{NiCl}_2(\text{PPh}_3)_2]$. This can be attributed to accommodating the bulky PPh_3 ligands around the nickel centre, with a wider spacing in the tetrahedral form. $[\text{NiCl}_2(\text{PPh}_3)_2]$ was synthesised, and used, in its tetrahedral form as a green-blue solid. In this paramagnetic form $[\text{NiCl}_2(\text{PPh}_3)_2]$ shows no $^{31}\text{P}\{^1\text{H}\}$ NMR signals. It has been established in the literature that when crystallised from chlorinated solvents, the tetrahedral form converts to the square-planar form.²²

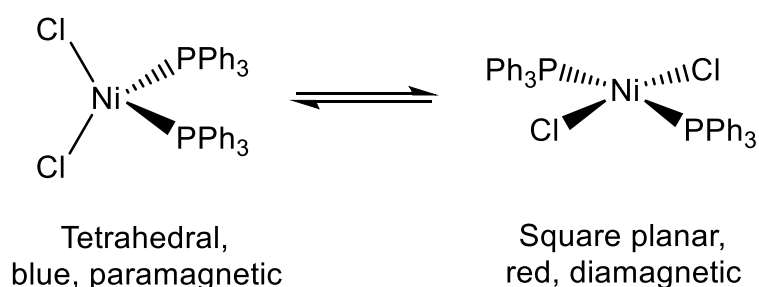
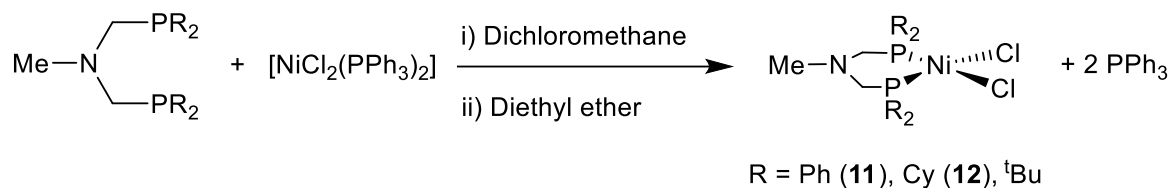


Figure 3.9. Tetrahedral and square-planar forms of $[\text{NiCl}_2(\text{PPh}_3)_2]$.



Scheme 3.3. General reaction scheme for reaction of nitrogen-bridged bisphosphine ligands with $[\text{NiCl}_2(\text{PPh}_3)_2]$.

The general reaction scheme for the coordination of nitrogen-bridged bisphosphine ligands to nickel is shown in Scheme 3.3. Dichloro nickel complexes of $\text{Me-N}(\text{CH}_2\text{PPh}_2)_2$ and $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ have been described previously.^{19,23–25} Again, dichloromethane was used to achieve full dissolution of both ligand and $[\text{NiCl}_2(\text{PPh}_3)_2]$ at RT, prior to addition of diethyl ether which precipitated a solid product.

In the reaction between $\text{Me-N}(\text{CH}_2\text{PPh}_2)_2$ and $[\text{NiCl}_2(\text{PPh}_3)_2]$, the reaction mixture quickly became red-orange in colour. By $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, a single peak was observed at -6 ppm, attributable to displaced triphenylphosphine. No other signals were observed. The absence of a free ligand signal indicated that full ligand coordination had occurred. The absence of any other signals suggested the formation of a paramagnetic complex, indicating that the nickel product was adopting a tetrahedral geometry. This can be rationalised by the reduced steric crowding of the bulky $\text{Me-N}(\text{CH}_2\text{PPh}_2)_2$ ligand around the smaller nickel centre in a tetrahedral geometry. After addition of diethyl ether, a red-orange solid precipitated. This was isolated in 53 % yield by cannula filtration, washed with diethyl ether and dried in vacuo. The displaced triphenylphosphine was removed by the washings, such that $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the product showed no signals.

Mass spectrometry confirmed the synthesis of the expected complex $[\text{Me-N}(\text{CH}_2\text{PPh}_2)_2\text{NiCl}_2]$ (**11**), found as $[\text{M-Cl+MeCN+H}]$ (calc. $m/z = 562.1005$, found $m/z = 562.1017$). Crystals of **11** were grown from vapour diffusion crystallisations in dichloromethane and diethyl ether. Although NMR spectra indicated the formation of the paramagnetic tetrahedral form in solution (by the lack of signals observed), the crystal structure of **11** adopted a square-planar geometry (Figure 3.10). The structure sits across a mirror plane passing through Ni(1), N(1) and C(4).

Table 3.8 collects key bond angles and bond lengths for **11**. Again, by looking at the bond angles around the nickel centre, there are some deviations from an idealised square planar geometry. Whilst the P-Ni-P bond angle is $93.19(3)^\circ$, this is less than 1° wider than the Cl-Ni-Cl bond angle. The P-Ni-P bond angle is $\sim 1^\circ$ wider than the P-Pd-P bond angle in the palladium analogue **4**. This is expected, owing to an increased need to relieve steric crowding around the smaller nickel centre. However, the Ni-P

bond lengths are almost 0.1 Å shorter than the corresponding Pd-P bond lengths, perhaps to a greater interaction between the Ni and P atoms which are more similar in size.

The reaction between $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ and $[\text{NiCl}_2(\text{PPh}_3)_2]$ proceeded in a similar way, resulting in a bright red reaction mixture. After stirring at RT overnight, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy again showed the presence of a signal for displaced PPh_3 , and the absence of a $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ signal. Unlike for the analogous PPh_2 reaction, a broad, poorly defined signal was observed at 17.4 ppm, which was attributed to the desired product $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{NiCl}_2]$ (**12**). The poor definition of the signal suggested some extent of paramagnetism, indicating that the product again is in equilibrium between tetrahedral and square-planar geometries. The intensity ratio of the product and PPh_3 signals was 1:1, as expected. A bright orange solid was isolated in the standard manner in 58 % yield. Mass spectrometry confirmed the synthesis of **12**, again found as $[\text{M-Cl+MeCN}]$ (calc. $m/z = 585.2804$, found $m/z = 585.2811$). Elemental analysis was also a match for the structure (calc. %C = 55.70, %H = 8.84, %N = 2.41, found %C = 55.99, %H = 9.15, %N = 2.29).

Crystals of **12** were again grown from vapour diffusion crystallisations in dichloromethane and diethyl ether and the product crystallised in a square-planar geometry, despite the paramagnetism observed in solution. Figure 3.10 shows the crystal structure, with bond angles and lengths collected in Table 3.8. There is further distortion from idealised square-planar geometry. The P-Ni-P bond angle is $\sim 3^\circ$ wider than for the PPh_2 analogue (**11**), attributed to the increased steric bulk of the PCy_2 groups.

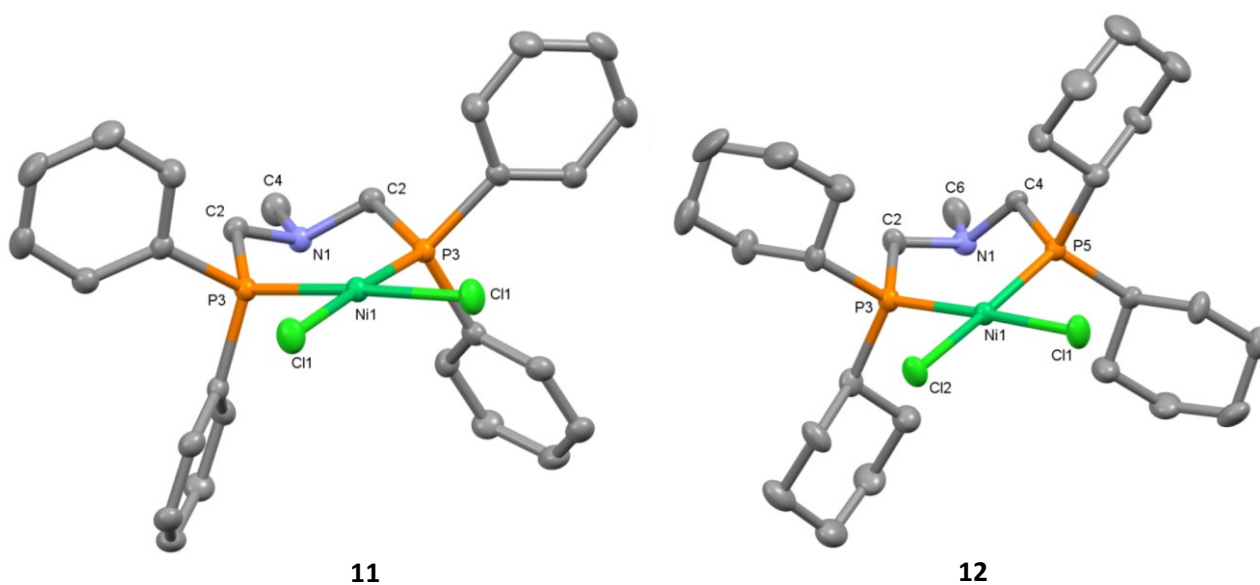


Figure 3.10. Crystal structures of $[\text{Me-N}(\text{CH}_2\text{PPh}_2)_2\text{NiCl}_2]$ (**11**) (left) and $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{NiCl}_2]$ (**12**) (right). Hydrogen atoms and solvent molecules omitted for clarity.

Table 3.8. Collected bond angles and bond lengths for nickel complexes **11** and **12**.

[Me-N(CH ₂ PPh ₂) ₂ NiCl ₂] (11)		[Me-N(CH ₂ PCy ₂) ₂ NiCl ₂] (12)	
Bond	Angle (°)	Bond	Angle (°)
P(3)-Ni(1)-P(3A)	93.19(3)	P(3)-Ni(1)-P(5)	96.37(5)
P(3)-Ni(1)-Cl(1)	87.09(2)	P(5)-Ni(1)-Cl(1)	85.99(5)
P(3A)-Ni(1)-Cl(1A)	87.09(2)	P(3)-Ni(1)-Cl(2)	87.22(5)
Cl(1)-Ni(1)-Cl(1A)	92.46(3)	Cl(1)-Ni(1)-Cl(2)	90.48(5)
	Length (Å)		Length (Å)
Ni(1)-P(3)	2.1585(6)	Ni(1)-P(3)	2.1673(14)
Ni(1)-P(3A)	2.1585(6)	Ni(1)-P(5)	2.1772(11)

The reaction between Me-N(CH₂P(^tBu)₂)₂ and [NiCl₂(PPh₃)₂] was less successful. The reaction mixture became a dark-blue colour, attributed to dominant formation of the tetrahedral form. Because of the increased steric bulk of the P(^tBu)₂ moieties, the tetrahedral geometry might be expected to dominate to position the bulky groups as far from each other as possible. After five hours stirring at RT, ³¹P{¹H} NMR spectroscopy only showed a signal at -5 ppm for PPh₃. The absence of a free Me-N(CH₂P(^tBu)₂)₂ ligand signal indicated the generation of a paramagnetic product through full coordination to nickel. After stirring overnight, a small additional ³¹P{¹H} NMR signal was observed at 35.3 ppm, which might tentatively be assigned to a Ni-P(^tBu)₂ moiety, in the expected chemical shift region. The analogous palladium complexes of the bisphosphine PCy₂ and P(^tBu)₂ ligands had ³¹P{¹H} NMR chemical shifts of 30.2 ppm and 37.8 ppm respectively. The ³¹P{¹H} NMR signal observed for the nickel complex of the bisphosphine PCy₂ ligand was at 17.4 ppm; any Ni-P(^tBu)₂ signal would be expected to be further downfield of that signal. Therefore, it is suggested that there is some conversion of the tetrahedral form to the square planar form.

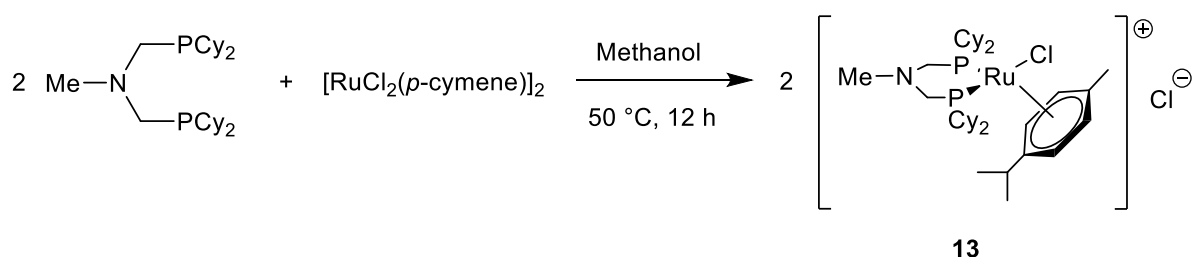
After addition of diethyl ether, a pale blue-green powder precipitated. This was isolated in trace amount and failed to yield NMR spectra, perhaps indicative of a paramagnetic species. A separate solid product was collected from the filtrate, which showed similar signals at +36.7 ppm and -5.3 ppm. Unfortunately, crystallisation attempts from dichloromethane and either diethyl ether or hexane failed to produce crystals suitable for X-ray crystallography. Furthermore, mass spectrometry failed to identify the expected structure, despite the identification of a M-Cl species.

3.3 Complexes of multidentate phosphine ligands with ruthenium

Given the success of coordinating both nitrogen-bridged bisphosphine and triphosphine ligands to palladium, attention turned to ruthenium. The reaction scheme used for the coordination of Me-N(CH₂PCy₂)₂ to ruthenium is shown in Scheme 3.4. The route was adapted from the synthesis of ruthenium dipyridylamine complexes reported by Fischmeister et al.²⁶ It was expected that the bisphosphine ligand would coordinate in a similar way to the bidentate dipyridylamine ligand.

The commercially available ruthenium precursor [RuCl₂(*p*-cymene)]₂ was used. Upon reaction with the bisphosphine ligand, [RuCl₂(*p*-cymene)]₂ is split homolytically. One of the chloride ligands is formally displaced as a chloride counter-ion, resulting in the formation of a singly charged ruthenium complex with a positive charge necessary to retain the 18-electron count. With heating to 50 °C, full dissolution of both Me-N(CH₂PCy₂)₂ and [RuCl₂(*p*-cymene)]₂ was achieved. After one hour, ³¹P{¹H} NMR spectroscopy showed a main signal at 27.1 ppm, alongside minor signals at 15, 39 and 47 ppm. The main signal was attributed to the expected product, owing to its proximity to the palladium analogue **1** (cf. 30.1 ppm). No signal was observed for the free ligand, indicating full ligand coordination. The reaction was continued overnight, with heating at 50 °C. The next day, ³¹P{¹H} NMR spectra of the reaction mixture appeared unchanged.

The reaction was cooled to RT without any precipitation. After solvent was removed to dryness, an orange-yellow solid residue remained. After washing with diethyl ether and drying in vacuo, the product was collected as a yellow powder in 60 % yield. Whilst the main ³¹P{¹H} NMR signal remained at 27.5 ppm, the small impurity signals remained. After washing further with diethyl ether, only a small signal remained at 45.7 ppm. This signal can be considered as a phosphine oxide R-P(O)Cy₂ (cf. 46.7 ppm). Crystallisations from a dichloromethane and diethyl ether combination successfully removed the ³¹P{¹H} NMR impurity signal. Mass spectrometry confirmed the identity of the product found as [Me-N(CH₂PCy₂)₂Ru(η⁶-*p*-cymene)Cl]Cl (**13**) as M⁺ with m/z = 722.3342 (calc. m/z = 722.3324). Elemental analysis results matched the product identity with the inclusion of two water molecules (calc. %C = 55.98, %H = 8.76, %N = 1.76, found %C = 55.70, %H = 9.12, %N = 1.95).



Scheme 3.4. Reaction scheme for reaction of Me-N(CH₂PCy₂)₂ with [RuCl₂(*p*-cymene)]₂.

The crystal structure of **13** was determined as two independent complexes. The complex ion can be described as adopting a piano-stool geometry (Figure 3.11 (a)). In this case, the *p*-cymene unit acts as the “seat” of the piano-stool, with the three “legs” composed of the two phosphines and the chloride ligand. This can be compared to a tetrahedral-type geometry, with the *p*-cymene adopting the apical position. This positions the *p*-cymene unit in a different plane to the bulky PCy₂ units, minimising any steric clashing.

The crystal structure of one of the independent complexes of **14** is shown in Figure 3.11 (b). Bond angles and bond lengths are collected in Table 3.9. All the Ru-P bonds are statistically equivalent in length, apart from Ru(1B)-P(3B) which is slightly shorter at 2.3295(7) Å. In every case, the Ru-Cl bond is longer than the Ru-P bond lengths. Concerning the phosphine and chloride ligands, the bond angles around the metal centre range from 81.00(2) to 90.20(2) °. For both independent complexes of the crystal structure, the P-Ru-P bond angle is larger than either of the P-Ru-Cl bond angles, as would be expected to accommodate the bulky PCy₂ groups.

In complex **13-B**, the two P-Ru-Cl angles are almost equivalent (84.89(2) and 85.22(2) Å). However, for complex **13-A** there is an almost 6 ° difference between the two P-Ru-Cl angles (81.00(2) and 87.05(2)). Overall, the bond angles around the metal centre are smaller than those expected for a standard tetrahedral geometry. This can be rationalised by the presence of the bulky *p*-cymene ligand in the apical position.

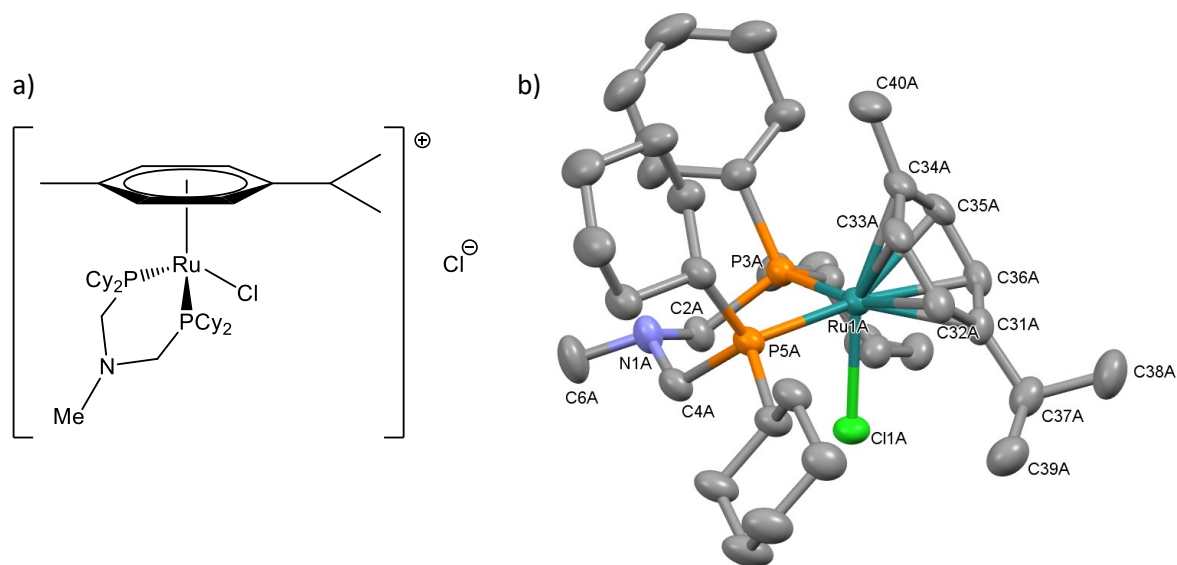


Figure 3.11. a) Illustration of the “piano-stool” geometry of [Me-N(CH₂PCy₂)₂Ru(η⁶-*p*-cymene)Cl]Cl (**13**), b) Crystal structure of **13** (one of the two independent molecules). Hydrogen atoms and solvent molecules omitted for clarity.

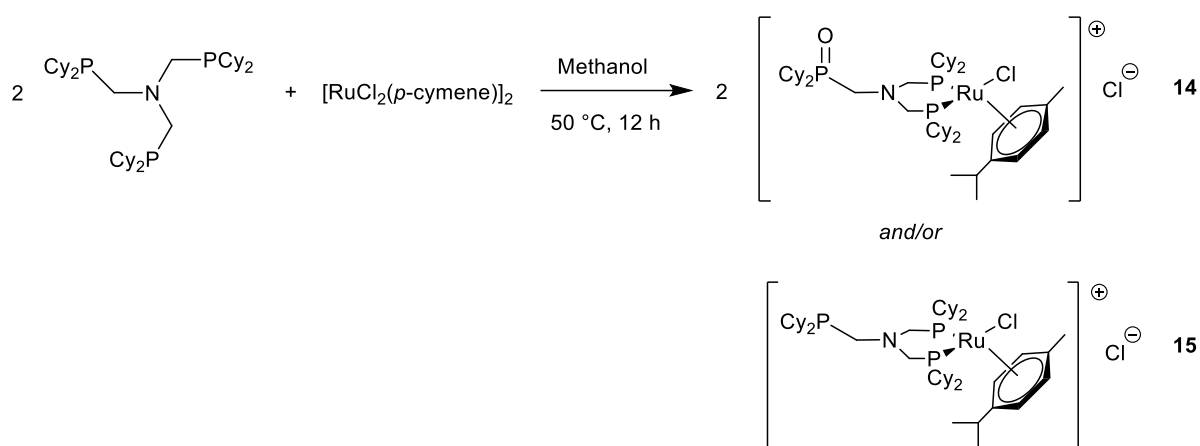
Table 3.9. Collected bond angles and bond lengths for [Me-N(CH₂PCy₂)₂Ru(η^6 -*p*-cymene)Cl]Cl (**13**).

Bond	Bond angle (°)
P(3A)-Ru(1A)-P(5A)	90.20(2)
P(3A)-Ru(1A)-Cl(1A)	87.05(2)
P(5A)-Ru(1A)-Cl(1A)	81.00(2)
P(3B)-Ru(1B)-P(5B)	87.40(2)
P(3B)-Ru(1B)-Cl(1B)	84.89(2)
P(5B)-Ru(1B)-Cl(1B)	85.22(2)
	Bond length (Å)
Ru(1A)-P(3A)	2.3482(7)
Ru(1A)-P(5A)	2.3511(7)
Ru(1A)-Cl(1A)	2.4040(7)
Ru(1B)-P(3B)	2.3295(7)
Ru(1B)-P(5B)	2.3477(7)
Ru(1B)-Cl(1B)	2.3976(6)

A reaction between the tridentate N-Triphos^{Cy} ligand and [RuCl₂(*p*-cymene)]₂ was performed in a similar way (Scheme 3.5). It was expected that two of the three phosphine arms would coordinate to ruthenium, leaving a pendant phosphine arm which could be converted to a phosphine oxide as with the palladium analogues described in Section 3.2.2.

After mixing N-Triphos^{Cy} and [RuCl₂(*p*-cymene)]₂ in methanol, the mixture was heated to 50 °C. After 90 minutes, ³¹P{¹H} NMR spectroscopy showed two main signals at 26.3 ppm and 47.4 ppm in a 2:1 ratio. The signal at 26.3 ppm was attributed to Ru-PCy₂ (cf. 27.5 ppm for **13**). The signal at 47.4 ppm was attributed to P(O)Cy₂ despite the lack of hydrogen peroxide addition. Several additional signals were observed, including at -17/-18 ppm for free ligand. After adding hydrogen peroxide solution, the main ³¹P{¹H} NMR signals at 26.3 ppm and 47.4 were observed. The free ligand signal had disappeared. Several small signals were present in the oxide region (50-55 ppm). A solid product was isolated by removing solvent to dryness. The product was collected as a free-flowing, yellow-brown coloured powder in 71 % yield. However, ³¹P{¹H} NMR spectra of the solid product were quite messy. The most intense signal was at 46.2 ppm, along with other signals in the oxide region. The Ru-PCy₂ signal appeared as two signals at 26.6/26.5 ppm.

Overall, the spectra indicated that the product had been over-oxidised and had suffered some degradation. Mass spectrometry identified a signal attributed to the expected product [P(O)Cy₂CH₂-N(CH₂PCy₂)₂Ru(η^6 -*p*-cymene)Cl]Cl (**14**) at *m/z* = 934.4679 (calc. *m/z* = 934.4654); however, the signal was of tiny intensity suggesting it was a minor species.



Scheme 3.5. Reaction scheme for reaction of N-Triphos^{Cy} with [RuCl₂(*p*-cymene)]₂.

The reaction was repeated without the addition of hydrogen peroxide. After 90 minutes, ³¹P{¹H} NMR spectroscopy showed a main signal at 26.2 ppm, alongside signals at -17.2, 39.1 and 47.3 ppm. This suggested that two phosphine arms had coordinated to ruthenium, whilst the third arm was in a mixture of states.

The product was collected in the same manner as a free-flowing orange powder in 62 % yield. The solid product showed ³¹P{¹H} NMR signals at 26.6 ppm and 40.4 ppm in a 2:1 ratio, as expected, along with other signals including those for free ligand. The reaction filtrate showed a major ³¹P{¹H} NMR signal at -17.0 ppm, attributable to free ligand. Mass spectrometry showed a major, unassigned signal at *m/z* = 738.3612. Small signals were identified at *m/z* = 918.4705, attributable to the complex with an unoxidised third arm, [PCy₂CH₂-N(CH₂PCy₂)₂Ru(η⁶-*p*-cymene)Cl]Cl (**15**) (calc. *m/z* = 918.4720) and at *m/z* = 934.4685, attributable to **14**.

Attempts to recrystallize the solid product from dichloromethane/diethyl ether were attempted. Two solid products were collected. The first produced a ³¹P{¹H} NMR spectrum with a signal at 26.5 ppm and no other major signals. This suggested tridentate coordination of the N-Triphos ligand, which had not been observed in the presence of hydrogen peroxide. The second product produced a ³¹P{¹H} NMR spectrum with a main signal at 40.4 ppm, indicating major oxidation of the product. Attempts to grow crystals suitable for X-ray crystallography were unsuccessful. Overall, the coordination of the N-Triphos^{Cy} ligand to ruthenium did not proceed in the straight-forward manner expected. Whilst coordination of the ligand to ruthenium was observed, the product appeared very susceptible to degradation by oxidation. It is possible that there is some competition with tridentate ligand coordination, but this would likely be hindered by the presence of three PCy₂ substituents and the *p*-

cymene ligand. Compared to the straight-forward reaction with $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$, the use of N-Triphos^{Cy} hindered the formation of a well-defined product, removing any benefit that might be associated with the easier synthesis and handling of N-Triphos^{Cy}. The relatively straight-forward coordination of N-Triphos ligands to palladium might be rationalised by the relatively unhindered coordination sphere (two chloride ligands) and the formation of stable, square-planar d^8 complexes.

3.4 Complexes of multidentate phosphine ligands with iridium

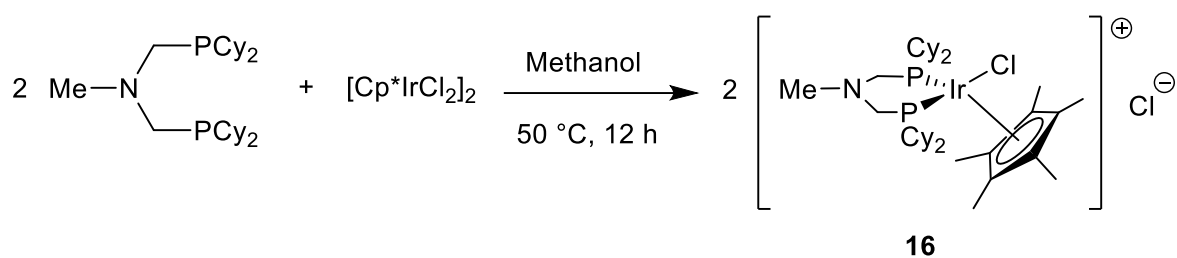
The next sections will discuss the coordination of both nitrogen-bridged bisphosphine ligands and N-Triphos ligands with different iridium precursors: with $[\text{Cp}^*\text{IrCl}_2]_2$ (3.4.1) and, more successfully, $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.4.2, 3.4.3). Further changes to the coordination chemistry were anticipated owing to the different steric and electronic requirements of iridium.

3.4.1 Complexes of multidentate phosphine ligands with $[\text{Cp}^*\text{IrCl}_2]_2$

$[\text{Cp}^*\text{IrCl}_2]_2$ was selected as an initial iridium precursor. Fischmeister et al. used $[\text{Cp}^*\text{IrCl}_2]_2$ for the formation of iridium complexes of dipyriddyamine ligands.²⁶ $[\text{Cp}^*\text{IrCl}_2]_2$ behaves in an analogous way to $[\text{RuCl}_2(p\text{-cymene})]_2$ as a dichloro-bridged iridium dimer which is homolytically split to generate two monometallic complexes. The Cp^* ligands are bound to iridium in a η^5 coordination mode. Accordingly, $[\text{Cp}^*\text{IrCl}_2]_2$ has 18 electrons at each iridium centre.

$[\text{Cp}^*\text{IrCl}_2]_2$ is available commercially, but can also be prepared from $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ and Cp^*H .²⁷ According to literature, $[\text{Cp}^*\text{IrCl}_2]_2$ is prepared by a 36 hour reflux in methanol. Initially, the mixture was dark-green/black in colour, but became a dark orange-red colour after ~12 hours. After 36 hours, the reaction mixture was cooled to RT and an orange solid precipitated. After washing with cold methanol and drying in vacuo, $[\text{Cp}^*\text{IrCl}_2]_2$ was collected as a gummy orange solid in 44 % yield. Although the long reaction time is inconvenient, $[\text{Cp}^*\text{IrCl}_2]_2$ is significantly more expensive to purchase than $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ [* £71.90 for 100 mg, compared to £87.30 for 1 g (Sigma Aldrich, retrieved: 22/02/2021)].

The standard reaction scheme for the reaction between $[\text{Cp}^*\text{IrCl}_2]_2$ and $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ is shown in Scheme 3.6. The resulting iridium complex retains an electron count of 18. The yellow-coloured reaction mixture resulting from $[\text{Cp}^*\text{IrCl}_2]_2$ and $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ was stirred with heating at 50 °C. After one hour, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed three signals, with a major signal at -17 ppm attributable

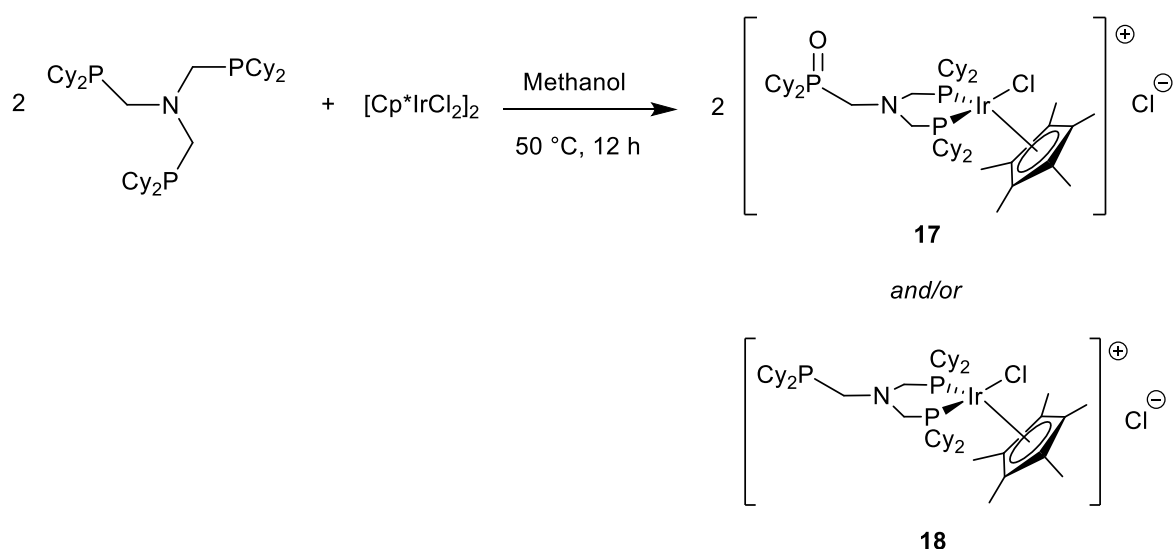


Scheme 3.6. Reaction scheme for reaction of Me-N(CH₂PCy₂)₂ with [Cp*IrCl₂]₂.

to free ligand in addition to signals at -1 and +15 ppm. The corresponding palladium and ruthenium analogues **1** and **13** showed product signals at 30.1 ppm and 27.5 ppm respectively. After continuing the reaction overnight, the three ³¹P{¹H} NMR signals remained, with some reduction in the signal at 15 ppm, and some increase in the signal at -1 ppm. After removing solvent to dryness in vacuo, a yellow oil residue remained. A yellow solid precipitated upon the addition of diethyl ether. After cannula filtration, washing with diethyl ether and drying in vacuo, the product was collected as a free-flowing yellow powder.

By ³¹P{¹H} NMR spectroscopy, three signals were observed at 14.5, -3.7 and -16.8 ppm, in integration ratio 0.2:1.0:1.0. This shows that the reaction made limited progress beyond the starting ligand. Each time the reaction was repeated, the same ³¹P{¹H} NMR signals were observed. Even with heating over 48 hours, no change in the ³¹P{¹H} NMR signals was observed. It was unclear if the presence of multiple ³¹P{¹H} NMR signals should be attributed to incomplete reaction progress, or due to impurities, and therefore inexact stoichiometries, resulting from either [Cp*IrCl₂]₂ or Me-N(CH₂PCy₂)₂. Surprisingly, mass spectrometry found a major molecular ion signal attributable to the expected product [Me-N(CH₂PCy₂)₂Ir(η⁵-Cp*)Cl]Cl (**16**) at *m/z* = 814.3990 (calc. *m/z* = 814.3990).

The reaction of N-Triphos^{Cy} with [Cp*IrCl₂]₂ was also attempted (Scheme 3.7). Following the same synthetic route, after two hours ³¹P{¹H} NMR spectroscopy showed signals at -0.8 ppm and -18.0 ppm in approximately a 2:1 ratio. With the signal at -18.0 ppm attributable to free N-Triphos^{Cy}, the signal at -0.8 ppm was attributed to Ir-PCy₂. As before, an additional signal was observed at 15.2 ppm. There was no change to these three signals overnight. After addition of hydrogen peroxide to oxidise the pendant phosphine arm, two signals at 51.2 ppm and -0.7 ppm were observed, with no other signals. The signal at 51.2 ppm was attributed to P(O)Cy₂. The reaction was ceased, and after solvent removal to dryness a free-flowing yellow powder was obtained. Unfortunately, the ³¹P{¹H} NMR spectrum of the solid product showed signals at 49.3/48.5 ppm, 13.3 ppm and -3.9 ppm. However, mass spectrometry again found the expected product [P(O)Cy₂CH₂-N(CH₂PCy₂)₂Ir(η⁵-Cp*)Cl]Cl (**17**) as the molecular ion peak at *m/z* = 1026.5319 (calc. *m/z* = 1026.5319).



Scheme 3.7. Reaction scheme for reaction of N-Triphos^{Cy} with [Cp*IrCl₂]₂.

The reaction between N-Triphos^{Cy} and [Cp*IrCl₂]₂ was repeated on a larger scale. Whilst the same ³¹P{¹H} NMR signals were observed, the unassigned signal at 15 ppm was less intense than previously. The product was collected as a free-flowing yellow-brown powder which showed the expected ³¹P{¹H} NMR signals as major peaks at 49.3 ppm and -3.6 ppm. However, the P(O)Cy₂ signal was the major signal, and several other signals ~ 50 ppm were observed. Additionally, small signals around -20 ppm were observed in the free ligand region. This suggests both incomplete coordination of the N-Triphos ligand to iridium, and over-oxidation of both the coordinated and uncoordinated phosphine groups.

Changing the solvent to methanol, no precipitation occurred until solvent was removed to dryness. In the palladium reactions, dichloromethane had been used as the solvent, with precipitation upon the addition of diethyl ether. Repeating the reaction in dichloromethane, after one hour ³¹P{¹H} NMR signals at -19.6 and 50.6 ppm were observed. After a further three hours, these signals were joined by additional signals at 14.1 and -28.0 ppm. Continuing the reaction overnight, the same signals remained with the loss of the signal at 50.6 ppm. The lack of a signal attributable to Ir-PCy₂, as observed in methanol, suggested the reaction was not proceeding. After removing dichloromethane, and adding methanol, ³¹P{¹H} NMR signals at 15.5, -18.0 and -28.1 ppm were found, again lacking the product signal seen previously.

Next, a commercial sample of [Cp*IrCl₂]₂ was purchased. To begin with, the reaction mixture was simpler to assign by ³¹P{¹H} NMR spectroscopy, with signals at -1.0 and -18.0 ppm as expected for Ir-PCy₂ and free PCy₂ respectively. After addition of hydrogen peroxide, new signals at 50.9 ppm (P(O)Cy₂) and 13.4 ppm (unassigned) were observed. However, the free ligand signal remained. The resistance of the free PCy₂ to oxidation by hydrogen peroxide as evidenced in these reactions suggests a possible interaction between the third phosphine arm and the metal centre. With continued reaction

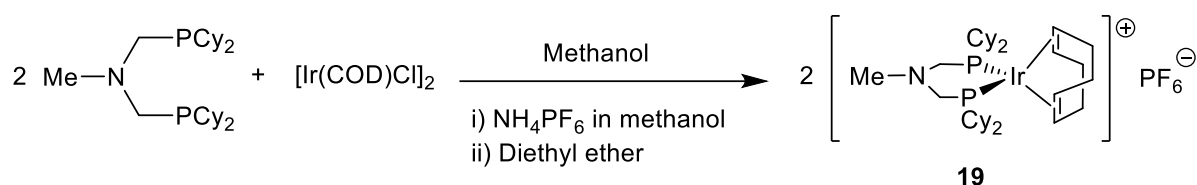
overnight, and with the addition of extra hydrogen peroxide, no change to the $^{31}\text{P}\{^1\text{H}\}$ NMR signals was observed. By solvent removal, a yellow solid was obtained. Whilst the major signals at -3.5 ppm and +49.4 ppm were observed, numerous oxide signals were observed around 50 ppm, and signals at -15.2 ppm, -17 and -20 ppm were observed. Again, this indicates a mixture of phosphine and phosphine oxide moieties in addition to the desired product.

Therefore, even with changes in ligand, solvent system, and the use of commercially purchased or self-prepared $[\text{Cp}^*\text{IrCl}_2]_2$, the reactions were not straight-forward. The reactions appeared to suffer from incomplete reaction progress, followed by a mixture of different states formed upon oxidation. Next a change in precursor was investigated, which proved to be much more successful.

3.4.2 Complexes of nitrogen-bridged bisphosphine ligands with $[\text{Ir}(\text{COD})\text{Cl}]_2$

The dichloro-bridged dimer $[\text{Ir}(\text{COD})\text{Cl}]_2$ is commercially available, and significantly less expensive than $[\text{Cp}^*\text{IrCl}_2]_2$. Alternatively, it can be prepared from $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ and 1,5-cyclooctadiene (COD). Adapting a literature method, $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ and COD were heated to 90 °C in an ethanol/water mixture for 24 hours. After cooling to RT, a bright red solid precipitated and was isolated by cannula filtration, washed with cold methanol and dried in vacuo. $[\text{Ir}(\text{COD})\text{Cl}]_2$ was collected as a brick-red solid in 61 % yield, with identity confirmed by ^1H NMR spectroscopy.^{28–30} Hence, compared to $[\text{Cp}^*\text{IrCl}_2]_2$, $[\text{Ir}(\text{COD})\text{Cl}]_2$ is cheaper to purchase, quicker to synthesise and easier to isolate as a homogeneous, free-flowing solid in good purity.

The reaction between $[\text{Ir}(\text{COD})\text{Cl}]_2$ and $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ is shown in Scheme 3.8. The method was adapted from a literature reaction between $[\text{Ir}(\text{COD})\text{Cl}]_2$ and the bisphosphine ligand dppe.³¹ The product was expected to form a bidentate iridium complex, with retention of the coordinated COD ligand. Displacement of the chloride ligand results in a singly charged complex ion with 16 valence electrons and a d^8 Ir(I) centre. Therefore, a square-planar geometry would be favoured. To aid precipitation, NH_4PF_6 was added to form an adduct with the bulky counter-ion PF_6^- .



Scheme 3.8. Reaction scheme for reaction of $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ with $[\text{Ir}(\text{COD})\text{Cl}]_2$.

After mixing $[\text{Ir}(\text{COD})\text{Cl}]_2$ and $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ together in methanol, the dark-red reaction mixture was heated to 50 °C. After one hour, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed a single peak at -1.3 ppm. This is similar to the signal observed for **16** (cf. -1 ppm). The lack of a free ligand signal indicated full ligand coordination. After addition of NH_4PF_6 in methanol, the mixture was heated for a further hour. Then, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed the same signal at -1.3 ppm, plus a PF_6^- multiplet at -144 ppm. After reducing the solvent volume to approximately one-third, a red solid began to precipitate. After addition of diethyl ether, a dark-red solid precipitated. After cooling, the product was isolated by cannula filtration, washed with diethyl ether and dried in vacuo. The product was collected as a dark-red free-flowing powder in 44 % yield. The product showed a single $^{31}\text{P}\{^1\text{H}\}$ NMR singlet at -1.63 ppm, alongside the PF_6^- multiplet centred at -144.3 ppm (observed as a quintet).

Mass spectrometry confirmed the identity of the expected product $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{Ir}(\text{COD})]\text{PF}_6$ (**19**) as $[\text{M}]^+$ at $m/z = 752.4074$ (calc. $m/z = 752.4065$). Elemental analysis also confirmed the product identity (found %C = 46.55, %H = 6.95, %N = 1.67; calc. %C = 46.86, %H = 7.08, %N = 1.56). Crystals of **19** suitable for X-ray crystallography were grown from vapour diffusion crystallisations in dichloromethane/diethyl ether. The structure shows the expected bidentate coordination of the bisphosphine ligand and the PF_6^- counter ion (Figure 3.12).

Because of the η^4 -coordination of the COD ligand, the geometry of **19** cannot be simply described. However, it can be approximated as a square-planar geometry. Considering the C-C bond lengths in the COD ligand, it is evident which carbon atoms are formally involved in the C=C double bonds: the bond lengths C(31)-C(32) and C(35)-C(36) are significantly shorter than the remaining C-C bond lengths (Table 3.10). The iridium centre binds to the COD across the two C=C bonds. There are two sets of equivalent Ir-C bond lengths – $\text{Ir}(1)\text{-C}(35)/\text{Ir}(1)\text{-C}(31)$ and $\text{Ir}(1)\text{-C}(32)/\text{Ir}(1)\text{-C}(36)$. Therefore, there is no significant difference between the binding across the two C=C double bonds. The two Ir-P bond lengths are equivalent to each other (2.3052(19) and 2.3114(17) Å) and slightly longer than each of the Ir-C bond lengths. To some approximation, Ir(1), P(3), P(5), C(32) and C(36) can be viewed as adopting positions lying along the same plane. Around the iridium centre, there is a relatively small deviation from idealised square-planar geometry. Whilst each bond angle is statistically distinct from each other, the P-Ir-P bond angle is widest at 93.22(6) °. As previously, this can be considered to minimise steric interactions between the bulky PCy_2 groups.

To obtain additional yield of **19**, the reaction filtrate was stored at 5 °C. Curiously, a yellow crystalline material was observed to form. The original solid product **19** was deep-red in colour. The yellow-coloured precipitate was isolated and dried in vacuo. Surprisingly, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed the presence of a multiplet centred at -32 ppm.

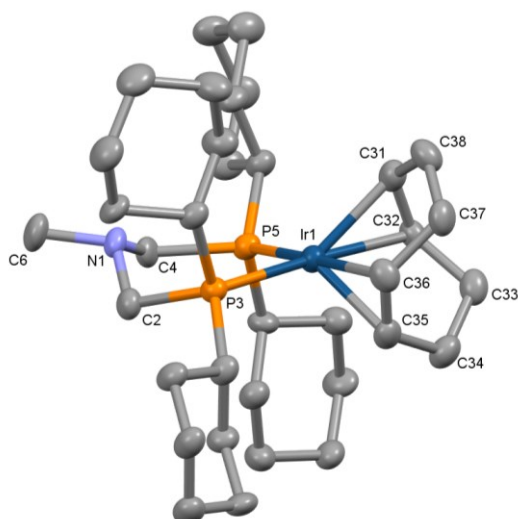


Figure 3.12. Crystal structure of [Me-N(CH₂PCy₂)₂Ir(COD)]PF₆ (**19**). Hydrogen atoms, counter-ion and solvent molecules omitted for clarity.

Table 3.10. Collected bond lengths and bond angles for [Me-N(CH₂PCy₂)₂Ir(COD)]PF₆ (**19**).

Bond	Bond length (Å)
C(31)-C(32)	1.408(10)
C(31)-C(38)	1.492(11)
C(32)-C(33)	1.533(10)
C(33)-C(34)	1.530(11)
C(34)-C(35)	1.485(10)
C(35)-C(36)	1.407(11)
C(36)-C(37)	1.517(11)
C(37)-C(38)	1.511(11)
Ir(1)-C(35)	2.165(7)
Ir(1)-C(31)	2.179(8)
Ir(1)-C(32)	2.240(7)
Ir(1)-C(36)	2.242(8)
Ir(1)-P(5)	2.3052(19)
Ir(1)-P(3)	2.3114(17)
	Bond angle (°)
P(5)-Ir(1)-P(3)	93.22(6)
C(36)-Ir(1)-P(3)	90.57(19)
C(32)-Ir(1)-P(5)	89.5(2)
C(32)-Ir(1)-C(36)	86.6(3)

The original product signal of **19** at -1.6 ppm was not observed, neither was a signal attributable to the free ligand Me-N(CH₂PCy₂)₂. A small PF₆⁻ signal remained. Therefore, ³¹P{¹H} NMR spectroscopy suggested the formation of a new, unassigned species. An expanded ³¹P{¹H} NMR spectrum is shown in Figure 3.13.

Initially, the ³¹P{¹H} NMR signal of the yellow crystalline material was assigned as a doublet of doublets centred at -31.7 ppm. Whilst the intensity distribution of the signals fit that of a quartet signal (1:3:3:1), the chemical shift distribution suggested a doublet of doublets. These observations match an NMR phenomenon generally referred to as an “AB quartet”. This occurs when two nuclei coupling to each other have a chemical shift difference comparable to the coupling itself. Therefore, the signal is in fact two doublet signals in close proximity to each other, centred at -31.6 ppm and -31.8 ppm. This means that there are two distinct, but only very slightly different, phosphorus environments which are coupling to each other. The difference in relative intensities of the signals in each doublet can be attributed to a “roofing effect”. The difference in the resonance frequencies of the two nuclei is comparable to the coupling constant between them, therefore the multiplets slant towards each other.

Considering that the “multiplet” in fact originates from two distinct signals, further analysis was performed. The coupling constants of the two doublets of P_A and P_B are both J = 22.7 Hz. The identical coupling constants indicate that the two signals are coupling to each other, potentially attributed to ²J_{p-p} coupling.

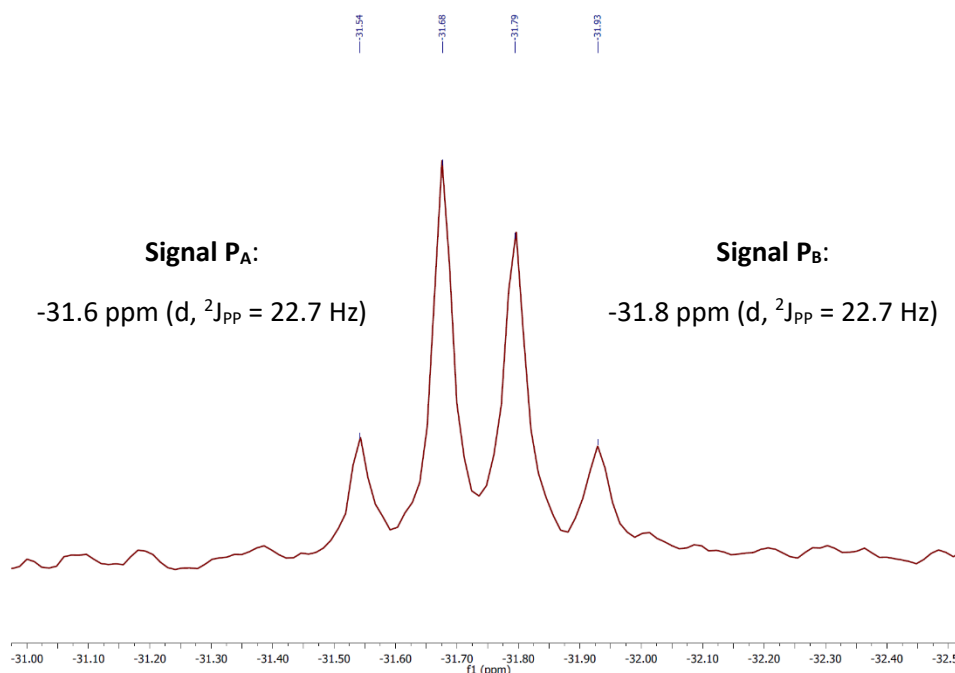


Figure 3.13. Expanded ³¹P{¹H} NMR spectrum showing the “AB quartet” of **21**.

The difference in resonance frequencies of the two signals (the distance between the centre of each doublet) is 40.5 Hz. This is on the same order of magnitude as the coupling constant (1.8 x), therefore the intensities of the two peaks in each doublet are different, owing to the roofing effect. Whilst **19** showed a single $^{31}\text{P}\{^1\text{H}\}$ environment, in the new species there must be a small, but definite, difference in chemical environment for each nucleus to couple to each other.

Furthermore, the chemical shift of these two signals was shifted far upfield relative to that of **19**. Additionally, whilst the original sample showed a PF_6^- signal, later samples of the yellow material lacked this signal, suggesting it was not a component of the unassigned species. Mass spectrometry identified a signal just three mass units heavier than $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{Ir}(\text{COD})]^+$.

Fortunately, single crystals of this species were grown through vapour diffusion crystallisation from chloroform/diethyl ether. The crystal structure was determined as $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{Ir}(\text{Cl})_3(\text{OH}_2)]$ (**20**) and was found as two independent complexes (Figure 3.14). Whilst the bisphosphine ligand remains bound to the iridium centre, the COD ligand has been displaced by three chloride ligands and one water ligand, resulting in the formation of an octahedral complex. The presence of the water ligand was the best fit for the crystallography data, which did not find the corresponding hydrogen atoms. The two independent complexes have different geometries with the axial water ligand placed on opposite sides of the complex relative to the N-methyl moiety. The bisphosphine ligand shows some puckering and does not lie entirely in the same plane.

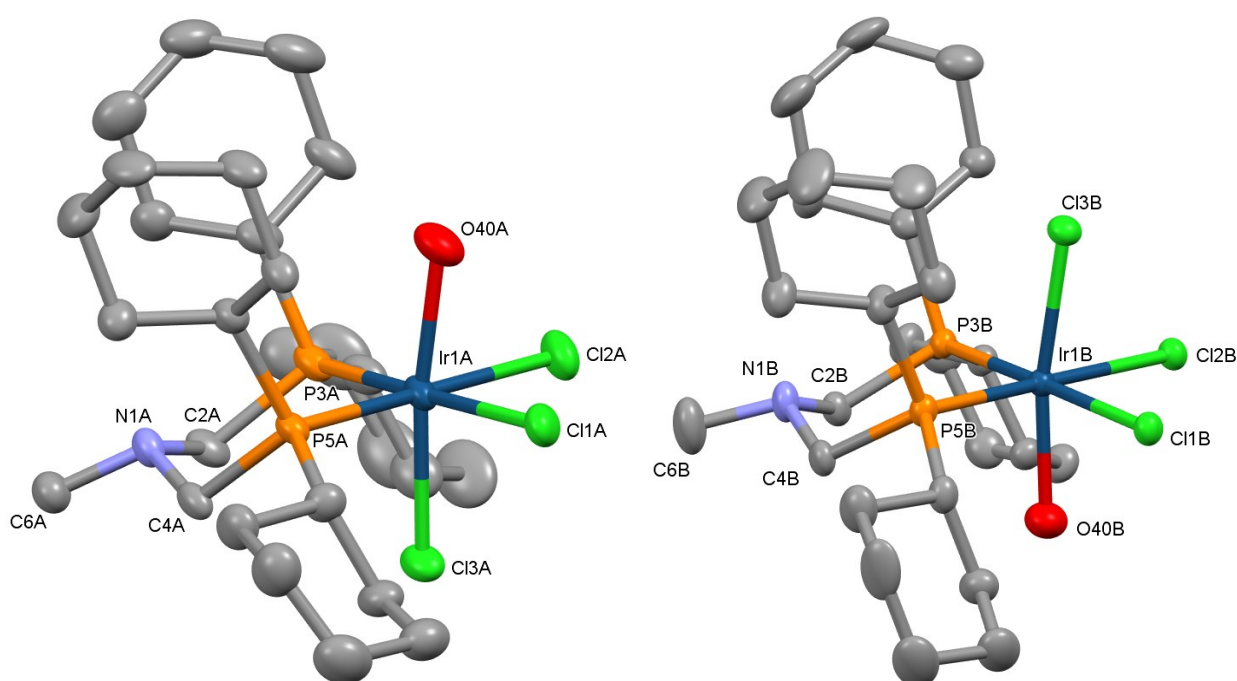


Figure 3.14. Crystal structures of $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{Ir}(\text{Cl})_3(\text{OH}_2)]$ (**20**). Hydrogen atoms and solvent molecules omitted for clarity.

However, there are some curiosities with the crystal structure of **20**. No chlorinated solvents were used in the reaction until the attempted crystallisation from chloroform/diethyl ether, suggesting that the chloride ligands originate from the addition of chloroform; or alternatively from the chlorides displaced from $[\text{Ir}(\text{COD})\text{Cl}]_2$. However, the inclusion of three chloride ligands in the complex rationalises the upfield chemical shift and the lack of a PF_6 signal. Furthermore, it is not immediately evident that each phosphorus centre is in a (very slightly) different chemical environment. Their chemical inequivalence, and the subsequent coupling between P_A and P_B , can likely be attributed to a small degree of structural variation in **20**; for example, the P-Ir-Cl bond angles in **20** are not equivalent.

An idealised octahedral complex would have bond angles of 90° between adjacent ligands, and 180° between opposite ligands. In both independent complexes of **20**, whilst all the bond angles between the equatorial ligands are statistically different from each other, they show a relatively insignificant deviation from idealised geometry (Table 3.11). The P-Ir-P bond angles are not the widest for either of the two complexes, indicating that there is no significant steric hindrance between the PCy_2 groups in an octahedral geometry in the presence of small water and chloride ligands. Furthermore, the P-Ir-P bond angles of $91.26(5)$ and $91.76(5)^\circ$ are over 1° narrower than that observed for **19** ($93.22(6)^\circ$). In both complexes, the two P-Ir bond lengths are statistically equivalent to each other. In each case, one of the equatorial Ir-Cl bond lengths is shorter than the other, with the axial Ir-Cl bond significantly shorter than both equatorial Ir-Cl bond lengths.

Table 3.11. Collected bond angles and bond lengths for $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{Ir}(\text{Cl})_3(\text{OH}_2)]$ (**21**).

	Angle ($^\circ$)		Angle ($^\circ$)
P3A-Ir-Cl2A	90.63(6)	P5B-Ir-Cl1B	93.94(5)
Cl2A-Ir-Cl1A	86.43(6)	Cl1B-Ir-Cl2B	87.88(5)
Cl1A-Ir-P5A	91.68(6)	Cl2B-Ir-P3B	90.98(5)
P5A-Ir-P3A	91.26(5)	P3B-Ir-P5B	91.76(5)
P3A-Ir-Cl1A	177.01(5)	P5B-Ir-Cl2B	177.21(5)
Cl2A-Ir-P5A	178.05(5)	Cl1B-Ir-P3B	177.89(5)
	Length ($\text{\AA}$)		Length ($\text{\AA}$)
P3A-Ir	2.2746(17)	P5B-Ir	2.2904(15)
P5A-Ir	2.2821(15)	P3B-Ir	2.2974(14)
Ir-Cl1A	2.4333(16)	Ir-Cl1B	2.4280(13)
Ir-Cl2A	2.4192(15)	Ir-Cl2B	2.4403(14)
Ir-O40A	2.117(4)	Ir-O40B	2.118(4)
Ir-Cl3A	2.3797(16)	Ir-Cl3B	2.3840(13)

It was stated that there was some uncertainty in the assignment of the oxygen-containing ligand as water. However, the Ir-O bond lengths are consistent with a single Ir-O bond. Furthermore, the inclusion of H₂O results in a stable 18 electron count with Ir(III). Pleasingly, elemental analysis results were a close match for the crystal structure (calc. %C = 42.21, %H = 6.95, %N = 1.82; found %C = 41.87, %H = 7.05, %N = 2.09). Mass spectrometry also supported the crystal structure, found as [M-Cl-H₂O+MeCN]⁺ at m/z = 755.2783 (calc. m/z = 755.2769).

The formation of **20** remains somewhat curious. An NMR sample of **19** in deuterated chloroform showed no change to its ³¹P{¹H} NMR signals over the course of one month, therefore **19** does not convert to **20** in the presence of a chlorinated solvent. This suggests that **20** is not formed as a direct result of displacement of COD from **19** by a chlorine source. Potentially, there is some competition between displacement of the chloride ligands and the COD ligand from the [Ir(COD)Cl]₂ precursor. The reaction filtrate, from which **20** crystallised, would have contained the displaced chlorides from [Ir(COD)Cl]₂, potentially displacing the coordinated COD ligand from **19** over extended periods of time. A summary of the reactivity of Me-N(CH₂PCy₂)₂ with [Ir(COD)Cl]₂ is presented in Figure 3.15.

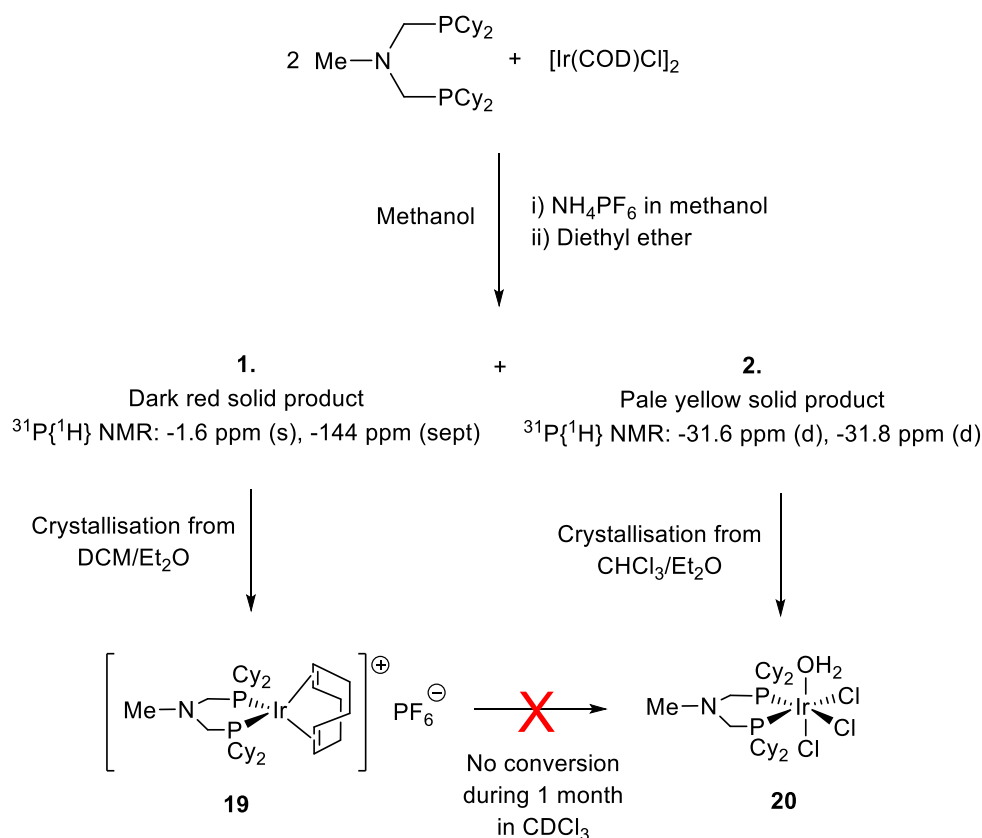


Figure 3.15. Summary of the reactivity of Me-N(CH₂PCy₂)₂ with [Ir(COD)Cl]₂.

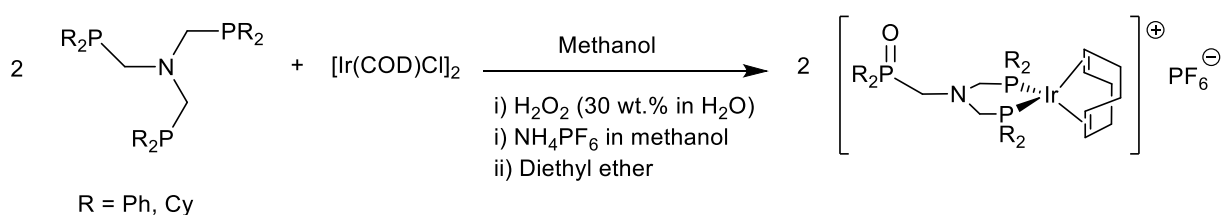
Section 3.5 will discuss the reactivity of similar rhodium phosphine complexes with chlorinated solvents, resulting in similarly unexpected products. Although **20** was well-defined and characterised, its synthesis could not be repeated.

However, despite the curious second product formed from the reaction between $[\text{Ir}(\text{COD})\text{Cl}]_2$ and $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$, $[\text{Ir}(\text{COD})\text{Cl}]_2$ was a far superior starting material than $[\text{Cp}^*\text{IrCl}_2]_2$. Full coordination of the ligand with $[\text{Ir}(\text{COD})\text{Cl}]_2$ was found within a short time, whilst this was never observed for $[\text{Cp}^*\text{IrCl}_2]_2$. This might be attributed to the formation of a stable, d^8 square-planar complex, or to a reduction in steric hindrance from the iridium precursor. The next section will discuss the coordination of tridentate N-Triphos ligands with $[\text{Ir}(\text{COD})\text{Cl}]_2$.

3.4.3 Complexes of N-Triphos ligands with $[\text{Ir}(\text{COD})\text{Cl}]_2$

Whilst the coordination of N-Triphos ligands to palladium was straight-forward, through bidentate ligand coordination and oxidation of the pendant arm, this was not the case for ruthenium. This section will discuss the coordination of N-Triphos^{Cy} and N-Triphos^{Ph} ligands to $[\text{Ir}(\text{COD})\text{Cl}]_2$. The general reaction scheme used is shown in Scheme 3.9. It follows the same general route used for the coordination of $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ to $[\text{Ir}(\text{COD})\text{Cl}]_2$, with the addition of hydrogen peroxide to oxidise the pendant phosphine arm.

After mixing $[\text{Ir}(\text{COD})\text{Cl}]_2$ and N-Triphos^{Cy} in methanol, the mixture was heated to 50 °C. After one hour, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed signals at -1.9/-2.5 ppm, which were attributed to the coordinated phosphine ligand (cf. -1.6 ppm for **19**), in addition to a signal at -16.4 ppm, attributed to the uncoordinated PCy₂ group. An extra signal was observed at -52.4 ppm which had not been observed previously. After addition of hydrogen peroxide, the signal at -1.4 ppm remained, but there were several signals in the region 48-53 ppm suggesting over-oxidation. No other signals were observed. After addition of NH_4PF_6 , the solvent level was removed to approximately one-third, diethyl ether was added, and the reaction mixture was cooled overnight. However, no solid precipitated.



Scheme 3.9. Reaction scheme for reaction of N-Triphos ligands with $[\text{Ir}(\text{COD})\text{Cl}]_2$.

After further solvent removal and addition of diethyl ether, a pale brown solid precipitated which was collected by cannula filtration, washed with diethyl ether and dried in vacuo. Based on the expected product, the yield was just 9 %. Removing the solvent from the filtrate led to the formation of a red-brown solid in 52 % yield. Both solids showed similar $^{31}\text{P}\{^1\text{H}\}$ NMR signals. A signal at -2.31 ppm was attributed to Ir-PCy₂ as expected, plus a PF₆⁻ multiplet at -144 ppm. Several signals were observed around 50 ppm (49.7, 49.2, 47.6 ppm). This suggested the formation of the expected product, alongside further oxidised species, likely oxidised N-Triphos^{Cy} ligand. The results indicate that the desired product is susceptible to degradation by oxidising agents such as hydrogen peroxide. Despite this, mass spectrometry confirmed the formation of the expected product [P(O)Cy₂CH₂-N(CH₂PCy₂)₂Ir(COD)]PF₆ (**21**) (found m/z = 964.5410, calc. m/z = 964.5395). Additional signals were also assigned to the fully oxidised N-Triphos^{Cy} ligand and to a version of the analogous iridium complex with an unoxidised pendant phosphine arm, [PCy₂CH₂-N(CH₂PCy₂)₂Ir(COD)]PF₆ (**22**). This suggested that there is some flexibility or uncertainty in the nature of the uncoordinated phosphine arm.

The reaction was repeated to avoid using hydrogen peroxide. After one hour, the same $^{31}\text{P}\{^1\text{H}\}$ NMR signals were observed at -1.87/-2.52 ppm, -16.4 ppm and -52.5 ppm. After addition of NH₄PF₆, the nitrogen atmosphere of the reaction was replaced by an atmosphere of air, as a gentler method of oxidising the pendant phosphine. The next day, small new signals were observed at 49 ppm and -27 ppm, however the NMR signals were mostly unchanged, indicating that air alone was insufficient for phosphine oxidation. Consequently, hydrogen peroxide was added, leading to the formation of a major signal at 51.2 ppm alongside signals at -1.7 ppm and -27.5 ppm (and -144 ppm). A pale-brown solid was collected in the standard manner, which showed a major signal at 49.1 ppm. Whilst signals at -27.4 ppm and -144 ppm were also present, it appeared that the expected product had completely degraded to an oxidised P(O)Cy₂ species.

The reaction was repeated in dichloromethane. Dichloromethane is a less coordinating solvent than methanol, which might have affected ligand coordination to iridium. After one hour, $^{31}\text{P}\{^1\text{H}\}$ NMR signals at -7.5, -16.3 and -52.4 ppm were observed. After addition of NH₄PF₆, $^{31}\text{P}\{^1\text{H}\}$ NMR signals at -2.4, -16.1 and -52.5 ppm were seen, and at -144 ppm (PF₆⁻). The signals at -2.4 and -16.1 ppm can be attributed to the expected product without oxidation. The signal at -52.5 ppm had been observed previously in the previous reaction of N-Triphos^{Cy} with [Ir(COD)Cl]₂, but was lost after addition of hydrogen peroxide. After continuing the reaction overnight, there was no further change to the $^{31}\text{P}\{^1\text{H}\}$ NMR signals. An orange-red solid product was isolated in the standard manner. The solid product showed $^{31}\text{P}\{^1\text{H}\}$ NMR signals at -2.2 and -16.0 ppm in a 2:1 ratio, without any phosphine oxidation observed. The signal at -52.6 ppm remained in greater intensity than had been previously observed. This signal was tentatively assigned to tridentate coordination of the N-Triphos^{Cy} ligand to iridium.

Potentially, the more coordinating solvent methanol had inhibited tridentate ligand coordination, which is in competition with the bidentate coordination mode in the less-coordinating solvent dichloromethane. The solid product was stored without protection from air. $^{31}\text{P}\{^1\text{H}\}$ NMR samples prepared over time showed no oxidation, indicating that the pendant PCy_2 group was more resistant to oxidation than expected. This might support the assignment of a mixture of bi- and tri-dentate coordination modes: if the third phosphine arm interacts with the iridium centre, it might be less readily oxidised in air.

Mass spectrometry showed a major signal attributable to the expected product **22** (found $m/z = 948.5458$, calc. $m/z = 948.5446$). Naturally, this does not discriminate between bi- and tridentate coordination modes. The mass spectrum was much cleaner than that seen for the product of the reaction using hydrogen peroxide, suggesting the formation of a single robust product.

In summary, in the reactions using hydrogen peroxide, over oxidation of the N-Triphos^{Cy} ligand was observed. However, NMR spectroscopy and mass spectrometry showed some presence of the expected product with the third phosphine arm unoxidised. In the reaction omitting hydrogen peroxide, little or no oxidation of the third phosphine arm was observed, even when the product was not protected from oxygen. This suggests that the complex is stable to oxidation unless a strong oxidising agent like hydrogen peroxide is used. This is quite surprising for a pendant PCy_2 arm, which is typically readily oxidised, especially in solution. This supports the hypothesis that there is some coordination of this third PCy_2 arm to the iridium centre, making it more resistant to oxidation. Unfortunately, attempts to grow single crystals suitable for X-ray crystallography were unsuccessful. This in itself might be attributed to a poorly defined coordination mode of the third phosphine arm. The bidentate and tridentate coordination modes are illustrated in Figure 3.16.

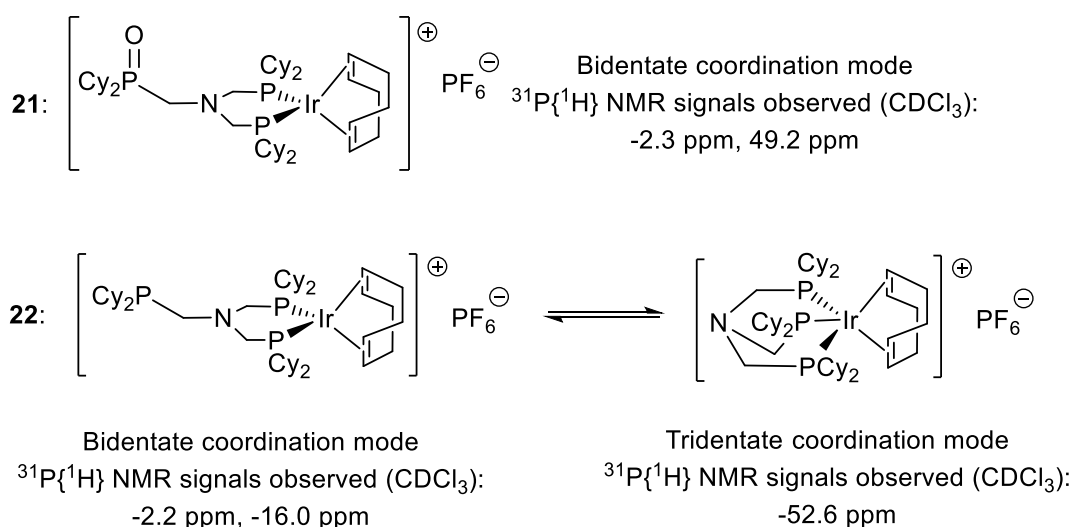


Figure 3.16. Bidentate and tridentate coordination modes of N-Triphos^{Cy} with iridium.

If there is some formation of a tridentate coordination mode of N-Triphos^{Cy} to iridium, this might be limited by the steric bulk of the PCy₂ groups. More straight-forward coordination was expected with the less bulky N-Triphos^{Ph} ligand. After mixing [Ir(COD)Cl]₂ and N-Triphos^{Ph} in methanol, a pale-yellow coloured reaction mixture was formed. This was in stark contrast to the reaction mixtures with N-Triphos^{Cy} which were dark red in colour. After heating at 50 °C for one hour, a sample was taken for ³¹P{¹H} NMR spectroscopy and showed one signal at -49.9 ppm. The lack of a free ligand signal showed that all three phosphine arms were in a new environment. The most reasonable assignment for this is to tridentate coordination of the N-Triphos^{Ph} ligand to iridium, [κ³-N(CH₂PCy₂)₃Ir(COD)]PF₆ (**23**). Curiously, the signal at -49.9 ppm is a close match for that observed at -52 ppm in the reaction of [Ir(COD)Cl]₂ and N-Triphos^{Cy}, which was tentatively assigned to a tridentate coordination mode of N-Triphos^{Cy}.

Owing to the lack of a free ligand signal in the ³¹P{¹H} NMR spectrum, hydrogen peroxide was omitted from the reaction. After addition of NH₄PF₆, the solvent level was reduced to approximately one-third in vacuo and after the addition of diethyl ether, a fine pale-yellow solid precipitated. The product was isolated by cannula filtration, washed with diethyl ether and after drying collected as a free-flowing beige-coloured powder. The solid product showed a ³¹P{¹H} NMR signal at -50.0 ppm and the PF₆⁻ multiplet at -144 ppm in the expected 3:1 ratio.

Whilst there are no examples of N-Triphos^{Ph} coordinating to iridium in a tridentate mode reported in the literature, there are examples of the carbon-centred Triphos ligand in this coordination mode. One relevant example is an iridium complex bound to the three phosphine arms of Triphos and to 1,3-butadiene. Its ³¹P{¹H} NMR signal was found at -23.4 ppm. Therefore, a negative chemical shift would be expected for the analogous N-Triphos complex **23**. Furthermore, the iridium-Triphos complex was described as pale-yellow in colour. These results support the assignment of a tridentate coordination mode of N-Triphos^{Ph} to iridium in **23**.³²

In such a complex, the electron count would be 18 electrons, perhaps providing a stimulus for the complex to adopt tridentate phosphine coordination. The assignment of the signal at -50.0 ppm to tridentate N-Triphos^{Ph} coordination might support the assignment of the signal observed at -52.6 ppm to a tridentate N-Triphos^{Cy} binding mode. Whilst there is typically a significant difference in ³¹P{¹H} NMR signals observed for N-Triphos^{Ph} and N-Triphos^{Cy} ligands (~ 10-20 ppm), this difference might be minimised in such a shielded, upfield ³¹P{¹H} NMR environment. Therefore, the mixture of coordination modes observed for N-Triphos^{Cy} could be attributed to the increased steric bulk of the PCy₂ groups inhibiting full adoption of a tridentate binding mode.

The two possible coordination modes of N-Tripos^{Ph} are illustrated in Figure 3.17. Although it is difficult to distinguish bi- or tridentate coordination modes from the phenyl protons by ¹H NMR spectroscopy, the N-Tripos^{Ph} N-CH₂ protons were assigned to a singlet at 4.37 ppm, indicating each phosphine arm is in the same environment. This again supports the identification of a tridentate coordination mode. Mass spectrometry confirmed the identity of **23**, with M⁺ at m/z = 912.2635 (calc. m/z = 912.2629). Furthermore, this was the only major signal identified by mass spectrometry without any fragmentation. This suggests that the product is robust and well-defined. Unfortunately, elemental analysis failed to match the product identity. Also, all crystallisation attempts failed to yield crystals suitable for X-ray crystallography. Although the structure of **23** was anticipated to feature well-defined tridentate coordination, intermolecular interactions are crucial in growing crystals. Therefore, the coordination mode of N-Tripos^{Ph} was unconfirmed by X-ray crystallography.

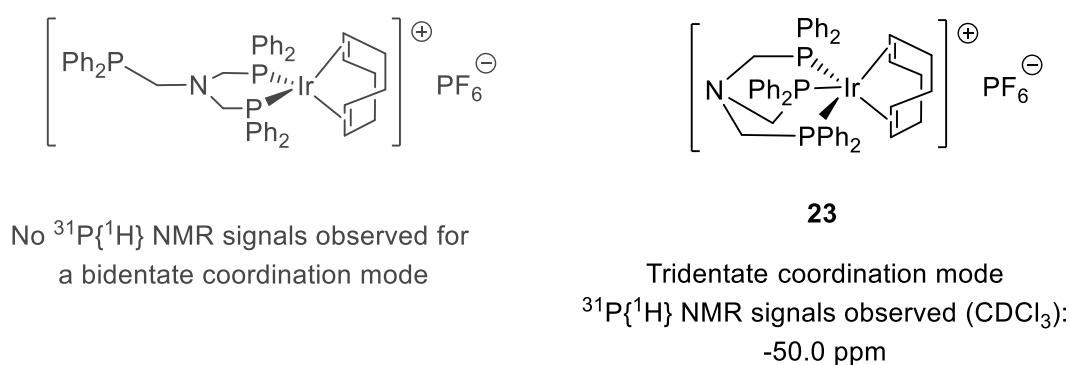


Figure 3.17. Bidentate and tridentate coordination modes of N-Tripos^{Ph} with iridium.

3.5 Complexes of multidentate phosphine ligands with rhodium

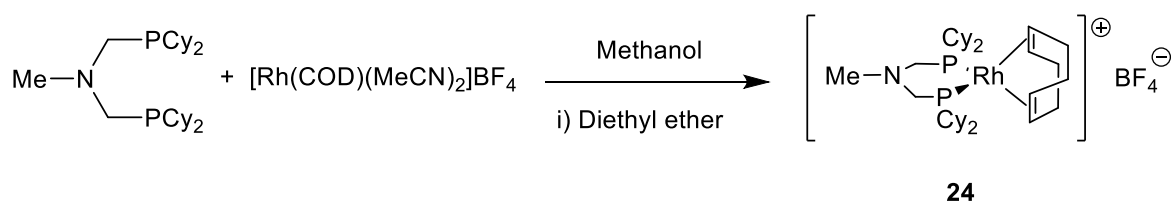
Following the reactions of the bi- and triphosphine ligands to palladium, ruthenium and iridium, attention turned next to rhodium. Nitrogen-bridged bisphosphine ligands were again expected to bind to rhodium in a bidentate manner, whilst with N-Tripos ligands some competition between bi- and tridentate coordination modes was anticipated, as observed with iridium. Earlier work in the Miller group investigated the coordination chemistry of N-Tripos^{Ph} with rhodium, achieving tridentate coordination;³³ however, the coordination chemistry of N-Tripos^{Cy} with rhodium was untested.

The commercially available precursor [Rh(COD)(MeCN)₂]BF₄ has a d⁸ Rh(I) centre with an overall electron count of 16. It can be considered as having square-planar geometry with labile acetonitrile ligands. Upon coordination of a bisphosphine ligand, the electron count and oxidation state are

maintained with a formal positive charge and BF_4^- counter-ion. A key difference with rhodium is that ^{103}Rh (100 % natural abundance) is NMR active with spin = $\frac{1}{2}$. This means that coupling between a coordinated phosphorus atom and rhodium can be observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.¹⁰

The reaction scheme for the coordination of $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ to $[\text{Rh}(\text{COD})(\text{MeCN})_2]\text{BF}_4$ is shown in Scheme 3.10. After mixing $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ and $[\text{Rh}(\text{COD})(\text{MeCN})_2]\text{BF}_4$ in methanol, a dark-orange coloured reaction mixture was formed. After heating to 50 °C for one hour, a solid precipitated. $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed a doublet at 10.7 ppm attributed to $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{Rh}(\text{COD})]\text{BF}_4$ (**24**) with a coupling constant of $^1J_{\text{P-Rh}} = 139.7$ Hz. No free ligand signal was observed, indicating full coordination had occurred. After cooling to RT, the solid product was isolated by cannula filtration, washed with diethyl ether and dried in vacuo. It was collected as a free-flowing yellow powder in just 21 % yield. However, when an NMR sample was prepared from the solid product the major $^{31}\text{P}\{^1\text{H}\}$ NMR signal appeared at 48.2 ppm (and at 49.6 ppm), attributable to $\text{R-P}(\text{O})\text{Cy}_2$. A minor product signal at 10.6 ppm was observed. This indicated that **24** was significantly air-sensitive, unlike its palladium, ruthenium and iridium analogues. Mass spectrometry also failed to find the expected product signal; however a major signal for the oxidised $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ ligand was observed at $m/z = 484.3960$.

Evidently the reaction needed to be repeated with strict exclusion of air throughout, and the solvent was changed to dichloromethane to aid product work-up. After one hour, the same product signal at 10.7 ppm was observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. No precipitate had formed. By reducing the solvent volume to approximately one-third, a yellow solid residue was formed. After complete solvent removal, the Schlenk tube was taken into a glovebox for isolation of the product as crystalline orange powder. Pleasingly, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of the product showed the doublet signal at 10.6 ppm ($^1J_{\text{P-Rh}} = 139.4$ Hz), without the presence of an oxide signal.



Scheme 3.10. Reaction scheme for reaction of $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ with $[\text{Rh}(\text{COD})(\text{MeCN})_2]\text{BF}_4$.

A sample of the product was prepared for mass spectrometry and tested immediately to minimise oxidation. Although the major MS signal observed at $m/z = 484.5443$ was again attributable to oxidised ligand, a signal was found at $m/z = 665.3740$. This is just three mass units heavier than the expected signal for **24**. This might be attributed to loss of the COD double bonds, or to fragmentation and addition of solvent molecules. Crystallisation attempts were complicated by the air-sensitivity of the product. Attempts at liquid-liquid diffusion crystallisations from acetonitrile/diethyl ether sealed inside Young's tap NMR tubes failed to produce suitable single crystals for analysis.

Surprisingly, when the original NMR sample was resubmitted for $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy after 48 hours, the product signal had been completely replaced by two doublet of doublets at 47.7 ppm and 38.6 ppm. They had equal signal intensity and near identical coupling constants ($J = 22.0, 112.1 \text{ Hz} / J = 22.0, 110.2 \text{ Hz}$). This suggested the presence of two phosphorus environments, coupling both to each other and to rhodium. No other $^{31}\text{P}\{^1\text{H}\}$ NMR signals were observed, suggesting complete transfer of the original product **24** to a new rhodium species. Relative to the original doublet signal, the doublet of doublets were significantly downfield, indicating that some oxidation had likely occurred. However, the splitting pattern indicated that the phosphines remained coordinated to rhodium, with the larger splitting probably attributable to $^1J_{\text{P-Rh}}$ coupling ($J = 112.1/110.2 \text{ Hz}$ vs. $J = 139.4 \text{ Hz}$), and the smaller splitting attributed to longer range $J_{\text{PA-PB}}$ coupling ($J = 22.0 \text{ Hz}$). Additionally, the reduction in the $^1J_{\text{P-Rh}}$ coupling constant from $J = 139.4 \text{ Hz}$ to $112.1/110.2 \text{ Hz}$ was consistent with oxidation of rhodium from Rh(I) to Rh(III) - in literature, $J_{\text{Rh-P}}$ coupling constants are larger for complexes of Rh(I) than for those of Rh(III).³⁴

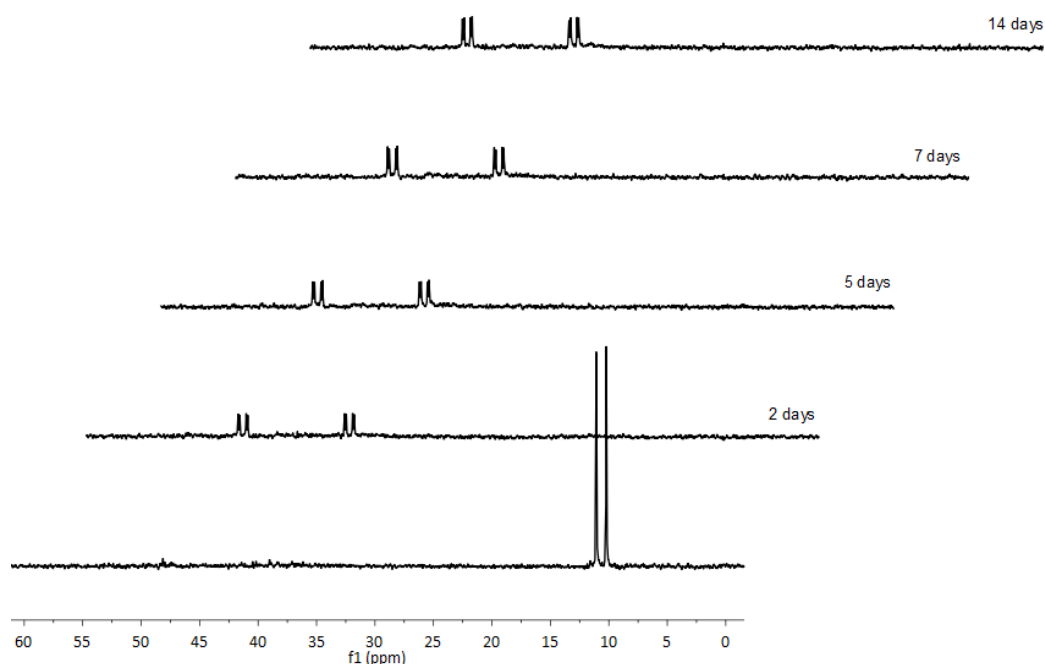


Figure 3.18. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showing change in signals observed for the product of reaction between $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ and $[\text{Rh}(\text{COD})(\text{MeCN})_2]\text{BF}_4$ over two weeks in CDCl_3 .

The same NMR sample was routinely resubmitted for $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy over the course of two weeks. Representative NMR spectra are presented in Figure 3.18. No further change was observed to the doublet of doublet signals. Preparing a fresh NMR sample from the solid product showed the original product doublet signal for **24**, indicating that the transfer of **24** to the new species was happening as a result of remaining in CDCl_3 solution for extended time periods.

A new NMR sample was prepared to determine at which point **24** transferred to the new species. The dd signals were first observed after 23 hours. There was a slow growth in these signals; after 55 hours, both the original d and the new dd signals were present. After 72 hours, the original doublet signal had been completely lost (Figure 3.19).

CDCl_3 was removed from the NMR sample in vacuo and replaced with MeCN-d_3 . Then, both the d and dd signals were observed (with changes to the chemical shift values owing to the change in solvent: $\delta = 31.9$ ppm, d, $J = 106.8$ Hz/ $\delta = 47.3$ ppm, dd, $J = 113.0, 23.6$ Hz and $\delta = 39.7$ ppm, dd, $J = 111.1, 21.8$ Hz). Therefore, the formation of the new species was reversible and dependent on the presence of CDCl_3 . This indicated that **24** reacted with CDCl_3 to form a new species, which reverted to **24** upon removal of CDCl_3 . The observation of some amount of the second species remaining in MeCN-d_3 was likely due to incomplete removal of CDCl_3 .

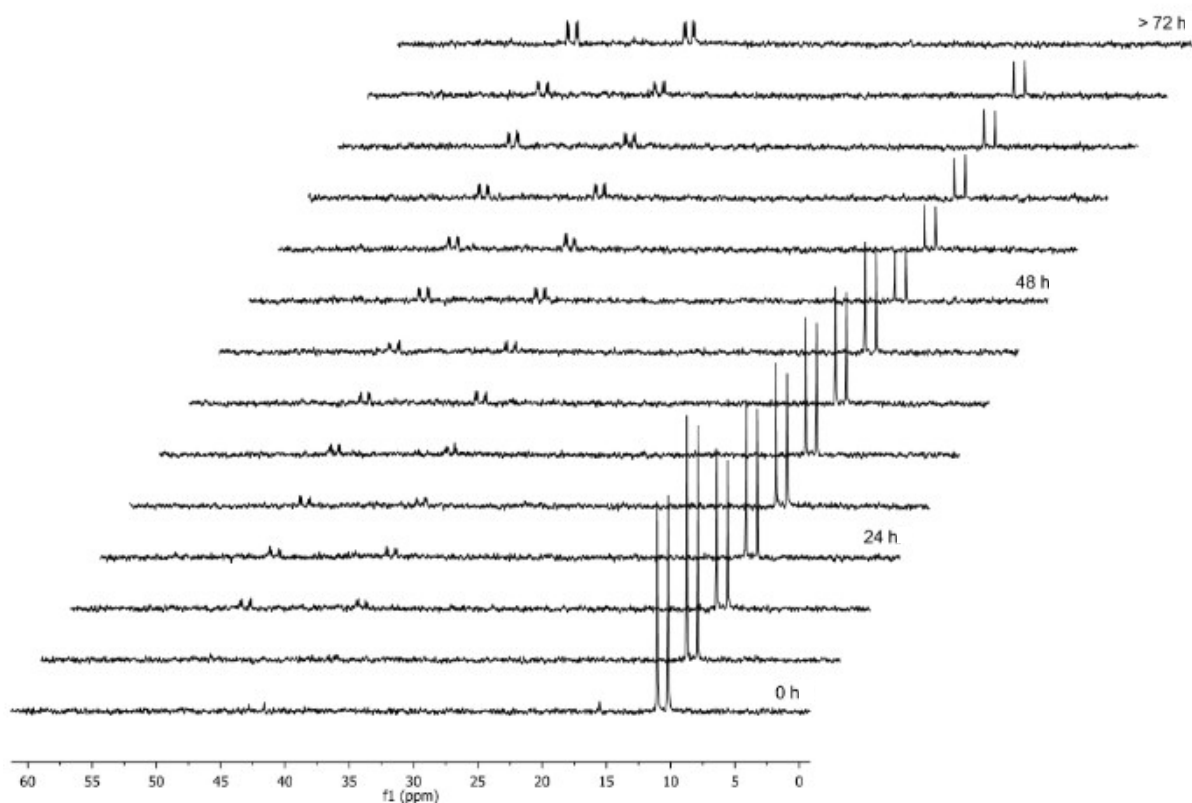


Figure 3.19. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showing gradual change in signals for the product of reaction between $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ and $[\text{Rh}(\text{COD})(\text{MeCN})_2]\text{BF}_4$ over the course of three days.

A new NMR sample was prepared from MeCN- d_3 . Although the doublet signal observed differed in both chemical shift (36.1 v 10.6 ppm) and coupling constant (166.3 v 139.4 Hz) from the original doublet observed in $CDCl_3$, these changes were attributed to the change in solvent. There was no change to this doublet signal observed over the course of a week, confirming that the transfer to the second species occurred only in $CDCl_3$ and not in MeCN- d_3 .

Single crystals of the unassigned species were successfully grown by layering hexane in the $CDCl_3$ NMR tube sample. The structure determined by X-ray crystallography is the tri-chloro bridged rhodium dimer $[\{Rh(Cl)(Me-N(CH_2PCy_2)_2)(\mu-Cl)_3\}BF_4]$ (**25**), with displacement of the coordinated COD ligand but retention of the bisphosphine ligand (Figure 3.20). The three bridging chlorides and a further chloride ligand at each rhodium centre is consistent with the observed reactivity of **24** with chloroform. The structure of **25** retains the BF_4^- counter-ion and is surrounded by three molecules of chloroform. The electron count of **25** is 18 electrons at each rhodium(III) centre. The complex is not centrosymmetric, owing to the presence of three bridging chlorides. The terminal chloride ligands are not pointing in the same direction, and so the bisphosphine ligands are orientated differently.

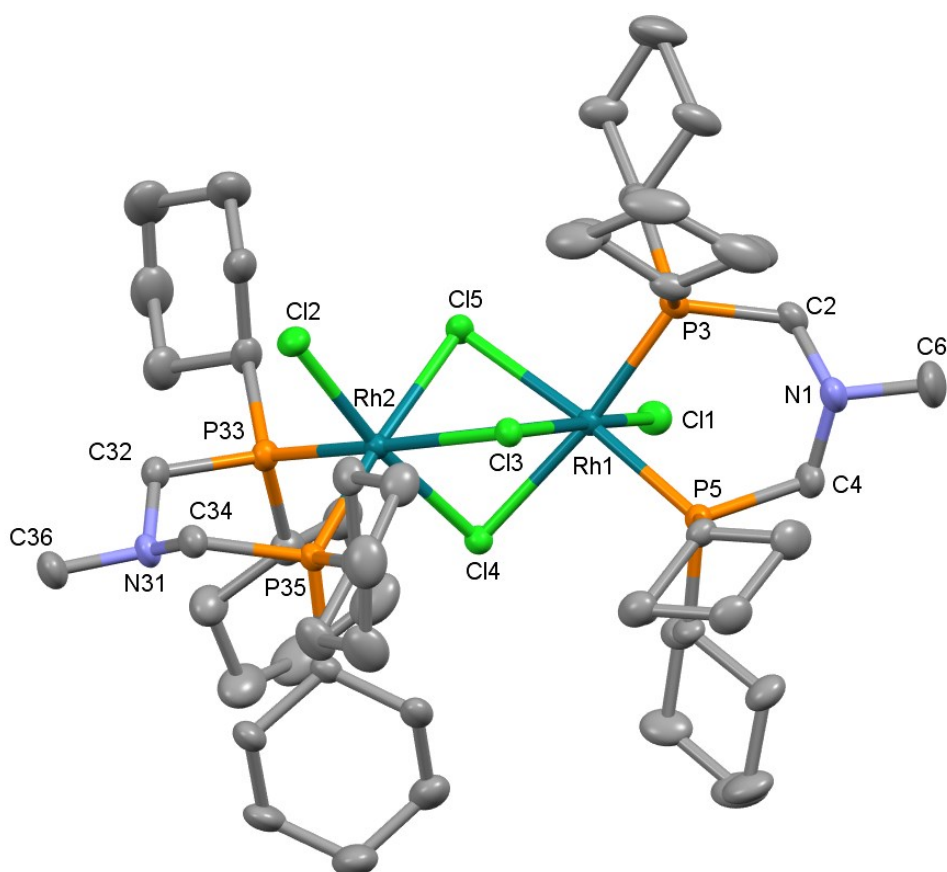


Figure 3.20. Crystal structure of $[\{Rh(Cl)(Me-N(CH_2PCy_2)_2)(\mu-Cl)_3\}BF_4]$ (**25**). Hydrogen atoms, solvent molecules and anion omitted for clarity.

By $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, two distinct phosphorus environments were determined. It is not immediately clear which two pairs of phosphorus atoms are equivalent to each other. Figure 3.21 presents the crystal structure with removal of the cyclohexyl rings. Viewing the complex along the Rh-Rh centre, P(5), P(35), Cl(3) and Cl(4) lie below the Rh-Rh centre. Above the Rh-Rh centre are found P(3), P(33), Cl(1), Cl(2) and Cl(5).

The presence of a Rh-Rh bond can be disregarded: the inclusion of a Rh-Rh bond would change the electron count at each rhodium centre from 18 to 19 electrons. Additionally, the Rh-Rh distance is 3.254 Å, significantly longer than would be expected for a Rh-Rh single bond (2.7 Å).³⁵ The terminal chloride ligands are pointing in different directions. Therefore, P(3) and P(33) can be considered as equivalent to each other, as can P(5) and P(35). In that way, $^1\text{J}_{\text{P-Rh}}$ coupling between each phosphorus to rhodium, and further $^2\text{J}_{\text{P-P}}$ coupling between P(3) and P(5), and between P(33) and P(35), results in the observed $^{31}\text{P}\{^1\text{H}\}$ NMR signals.

The incorporation of the five chloride ligands in **25** – none of which were present in **24** – account for the strong downfield shift in the dd signals relative to the original doublet. The proximity of the two signals at 39 and 48 ppm indicates two similar phosphorus environments, consistent with the obtained crystal structure. In **25**, each rhodium is in oxidation state +3. This is a change from the Rh(I) species **24**. The reduction in coupling constants between **24** and **25** is supported by the increase in oxidation state. Similar tri-chloro bridged rhodium dimers with carbon-centred Triphos ligands have been reported previously in the literature; examples are shown in Figure 3.22.^{36–38}

Table 3.12 collects selected Rh-P bond lengths from **25**. There is some variation in the Rh-P bond lengths. Rh(1)-P(5) and Rh(2)-P(33) can be considered as equivalent, at 2.2810(8) and 2.2786(8) Å. The Rh(1)-P(3) bond length of 2.2662(8) Å is slightly shorter, and the Rh(2)-P(35) bond length of 2.2876(8) Å is slightly longer.

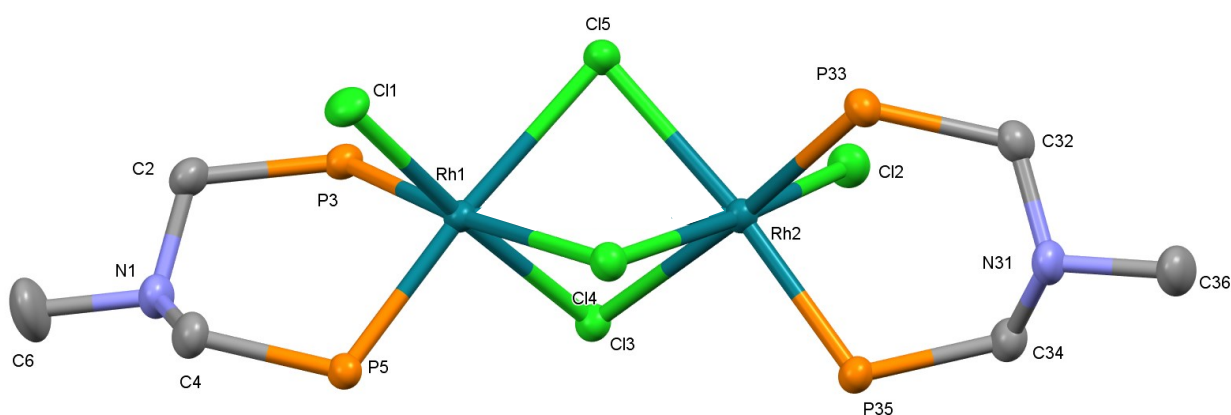


Figure 3.21. Magnified crystal structure of $[\{\text{Rh}(\text{Cl})(\text{Me}-\text{N}(\text{CH}_2\text{PCy}_2)_2\}_2(\mu\text{-Cl})_3]\text{BF}_4$ (**26**) with cyclohexyl rings removed for clarity.

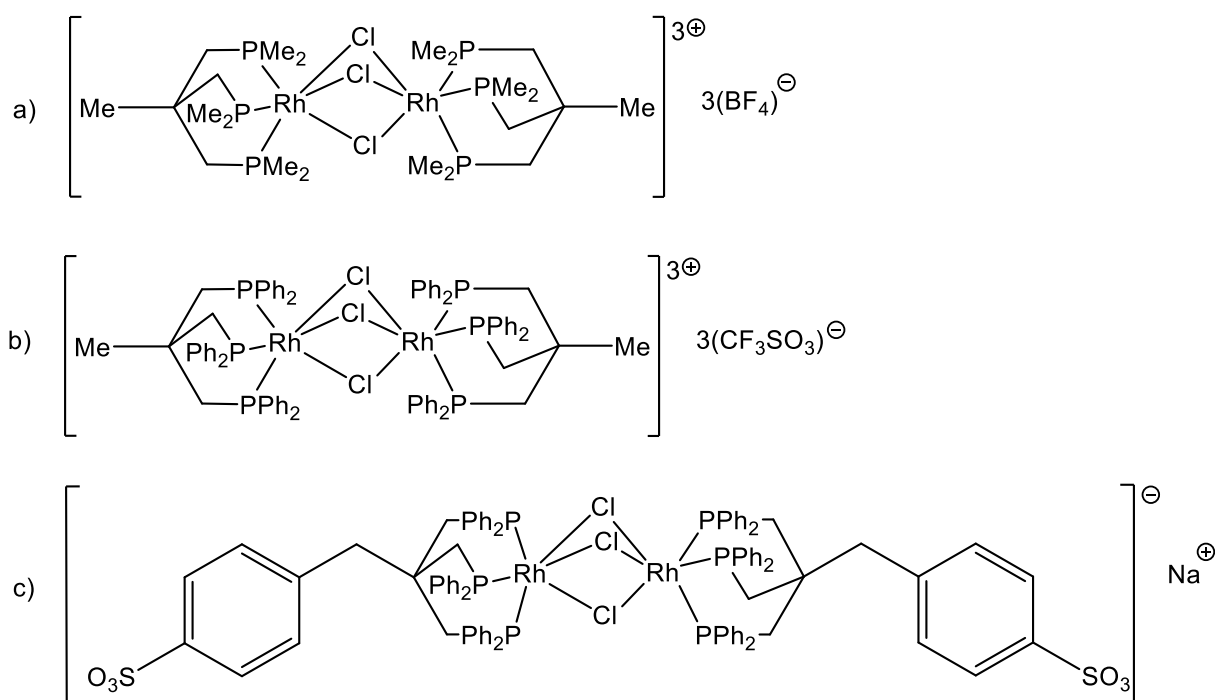


Figure 3.22. Examples of tri-chloro bridged rhodium dimers of Triphos ligands from the literature.^{36–38}

Table 3.12. Selected bond lengths from $[\{\text{Rh}(\text{Cl})(\text{Me}-\text{N}(\text{CH}_2\text{PCy}_2)_2\}_2(\mu\text{-Cl})_3]\text{BF}_4$ (**25**).

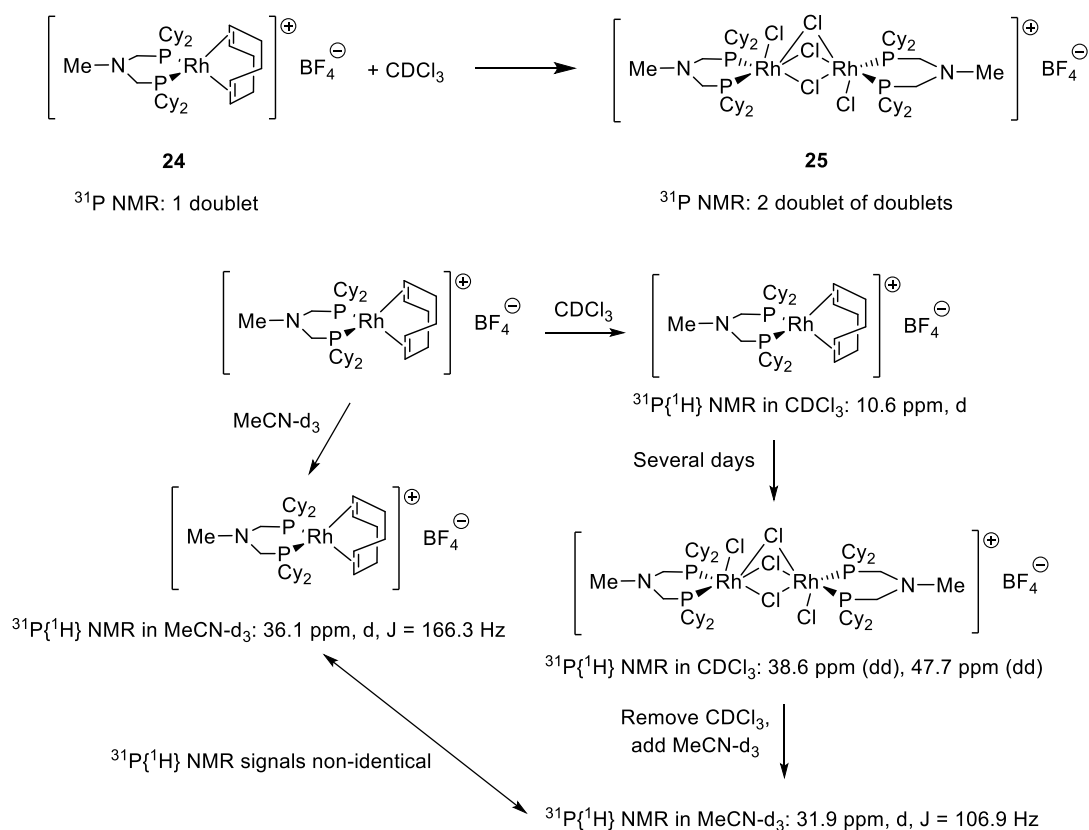
Bond	Bond length (Å)
Rh(1)-P(3)	2.2662(8)
Rh(1)-P(5)	2.2810(8)
Rh(2)-P(33)	2.2786(8)
Rh(2)-P(35)	2.2876(8)

After identification of the rhodium dimer **25** by crystallography, the product was further characterised. The $^{31}\text{P}\{^1\text{H}\}$ NMR signals were fully characterised as 38.6 ppm (2P, dd, $^2J_{\text{P-P}} = 22.0$ Hz, $^1J_{\text{P-Rh}} = 110.1$ Hz) and 47.7 ppm (2P, dd, $^2J_{\text{P-P}} = 22.1$ Hz, $^1J_{\text{P-Rh}} = 112.3$ Hz). After exposing the NMR sample to air for five days and resubmitting, no change to the $^{31}\text{P}\{^1\text{H}\}$ NMR signals was observed, indicating that **25** has good air stability (in stark contrast to **24**). Mass spectrometry supported the identification of **25**, with M^+ found at $m/z = 1285.3544$ (calc. $m/z = 1285.3517$). The lack of major fragmentation suggested **25** is particularly stable. Elemental analysis also supported the product identity (found %C = 47.23, %H = 7.49, %N = 2.04; calc. $m/z = 47.07$, %H = 7.61, %N = 2.16).

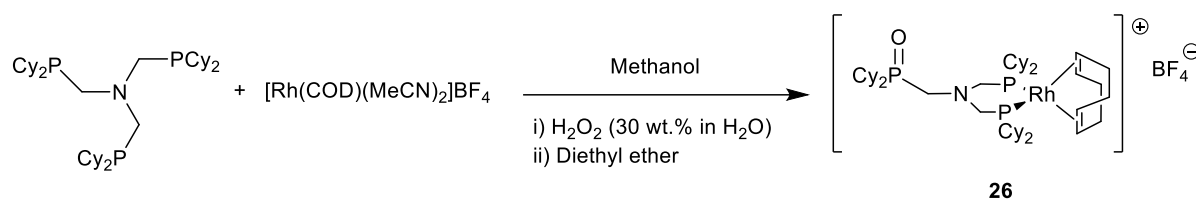
A schematic of the rhodium complexes of $\text{Me}-\text{N}(\text{CH}_2\text{PCy}_2)_2$ is shown in Scheme 3.11. There remains a small uncertainty. When a sample of **24** was prepared directly in $\text{MeCN}-d_3$, the doublet signal appeared at 36.1 ppm with $J = 166.3$ Hz. Upon preparation of an NMR sample in CDCl_3 , the monomeric

complex **24** converted to the dimer **25** over the course of several days. By completely removing CDCl₃ and refilling with MeCN-d₃, a doublet signal was regained at 31.9 ppm with J = 106.9 Hz. There is a discrepancy in both chemical shift and coupling constant between this signal and that of **24**. ¹H NMR spectra of the new sample did not show signals attributable to coordinated COD, indicating that **24** itself is not reformed from **25**. However, complete loss of **25** was observed upon removal of CDCl₃. Unfortunately, no crystallographic data was obtained for **24** or the new species observed in MeCN-d₃.

Next, the reactivity of N-Triphos^{Cy} with [Rh(COD)(MeCN)₂]BF₄ was tested (Scheme 3.12). Initially in methanol, a dark-orange mixture was formed. After one hour, ³¹P{¹H} NMR spectroscopy showed the presence of three multiplets centred at 30, 17 and 10 ppm. A trace signal for free ligand at -16.8 ppm was also observed. However, it appeared that all three phosphine arms were interacting with rhodium. After heating the reaction at 50 °C overnight, there was little change to the ³¹P{¹H} NMR signals. Whilst the free ligand signal had disappeared, a small P(O)Cy₂ signal was observed. The multiplet centred at 30.4 ppm was tentatively assigned to a doublet of triplets, and the multiplet centred at 16.4 ppm was tentatively assigned to a doublet of doublet of doublets.



Scheme 3.11. Schematic of reactivity of products from reaction of Me-N(CH₂PCy₂)₂ with [Rh(COD)(MeCN)₂]BF₄.



Scheme 3.12. Reaction scheme for reaction of N-Triphos^{Cy} with [Rh(COD)(MeCN)₂]BF₄.

The signal at 9.4 ppm was a doublet, with $J = 139.6$ Hz. This is a close match to the doublet observed through reaction of Me-N(CH₂PCy₂)₂ with [Rh(COD)(MeCN)₂]BF₄ (cf. 10.6 ppm, $J = 139.4$ Hz). After reducing the solvent volume to $\sim$ one-third, addition of diethyl ether and cooling, a fine yellow precipitate began to form.

The precipitate was isolated by cannula filtration, washed with diethyl ether and dried in vacuo. A crystalline sandy-brown free-flowing solid was collected. The solid was not protected from air exposure. Although the NMR sample was prepared under inert conditions, the ³¹P{¹H} NMR spectrum showed just one signal at 50 ppm, attributable to P(O)Cy₂. This demonstrated that the rhodium complex of N-Triphos^{Cy} is even more air-sensitive than **24**.

Although it was evident that repeat attempts needed to strictly avoid air exposure, the observation of the three ³¹P{¹H} NMR multiplets was not straight-forward to analyse. In previous work by the Miller group, N-Triphos^{Ph} achieved full tridentate coordination to [Rh(COD)(MeCN)₂]BF₄ in dichloromethane.³³ When acetonitrile, a more coordinating solvent, was used, a mixture of bidentate (major) and tridentate (minor) coordination modes were observed. This is similar to the reaction between N-Triphos^{Cy} and [Ir(COD)Cl]₂ (described in Section 3.4.3), where the use of dichloromethane led to the observation of greater tridentate ligand coordination than seen in methanol. Methanol is considered as a coordinating solvent similar to acetonitrile.³⁹ Therefore, the next reaction between N-Triphos^{Cy} and [Rh(COD)(MeCN)₂]BF₄ was performed in dichloromethane.

After heating at 30 °C for one hour, a sample was taken for ³¹P{¹H} NMR spectroscopy in CDCl₃. The signals were entirely different to those observed in the previous reaction. Representative ³¹P{¹H} NMR spectra are shown in Figure 3.23. A major and minor pair of doublets and singlets was found: a major doublet at 10.80 ppm ($J = 139.4$ Hz) and a minor doublet at 9.57 ppm ($J = 139.7$ Hz); a major singlet at -16.65 ppm and a minor singlet at -17.92 ppm. Each of the major and minor doublets and singlets have a 2:1 ratio, suggesting two coordinated PCy₂ arms and one uncoordinated PCy₂ arm. The chemical shift and coupling constants of the doublets resemble those previously observed for the product of reaction

between $[\text{Rh}(\text{COD})(\text{MeCN})_2]\text{BF}_4$ and $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ (cf. $\delta = 10.6$ ppm, $J = 139.4$ Hz). The singlets can be assigned to an uncoordinated PCy_2 arm. Therefore, the use of dichloromethane appeared to have facilitated exclusively bidentate coordination of $\text{N-Triphos}^{\text{Cy}}$ to rhodium.

It was considered that oxidation of the pendant phosphine through addition of hydrogen peroxide would likely destroy the complex. After cooling to RT, the solvent level was reduced to $\sim$ one-third in vacuo. After addition of diethyl ether and cooling, an orange solid precipitated. This was isolated by cannula filtration, washed with diethyl ether and dried in vacuo. The Schlenk tube was taken directly into a glovebox for isolation and storage of the product. The expected $^{31}\text{P}\{^1\text{H}\}$ NMR signals in CDCl_3 for $[\text{PCy}_2\text{CH}_2\text{-N}(\text{CH}_2\text{PCy}_2)_2\text{Rh}(\text{COD})]\text{BF}_4$ (**26**) were observed: a doublet at 10.3 ppm ($J = 139.4$ Hz) and a singlet at -16.6 ppm in a 2:1 ratio. Unfortunately, small oxide signals ~ 50 ppm were also observed, again demonstrating the high air-sensitivity of **26**. Resubmitting the same (sealed under inert conditions) NMR samples after four days showed complete oxidation/degradation, suggesting that **26** is unstable in solution or highly susceptible to trace amounts of oxygen.

Fresh NMR samples were prepared in the glovebox from MeCN-d_3 . Although the same signals were observed, the doublet signal experienced a large change in chemical shift from 10.3 ppm to 36.5 ppm (similar to that observed for **24** cf. $\delta = 36.1$ ppm). Additional minor doublets were observed around the major doublet with equivalent coupling constants. Attempted liquid-liquid diffusion crystallisation from chloroform/hexane was unsuccessful. By mass spectrometry, an exact match for **26** was not observed. However, a signal at $m/z = 872.4420$ is just two mass units lighter than the product with an oxidised third arm.

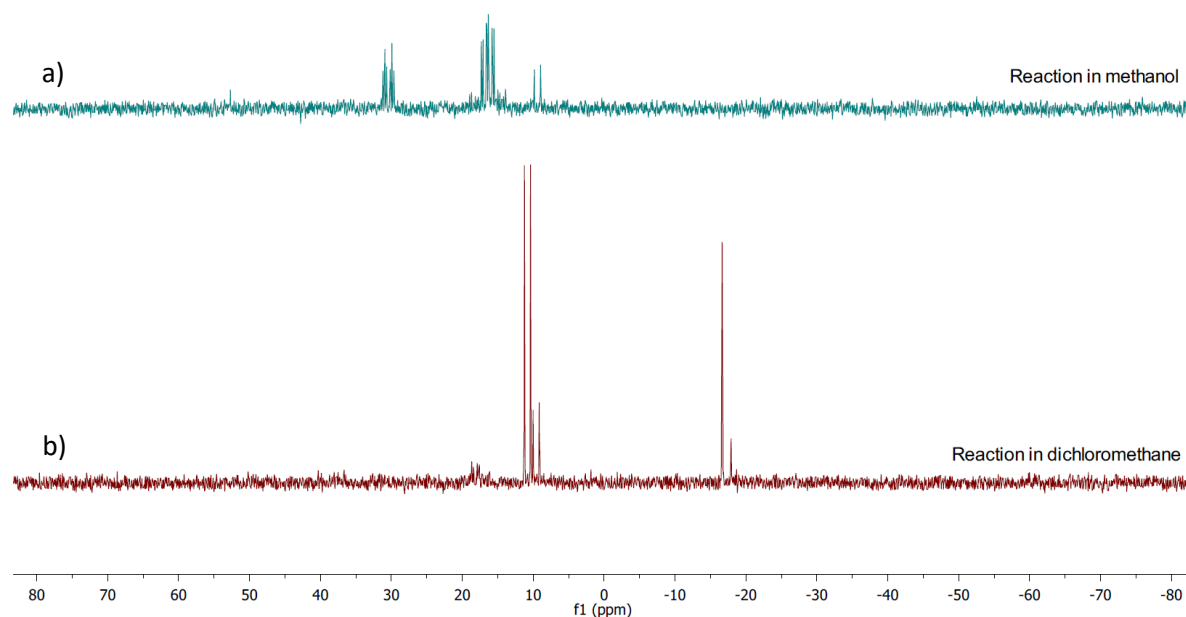


Figure 3.23. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of reaction between $\text{N-Triphos}^{\text{Cy}}$ and $[\text{Rh}(\text{COD})(\text{MeCN})_2]\text{BF}_4$ (a) in methanol b) in dichloromethane.

Ultimately, although the reactions of $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ and $\text{N-Triphos}^{\text{Cy}}$ with $[\text{Rh}(\text{COD})(\text{MeCN})_2]\text{BF}_4$ appeared to proceed by the formation of the expected coordination modes (dependent on solvent), their high air-sensitivity severely limited their characterisation. Furthermore, this makes them less attractive candidates as catalysts relative to the palladium, ruthenium and iridium analogues which can be handled without air protection.

3.6 Summary and outlook

This chapter has described the coordination chemistry of both bidentate nitrogen-bridged bisphosphine ligands and tridentate N-Triphos ligands to a range of transition metals.

Palladium complexes of the bidentate nitrogen-bridged phosphine ligands with $\text{R} = \text{Ph}$, Cy and ^tBu were synthesised. The reactions all proceeded in the expected manner, with bidentate coordination of the bisphosphine ligand. Crystal structures determined by X-ray crystallography confirmed that square-planar geometries were obtained in every case, with some variation in bond angles around the metal centre attributed to the steric requirements of the different ligand substituents. The reaction of the $\text{P}(^t\text{Bu})_2$ bisphosphine ligand $\text{Me-N}(\text{CH}_2\text{P}(^t\text{Bu})_2)_2$ suffered from a slightly reduced yield and purity, perhaps attributable to an increased solubility of the product in the reaction mixture. Small variations in the amine substituent were investigated ($\text{R}' = \text{Me}$, Bn , $\text{CH}_2\text{CH}(\text{OEt})_2$), which were found to have little effect on the products formed or the structures of the resulting complexes. Modification of the amine substituent can be considered as a route to modify the solubility of the complex, whilst the phosphine substituent is considered to have a larger effect on the stereo-electronic properties, and therefore catalytic behaviour, of the complex. The reaction between $\text{C}(\text{OEt})_2\text{HCH}_2\text{-N}(\text{CH}_2\text{PCy}_2)_2$ and $[\text{PdCl}_2(\text{COD})]$ proceeded in the standard manner and the expected crystal structure was determined.

Similar palladium complexes were prepared by reactions of N-Triphos ligands ($\text{R} = \text{Ph}$, Cy and ^tBu) with $[\text{PdCl}_2(\text{COD})]$. In each case, bidentate phosphine coordination was observed, with the third phosphine arm remaining uncoordinated. The strategy of adding hydrogen peroxide to oxidise the pendant phosphine group to a phosphine oxide was successful. In each case, the complexes adopted the expected square-planar geometry as determined by crystallography. Again, the reaction with $\text{N-Triphos}^{^t\text{Bu}}$ was more difficult to work-up and resulted in low yield.

Reactions of the bidentate nitrogen-bridged phosphine ligands ($\text{R} = \text{Ph}$, Cy and ^tBu) with $[\text{NiCl}_2(\text{PPh}_3)_2]$ were also performed. Although the products appeared to adopt paramagnetic, tetrahedral geometries, their crystal structures were determined with the square-planar geometries as seen for

their palladium analogues. Although the reaction with $\text{Me-N}(\text{CH}_2\text{P}^t\text{Bu})_2$ appeared to proceed in the same manner, its characterisation was largely unsuccessful.

The reaction of $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ with $[\text{RuCl}_2(p\text{-cymene})]_2$ proceeded with bidentate phosphine coordination, and the resulting crystal structure showed a complex with a “piano-stool” geometry. However, reaction of N-Triphos^{Cy} with $[\text{RuCl}_2(p\text{-cymene})]_2$ was not as straight-forward as for its palladium analogue. Whilst bisphosphine coordination was observed, the third phosphine appeared to be poorly defined. This might be attributed to a mixture of bi- and tridentate coordination modes in competition.

Using $[\text{Cp}^*\text{IrCl}_2]_2$ as an initial iridium precursor, coordination reactions of $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ and N-Triphos^{Cy} showed both incomplete reaction progress and with N-Triphos^{Cy}, a poorly defined third phosphine arm. Again, a mixture of coordination modes were suggested, in addition to a mixture of phosphine and phosphine oxide moieties. Generally, the pendant phosphine arm appeared to be resistant to oxidation by hydrogen peroxide, making this route less straight-forward than it was for the palladium analogues.

Pleasingly, the use of $[\text{Ir}(\text{COD})\text{Cl}]_2$ facilitated more straight-forward reactions. With $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$, full bidentate conversion was achieved, resulting in the formation of a dark-red coloured product. Its crystal structure confirmed the expected product, with distorted square-planar geometry (owing to the inclusion of the COD ligand). A separate, yellow coloured product was collected from the same reaction, which showed entirely different NMR signals. Through crystallography, this was determined as an octahedral complex $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{Ir}(\text{Cl})_3(\text{OH}_2)]$ (**20**). The route to this second product is uncertain; its formation from the original product was not observed in CDCl_3 for extended time periods.

Reactions of the N-Triphos^{Cy} ligand with $[\text{Ir}(\text{COD})\text{Cl}]_2$ in methanol showed the presence of multiple $^{31}\text{P}\{^1\text{H}\}$ NMR signals, and the product appeared to be susceptible to degradation by hydrogen peroxide. Changing the solvent to dichloromethane, the $^{31}\text{P}\{^1\text{H}\}$ NMR signals were attributed to a mixture of both bi- and tridentate N-Triphos^{Cy} coordination. Unfortunately, suitable crystals for crystallography could not be grown, so the nature of the third phosphine arm remained uncertain. With N-Triphos^{Ph}, however, full tridentate coordination of the ligand to iridium was observed. This could be attributed to presence of the less bulky PPh_2 moieties.

Finally, reactions with $[\text{Rh}(\text{COD})(\text{MeCN})_2]\text{BF}_4$ were studied. Full coordination of $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ to rhodium was observed, however the rhodium complex was highly air-sensitive, making it difficult to fully characterise. Curiously, its $^{31}\text{P}\{^1\text{H}\}$ NMR signals were observed to change over the course of a few

days in chloroform to a second species. This was determined by crystallography as a tri-chloro bridged rhodium dimer. With N-Triphos^{Cy}, formation of the expected bidentate coordination mode was observed, with a pendant third phosphine arm. Owing to the air-sensitivity of the rhodium complexes, the product was collected without addition of hydrogen peroxide. Again, whilst the expected product was collected, it was found to be highly air-sensitive.

Figure 3.24 summarises the main findings discussed in this chapter. Overall, the coordination chemistry of both the bidentate nitrogen-bridged bisphosphine ligands and the tridentate N-Triphos ligands was most straight-forward with palladium. The reactions proceeded with full reaction progress (as observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy) and their products could be easily worked-up by addition of diethyl ether to the reaction mixtures. Therefore, the catalytic studies described in the next chapter will primarily focus on the use of these palladium catalysts.

Whilst the reactions with ruthenium and iridium were observed to form the expected products, their reactions were not as straight-forward and required more difficult work-up procedures. Furthermore, the use of N-Triphos ligands (which are easier to prepare and handle than the bisphosphine ligands) led to the formation of less well-defined coordination modes; the strategy of oxidising the third phosphine arm to a phosphine oxide did not proceed as smoothly as with palladium. The rhodium complexes were further complicated by their high degree of air-sensitivity.

Overall, it has been demonstrated that the multidentate phosphine ligands described herein are able to form a range of complexes with a series of transition metals, with coordination modes and geometries affected by the ligand denticity; the organic substituents on the phosphine ligands; the choice of metal precursor; and reaction conditions such as the solvent system. It is also evident that there is wide scope for the investigation of a wider range of ligands with different phosphine substituents, and with different transition metals. However, with the intention of developing straight-forward, well-defined, robust catalysts for hydrogenation processes, this work represents a general survey on the coordination chemistry of the lesser-studied nitrogen-centred multiphosphine ligands.

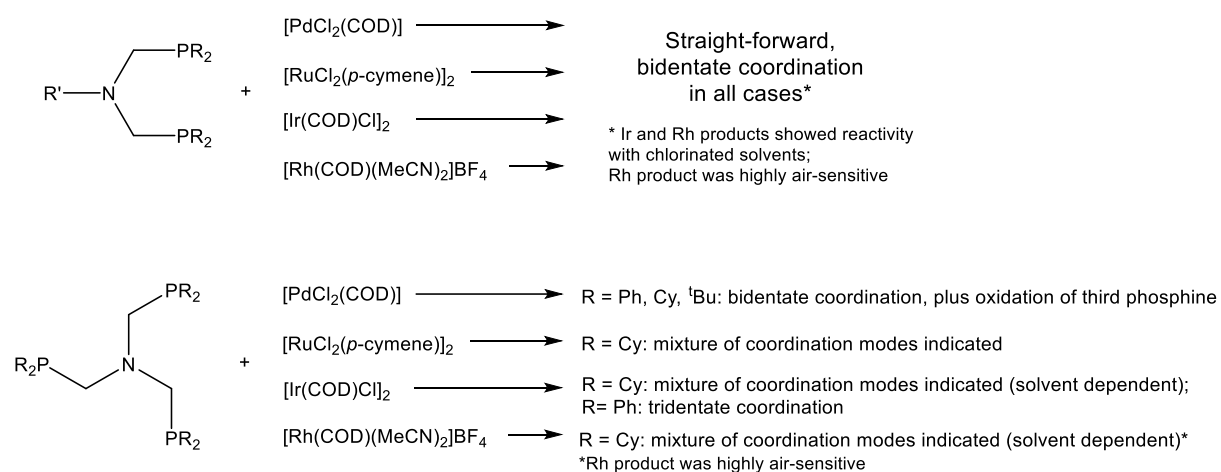


Figure 3.24. Summary of coordination of nitrogen-bridged bisphosphine ligands and N-Triphos ligands with palladium, ruthenium, iridium and rhodium.

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Chapter 4

Transfer hydrogenation of levulinic acid

“Do. Or do not. There is no try”, *Star Wars: The Empire Strikes Back* (1980)

4.1 Introduction

Chapter 1 introduced transfer hydrogenations as an alternative to hydrogenation reactions using high-pressures of hydrogen gas. Several benefits of transfer hydrogenation reactions were highlighted. These include an increased overall safety, reduced operating costs, their simplicity of operation, a wider availability of materials and equipment, better product selectivity, and certain “green chemistry” credentials. Through a combination of these factors, research interest in transfer hydrogenation reactions has significantly increased in recent years. Figure 4.1 shows a graph of the number of references containing the term “transfer hydrogenation” per year. This has increased drastically in the past twenty years. This can be attributed to, at least in part, a global drive towards the development of more sustainable chemical processes. Figure 4.2 shows the number of references to both “transfer hydrogenation” and “biomass”, a field which remains in its infancy. The sharp increase in the number of publications in the past decade highlights the need for processes based upon renewable feedstocks as an alternative to fossil fuel-derived feedstocks.

More specifically, publications referring to both “transfer hydrogenation” and “levulinic acid” have only started to appear within the past decade (Figure 4.3). With levulinic acid (LA) as one of the key highlighted biomass-derived feedstocks (Chapter 1), this is likely to become an increasingly active research field in coming years. Whilst most systems utilise heterogeneous catalysts, Chapter 1 discussed some of the advantages of homogeneously catalysed systems. Many of the complexes described in Chapter 3 are examples of well-defined transition metal complexes of multidentate phosphine ligands. As such, they have the potential for application as homogeneous catalysts for the transfer hydrogenation of LA into γ -Valerolactone (GVL).

4.1.1 Transfer hydrogenation of LA to GVL

The standard reaction scheme used for transfer hydrogenation in this work is shown in Scheme 4.1. Generally, the reactions were performed on a relatively small scale with ~ 3 mmol LA (~ 0.4 mL). The low melting point of LA (30-33 °C) makes it difficult to handle at RT, where it is either a “wet” solid or a viscous liquid. Generally it was easiest to store LA as a solid at 5 °C and weigh it as a solid when required. Owing to the small volumes used, it was found to be most efficient to prepare large volumes of a stock solution of LA and triethylamine from which aliquots could be taken for individual reactions.

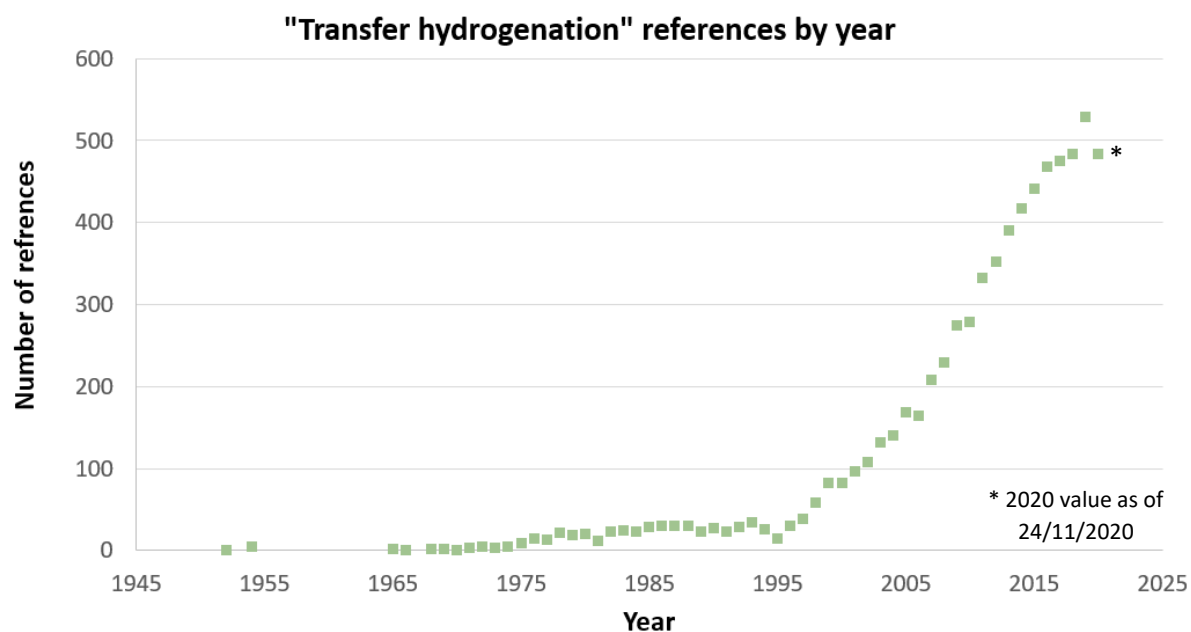


Figure 4.1. Number of references to “transfer hydrogenation” per year.

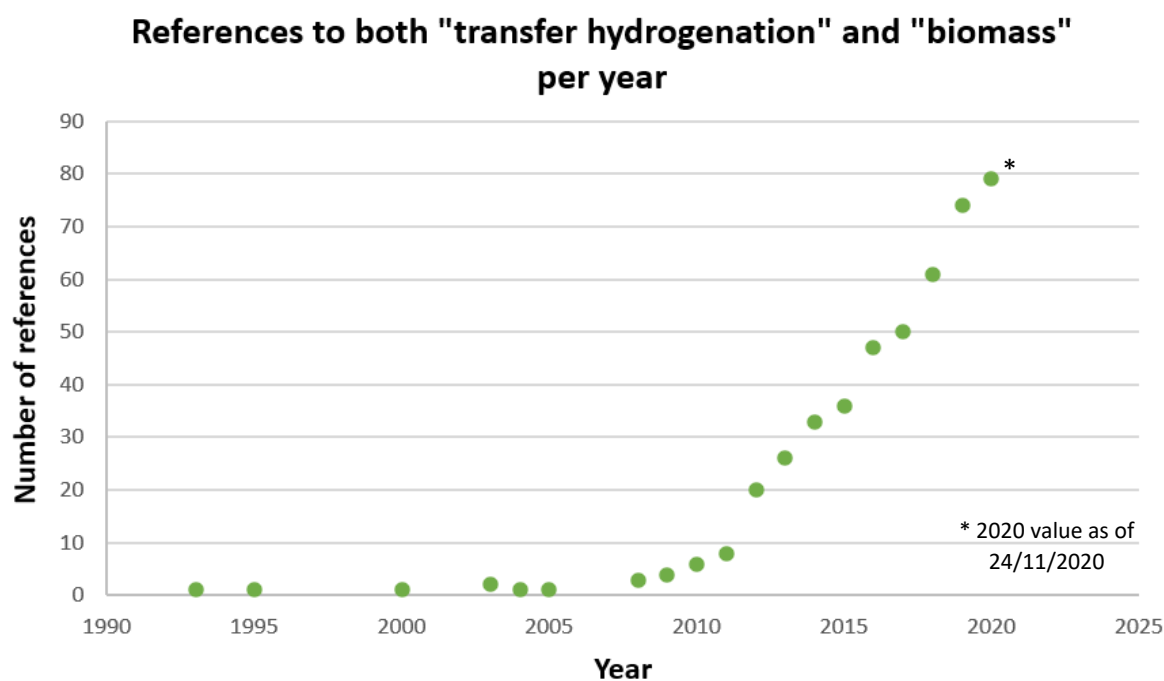


Figure 4.2. Number of references to “transfer hydrogenation” and “biomass” per year.

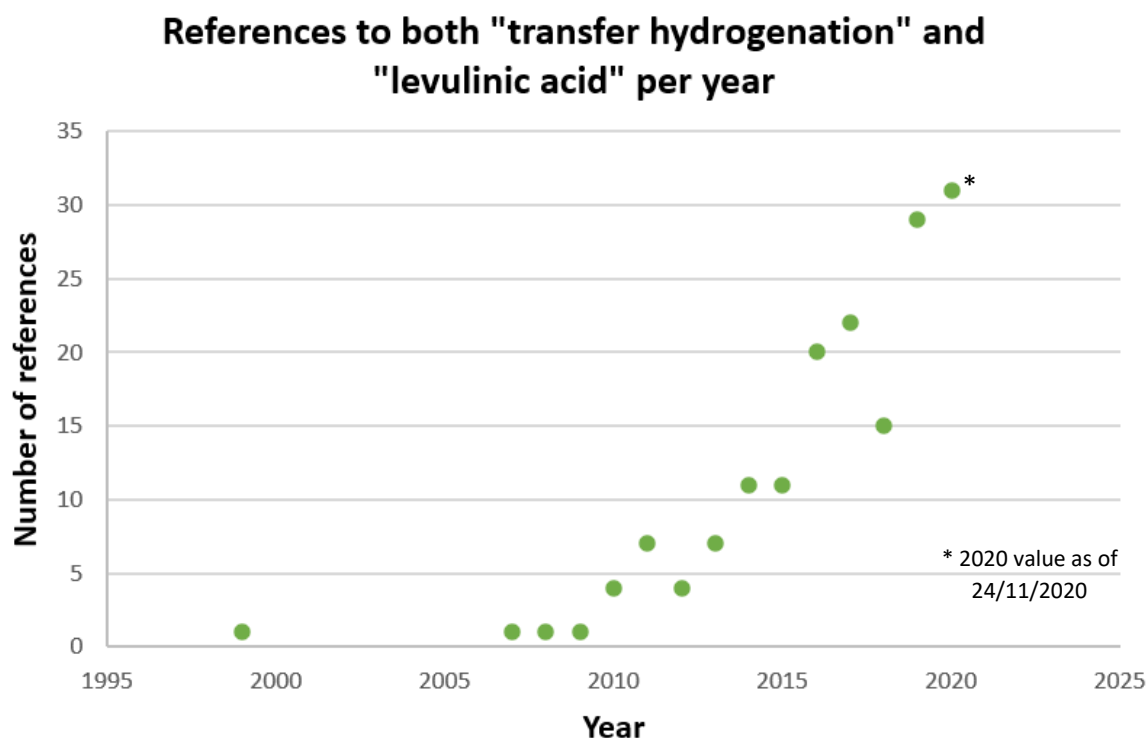
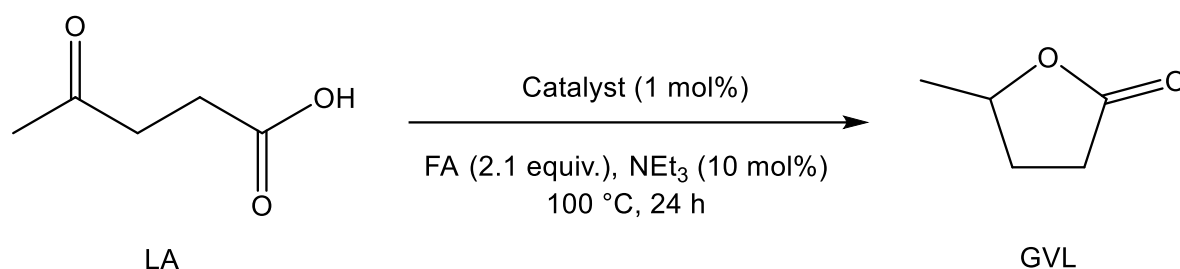


Figure 4.3. Number of references to “transfer hydrogenation” and “levulinic acid” per year.

The standard reaction conditions were adapted from those described by Garcia et al., which were found to be highly effective with their series of palladium catalysts (Chapter 1). Their most successful catalyst used the dtbpe ligand with $P(^i\text{Bu})_2$ substituents; this achieved quantitative hydrogenation of LA to GVL under both transfer hydrogenation and high-pressure conditions. Their PPh_2 and PCy_2 -analogues achieved no LA hydrogenation under transfer hydrogenation conditions, and moderate GVL yields of 9 % and 34 % respectively using hydrogen gas. Nickel analogues of their palladium catalysts showed no activity under the conditions tested. Their reactions were performed in Schlenk tubes fitted with Rotaflo valves, with the addition of 5 mL water as solvent.¹ The next sections will highlight the key components of the transfer hydrogenation system used in this work in turn.

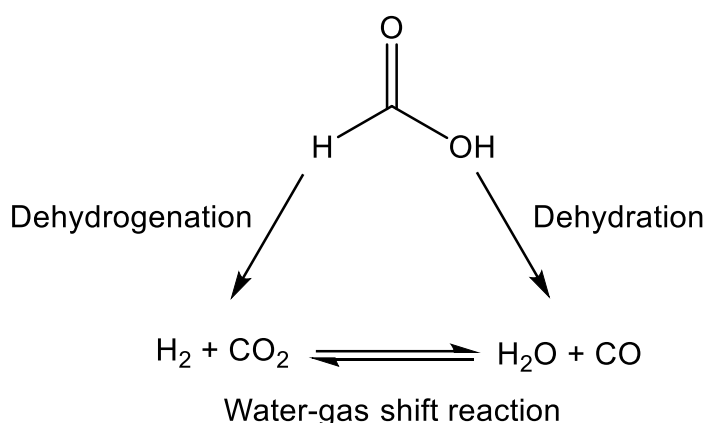


Scheme 4.1. General catalytic procedure used for the transfer hydrogenation of LA to GVL.

4.1.2 Role of formic acid

Formic acid (FA) was chosen as the source of hydrogen. FA is the most commonly used hydrogen source for transfer hydrogenations of LA, as introduced in Chapter 1. The production of LA from cellulose generates equimolar amounts of FA; therefore there is the potential for the FA generated during LA production to be used directly for hydrogenation of LA to GVL, without addition of an external hydrogen source. This can be considered to increase the sustainability of the transfer hydrogenation process. Furthermore, FA decomposes to gaseous products which allows for ready separation from the product. Its boiling point lies just above that of water (100.7 °C). The standard reactions in this work used 2.1 equivalents of FA relative to LA.

There are two possible decomposition routes accessible to FA: dehydrogenation (decarboxylation) to H₂ and CO₂ or dehydration to H₂O and CO. These two sets of decomposition products are linked by the water-gas shift reaction. These reactions are shown in Scheme 4.2.



Scheme 4.2. Decomposition pathways accessible to formic acid.

There are a number of reports on the chemistry of the competing, parallel dehydrogenation and dehydration decomposition pathways of FA. It has become established that in the gaseous phase dehydration is favoured, whilst in the aqueous phase dehydrogenation is favoured. To this end, water has a significant effect on FA decomposition. Studies have found that water acts as a homogeneous catalyst and lowers the activation energies for both dehydrogenation and dehydration, but that the dehydrogenation route becomes more favourable in the presence of water. Water molecules are actively involved in bond-breaking/making.^{2,3}

FA can adopt one of two isomers. In the trans-isomer, the hydrogen atoms are on opposite sides of the C-O bond which facilitates the formation of CO and H₂O. In the cis-isomer, the hydrogen atoms

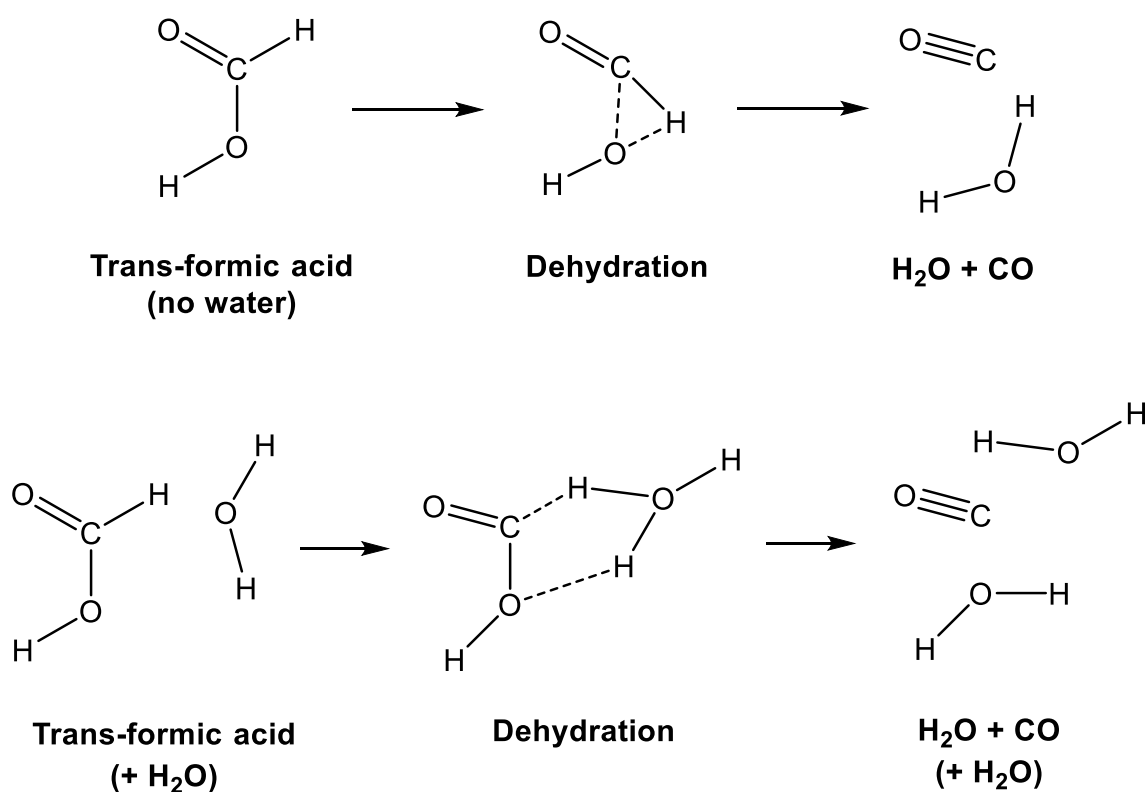
are on the same side of the C-O bond, which facilitates the formation of CO₂ and H₂. Incorporating a molecule of water into either decomposition route does not lead to consumption of the water molecule, but the identity of the atoms in the water molecule is not retained; water is implicitly involved in the nature of the bond-breaking and bond-forming. The decomposition pathways of trans- and cis-formic acid are shown in Schemes 4.3 and 4.4.

Figure 4.4 shows qualitative energy level diagrams for the dehydrogenation and dehydration pathways in the absence and presence of water, adapted from calculations reported in the literature. It can be seen that in the absence of water, the trans-isomer is more stable than the cis-isomer; therefore, in the absence of water the majority of FA can be assumed to adopt the trans-isomeric state. Therefore, the dehydration pathway to form H₂O and CO is favoured. Although the dehydrogenation pathway actually has a lower activation energy than for dehydration, the trans-formic acid must first isomerise to cis-formic acid, so the overall energy difference for dehydrogenation is less favoured.²

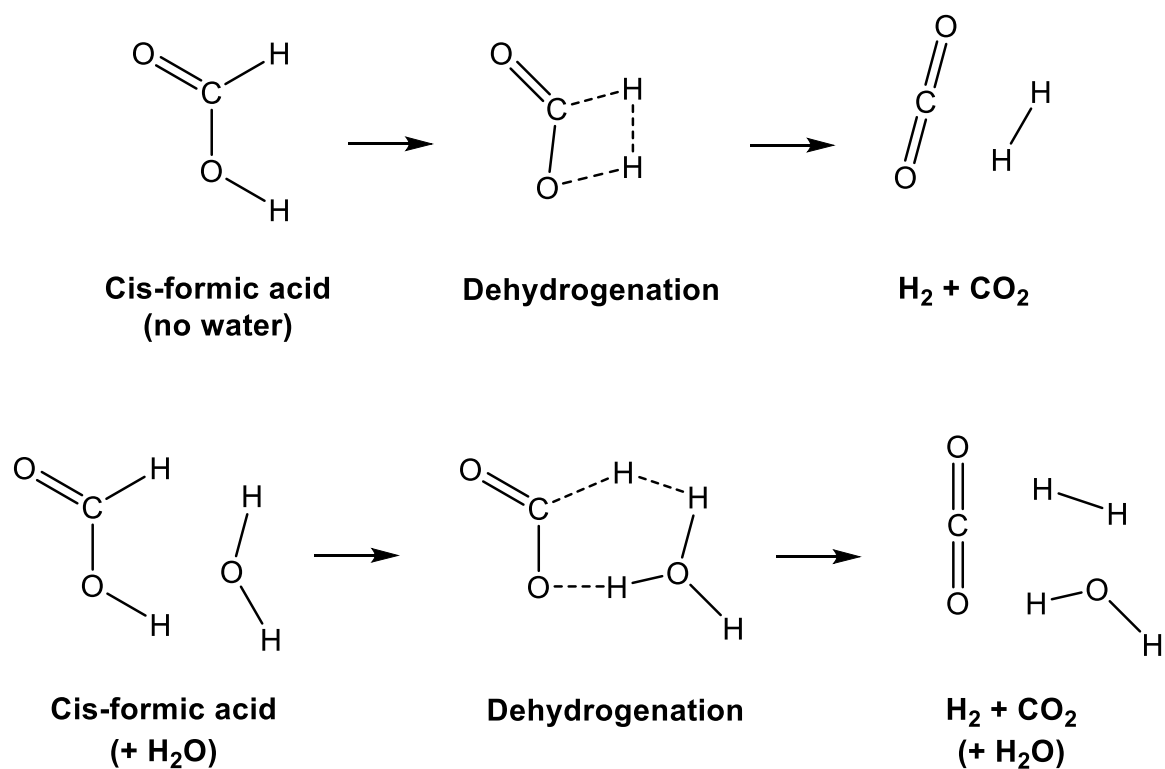
In the presence of water, cis-formic acid is more stable than trans-formic acid. Both activation energies for dehydrogenation and dehydration are lowered relative to the reactions without water; however, the dehydrogenation transition state is now lower in energy than the dehydration transition state, favouring dehydrogenation and the formation of H₂ and CO₂. Whilst a “real” system will involve a large number of configurations, the general trends described above have been found to correspond well with experimental findings.²

4.1.3 Role of base additive

A base additive is commonly included in transfer hydrogenation reactions. In this work, whilst a range of bases were trialled (see Section 4.2.8), triethylamine was found to be the most suitable and effective base. In this context, the main purpose of the triethylamine base is for chloride abstraction from the catalyst (as [HNEt₃]⁺) as the initial step in formation of an active catalyst species.¹ As a liquid base with a relatively high boiling point (88.8 °C), it is compatible with the transfer hydrogenation system. The base is also considered to accelerate the decomposition of FA. Others have found that the catalytic conversion of FA is very slow in the absence of tertiary amine bases, with an increase in FA decomposition achieved with increasing base loading.⁴ The standard reactions in this work used a triethylamine loading of 10 mol% relative to LA.



Scheme 4.3. Dehydration pathways of trans-formic acid.²



Scheme 4.4. Dehydrogenation pathways of cis-formic acid.²

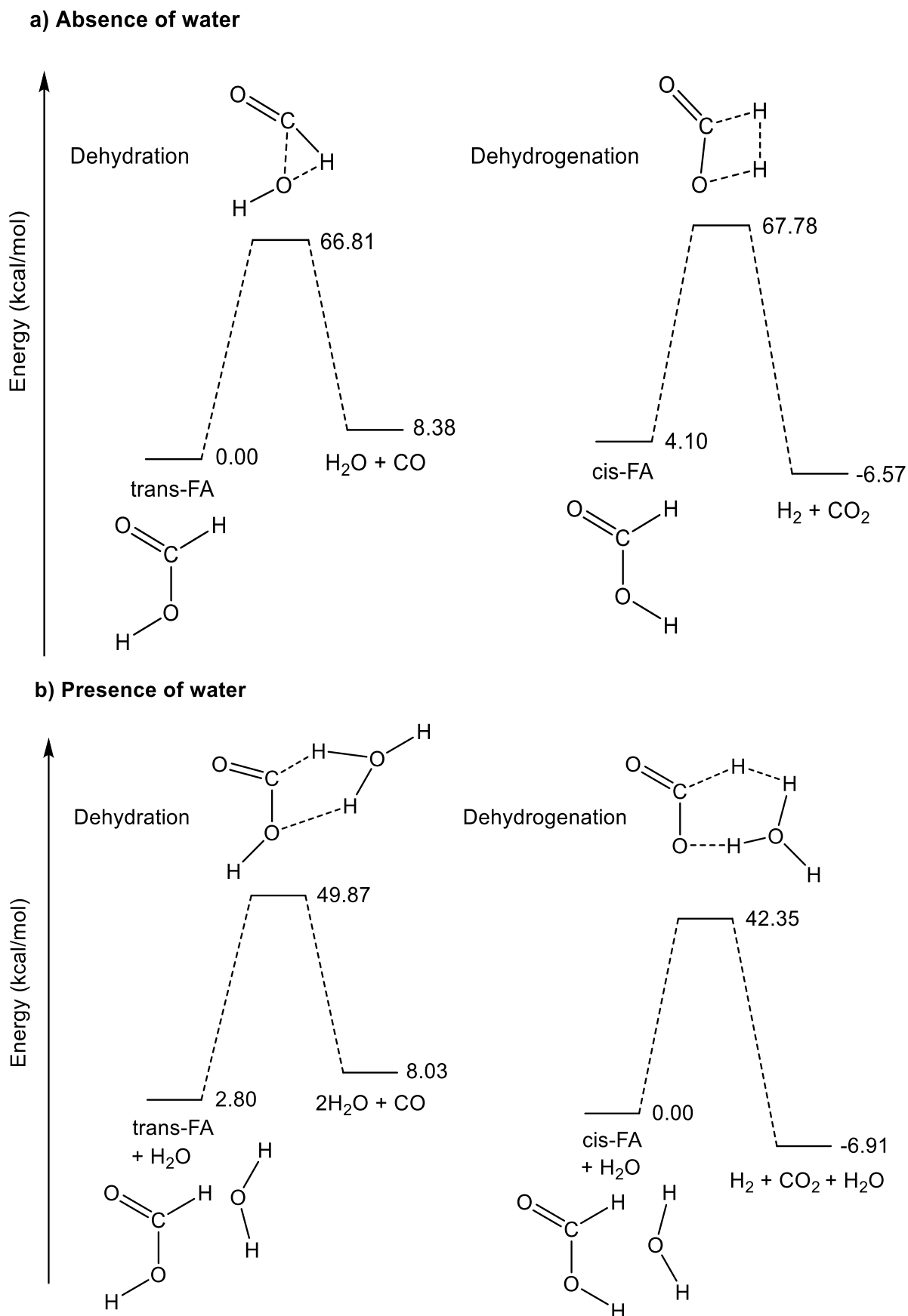


Figure 4.4. Energy level diagrams for FA decomposition in a) the absence of water and b) the presence of water.²

4.1.4 Role of solvent

Whilst the benefits of water with regards to FA decomposition have already been described, the use of water as a solvent has numerous other advantages. It is environmentally benign, non-hazardous, low-cost and widely available. Unfortunately, the catalysts applied in this study have no appreciable water solubility, even at elevated temperatures. An initial solvent scope was investigated and found that in water, no LA hydrogenation was achieved under all conditions trialled. Solvent mixtures of water with either 1,4-dioxane or THF provided small improvements; however any benefit of increasing the proportion of water was quickly outweighed by an increasing catalyst insolubility. Furthermore, all of the alternative solvents trialled (THF, 1,4-dioxane, DMSO, DMF, propan-2-ol) had a strong inhibitory effect on LA hydrogenation. This is potentially attributed to a dilution effect, or to an inhibiting effect of the solvent on, for example, FA dehydrogenation. Therefore, the standard transfer hydrogenation reactions which will be discussed in this Chapter were performed without an additional solvent. The use of solventless, or “neat”, conditions, can be considered as beneficial from a green chemistry perspective. However, this means that most reactions were performed on a particularly small scale (~ 1 mL in total). Although the reaction mixtures were homogeneous, the small reaction scale could be expected to reduce the efficiency of mixing. The lack of a solvent makes further scale-up of the reactions more difficult. The solvent effect will be further discussed in Section 4.5.

4.1.5 Apparatus for transfer hydrogenation reactions

Whilst transfer hydrogenation reactions do not require specialist reactors able to withstand high pressures of hydrogen gases, they nonetheless must be performed in equipment with a suitable pressure tolerance. As introduced in Chapter 1, there is some discussion over the exact mechanisms operating under transfer hydrogenation conditions: whether true inner-sphere or outer-sphere transfer hydrogenation is occurring, or if the hydrogen source is decomposing to hydrogen gas and hydrogenating LA in the traditional manner. There are examples of transfer hydrogenation procedures in the literature which recorded the generation of a significant pressure, attributed to decomposition of the hydrogen source.^{5,6} Regardless of the exact mechanism taking place, at elevated temperatures there will be an increase in pressure through the generation of gases, with each mole of FA potentially forming two moles of gaseous products.

Several set-ups were trialled in this work. Initial reactions were performed in Schlenk tubes (as per Garcia et al.¹), which allowed the reaction mixtures to be prepared under inert conditions and then sealed either with a J Young tap or a subaseal. Whilst this reaction set-up allows for the formation of

a sealed system, and with Schlenk tubes available which can tolerate elevated pressures, in the case of an over-pressure being generated there is no safe means of pressure release. Furthermore, the length of a Schlenk tube introduces difficulties in mixing and an inhomogeneity of the reaction mixtures, especially on the small scales at which these reactions were performed. Also, the use of Schlenk tubes limits the number of reactions which can be performed, as each tube requires its own heating mantle. This is especially limiting during an initial investigation of reaction variables. Preliminary investigations found that using Schlenk tubes for these reactions introduced a high degree of variability in the results collected, especially with regards to the methods of sample preparation. Several “open” systems were also investigated in which the Schlenk tube itself was not completely sealed. This served to avoid the possibility of an over-pressure being generated in the reactions. Similar GVL yields could be obtained given that a nitrogen atmosphere was maintained and that the vessels were closed to the outside environment.

To combat these obstacles, reactions were generally performed in glass reaction vials which fit on a bespoke heating block atop a standard hotplate. This allowed for numerous reactions to be performed in parallel. Initial attempts used vials fitted with simple PTFE/silicone septa caps. The results achieved were lower than expected based upon the Schlenk tube reactions, which was largely attributed to the poor quality of sealed closure provided. The caps were found to be less effective at preventing the loss of reaction gases, maintaining a reaction pressure and controlling the inert atmosphere.

Whilst vials are available which can be sealed with crimped metal lids, again these have no tolerance for an “over-pressure”. Vials fitted with screw-top plastic lids with pressure-relief valves were found to be an effective alternative (Figure 4.5). The pressure-relief valves expand with increasing pressure, up to a designated pressure-limit. In the event of the pressure inside the vial exceeding the pressure tolerance of the pressure-relief valve, the plastic valve itself ruptures open without damage to the lid, glass vial or the reaction mixture itself. Whilst it was not facile to measure the pressures generated inside the reaction vials, the expansion of the pressure-relief valves over the course of a reaction was a visual indication of gas evolution. This is illustrated in Figure 4.6. With this system, any risk of over-pressure to the equipment or user is effectively negated. After allowing the reaction vials to cool to RT, careful unscrewing of the vial lids was accompanied by a small pressure release. This was a further indication of a pressure increase during the transfer hydrogenation reaction and confirmed that the pressure was maintained over the course of the reaction.

The reaction mixtures were prepared inside a vial within a Schlenk tube under nitrogen, to ensure an inert atmosphere. The sealing of the vial by screwing on the lid allowed for the introduction of some

air, but this could be performed under a flow of nitrogen. The effect of an inert atmosphere on the transfer hydrogenation reactions will be discussed in Section 4.2.2.

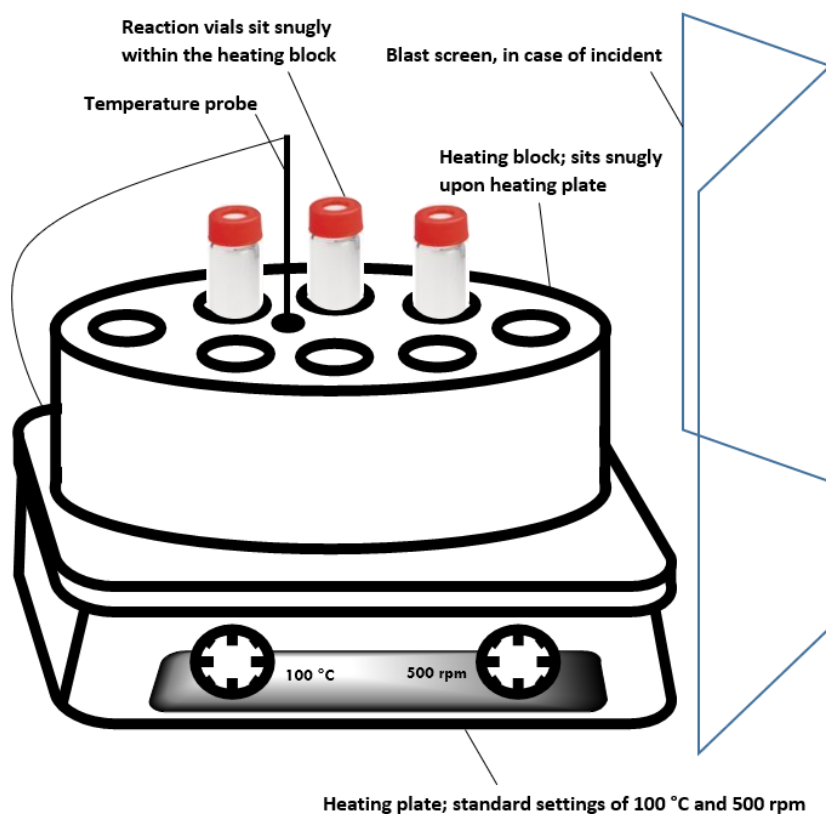


Figure 4.5. An illustration of the transfer hydrogenation reaction set-up with reaction vials.

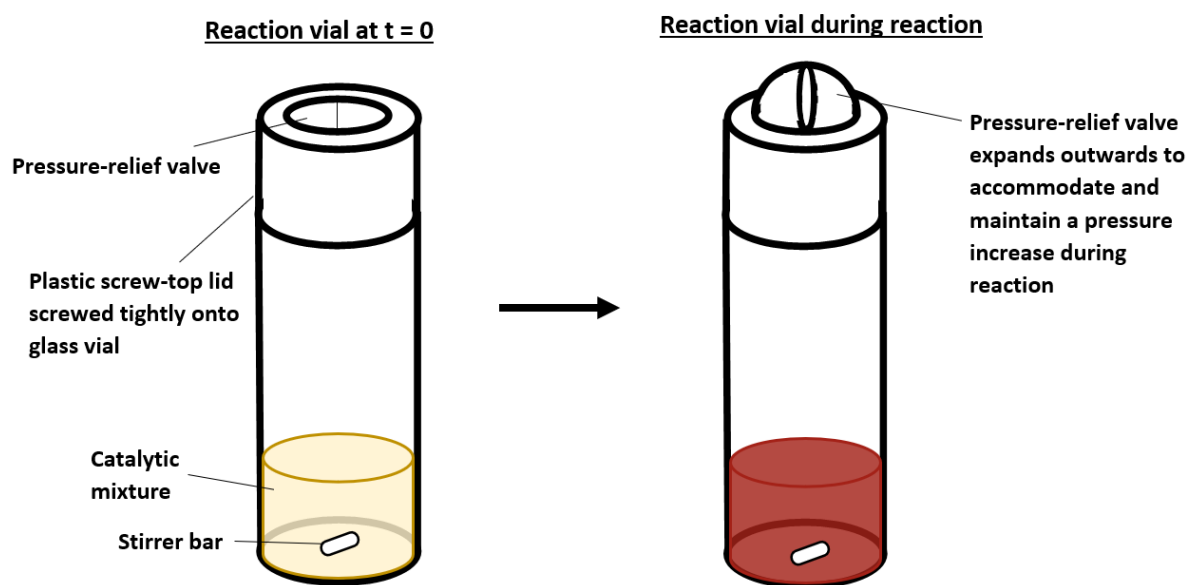


Figure 4.6. An illustration of the reaction vials with pressure-release valves used.

4.1.6 Analysis methods

In the literature, there are two main methods used for analysing the yields of LA hydrogenation reactions. Gas chromatography is the prevalent technique, allowing for the detection and quantification of LA and GVL signals. However, in this context, ^1H NMR spectroscopy can also be used.

Both LA and GVL have four ^1H NMR environments. Most of their ^1H NMR signals are multiplets which appear in similar chemical shift regions (2-3 ppm). However, LA and GVL have a methyl (3H) environment in common with each other. For LA, the methyl signal appears at 2.09 ppm as a singlet (in DMSO- d_6).⁷ For GVL, the methyl signal appears at 1.30 ppm as a doublet ($^3J_{\text{H-H}} = 6.2$ Hz). Their singlet and doublet signals are easy to identify and characterise. Furthermore, their ^1H NMR signals appear at chemical shifts distinct from the remainder of their environments, so that there is no overlap with other signals. This means that the methyl signals can be integrated accurately. The coupling constant of the GVL doublet can be confirmed by comparing to the expected value. A representative ^1H NMR spectrum is shown in Figure 4.7. Given that the methyl signal for both LA and GVL represents three protons (out of a total eight protons for each), the methyl signal can be taken to represent the entire compound. In this way, a percentage yield of GVL can be calculated using the equation shown in Figure 4.8. This assumes that all of the LA present at the start of the reaction had one of two fates: either it remained as unconverted LA, or it was hydrogenated to GVL. This is a valid assumption for LA hydrogenation under transfer hydrogenation conditions, which are generally ineffective for hydrogenation beyond GVL to 1,4-PDO or 2-MTHF. Furthermore, both 1,4-PDO and 2-MTHF have characteristic methyl doublet signals which can be identified by chemical shift and coupling constant in the case of their production.^{8,9} This means that NMR yields of GVL can be calculated for each reaction, given that LA hydrogenation is 100 % selective for GVL.

The other species present in the hydrogenation mixtures do not interfere with the analysis of LA conversion by ^1H NMR spectroscopy. The low catalyst loading does not allow for the observation of catalyst ^1H NMR signals (although $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy was used to study the behaviour of the catalyst). ^1H NMR signals for FA and triethylamine are observed but do not interfere with the LA or GVL signals. The lack of an additional reaction solvent in most of the transfer hydrogenations performed in this study also facilitates analysis without any additional work-up; without dilution by a solvent, the catalytic mixtures themselves provide well defined NMR signals.

Therefore, the use of ^1H NMR spectroscopy is a convenient way to determine GVL yields allowing for facile comparisons between those achieved with different reaction variables. Therefore, it was found to be an effective means of analysis for catalyst screening.

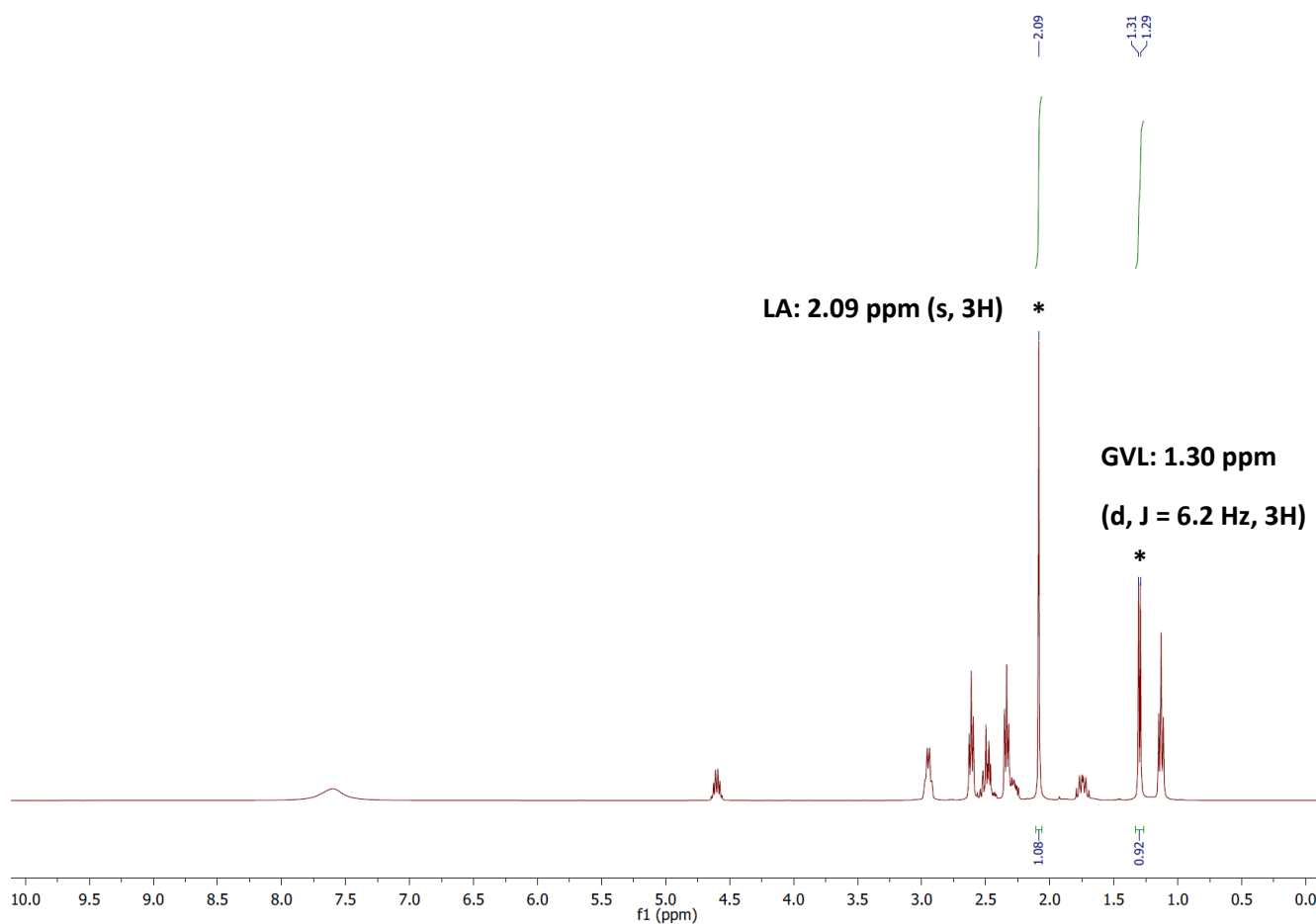
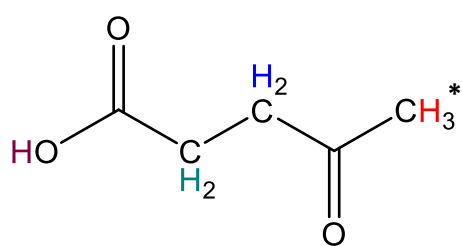
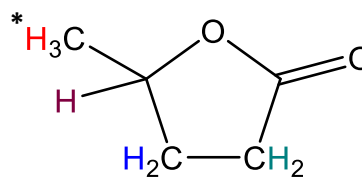


Figure 4.7. Representative ^1H NMR spectrum showing the LA and GVL signals of interest.



Levulinic acid



γ -Valerolactone

$$\text{GVL yield (\%)} = \left(\frac{\text{Integration of GVL methyl signal}}{\text{Integration of GVL methyl signal} + \text{Integration of LA methyl signal}} \right) \times 100$$

Figure 4.8. Analysis of transfer hydrogenation reactions by ^1H NMR spectroscopy.

4.1.7 Scope of catalysts tested

Chapter 3 described the synthesis of a number of complexes formed from a series of different metal centres with both di- and tri-phosphine ligands. Throughout this Chapter, the properties and activities of these complexes as catalysts will be highlighted. Figure 4.9 provides a summary of the catalysts which have been trialled in this body of work and which will be introduced at the appropriate sections within this Chapter. The complexes have been given Catalyst (C) numbering codes as shown in Figure 4.9 to aid facile discussion. The standard reactions in this work used a catalyst loading of 1 mol% relative to LA.

4.2 Transfer hydrogenation experiments

After preliminary experiments using Schlenk tubes or standard screw-top vials, the widest investigation into the transfer hydrogenation of LA to GVL was performed using reaction vials fitted with pressure-relief caps as introduced in 4.1.5. These allowed for the investigation of a wide range of variables which will be discussed in turn in this Section. The standard reactions were performed at 100 °C with a 24-hour reaction time. Reactions were performed in duplicate (or greater), and results are presented in tables as the mean GVL yields as determined by ^1H NMR spectroscopy. Where repeat results showed a disparity of greater than $\pm 7\%$, additional repeats were performed as appropriate.

4.2.1 Type of catalyst

Firstly, a wide catalyst scope was performed with the complexes shown in Figure 4.9. Results are collated in Table 4.1, achieved under the standard reaction conditions outlined in 4.1.1. Catalysts **C1** and **C2**, the palladium complexes of $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ and N-Triphos^{Cy}, achieved very similar GVL yields of 47 and 46 % respectively (Table 4.1, Entries 1-2). This demonstrates that the identity of the substituent at the amine position does not significantly affect the catalytic activity.

The iodo-analogue to **C1**, $\text{Me-N}(\text{CH}_2\text{PCy}_2)\text{PdI}_2$ (**C3**), achieved a reduced 34 % GVL yield (Table 4.1, Entry 3), showing that replacement of the chlorides for iodides has a small inhibitory effect on the conversion achieved. Given that halide abstraction is considered as important for catalyst activation, the greater leaving group ability of iodides might have been expected to facilitate higher GVL yields.

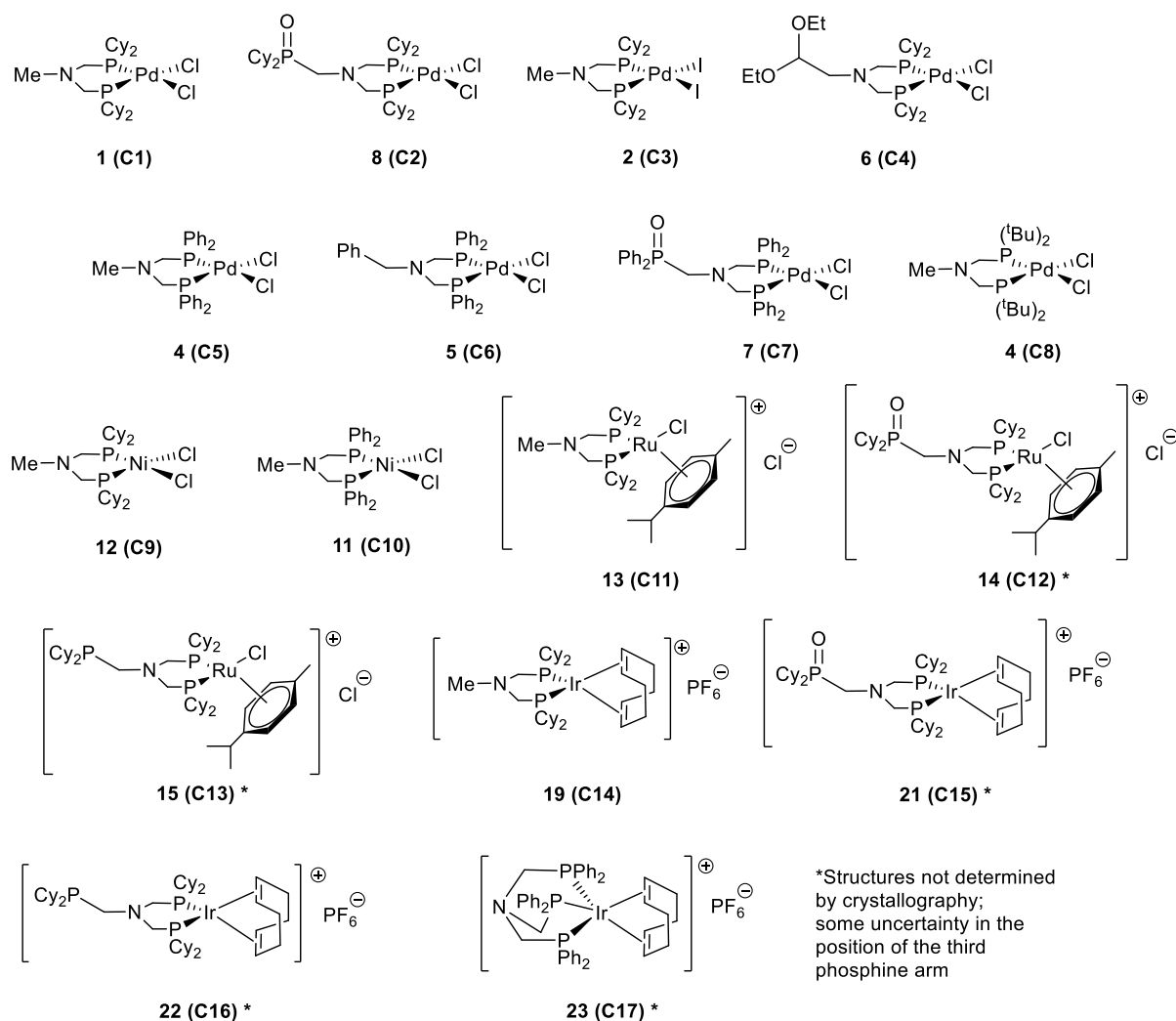


Figure 4.9. A summary of the catalysts **C1** – **C17** trialed in this work.

The inhibitory effect might be attributed to a steric effect, impeding substrate approach, or to poorer solubility, evidenced by more inhomogeneous mixtures.

The PCy₂-catalyst **C4**, containing a CH₂CH(OEt)₂ moiety at the amine position, achieved a GVL yield of 37 %. Further investigation with **C4** will be discussed in Section 4.5.3.

The PPh₂-catalysts **C5-C7** achieved no LA hydrogenation under the standard conditions (Table 4.1, Entries 5-7). This demonstrates the importance of the phosphine substituent. This effect can be attributed to the electron-donating nature of the phosphine substituent, with more electron-donating phosphine substituents generally found to facilitate higher GVL yields. This is supported by the greater

electron-donating nature of cyclohexyl substituents relative to phenyl groups. Therefore, the PPh_2 -palladium complexes **C5-C7** were considered to have no potential for further study.

The $\text{P}(\text{tBu})_2$ -catalyst **C8** was anticipated to have a greater activity than the corresponding PCy_2 and PPh_2 complexes. However, a GVL yield of just 8 % was achieved under the standard conditions (Table 4.1, Entry 8). In the work reported by Garcia et al., their analogous $\text{P}(\text{tBu})_2$ complex showed the highest activity of all, which was attributed to several factors.¹ The greater steric bulk of the $\text{P}(\text{tBu})_2$ moieties was considered to offer a stabilising effect by minimising catalyst decomposition. Furthermore, the greater electron-donating nature of the $\text{P}(\text{tBu})_2$ moieties relative to other PR_2 groups is considered to promote FA decomposition into H_2 .¹⁰ From these factors, replacing **C1** for **C8** was expected to promote the LA hydrogenation. However, the opposite effect was observed.

A black precipitate was observed in the reactions with **C8**, attributed to catalyst decomposition into palladium black. This suggests that there is a decomposition pathway accessible to **C8** that is not available to **C1**. Hydride elimination reactions are commonly described decomposition pathways for transition metal complexes, most commonly α - and β -hydride eliminations. In **C8**, with the phosphorus atoms at the α -positions, there are no α -hydrides. There are β -hydrides at the $\text{N-CH}_2\text{-PR}_2$ site; however, these same hydrides are present in **C1**, with which the same level of decomposition was not observed. In the $\text{P}(\text{tBu})_2$ moieties there are no β -hydrides, however there are γ -hydrides. γ -hydride eliminations are less common than α - and β -hydride eliminations but are encountered, primarily with late transition-metals.¹¹ In **C8**, there are 36 γ -hydrides. **C1** has 16 γ -hydrides (and four β -hydrides from the PCy_2 moieties). Potentially the very high number of γ -hydrides present in **C8** promotes a decomposition pathway involving γ -hydride elimination. Figure 4.10 illustrates several hypothetical γ -hydride pathways.

The nickel complexes **C9** and **C10** were found to have no activity for LA hydrogenation under the standard conditions (Table 4.1, Entries 9-10). It was relatively unsurprising that directly replacing palladium for nickel did not achieve the same activity; however, the development of earth-abundant metal catalysts for these processes is becoming an increasingly active area of research.

C11, the ruthenium complex of $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$, achieved an average 36 % GVL yield, slightly lower than that achieved with the palladium analogue **C1** (Table 4.1, Entry 11). The coordination of $\text{N-Triphos}^{\text{Cy}}$ to ruthenium did not proceed in the straight-forward manner anticipated, with a mixture of coordination modes and levels of oxidation observed. Crystallography failed to elucidate the exact structures of the reaction products (Chapter 3).

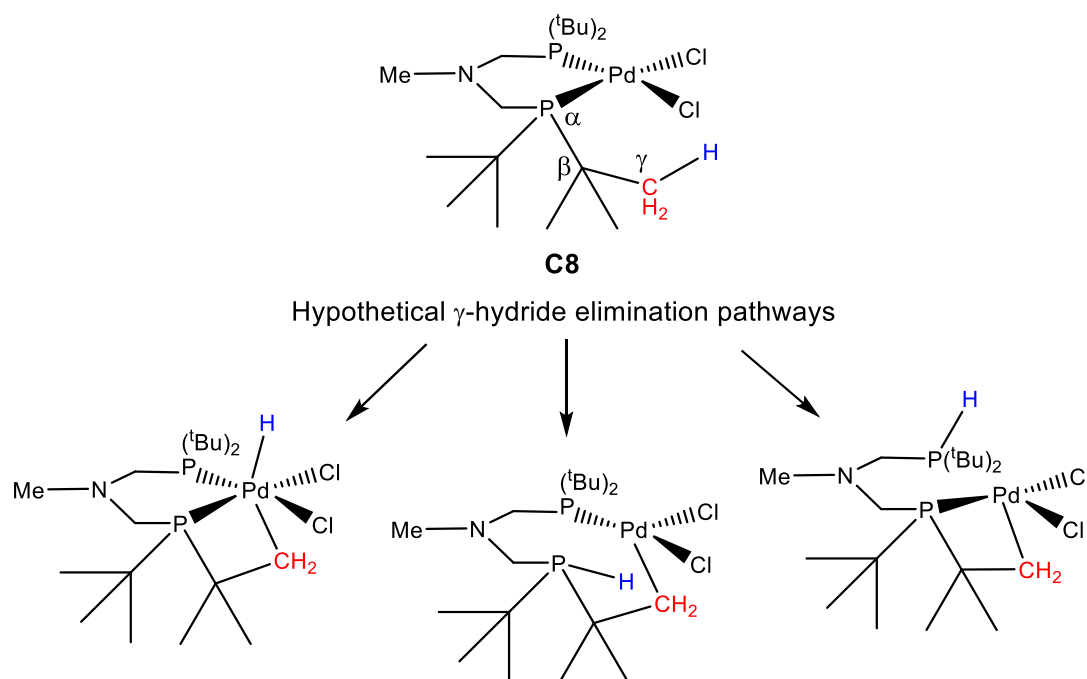


Figure 4.10. Hypothetical γ -hydride pathways accessible to **C8**.

Nonetheless, samples were tested as transfer hydrogenation catalysts: **C12** (in which the third phosphine arm was identified as $P(O)Cy_2$) and **C13** (in which the third phosphine arm was unoxidised). The GVL yields achieved were 34 and 26 % respectively (Table 4.1, Entries 12-13), similar to those achieved with **C11**. The slight reduction in the yields achieved could be attributed to the poorly defined nature of the third phosphine arm and consequently of the complex itself. Regardless, the results demonstrate no catalytic advantage in incorporating the N-Triphos^{Cy} ligand. Owing to the straight-forward coordination of Me-N(CH_2PCy_2)₂ to ruthenium, **C11** is a more promising candidate.

C14, the iridium complex of Me-N(CH_2PCy_2)₂, achieved a GVL yield of 40 % (Table 4.1, Entry 14). This is slightly lower than the yield achieved with the palladium analogue **C1** (47 %), but slightly higher than that achieved with the ruthenium analogue **C11** (36 %). These results show no significant difference in the yields achieved between analogous palladium, ruthenium and iridium complexes.

The coordination chemistry of N-Triphos ligands to iridium was also less straight-forward than expected. The inclusion or omission of hydrogen peroxide generated iridium complexes of N-Triphos^{Cy} where the third phosphine was determined to be oxidised or unoxidised respectively. Unfortunately, crystallographic analysis of these complexes was unsuccessful (Chapter 3). These complexes were also trialled as catalysts for the transfer hydrogenation of LA, as **C15** and **C16** respectively. **C15** achieved

an average 51 % GVL yield, an increase over that achieved with **C14** (40 %) (Table 4.1, Entry 15). Surprisingly, **C16** achieved an average GVL yield of 71 %, the highest yet described (Table 4.1, Entry 16). This suggests that the inclusion and identity of a pendant third phosphine arm can have a significant effect on the yield achieved. A mixture of bi- and tri-dentate coordination modes had been tentatively assigned to **C16**, and perhaps an increased catalyst stability was responsible.

The complex formed through coordination of N-Triphos^{Ph} to iridium could not be characterised by crystallography; however, NMR spectroscopy had indicated tridentate coordination of the ligand to iridium (Chapter 3). **C17** achieved a GVL yield of 43 % under the standard conditions (Table 4.1, Entry 17). Given that the PPh₂-containing palladium complexes **C5-C7** showed no catalytic activity, this result was surprising. This suggests that it is not just the identity of the phosphine substituent itself which determines the activity, but also the denticity of the phosphine ligand and its interaction with the metal centre. Potentially, the coordination of three PPh₂ moieties to iridium sufficiently activates the metal centre for transfer hydrogenation or increases the robustness of the catalyst under transfer hydrogenation conditions.

Table 4.1. Results from investigation into catalyst scope.

Entry	Catalyst	GVL yield (%)
1	C1	47
2	C2	46
3	C3	34 ^a
4	C4	37
5	C5	nd
6	C6	nd
7	C7	nd
8	C8	8
9	C9	nd
10	C10	nd
11	C11	36
12	C12	34
13	C13	26
14	C14	40 ^b
15	C15	51 ^c
16	C16	71
17	C17	43 ^b

*Reactions performed using standard transfer hydrogenation conditions, with levulinic acid (3.4 mmol), the stated catalyst (1 mol%), formic acid (2.1 equivalents) and triethylamine (10 mol%) at 100 °C for 24 hours. Reactions were performed in duplicate and yields were determined by ¹H NMR spectroscopy. nd = not detected. a) Reaction performed on half-scale. b) Reaction performed in triplicate. c) Reaction performed in quadruplicate.

4.2.2 Effect of air-protection

Most of the complexes trialled as TH catalysts showed remarkable similarity, excluding the inactive PPh_2 -complexes **C5-C7**. Generally, the ruthenium complexes gave less impressive yields relative to their palladium and iridium analogues. Whilst some of the iridium complexes achieved the highest GVL yields, there is some degree of uncertainty regarding the exact identity of the complexes based upon N-Triphos ligands. The poorly defined nature of the third phosphine arm appears to introduce a wider-than-expected variety in results. Therefore, the palladium complexes **C1** and **C2** were deemed as the most promising candidates for further work. They show similar activity to each other, demonstrating that the identity of the third arm is not highly significant. The syntheses of **C1** and **C2** are straight-forward and high-yielding and the complexes are well defined. Their initial GVL yields of ~ 50 % with this system showed the most promise for further optimisation.

The effect of air-protection on the GVL yields achieved was studied with **C1**. Results are collated in Table 4.2. The standard reaction set-up prepared the reaction mixture inside a reaction vial sitting inside a Schlenk tube under a nitrogen atmosphere. When all the reaction components had been added, with degassing of the liquid components, the Schlenk tube was opened and the reaction vial was quickly sealed with the screw-top lid. Using this set-up, the average GVL yield of 47 % presented in Section 4.2.1 was achieved (Table 4.2, Entry 1). When no attempts to exclude oxygen from the reaction mixtures were taken, a 48 % GVL yield was achieved (Table 4.2, Entry 2). Therefore, the yield was unchanged with the use of an uncontrolled atmosphere.

This led to two possible conclusions. Either the reactions are not sensitive to air, or the steps taken to exclude air were insufficient. When the original set-up was modified to seal the reaction vessel under a flow of nitrogen provided by a funnel placed above the Schlenk tube, an average GVL yield of 48 % was achieved, demonstrating no further improvement (Table 4.2, Entry 3). One final modification to the reaction set-up was trialled. After preparing the reaction vial within the Schlenk tube, the sealed Schlenk tube itself was transferred into a glovebox where the Schlenk tube was opened and the reaction vial was sealed with a screw-top lid. The sealed vial was then removed from the glovebox directly for the transfer hydrogenation reaction. Using this route, a slightly improved average yield of 54 % was achieved (Table 4.2, Entry 4). This might represent a small improvement with the complete exclusion of air; however, the small improvement was insignificant relative to the inconvenience of using the glovebox. Therefore, most catalytic reactions described in this study maintained the original set-up. Although the reactions appeared to lack sensitivity to air, this was used to maintain consistency throughout the reactions.

Garcia et al. reported that catalyst decomposition was observed when their mixtures were prepared in air. However, with the standard catalyst loading they found no difference in the yield, TON or TOF achieved between reactions using inert or uncontrolled atmospheres. With a reduced catalyst loading of one-third, their yield dropped from 70 % to 27 % when the mixtures were prepared in air. This suggests that the inclusion of air, and subsequent catalyst decomposition, is significant only when there is a relatively low catalyst loading available.¹

Table 4.2. Results from investigation into the effect of air-protection.

Entry	Conditions	GVL yield (%)
1	Sample prepared in Schlenk tube	47
2	No protection from air	48
3	Sample prepared in Schlenk tube and sealed under N ₂ flow	48
4	Sample prepared in Schlenk tube and sealed inside glovebox	54

Reactions performed using standard transfer hydrogenation conditions, with levulinic acid (3.4 mmol), **C1 (1 mol%), formic acid (2.1 equivalents) and triethylamine (10 mol%) at 100 °C for 24 hours. Reactions were performed in duplicate and yields were determined by ¹H NMR spectroscopy.

4.2.3 Effect of in situ catalyst mixtures

C1 and **C2** are made through straight-forward reactions of [PdCl₂(COD)] with Me-N(CH₂PCy₂)₂ and N-Triphos^{Cy} respectively, as described in Chapter 3. However, time and resources would be saved if the synthesis of the complexes could be avoided. Therefore, it was considered that in situ mixtures of [PdCl₂(COD)] and ligand might be a suitable replacement for the preformed catalyst, with the catalyst generated in situ during the hydrogenation reaction. Results from this study are collected in Table 4.3.

First, reactions performed with [PdCl₂(COD)] and [Pd₂I₆](TBA)₂ in the absence of ligand achieved no LA hydrogenation (Table 4.3, Entries 3-4). This shows that the phosphine ligand is a crucial component in attaining catalytic activity. In these reactions there was no observable pressure generated. By ¹H NMR spectroscopy the presence of FA signals indicated no decomposition of FA had occurred. This indicates that heat alone is not sufficient for FA dehydrogenation. Decomposition of [PdCl₂(COD)] to palladium-black was observed.

An in situ mixture of $[\text{PdCl}_2(\text{COD})]$ and $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ achieved a GVL yield of 33 %, down from 47 % achieved with **C1** under the same conditions (Table 4.3, Entry 5). Pressure generation within the reaction vials was observed, hence an in situ catalytic mixture was seen to enable FA decomposition. The reduced conversion achieved with an in situ mixture might be attributed to an incomplete formation of **C1**.

With an in situ mixture of $[\text{PdCl}_2(\text{COD})]$ and N-Triphos^{Cy}, pressure generation was not observed until after several hours, with the expected expansion of the pressure-relief valves not observed until the next day. The delayed pressure generation suggests an inductive period, perhaps attributable to a longer time required for **C2** to form from $[\text{PdCl}_2(\text{COD})]$ and N-Triphos^{Cy}. This also indicates that it is more difficult for **C2** to form in situ than for **C1**, likely attributable to the bulkier coordination sphere of the N-Triphos^{Cy} ligand. After 24 hours, a GVL yield of just 21 % was determined, down from the 46 % achieved with **C2** under the same conditions (Table 4.3, Entry 6). This reveals that in situ catalyst mixtures are not a suitable replacement for the preformed catalysts. Given the observation of an “inductive period”, it might be the case that the activity of the in situ mixtures improves over extended reaction times. However, reaction times of above 24 hours are prohibitively long for these reactions.

Table 4.3. Results from investigation into the use of in situ catalyst mixtures.

Entry	Catalyst	GVL yield (%)
1	C1	47
2	C2	46
3	$[\text{PdCl}_2(\text{COD})]$	nd
4	$[\text{Pd}_2\text{I}_6](\text{TBA})_2$	nd
5	$[\text{PdCl}_2(\text{COD})] + \text{Me-N}(\text{CH}_2\text{PCy}_2)_2$	33
6	$[\text{PdCl}_2(\text{COD})] + \text{N-Triphos}^{\text{Cy}}$	21

*Reactions performed using standard transfer hydrogenation conditions, with levulinic acid (3.4 mmol), the stated catalyst (1 mol%), formic acid (2.1 equivalents) and triethylamine (10 mol%) at 100 °C for 24 hours. Reactions were performed in duplicate and yields were determined by ¹H NMR spectroscopy. nd = not detected.

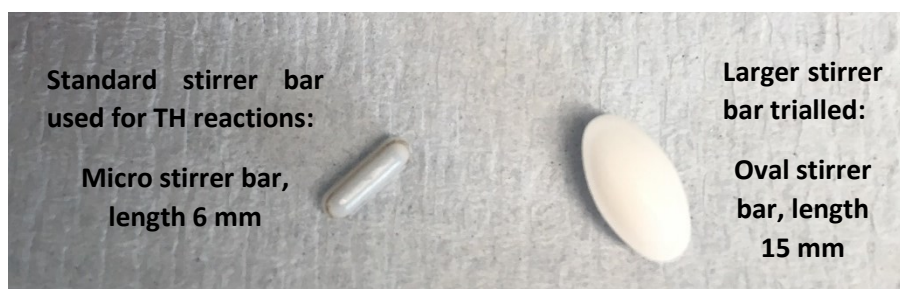


Figure 4.11. Photograph of stirrer bars trialled during TH reactions.

4.2.4 Effect of other system variables

Several changes to the reaction set-up itself were investigated with **C1** and **C2**. These results are collated in Table 4.4.

With **C1**, an overall reduction in the scale of the reaction by $\frac{1}{2}$ had little effect on the yield achieved, with a small change from 47 % to 51 % (Table 4.4, Entries 1-2). Larger scale reactions were not trialled at this point owing to the pressure tolerance of the pressure-relief valves.

The small volumes of the reaction mixtures raised concerns over their mixing efficiency. Generally, the reactions used the smallest available stirrer bar (micro stirrer bar, length: 6 mm (Figure 4.11)). Concerned that this limited the efficacy of the mixing, a larger stirrer bar was trialled (oval stirrer bar, length: 15 mm (Figure 4.11)). Comparing otherwise equivalent reactions with **C2**, yields of 40 and 37 % were achieved with the “small” and “large” stirrer bars respectively, justifying the use of the smallest stirrer bar as appropriate for the reaction volume (Table 4.4, Entries 3-4). The flat-bottomed vials might also be considered as a barrier to highly efficient mixing; using round-bottomed vials instead might be an alternative route to improve this.

Generally the reaction mixtures were prepared by initial addition of the solid catalyst to the reaction vial, followed by degassing and filling the vial with an atmosphere of nitrogen. Then, a stock solution of LA/ NEt_3 was added, followed by FA. To confirm that the order of addition does not affect the conversion achieved, the order of addition was switched (FA, then LA/ NEt_3). This achieved a 40 % yield with **C2** in 4 hours, in line with that achieved under the same conditions with the standard order of addition (Table 4.4, Entries 5-6).

Table 4.4. Results from investigation into further system variables.

Entry	Conditions	GVL yield (%)
1	Standard scale	47 ^a
2	Half-scale	51 ^a
3	Standard stirrer bar	40 ^{bc}
4	Larger stirrer bar	37 ^{bc}
5	LA/ NEt_3 , then FA	40 ^{bc}
6	FA, then LA/ NEt_3	40 ^{bc}

*Reactions performed using standard transfer hydrogenation conditions, with levulinic acid (3.4 mmol), the stated catalyst (1 mol%), formic acid (2.1 equivalents) and triethylamine (10 mol%) at 100 °C for 24 hours. Reactions were performed in duplicate and yields were determined by ^1H NMR spectroscopy. a) With **C1**. b) With **C2**. c) Reaction time of 4 hours.

4.2.5 Catalyst loading

The effect of catalyst loading was trialled with **C1**, recognising that this is an important consideration with precious metal catalysts. These results are collated in Table 4.5. Reducing the catalyst loading from 1 mol% to 0.5 mol% reduced the average GVL yield achieved only from 47 % to 41 %, indicating that the reactions proceed almost as well with half the catalyst loading (Table 4.5, Entries 1-2). Whilst a 1 mol% loading continued to be used for optimisation of the catalyst system, a lower catalyst loading would perhaps make the reactions more widely applicable.

Surprisingly, doubling the catalyst loading to 2 mol% had a small negative effect, achieving an average 42 % GVL yield (Table 4.15, Entry 3). The variation is likely within the experimental error of these methods. The results suggest that at 1 mol% there is already a maximum amount of catalyst effective for this reaction. This might be attributed to catalyst saturation, with the mixtures observed to be thicker and less homogeneous with a higher catalyst loading. Again, this might be an issue with catalyst solubility, complicated by the lack of a bulk solvent.

Table 4.5. Results from investigation into the effect of catalyst loading.

Entry	Conditions	GVL yield (%)
1	Standard loading (1 mol%)	47
2	Half-loading (0.5 mol%)	41
3	Double-loading (2 mol%)	42

*Reactions performed using standard transfer hydrogenation conditions, with levulinic acid (3.4 mmol), **C1**, formic acid (2.1 equivalents) and triethylamine (10 mol%) at 100 °C for 24 hours. Reactions were performed in duplicate and yields were determined by ¹H NMR spectroscopy.

4.2.6 Loading of formic acid

The effect of FA loading was investigated with both **C1** and **C2**, with results collected in Table 4.6. Reactions which doubled the FA loading were performed on an overall reduction of reaction scale to ½, given the pressure tolerance of the reaction vials. Section 4.2.4 illustrated that a change of reaction scale did not have a significant effect on the LA hydrogenation. With a doubled FA loading (from 2.1 equivalents to 4.2 equivalents) and with **C1** and **C2**, GVL yields of 42 and 47 % were achieved (Table 4.16, Entries 2-3). Therefore, the addition of further FA is not beneficial and the original results were not limited by a lack of FA. With an increased loading of FA, there is a greater availability of its

decomposition products. In the absence of water, it is understood that FA primarily decomposes to CO and H₂O. Therefore, there is the potential for catalyst poisoning by the increased presence of these decomposition products (this will be discussed further in Section 4.4).

With a reduction in FA loading by ½ (from 2.1 equivalents to one equivalent), GVL yields of 35 and 33 % were obtained with **C1** and **C2** respectively (Table 4.6, Entries 4-5). A decrease in yield was expected with a reduction in the hydrogen source; therefore, the use of 2.1 equivalents of FA is warranted.

Table 4.6. Results from investigation into the effect of loading of formic acid.

Entry	Catalyst	FA loading	GVL yield (%)
1	C1	Standard FA loading (2.1 equivalents)	48
2	C1	2 x FA loading (4.2 eq.)	42 ^a
3	C2	2 x FA loading (4.2 eq.)	47 ^{ab}
4	C1	½ x FA loading (1 eq.)	35 ^b
5	C2	½ x FA loading (1 eq.)	33

*Reactions performed using standard transfer hydrogenation conditions, with levulinic acid (3.4 mmol), the stated catalyst (1 mol%), formic acid and triethylamine (10 mol%) at 100 °C for 24 hours. Reactions were performed in duplicate and yields were determined by ¹H NMR spectroscopy. a) Reactions performed on half-scale. b) Reactions performed in triplicate.

4.2.7 Base loading

Next, both **C1** and **C2** were used to study the effect of base loading, with results collected in Table 4.7. A doubling of NEt₃ loading (from 10 mol% to 20 mol%) had a small, negative effect with both catalysts, with GVL yields of 39 % and 38 % achieved respectively (Table 4.7, Entries 3-4). The main role of triethylamine is to aid chloride abstraction by [HNEt₃]⁺. Clearly, this is not improved with addition of further triethylamine. Potentially, the presence of additional triethylamine facilitates excess chloride abstraction, perhaps favouring the formation of an inactive catalyst species (this will be discussed further in Section 4.4). Triethylamine is also considered to accelerate FA decomposition. As per the study of FA loading in 4.2.6, if additional triethylamine causes additional FA dehydration to CO and H₂O, this might have a negative effect on the reaction.

Reducing the triethylamine loading from 10 mol% to 5 mol% had a small, positive effect, with GVL yields of 52 and 53 % found for **C1** and **C2** respectively (Table 4.7, Entries 5-6). Very similar conversions

were found with a further reduction triethylamine loading to a quarter (2.5 mol%), of 54 and 52 % respectively (Table 4.7, Entries 7-8). This indicates that triethylamine loadings of less than 10 mol% are sufficient for it to fulfil its role in chloride abstraction. This might affirm that “excess” triethylamine has a negative effect, potentially in catalyst deactivation.

Omitting triethylamine entirely achieved GVL yields of just 7 and 3 % with **C1** and **C2** respectively (Table 4.7, Entries 9-10). The low conversions achieved illustrate the necessity of including a base. However, the non-zero yields achieved indicate that a small extent of chloride abstraction is achieved even in the absence of a base.

Table 4.7. Results from investigation into the effect of base loading.

Entry	Catalyst	NEt ₃ loading	GVL yield (%)
1	C1	10 mol %	47
2	C2	10 mol %	46
3	C1	20 mol %	39
4	C2	20 mol %	38
5	C1	5 mol %	52
6	C2	5 mol %	53 ^a
7	C1	2.5 mol%	54 ^a
8	C2	2.5 mol%	52
9	C1	-	7
10	C2	-	3

*Reactions performed using standard transfer hydrogenation conditions, with levulinic acid (3.4 mmol), the stated catalyst (1 mol%), formic acid (2.1 equivalents) and triethylamine at 100 °C for 24 hours. Reactions were performed in duplicate and yields were determined by ¹H NMR spectroscopy. a) Reactions performed in triplicate.

4.2.8 Base screening

A wider base scope was investigated with **C1**, with results collected in Table 4.8. The standard 48 % yield achieved with triethylamine was used for a comparison. The GVL yields achieved with the different bases can be summarised as: K₃PO₄ > K₂CO₃ > NEt₃ > sodium formate > DIPEA > pyridine > sodium bicarbonate > KOH ~ imidazole > DBU.

It is not facile to elucidate trends based on the efficacy of the individual bases. Grouping the nitrogen-centered amines shows a range of yields from DBU (31 %) to NEt₃ (48 %). The solid bases gave yields in the range of 34 % (imidazole, potassium hydroxide) to 64 % (K₃PO₄), and the liquid bases give yields in the range of 31 % (DBU) to 48 % (NEt₃). The slightly higher yields achieved with K₂CO₃ and K₃PO₄ might be attributed to their dibasic and tribasic nature respectively. The GVL yield generally increases

with decreasing pK_b (increasing base strength) but there are strong outliers to this trend. Table 4.9 collates the base strengths with the yields achieved, and a summary is shown in Figure 4.12. DBU and KOH are the strongest bases but give some of the lowest GVL yields. Sodium formate is the weakest of the bases trialled but gives a moderate GVL yield of 46 %. A similar trend was found by Fischmeister et al., who investigated a base scope consisting of sodium formate, K_2CO_3 , NEt_3 , $(iPr)_2NH$ and K_3PO_4 . There was a rough correlation between increasing base strength and increasing LA hydrogenation. However, the strong base $(iPr)_2NH$ gave a conversion of just 30 %.¹² Therefore, base strength can be used as a general guide to the resulting GVL yield but there are several large exceptions.

With sodium formate, the reaction was initially performed on a half-scale in case of an excess pressure build-up. Although a GVL yield of 54 % was determined, the reaction mixture was very inhomogeneous and only a small pressure was generated. Repeating the reaction on the standard scale achieved a reduced yield of 46 %, despite an observed increase in the generated pressure and homogeneity.

Although the use of both K_3PO_4 and K_2CO_3 facilitated higher GVL yields than with triethylamine, the solid bases resulted in less homogeneous reaction mixtures which were more difficult to work with. For example, the mixtures had to be filtered to remove the solid base prior to analysis by NMR spectroscopy.

Table 4.8. Results from investigation into the effect of different bases.

Entry	Base	GVL yield (%)
1	NEt_3	48
2	Pyridine	36 ^a
3	DIPEA	42 ^a
4	K_2CO_3	56
5	K_3PO_4	64
6	DBU	31
7	$NaHCO_3$	35
8	Imidazole	34
9	KOH	34
10	Sodium formate	54 ^b
11	Sodium formate	46

*Reactions performed using standard transfer hydrogenation conditions, with levulinic acid (3.4 mmol), **C1** (1 mol%), formic acid (2.1 equivalents) and the stated base (10 mol%) at 100 °C for 24 hours. Reactions were performed in duplicate and yields determined by ^1H NMR spectroscopy. a) Reactions performed in triplicate. b) Reaction performed on half-scale.

Table 4.9. Comparison of base strength to GVL yield achieved.

Base	pKa of conjugate acid (in water)	pKb	GVL yield (%)
Sodium formate	3.77	10.23 (<i>Weakest base</i>)	(54)/46 *
Pyridine	5.25	8.75	36
Sodium hydrogen carbonate	6.3	7.7	35
Imidazole	6.95	7.05	34
DIPEA	8.5*	5.5*	42
Potassium carbonate	10.25	3.75	56
Triethylamine	10.75	3.25	48
Potassium phosphate, tribasic	12.32	1.68	64
DBU	13.5	0.5 (<i>Strongest base</i>)	31
Potassium hydroxide	13.5	0.5 (<i>Strongest base</i>)	34

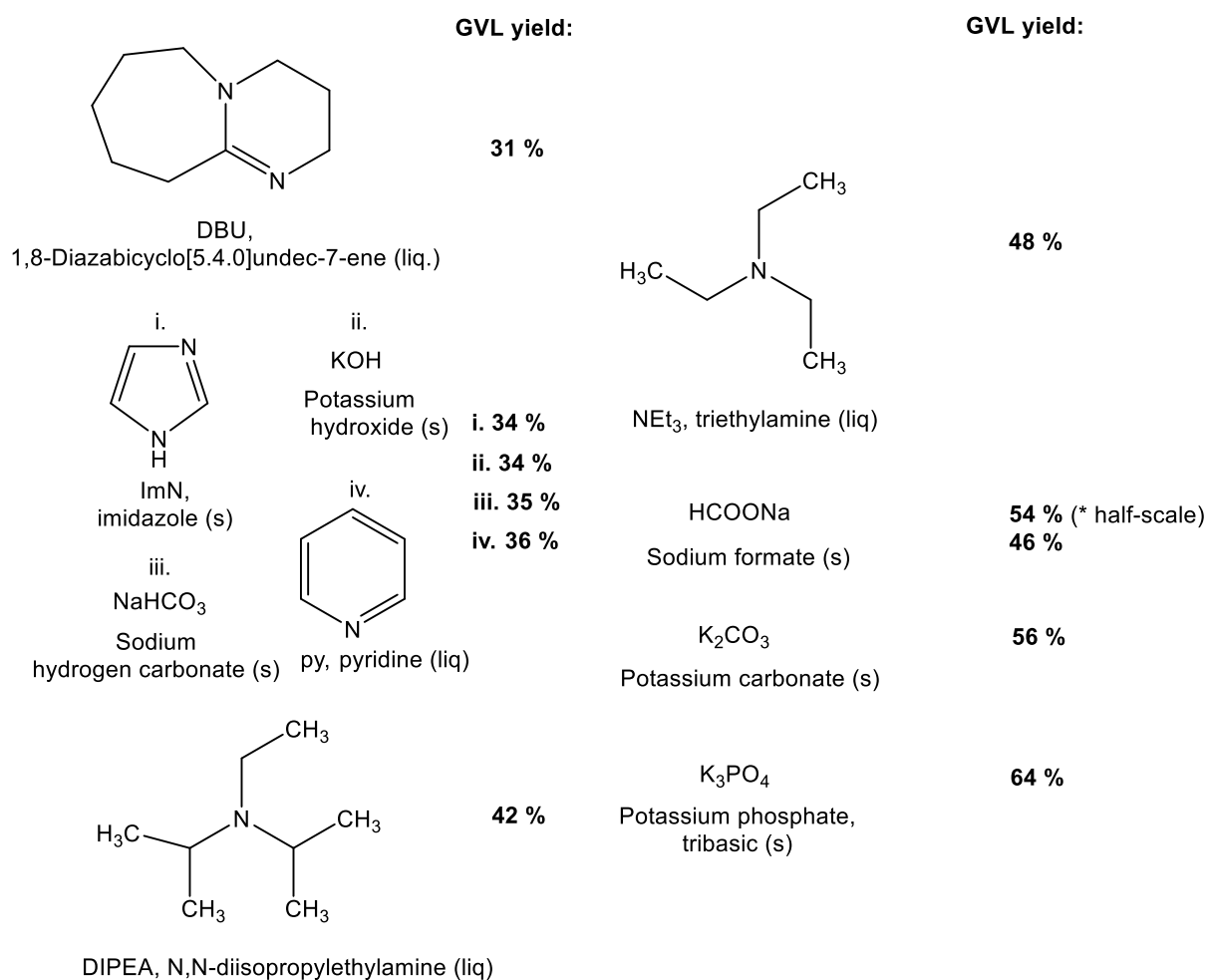


Figure 4.12. Summary of base scope trialled.

4.2.9 Temperature

The effect of reaction temperature was investigated with both **C1** and **C2**. Results are collated in Table 4.10. Whilst temperatures above 100 °C would generally be expected to promote the yields achieved, the use of elevated temperatures would generate unsuitable pressures for the current set-up. Instead, comparisons between temperatures of 80 and 100 °C were made. (An investigation into temperatures above 100 °C will be described in Section 4.6.1). At 100 °C, **C1** achieved 43 % GVL in 4 hours, which increased to 47 % at 24 hours (Table 4.10, Entries 3-4).

Reducing the temperature to 80 °C gave a slightly reduced yield of 37 % within four hours (Table 4.10, Entry 1). However, over 24 hours at 80 °C the final yield of 48 % matched that at 100 °C (Table 4.10, Entry 2). This suggests that the reaction profile is slightly faster at 100 °C compared to 80 °C, but the maximum yields achieved at both temperatures are very similar.

With **C2** at 100 °C, a yield of 40 % at four hours increased to 46 % at 24 hours (Table 4.10, Entries 7-8). Again, this shows that most of the LA hydrogenation occurs in the first four hours. However, at 80 °C the findings were very different. In four hours, just a 10 % yield was achieved (Table 4.10, Entry 5). However, this increased to 50 % over 24 hours (Table 4.10, Entry 6). Therefore, 80 °C is again sufficient to reach the same maximum yield. However, almost no hydrogenation was achieved in the first four hours, meaning that the reaction is much slower with **C2** at 80 °C compared to **C1**. At 80 °C, poor catalyst dissolution was observed within four hours. However, the mixtures were more homogeneous in the 24-hour experiments, suggesting that the low yields achieved within four hours might be attributable to catalyst insolubility. With longer reaction times, dissolution improved allowing for maximum yields to be achieved. Figure 4.13 shows a graph collating the results described in this section.

Table 4.10. Results from investigation into the effect of temperature.

Entry	Catalyst	Temperature (°C)	Time (h)	GVL yield (%)
1	C1	80	4	37
2	C1	80	24	48
3	C1	100	4	43
4	C1	100	24	47
5	C2	80	4	10
6	C2	80	24	50
7	C2	100	4	40
8	C2	100	24	46

*Reactions performed using standard transfer hydrogenation conditions, with levulinic acid (3.4 mmol), the stated catalyst (1 mol%), formic acid (2.1 equivalents) and triethylamine (10 mol%) at the stated temperature for the stated time. Reactions were performed in duplicate and yields were determined by ¹H NMR spectroscopy.

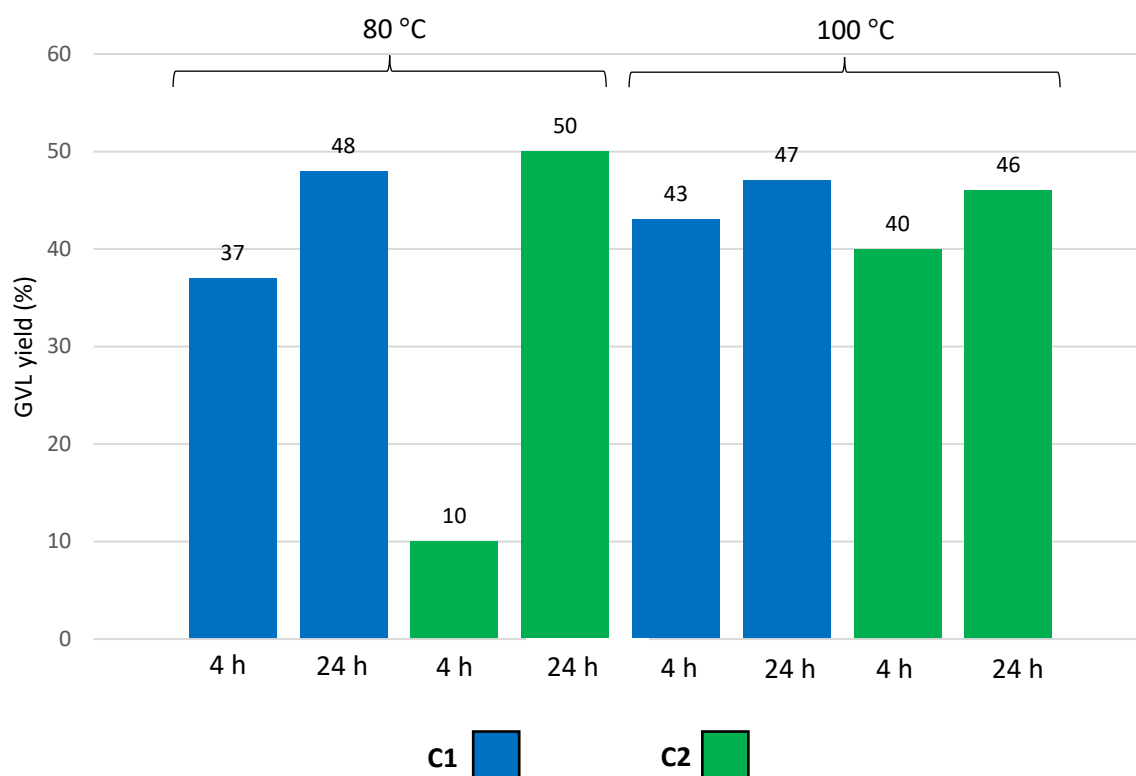


Figure 4.13. Graphs showing GVL yields achieved at 80 °C and 100 °C with **C1** and **C2**.

4.2.10 Reaction time

An attempt to further study the reaction profile over time was performed with **C2**, with results collated in Table 4.11. Under the standard conditions, it has already been described that **C2** reaches an average GVL yield of 46 % in 24 hours. With the same conditions, an average yield of 31 % was achieved within one hour (Table 4.11, Entry 1). Therefore, the majority of LA hydrogenation occurs within the first hour. After two hours, an average yield of 40 % was achieved (Table 4.11, Entry 2).

Therefore, within just two hours, the reaction approaches the maximum yield achieved in 24 hours. At four hours, the same average yield of 40 % was found, indicating that after the initial two hours, additional hydrogenation occurs at a far slower rate (Table 4.11, Entry 3). Extending the reaction time to 48 hours provided no benefit with an average yield of 42 % (Table 4.11, Entry 5). With **C1**, an average GVL yield of 43 % was obtained after four hours, close to the 47 % yield achieved after 24 hours (Table 4.11, Entries 6-7).

There are several possible explanations for the lack of catalytic activity after the first two hours. Potentially the catalyst is decomposing or converting to an inactive form within the first two hours, so that there is little or no active catalyst remaining beyond this time. Alternatively, there is insufficient FA (and/or hydrogen gas) remaining after this time for additional hydrogenation. However, the standard reaction set-up uses 2.1 equivalents of FA, therefore there should be sufficient FA for each molecule of LA to be hydrogenated twice. Therefore, FA might not be in a useful form for hydrogenation to occur. In the absence of water, FA dehydration is considered to dominate over dehydrogenation. Therefore, if FA decomposes entirely within a short time (into predominantly CO and H₂O), then there might be little available H₂ for further hydrogenation.

Although it was disappointing that extending the reaction time did not allow higher yields to be accessed, the fact that near-maximum conversions are achieved within just two hours greatly improves the applicability of these reactions, compared to a 24-hour reaction time.

Garcia et al. achieved quantitative LA hydrogenation within one hour. Therefore, the difference in behaviour between the two systems within the first hour is critical. Given that the major difference between the two systems is the presence or absence of water, and given the established effect of water on FA decomposition, it appeared that this is a critical factor that needed to be investigated.¹

Table 4.11. Results from investigation into different reaction times.

Entry	Catalyst	Time (h)	GVL yield (%)
1	C2	1	31
2	C2	2	40
3	C2	4	40
4	C2	24	46
5	C2	48	42
6	C1	4	43
7	C1	24	47

*Reactions performed using standard transfer hydrogenation conditions, with levulinic acid (3.4 mmol), the stated catalyst (1 mol%), formic acid (2.1 equivalents) and triethylamine (10 mol%) at 100 °C for the stated time. Reactions were performed in duplicate and yields were determined by ¹H NMR spectroscopy.

4.2.11 Alternative substrates

The experiments described in this section were performed by BSc. students Madeleine Hardstaff (MH) and Lu Lu (LL) under supervision.^{13,14}

Ethyl levulinate (EL) is the ethyl ester of LA. Like LA, EL is a colourless liquid with a low melting point of 25 °C. Its primary hydrogenation product is GVL, obtained with the elimination of ethanol via ethyl 4-hydroxypentanoate. Analogous transfer hydrogenation reactions were performed using EL as the substrate (Table 4.12). In every case, the GVL yields achieved were lower than the corresponding yields achieved from LA. With **C1**, a maximum GVL yield of 28 % was achieved after four hours, with no improvement over longer times (Table 4.12, Entries 1-4). **C2** achieved a maximum GVL yield of just 17 % from EL (Table 4.12, Entries 5-6). Trialling **C5**, **C8** or in situ catalyst mixtures achieved near-zero yields in all cases (Table 4.12, Entries 7-13).

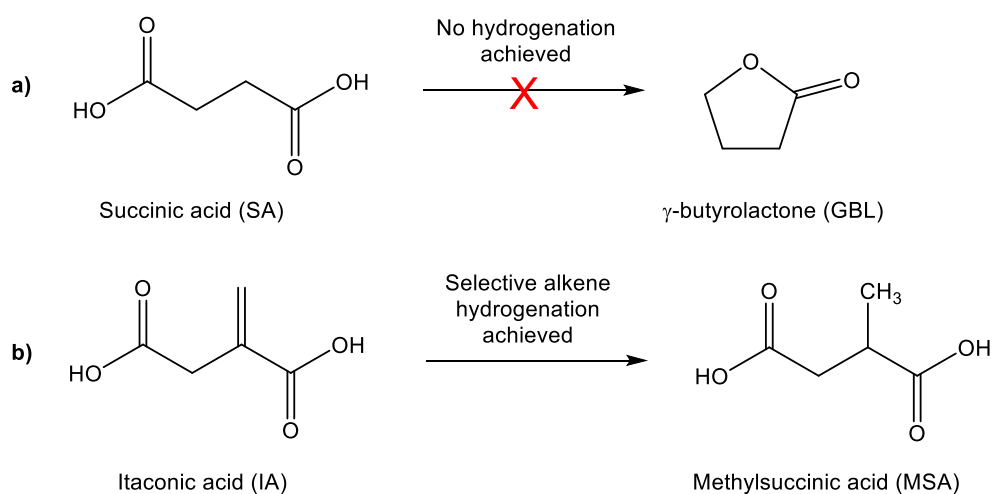
Succinic acid (SA) is the di-carboxylic acid analogue of LA, with an analogous hydrogenation product γ -Butyrolactone (GBL). Although SA and GBL lack the distinctive $-\text{CH}_3$ ^1H NMR signals which were used to analyse the hydrogenation reactions of LA to GVL, their ^1H NMR signals are characterised more-straightforwardly owing to the relative simplicity of SA and GBL. Hydrogenations of SA to GBL, which can be applied as a green solvent, via succinic anhydride have become well-established in the literature, typically using heterogeneous precious metal catalysts.¹⁵ The hydrogenation of SA to GBL is shown in Scheme 4.5. With **C1**, no SA hydrogenation was achieved under the standard TH conditions (Table 4.12, Entry 14). This demonstrates a stark contrast in reactivity upon the replacement of a ketone for a second carboxylic acid. As discussed in Chapter 1, the hydrogenation of LA to GVL proceeds through ketone hydrogenation followed by nucleophilic attack on the carboxylic acid with ring-closure to form GVL. Recognising that it is the ketone of LA which is initially hydrogenated, the omission of such a functional group in SA appears to be highly significant. Carboxylic acids are generally less reactive towards hydrogenation than carbonyl functional groups such as ketones. Therefore, it appears that the catalytic system under study is sufficiently active to hydrogenate the ketone functionality of LA and EL, but not the carboxylic acid moiety of SA. Given the otherwise identical structures of LA and SA, factors such as hindrance towards ring-closure can be discounted.

The structures of LA, EL and SA can further be compared. LA has been the most successful hydrogenation candidate, suggesting the incorporation of both ketone and carboxylic acid moieties is optimal. Whilst the ketone of EL can be hydrogenated in the same manner as LA, ring-closure by attack at the ester of EL appears to be limited compared to attack at the carboxylic acid of LA, perhaps attributable to the nature of the leaving group: OH^- (H_2O) is classed as a better leaving group than

$\text{OCH}_2\text{CH}_3^-$ ($\text{CH}_3\text{CH}_2\text{OH}$). Therefore, ring-closure to generate GVL can be considered as more favourable with LA than with EL. Given that GVL is produced via an intramolecular ring-closing reaction, the ethyl moiety might add a small degree of steric hindrance, relative to a hydroxyl group. The lack of SA hydrogenation can be attributed to its lack of ketone functional groups.

Itaconic acid (IA) (methylidenesuccinic acid) is another biogenic acid with strong structural similarities to LA. Its structure is shown in Scheme 4.5. Its carbonyl functionality is identical to SA, therefore hydrogenation of its carboxylic acids was not expected. Indeed, no carbonyl hydrogenation was observed under any of the conditions tested.

However, quantitative and selective hydrogenation of IA to methylsuccinic acid (MSA) was observed in four hours (Table 4.12, Entries 15-17). This involves hydrogenation of the alkene bond (Scheme 4.5). The synthesis of MSA by partial hydrogenation of itaconic acid with Raney nickel is well-established.¹⁶ MSA is a prevalent chemical used in aerosols¹⁷ and has important applications within the pharmaceutical industry.¹⁸ With a reduction in catalyst loading from 1 mol % to 0.5 mol%, quantitative conversion of IA to MSA was still achieved, in 24 hours. No hydrogenation was achieved in the absence of catalyst. As for GVL, the presence of a chiral centre in MSA raises the potential for development of stereo-selective catalysis; this was not explored in the present study. Although further optimisations were not performed, the results demonstrate the relative ease of alkene hydrogenation compared to carbonyl hydrogenation. This is consistent with SA, necessitating the presence of ketone functionality for carbonyl hydrogenation with this system. Therefore, the available substrate scope might not be as wide as initially hoped if both ketone and carboxylic acid moieties are necessary. Longer-chain analogues of LA could be investigated, for example 5-oxo-hexanoic acid (to 5-hexanolide¹⁹) or 6-oxo-heptanoic acid. However, the formation of a stable 5-membered ring is likely to play a role in the success of GVL formation which might be suppressed with the use of longer chains.



Scheme 4.5. a) Hydrogenation of SA to GBL. b) Hydrogenation of IA to MSA.

Table 4.12. Results from investigation into different substrates.

Entry	Substrate	Catalyst	Temperature	Time (h)	Yield (%)
1	EL	C1	100	2	25 ^b
2	EL	C1	100	4	28 ^b
3	EL	C1	100	24	28 ^b
4	EL	C1	100	67	28 ^b
5	EL	C2	100	24	17 ^b
6	EL	C2	150	24	5 ^b
7	EL	C5	100	24	nd ^b
8	EL	C8	100	24	2 ^b
9	EL	-	100	24	nd ^b
10	EL	-	150	24	nd ^b
11	EL	[PdCl ₂ (COD)] + N-Triphos ^{Ph}	100	24	nd ^b
12	EL	[PdCl ₂ (COD)] + N-Triphos ^{Cy}	100	24	6 ^b
13	EL	[PdCl ₂ (COD)] + N-Triphos ^{Cy}	150	24	11 ^b
14	SA	C1	100	24	nd ^c
15	IA	C1	100	4	100 ^d
16	IA	C1	100	24	100 ^d
17 ^a	IA	C1	100	24	100 ^d

*Reactions performed using standard transfer hydrogenation conditions, with the stated substrate (3.4 mmol), stated catalyst (1 mol%), formic acid (2.1 equivalents) and triethylamine (10 mol%) at the stated temperature for the stated time. Reactions were performed in duplicate and yields were determined by ¹H NMR spectroscopy. a) 0.5 mol% catalyst loading. b) Yield of GVL. c) Yield of GBL. d) Yield of MSA.

4.3 Gas evolution studies

Investigation of all the variables discussed in Section 4.2 failed to significantly improve the GVL yields achieved relative to the standard conditions. Therefore, attention turned to better understanding the transfer hydrogenation processes themselves.

4.3.1 Measurements of quantity and rate of gas evolution

In the standard transfer hydrogenation conditions, 7.2 mmol of FA (2.1 equivalents) was added. Given the potential for each molecule of FA to decompose into two molecules of gaseous products, there was the potential for a maximum of 14.4 mmol gaseous products to be generated in each reaction. Taking that one mole of any gas occupies a volume of 24 dm³ (24,000 cm³) at room temperature and

pressure, there was the potential for a maximum of 346 mL gas to be generated in a standard transfer hydrogenation experiment. Using a standard water-displacement experimental set-up as illustrated in Figure 4.14, a series of gas evolution tests were performed. Results are collected in Table 4.13. Collected gas was allowed to cool to RT before measuring the volumes.

Under the standard transfer hydrogenation conditions at 100 °C with LA, catalyst, FA and triethylamine, an average volume of 225 mL of gas was collected within one hour, equivalent to 65 % of the theoretical maximum gas volume (Table 4.13, Entry 1). Over a total of two hours, this had increased to an average collected gas volume of 273 mL, or 79 % of the theoretical maximum gas volume (Table 4.13, Entry 2). Over a total of 24 hours, a gas volume of 256 mL was collected (74 % of the theoretical maximum) (Table 4.13, Entry 3). This shows that there is no further increase in the gas volume produced after the first two hours, and that the volume of gas produced within the first two hours can be considered as the total gas volume produced by this system under those conditions.

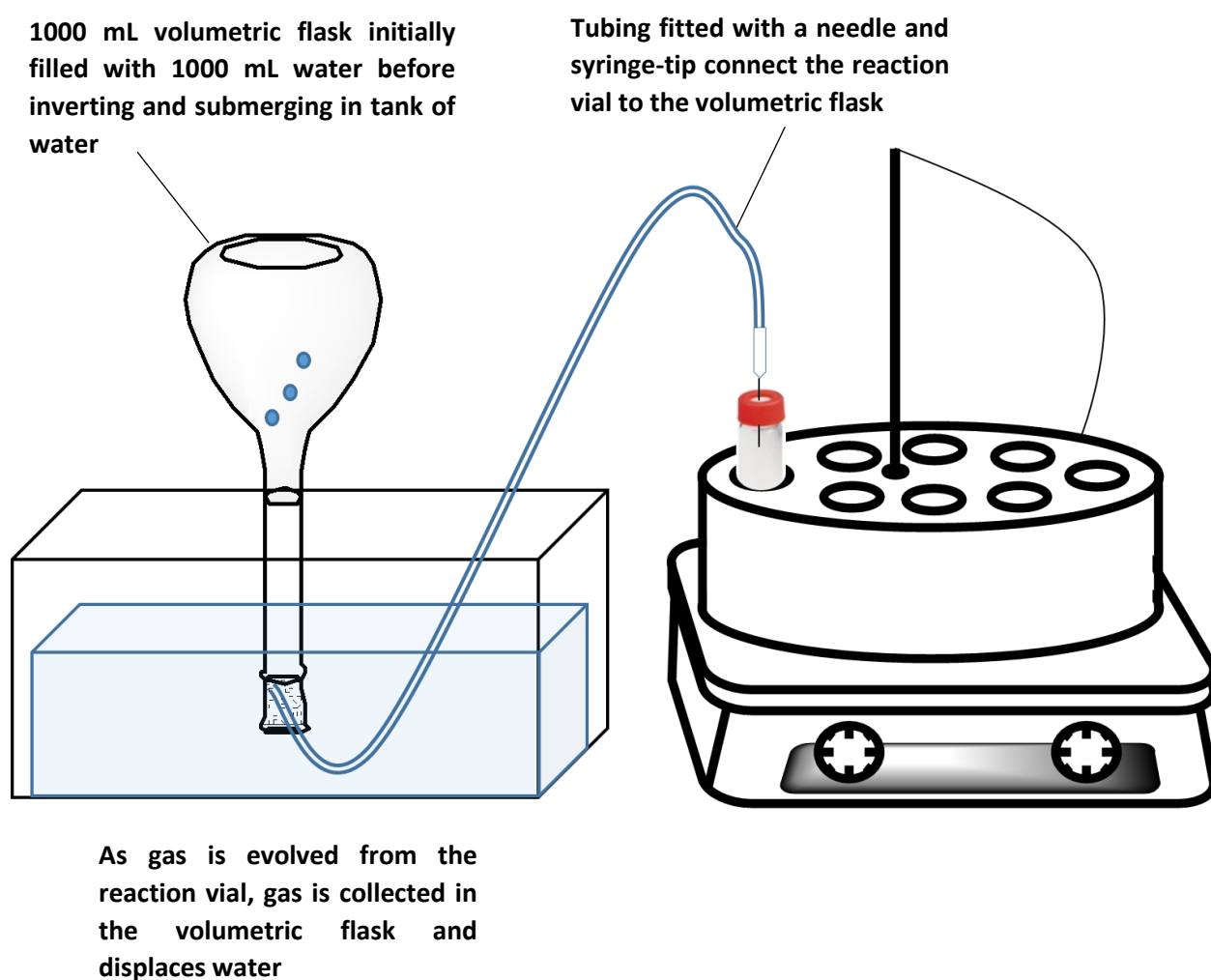


Figure 4.14. Diagram of the water-displacement experimental set-up.

The numbers of gas bubbles produced over the first two hours at 100 °C were counted and collected into five-minute intervals. A total gas volume of 280 mL was collected and in this time 4276 bubbles were counted (giving an average volume per bubble of 0.65 mL). Figure 4.15 shows graphs of gas evolution across the reaction timescale. The graphs illustrate that at 100 °C the volume of gas formed in each interval over the first 90 minutes is quite constant, showing that the rate of gas evolution remains at a steady level in this period. After ~ 90 minutes, the rate of gas evolution falls drastically, and beyond two hours gas is being produced only at a very slow rate. The graph showing the cumulative volume of gas evolved also shows this, with the gradient of the line changing drastically after 90 minutes.

These observations are consistent with the findings described in the previous section that the maximum GVL yields are achieved within the first two hours and that there is very little further hydrogenation of LA after the first two hours. These results suggest that the lack of further gas evolution beyond two hours correlates with the lack of conversion achieved beyond the same timepoint.

Increasing the temperature to 120 °C, an average ($n=2$) gas volume of 319 mL was collected, or 92 % of the theoretical maximum (Table 4.13, Entry 4). This is a significant increase compared to the volume of gas collected at 100 °C. Again, the number of bubbles produced over the first two hours at 120 °C were counted and collected into five-minute intervals. With a total gas volume of 314 mL collected and a total of 3,319 bubbles counted, an average volume per bubble of 0.095 mL was determined. The number of bubbles counted is lower than at 100 °C despite an overall larger volume of gas collected. This is attributed to the extremely fast rate of gas evolution at 120 °C, making a reliable count of the bubbles produced more difficult. Nonetheless, the graphs show an entirely different profile for gas evolution at 120 °C compared to 100 °C. The rate of gas evolution peaks at the very start of the experiment and drastically plummets within the first 30 minutes. Beyond this time, additional gas evolution is near-negligible. Therefore, at 120 °C, both a larger volume of gas is generated than at 100 °C and the gas is produced much more quickly.

With a further increase in temperature to 150 °C, a slightly larger average gas volume of 328 mL was collected over two hours (95 % of the theoretical maximum volume) (Table 4.13, Entry 5). This demonstrates that this system is capable of fully decomposing FA into its decomposition products. Furthermore, the gas was produced more quickly than at both 100 and 120 °C, with the rate of gas evolution slowing after just 20 minutes and with near-zero gas formation after the first hour. The profiles of gas evolution are very similar for 120 °C and 150 °C, with 150 °C facilitating a slightly larger volume of gas evolution slightly more quickly.

Table 4.13. Results from water displacement experiments.

Entry	Catalyst	Temperature (°C)	Time (h)	Average gas volume evolved (mL)	Percentage of maximum volume (%)
1	C2	100	1	225	65
2	C2	100	2	273	79 ^a
3	C2	100	24	256	74
4	C2	120	2	319	92
5	C2	150	2	328	95
6 ^b	C2	100	1	29	8
7 ^b	C2	100	2	44	13
8 ^b	C2	100	24	257	74
9	C7	100	2	18	5
10	-	100	1	12	3

*Reactions performed using standard transfer hydrogenation conditions, with levulinic acid (3.4 mmol), the stated catalyst (1 mol%), formic acid (2.1 equivalents) and triethylamine (10 mol%) at the stated temperature for the stated time. Reactions were performed in duplicate and yields determined by ¹H NMR spectroscopy. a) Reaction performed in triplicate. b) Triethylamine omitted.

Whilst reaction temperatures of above 100 °C had not been trialled for transfer hydrogenation using the reaction vials, these results indicate that the use of 120 °C might be expected to facilitate higher GVL yields, given that FA decomposition is both accelerated and augmented. This suggests that a small increase in operating temperature from 100 to 120 °C might be useful in facilitating higher GVL yields.

Similar reactions were performed at 100 °C with the omission of triethylamine. In one hour, just 29 mL gas was collected (8 %), however this increased to 44 mL after two hours (13 %) (Table 4.13, Entries 6-7). Gas was still being evolved at this point; therefore, the reaction was continued for a full 24 hours. After 24 hours, a total gas volume of 257 mL was produced (74 %) (Table 4.13, Entry 8). Interestingly, this is in-line with the total volume of gas generated at 100 °C in the presence of triethylamine. This indicates that the inclusion of triethylamine plays a key role in accelerating the decomposition of FA but is not itself essential for gas evolution. This is consistent with other reports in the literature.

Replacing the PCy₂-catalyst **C2** for the analogous PPh₂-catalyst **C7** facilitated the evolution of just 18 mL gas (5 %) in two hours (Table 4.13, Entry 9). Therefore, the inactivity of the PPh₂-catalysts can be attributed to their inability to facilitate the decomposition of FA. Furthermore, in the absence of catalyst just 12 mL of gas was generated within one hour (just 3 % of the theoretical maximum) (Table 4.13, Entry 10). This again illustrates that a catalyst is essential for FA decomposition.

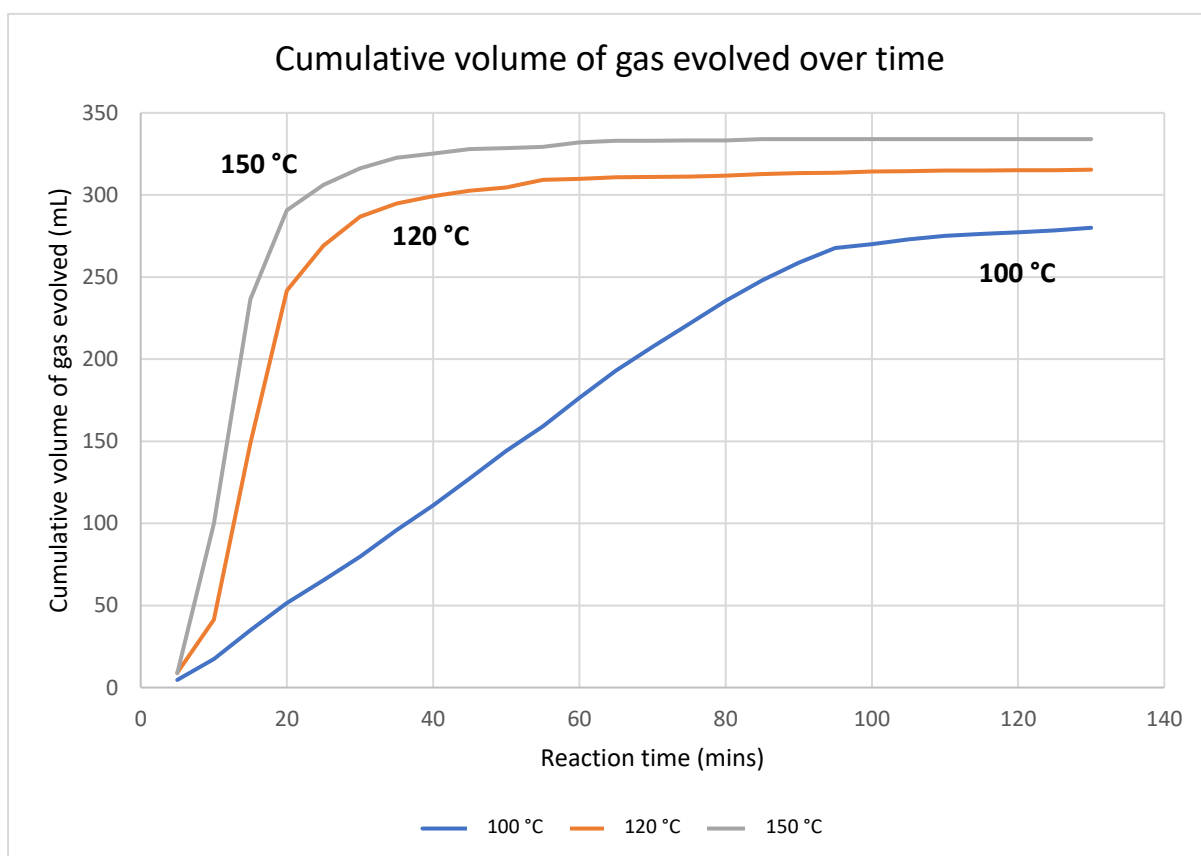
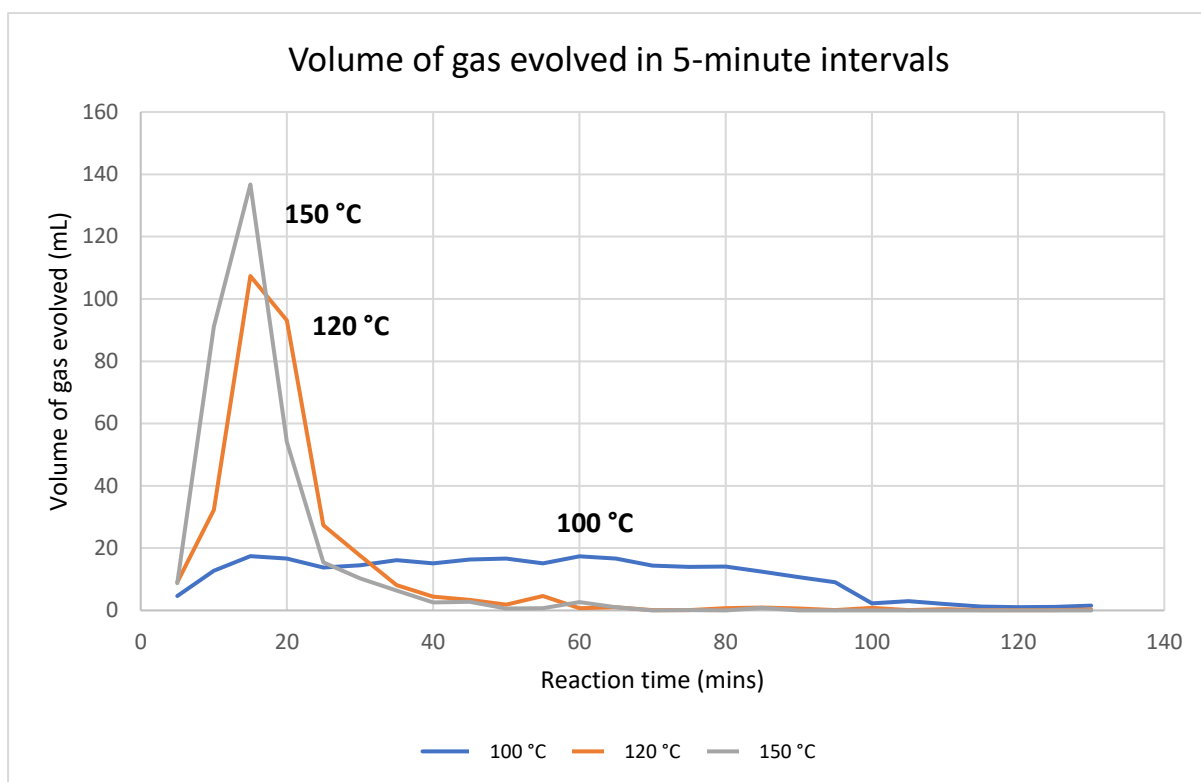
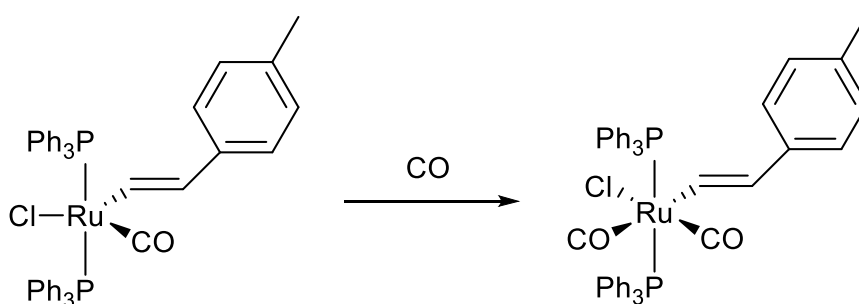


Figure 4.15. Graphs showing a) the volume of gas evolved over time and b) the cumulative volume evolved from water-displacement experiments.

4.3.2 Detection of carbon monoxide gas

To better understand the gases being produced from FA in the transfer hydrogenation reactions, a ruthenium probe complex was provided by the Wilton-Ely group. The 5-coordinate ruthenium tolyl complex, $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me}-4)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$, undergoes an irreversible colour change from orange-red to pale-yellow upon the coordination of carbon monoxide. The probe has been shown to be selective for CO over other gases (e.g. H_2O , CO_2).^{20–22}. The structures, and colours, of the ruthenium complexes are shown in Scheme 4.6 and Figure 4.16.



Scheme 4.6. Addition of carbon monoxide to the 5-coordinate ruthenium tolyl probe complex.

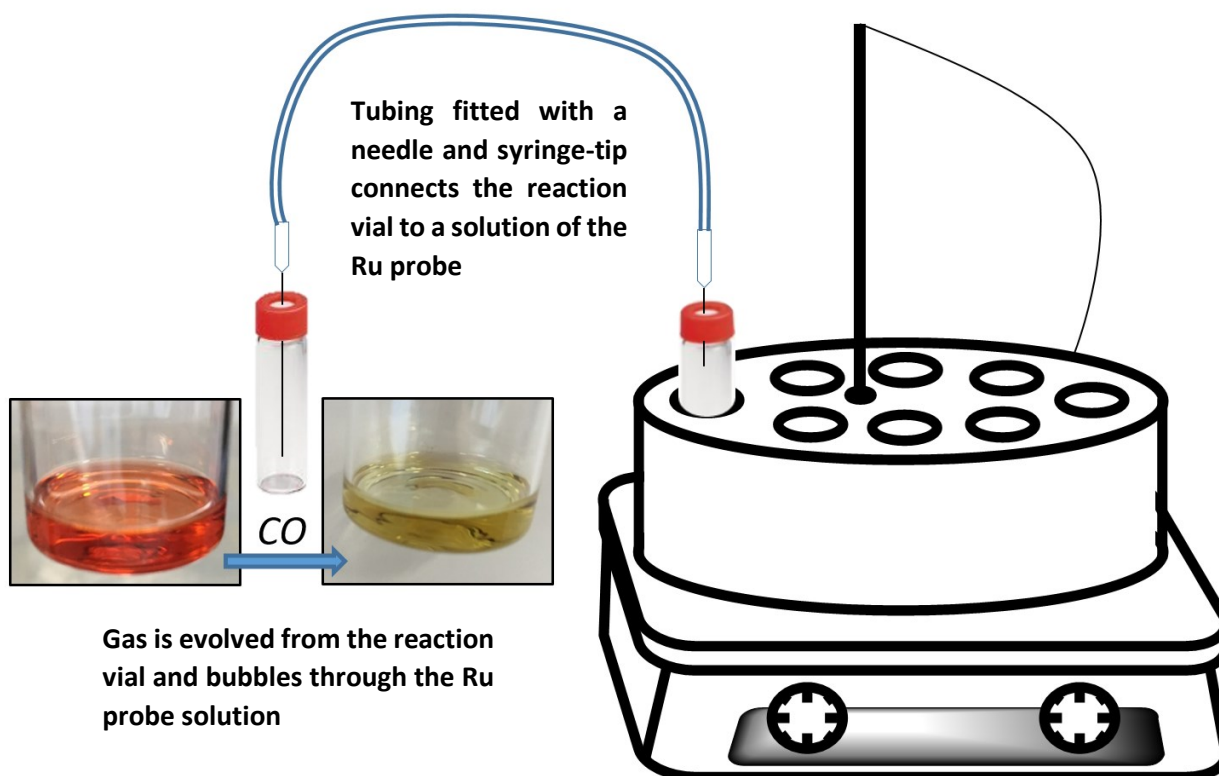


Figure 4.16. Diagram of the carbon monoxide detection set-up.

The gases produced from a standard transfer hydrogenation experiment were bubbled through a solution of the Ru probe in dichloromethane (5 mg/mL). After ~ 15 mins, discolouration of the Ru probe solution was observed, with a complete colour change identified after ~ 20 mins. The delay in the colour change suggests that there is a small time period before CO is generated in sufficient volume to saturate the probe solution. After 90 minutes, the gases produced were bubbled through a freshly prepared Ru probe solution; again the colour changed from red to yellow within 10 minutes.

A fresh transfer hydrogenation reaction mixture was set-up and kept sealed for one hour with heating. After this time, bubbling the reaction atmosphere through a solution of the Ru probe gave an immediate colour change from red to yellow. The same observations were found after keeping a fresh reaction mixture sealed for 24 hours.

The findings show that CO is generated near the start of the transfer hydrogenation experiment (in sufficient quantities to saturate the Ru CO probe solution). The atmosphere of the transfer hydrogenation reaction after both one hour and 24 hours (i.e. throughout the transfer hydrogenation experiment) also have sufficient CO compositions to saturate the Ru CO probe solution. The presence of CO confirms that FA dehydration plays a significant role in the FA decomposition processes within this system.

4.3.3 Headspace analysis

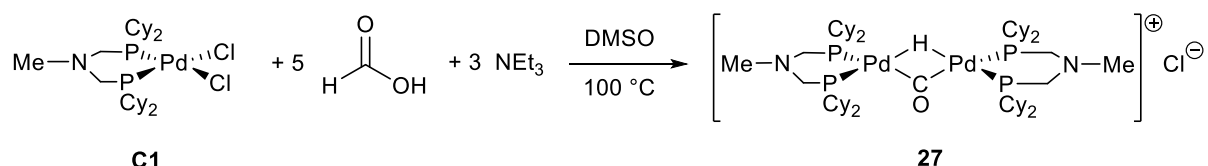
Although the previous experiments had studied the rate and volume of gas evolution, and detected the presence of CO gas, the exact composition of the transfer hydrogenation atmosphere is uncertain. Attempts were made to collect the gases from a typical transfer hydrogenation experiment by bubbling the gas mixture into a cooled NMR tube of CDCl₃ fitted with a Young's tap. However, by ¹H and ¹³C NMR spectroscopy, no signals attributable to H₂, CO or CO₂ were observed.

4.4 Investigation of catalyst deactivation

Given that quantitative hydrogenation of LA to GVL had not been achieved under any of the transfer hydrogenation systems trialled, it appeared that there was a more fundamental limitation to the catalytic system under study. The transfer hydrogenation mechanism reported by Garcia et al. described the formation of an inactive catalyst species - a CO-bridged palladium dimer - formed through an off-cycle reaction.¹ Given that the presence of CO in the present transfer hydrogenations

had been identified, it was considered that a similar deactivated form of the catalysts used in this work might be responsible for the moderate yields achieved.

To study the proposed catalyst deactivation, the reactivity of **C1** and **C2** with FA and triethylamine were investigated. The reaction scheme, showing the anticipated form of inactivated catalyst, is shown in Scheme 4.7.



Scheme 4.7. Reactivity of **C1** with formic acid and triethylamine.

To a solution of **C1** in DMSO was added 5 equivalents of FA and 3 equivalents of triethylamine. After heating to 100 °C, the mixture changed from pale-yellow to deep-red in colour within 30 minutes. At this point, ³¹P{¹H} NMR spectroscopy showed that the initial catalyst signal at 29.9 ppm had been almost completely replaced by a new signal at 12.5 ppm. This matched a signal which had been observed in many ³¹P{¹H} NMR spectra of the TH reaction mixtures, alongside or in place of the original catalyst signal. This new signal was observed over the course of four hours, with complete loss of the original catalyst signal. After heating overnight, a mixture of signals at 12.5, 29.9 and 46.8 ppm were observed. This indicated that some of the “new” species had reverted to **C1**, alongside a small degree of oxidation. After cooling to RT and full solvent removal in vacuo, a brown-red solid was collected which showed a major ³¹P{¹H} NMR signal at 29.9 ppm and a minor signal at 12.5 ppm. Whilst Garcia et al. identified a number of species formed from the reaction of [(dtbpe)PdCl₂] with FA and triethylamine, the expected product was an analogous Pd dimer bridged by H and CO ligands, [{Pd(Me-N(CH₂PCy₂)₂)(μ-H)(μ-CO)]Cl (**27**).¹ Originally, ³¹P{¹H} NMR spectroscopy had indicated full conversion of the original catalyst to a product species containing a single phosphorus environment. However, subsequent NMR samples showed that this product had reverted to **C1**. After three weeks, preparing a fresh NMR sample or resubmitting the original NMR sample both showed ³¹P{¹H} NMR signals for **C1** alone, indicating that the product species is unstable both in solution and as a solid. By storing the NMR sample at 5 °C, the product signal was maintained over three days.

The reaction was repeated in DMSO in an identical fashion with full conversion of **C1** observed after two hours by ³¹P{¹H} NMR spectroscopy, at which point heating was ceased. However, the solid

product showed a major signal at 29.9 ppm and a minor signal at 12.5 ppm, as seen previously. Over the course of four days, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed complete loss of the product signal.

Therefore, both a short reaction time and a reaction solvent that could be removed readily were necessary to isolate the new species. An analogous reaction was performed in dichloromethane at 50 °C. Although the same colour change was observed, $^{31}\text{P}\{^1\text{H}\}$ NMR spectra after five hours showed no change from **C1**.

However, after heating overnight $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed a major signal at 12.3 ppm. After removing dichloromethane in vacuo, a brick-red solid was isolated. This showed a major signal at 12.3 ppm and a small signal at 30.6 ppm. This was a large improvement over the spectra achieved from the reactions performed in DMSO, illustrating that whilst some reversion to **C1** had occurred, the facile removal of dichloromethane had facilitated the isolation of the product species. ^1H NMR spectroscopy showed a quintet at -5.20 ppm. The highly upfield chemical shift suggested Pd-H bonding, and the quintet indicated coupling to four equivalent phosphorus centres. Furthermore, both the chemical shift and coupling constant ($^2J_{\text{H-P}} = 42$ Hz) were a close match for the dtpbe analogue reported by Garcia et al. ($\delta = -5.45$ ppm, $^2J_{\text{H-P}} = 42$ Hz).¹ IR spectroscopy showed the presence of a C=O band at 1747 cm^{-1} (and 1782 cm^{-1}); supporting the inclusion of a bridging CO moiety. Mass spectrometry found that the solid products from all three attempts matched the expected product identity, **27**, with $m/z = 1145.5104$ (calc. $m/z = 1145.5095$).

Attempts to grow single crystals of **27** by diffusion of diethyl ether into dichloromethane were attempted. Whilst crystals were analysed by X-ray crystallography, the determined crystal structure was that of the original catalyst **C1**, the structure of which had been previously obtained (Chapter 3). The crystal structure is shown in Figure 4.17. The new crystal structure differed only in the lack of solvation of the complex. Although disappointing, the crystal structure was not surprising. The palladium dimer **27** had already been found to be unstable with respect to reversion to the original catalyst in solution over several days. It was considered that crystallisations kept at low temperatures might aid crystallisation of the palladium dimer **27**; however suitable crystals failed to grow at 5 °C. The iodo-analogue to **C1**, $[\text{Me-N}(\text{CH}_2\text{PCy}_2)\text{PdI}_2]$ (**C3**), was also found to convert readily to the same dimeric product **27** in the presence of excess FA and triethylamine within one hour.

During transfer hydrogenation reactions using **C2**, an analogous, unassigned signal had also been observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. This was now attributed to an analogous palladium dimer to **27**. The increased steric bulk of the additional $\text{P}(\text{O})\text{Cy}_2$ arm was considered to aid product isolation and crystallisation of its palladium dimer.

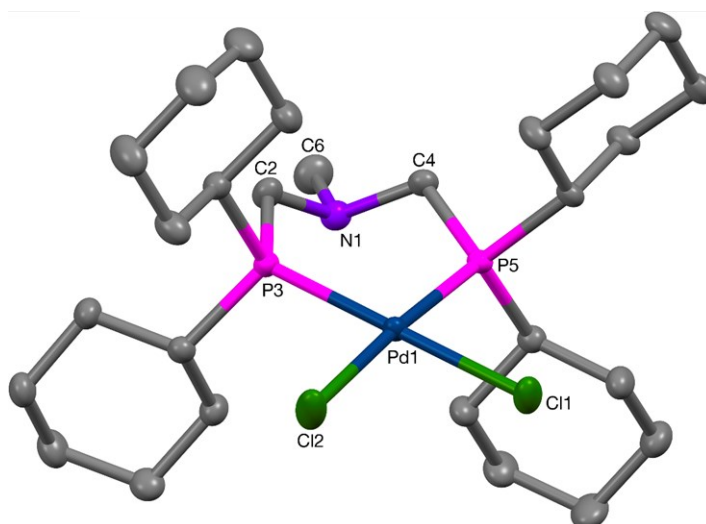
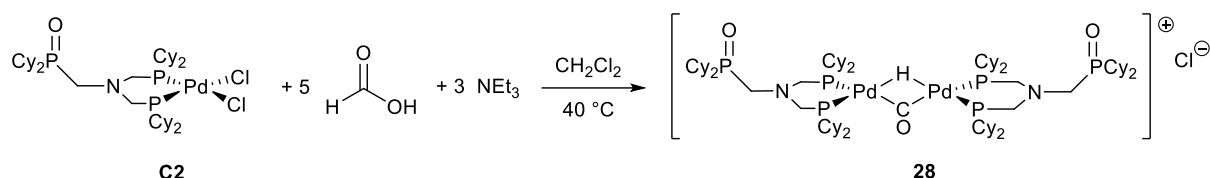


Figure 4.17. Crystal structure of **C1**. Hydrogen atoms and solvent molecules omitted for clarity.

A reaction between **C2**, triethylamine and FA was performed in dichloromethane as shown in Scheme 4.8. No change to the original $^{31}\text{P}\{^1\text{H}\}$ NMR signals at 28.5 and 46.2 ppm were observed over 19 hours of heating at 40 °C. After addition of extra triethylamine and FA, new signals were observed at 11.9 and 46.2 ppm, attributed to the product dimer $[\{\text{Pd}(\text{P}(\text{O})\text{Cy}_2\text{-N}(\text{CH}_2\text{PCy}_2)_2)(\mu\text{-H})(\mu\text{-CO})\}]$ (**28**). However, these remained small relative to the original signals. After a further 23 hours of heating, extra triethylamine and FA were added. After a total reaction time of 66 hours, $^{31}\text{P}\{^1\text{H}\}$ NMR showed only signals at 11.9 and 45.7 ppm, in a 2:1 ratio, indicating reaction completion. After cooling to RT, solvent removal in vacuo and drying in vacuo overnight, the product was collected as a bright-red oil/viscous liquid. The product showed initially only the expected $^{31}\text{P}\{^1\text{H}\}$ NMR signals for **28**, at 48.1 and 12.3 ppm, showing no reversion to **C2**, although higher-resolution spectra showed additional signals at 48.9/30.1 ppm. Nonetheless, ^1H NMR spectroscopy showed the characteristic hydride quintet signal at -5.02 ppm, $^2J_{\text{H-P}} = 42$ Hz. IR spectroscopy showed a C=O stretch at 1737 cm^{-1} , close to that observed for **27**. Mass spectrometry found a product signal at $m/z = 1569.7804$ (calc. $m/z = 1569.7755$) attributable to **28** without significant fragmentation.

Crystallisations of **28** were again attempted from vapour diffusion of diethyl ether into dichloromethane. Fine needles were obtained but these were of insufficient quality for crystallographic analysis. NMR analysis of the crystalline material suggested reversion to **C2**.



Scheme 4.8. Reactivity of **C2** with formic acid and triethylamine.

The determination of the palladium dimer species formed through reaction of **C1** and **C2** with FA and triethylamine, and their similarity to the “inactive catalyst species” described by Garcia et al., allowed for the tentative assignment of **27** and **28** as inactive forms of the catalysts **C1** and **C2** used in the present study.¹ ³¹P{¹H} NMR signals corresponding to the dimer species **27** and **28** were observed in many of the transfer hydrogenation reactions described in this Chapter. Although their formation from the original catalysts appears to be reversible, it is likely that under transfer hydrogenation reaction conditions with a maintained pressure, their reversion to the original catalyst would be less favoured. If **27** and **28** are correctly assigned to inactive forms of **C1** and **C2**, their formation might help to rationalise the lower-than-expected GVL yields achieved. The palladium dimers have no vacant sites for substrate coordination, and the bidentate phosphine ligands are non-trivial to displace.

The formation of the palladium dimer species **27** and **28** from their corresponding catalyst, FA and triethylamine was accompanied by a stark colour change from pale-yellow to deep-red; a similar colour change was observed in the majority of transfer hydrogenation reactions within a short time. This suggests that the dimers were forming within the early stages of the transfer hydrogenation reactions, perhaps preventing quantitative hydrogenations from being achieved. ³¹P{¹H} NMR spectra collected at the end of each transfer hydrogenation reaction tended to show a mixture of signals attributable to both the original catalyst and the dimer species. It is uncertain if this demonstrates incomplete conversion of the original catalyst into the dimer species, or if there had been some reversion of the dimer species back to the original catalyst.

The palladium dimer species **27** and **28** have an electron count of 16 valence electrons at each palladium centre, which are formally Pd(I) owing to the inclusion of a single positive charge and the bridging-hydride ligand (3-centre-2-electron bonding)²³. This is illustrated in Figure 4.18. Although Pd(I) oxidation states are less common, there is precedent in the literature for the formation of similar palladium dimer species of carbon-centred diphosphine ligands.^{24–26}

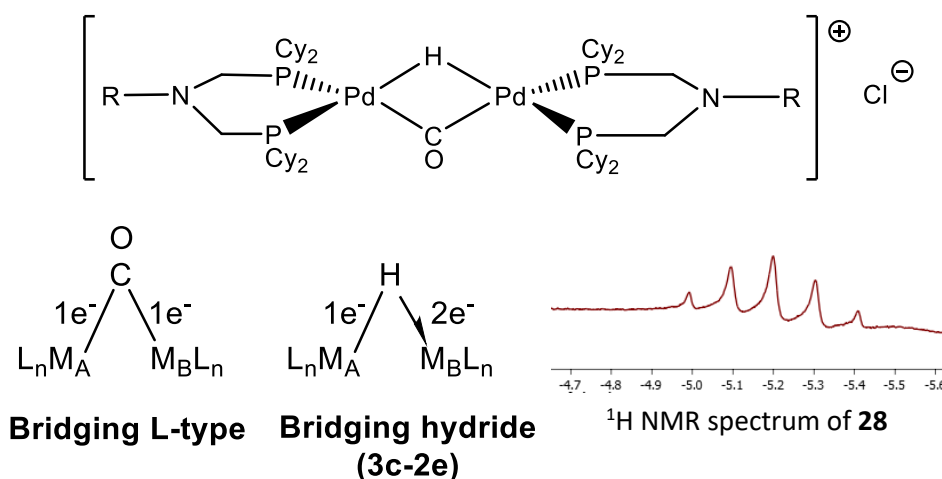


Figure 4.18. Structure of the palladium dimers **27** and **28**.

It was discussed previously that FA has the potential to decompose into H_2 and CO_2 (the favoured route for hydrogenation) or into H_2O and CO (detrimental for hydrogenation). The latter decomposition route is responsible for the formation of the inactive CO -bridged palladium dimer species. The decomposition of FA into CO and H_2O is disfavoured in the presence of water (Section 4.1.2).

This might rationalise why Garcia et al. reported the minor formation of an analogous palladium dimer species amongst other species, as their reactions were performed in water. Here, in non-aqueous media, the decomposition of FA into CO and H_2O dominated and full conversion of the original catalysts to their corresponding Pd dimer was achieved. A reaction mechanism for the formation of the palladium dimers **27** and **28** is shown in Scheme 4.9.¹

This illustrates a fundamental difference between the catalytic reactions described here and those reported by Garcia et al. Their catalysts are water-soluble at high temperatures, allowing for the use of water as a solvent for their transfer hydrogenation reactions. This minimises the decomposition of FA into CO and H_2O , minimising the formation of the inactive catalyst dimer, and maximising the LA hydrogenation achieved. The catalysts described in this work have no water-solubility (even at high temperatures), therefore water cannot be used as the transfer hydrogenation solvent. This means that decomposition of FA into CO and H_2O is uncontrolled and the formation of the inactive catalyst dimer is prevalent.

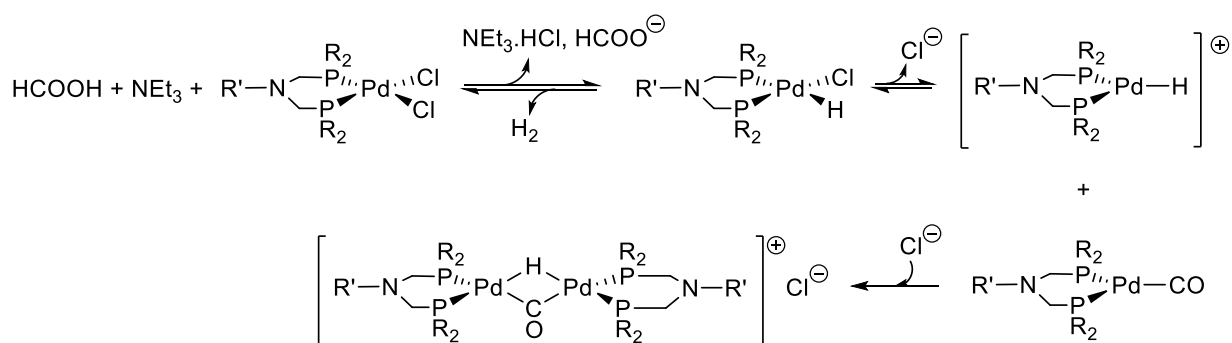
This ties together several observations which have been discussed in this chapter. The maximum GVL yield was generally achieved within the first two hours of the transfer hydrogenation reaction, with very limited additional hydrogenation achieved after this timepoint. Gas evolution studies found that

the maximum gas volume was generated within the first two hours, again with very limited further gas evolution beyond this timepoint. The catalyst converted to a CO-bridged palladium dimer within a short time (~ one hour), invoking the presence of CO gas.

Interestingly, reacting **C1** with excess FA and triethylamine in aqueous media also led to the formation of **27**, observed through $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy. Whilst **C1** remained insoluble in water even with heating at 100 °C, the expected colour change from yellow to deep-red was observed within a short time. Whilst the reaction could not be monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy owing to catalyst insolubility, after product isolation major conversion to the dimer species **27** was identified. This suggests that the presence of water does not prevent **C1** from converting to **27**.

Furthermore, trialling the two palladium dimers **27** and **28** as TH catalysts themselves achieved GVL yields of 33 % and 55 % respectively under the standard conditions. The difference in results can likely be attributed to a differing extent of reversion to their original catalyst species; however, the results clearly demonstrate that the presence of the dimer species is not a barrier towards achieving catalytic activity. Again, $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showed a mixture of signals attributable to monomeric and dimeric complexes, suggesting that the two forms readily interconvert. Therefore, whilst the dimeric form could be considered as an inactive form, it is readily able to convert to an active catalyst species and participate in hydrogenation. It might also be the case that the lack of chloride abstraction necessary primes the dimer to attain an active form more readily than the monomeric catalysts.

Therefore, it appears that formation of the palladium dimer itself is not responsible for the lack of quantitative hydrogenation achieved. This suggests that a lack of hydrogen (rather than a lack of catalyst) is responsible, attributed to FA dehydration in non-aqueous conditions. These findings combined suggest that the competing decomposition pathways of FA form a barrier towards achieving higher GVL yields. The next Section will discuss several routes towards incorporating water in the transfer hydrogenation reactions to minimise FA dehydration and catalyst deactivation.



Scheme 4.9. Formation of palladium dimers **27** and **28** from the original palladium catalysts.

4.5 Incorporation of water

Given the established benefits of using aqueous mixtures for transfer hydrogenation reactions, a few routes towards including water were trialled. Some of this work was performed by BSc. student Fraser Gaines (FG) under supervision.²⁷ These parts of work will be clearly highlighted.

The routes can be summarised as:

- 1) The addition of small volumes of water (4.5.1)*
- 2) Trialling water-soluble complexes incorporating PTA ligand (M = Pd, Ir, Ru) (4.5.2)*
- 3) The incorporation of water-soluble amine moieties within the catalyst structure (4.5.3)

(* Experiments performed by FG under supervision)

4.5.1 The addition of small volumes of water

Trialling the addition of “bulk” volumes of water to the transfer hydrogenation reactions completely inhibited LA hydrogenation. Every other solvent combination trialled was also detrimental. It was considered that the addition of trace volumes of water might allow for increased activity whilst minimising dissolution of the catalyst.

The reactions were performed on a standard scale with **C2**. Results are collected in Table 4.14. The volumes of water used were in the range of 0.1 – 0.7 mL, in increments of 0.1 mL. This reflects the very poor solubility of **C2** in water.

Although the results do not show large improvements, there is some indication that the inclusion of water volumes of up to 0.3 mL has a small, positive effect on the GVL yields achieved. From an average yield of 46 % in the absence of water, the yield increased to 63 % with the addition of 0.3 mL water (Table 4.14, Entries 1-4). This suggests that the trace volume of water has a positive effect on FA dehydrogenation. However, with the addition of water volumes in the range 0.4 – 0.7 mL, the yields decreased (Table 4.14, Entries 5-8). This indicates that even with such small volumes of water, catalyst insolubility outweighs any benefit gained from water inclusion. Analogous reactions were performed with volumes of DMSO in the range 0.1-0.3 mL (Table 4.14, Entries 9-11). With the addition of DMSO, the GVL yield decreased to 33 % at 0.3 mL DMSO. Comparing the addition of 0.3 mL water to 0.3 mL DMSO shows a large difference in GVL yield of 63 % and 33 % respectively.

Table 4.14. Effect of incorporating small volumes of water and DMSO to the TH reactions.

Entry	Additive	GVL yield (%)
1	-	46
2	0.1 mL H ₂ O	47
3	0.2 mL H ₂ O	55
4	0.3 mL H ₂ O	63
5	0.4 mL H ₂ O	57
6	0.5 mL H ₂ O	46
7	0.6 mL H ₂ O	54
8	0.7 mL H ₂ O	50
9	0.1 mL DMSO	44
10	0.2 mL DMSO	39
11	0.3 mL DMSO	33

*Reactions performed using standard transfer hydrogenation conditions, with levulinic acid (3.4 mmol), **C2** (1 mol%), formic acid (2.1 equivalents) and triethylamine (10 mol%) at 100 °C for 24 hours. Reactions were performed in duplicate and yields were determined by ¹H NMR spectroscopy.

4.5.2 Water-soluble PTA complexes

Chapter 1 introduced several water-soluble phosphine ligands which have been applied in catalytic systems for LA hydrogenation reactions. Whilst the PCy₂ moieties incorporated within the catalysts in this study are important for the activity of the catalysts, they fail to impart water solubility to their complexes. 1,3,5-Triaza-7-phosphadamantane (PTA) is a commercially available water-soluble monodentate phosphine ligand, which has been used for the formation of water-soluble transition metal complexes in the literature. The syntheses of three previously reported PTA complexes (M = Pd, Ir, Ru) were performed. Their structures are shown in Figure 4.19 and their syntheses are summarised in Scheme 4.10. These complexes were selected for their similarity to the previously described palladium, iridium and ruthenium complexes of the nitrogen-bridged phosphine ligands. However, they have not previously been applied as catalysts in this context. The precursors [PdCl₂(COD)] and [Ir(COD)Cl]₂ were prepared following standard procedures; [Ru(η⁶-*p*-cymene)Cl₂]₂ was purchased from a commercial source.

[Pd(PTA)₂Cl₂] (**29**) was prepared from [PdCl₂(COD)] and PTA in dichloromethane.²⁸ [Ir(PTA)₃COD]Cl (**30**) was synthesised from [Ir(COD)Cl]₂ and PTA in dichloromethane.²⁹ [Ru(η⁶-*p*-cymene)(PTA)Cl₂] (**31**) (also known as RAPTA-C) was synthesised from [Ru(η⁶-*p*-cymene)Cl₂]₂ and PTA in methanol.³⁰ The identity of all three complexes was confirmed by ¹H and ³¹P{¹H} NMR spectroscopy and mass spectrometry.

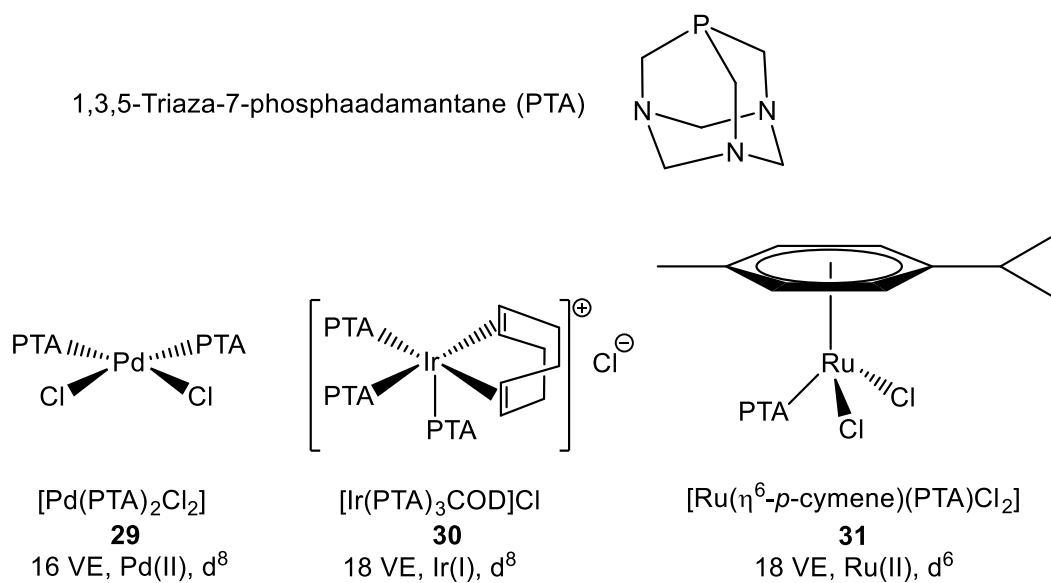
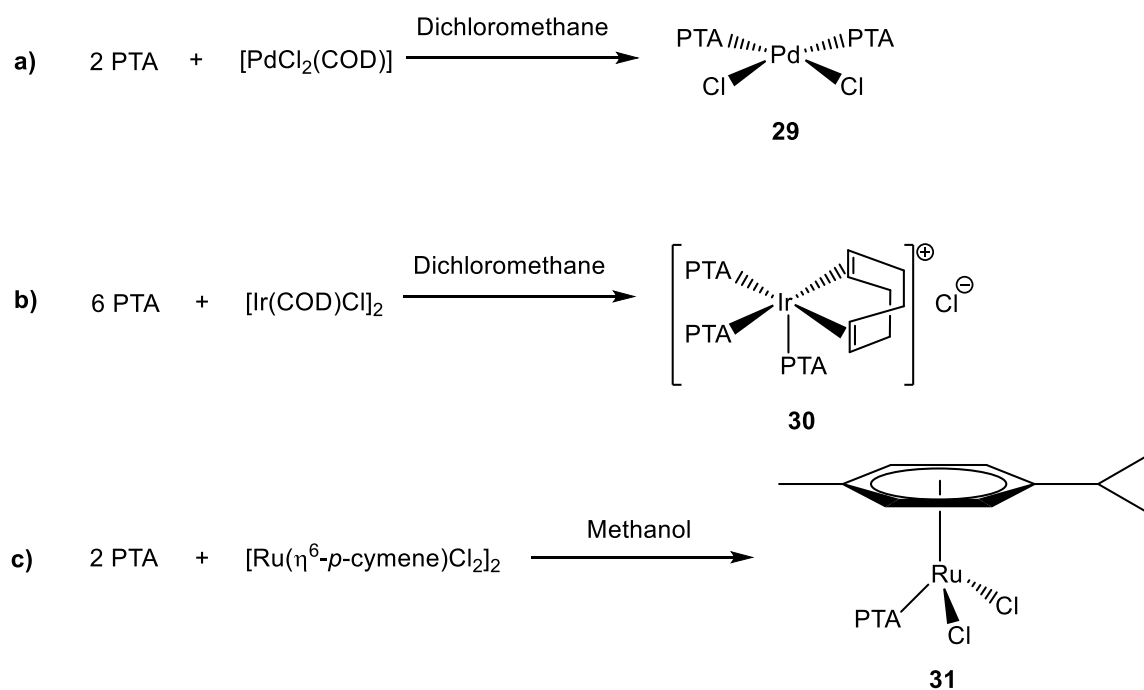


Figure 4.19. Structures of the PTA complexes **29-31** studied in this work.



Scheme 4.10. Syntheses of a) $[\text{Pd}(\text{PTA})_2\text{Cl}_2]$ (**29**) b) $[\text{Ir}(\text{PTA})_3\text{COD}]\text{Cl}$ (**30**) c) $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{PTA})\text{Cl}_2]$ (**31**).

Table 4.15. Results of TH reactions using water-soluble catalysts.

Entry	Catalyst	Additive	GVL yield (%)
1	[Pd(PTA) ₂ Cl ₂] (29)	-	2
2	[Pd(PTA) ₂ Cl ₂] (29)	0.5 mL H ₂ O	nd
3	[Pd(PTA) ₂ Cl ₂] (29)	1 mL H ₂ O	nd
4	[Pd(PTA) ₂ Cl ₂] (29)	2 mL H ₂ O	nd
5	[Pd(PTA) ₂ Cl ₂] (29)	3 mL H ₂ O	nd
6	[Ir(COD)(PTA) ₃ Cl] (30)	-	29
7	[Ir(COD)(PTA) ₃ Cl] (30)	0.5 mL H ₂ O	41
8	[Ir(COD)(PTA) ₃ Cl] (30)	1 mL H ₂ O	39
9	[Ir(COD)(PTA) ₃ Cl] (30)	2 mL H ₂ O	44
10	[Ir(COD)(PTA) ₃ Cl] (30)	3 mL H ₂ O	47
11	[Ir(COD)(PTA) ₃ Cl] (30)	3 mL H ₂ O	52 ^a
12	[Ru(PTA)(<i>p</i> -cymene)Cl ₂] (31)	-	31
13	[Ru(PTA)(<i>p</i> -cymene)Cl ₂] (31)	0.5 mL H ₂ O	25
14	[Ru(PTA)(<i>p</i> -cymene)Cl ₂] (31)	1 mL H ₂ O	15
15	[Ru(PTA)(<i>p</i> -cymene)Cl ₂] (31)	2 mL H ₂ O	13
16	[Ru(PTA)(<i>p</i> -cymene)Cl ₂] (31)	3 mL H ₂ O	13
17	C4	-	37
18	C4	0.5 mL H ₂ O	56
19	C4	0.5 mL H ₂ O	51 ^a
20	C4	1 mL H ₂ O	59
21	C4	2 mL H ₂ O	36
22	C4	3 mL H ₂ O	19

*Reactions performed using standard transfer hydrogenation conditions, with levulinic acid (3.4 mmol), stated catalyst (1 mol%), formic acid (2.1 equivalents) and triethylamine (10 mol%) at 100 °C for 24 hours. Reactions were performed in duplicate and yields determined by ¹H NMR spectroscopy. a) mixtures prepared under inert conditions.

The three PTA complexes **29-31** were trialled as catalysts with varying volumes of water added. Their high water-solubility allowed for the addition of larger volumes of water than those trialled with **C2**. The results are summarised in Table 4.15.

Disappointingly, [Pd(PTA)₂Cl₂] (**29**) was found to have no activity for the transfer hydrogenation of LA under the standard conditions, even with the incorporation of water volumes up to 3 mL (Table 4.15, Entries 1-5). Therefore, directly replacing the bidentate nitrogen-bridged PCy₂ ligand for two monodentate PTA ligands is not an effective strategy, despite the increased water-solubility.

[Ir(PTA)₃COD]Cl (**30**) was found to be more active. In the absence of water, an average GVL yield of 29 % was achieved. This gradually increased up to an average 47 % yield with the addition of 3 mL H₂O (Table 4.15, Entries 6-10). Strictly excluding air from the mixtures facilitated a slightly higher conversion of 52 % (Table 4.15, Entry 11). This demonstrates that the addition of water does have a positive effect on LA hydrogenation achieved with this catalyst, but that the addition of water alone is not sufficient to reach high yields of GVL.

[Ru(η^6 -*p*-cymene)(PTA)Cl₂] (**31**) achieved a similar average yield as [Ir(PTA)₃COD]Cl (**30**) in the absence of water (31 %) (Table 4.15, Entry 12). Surprisingly, the GVL yields achieved decreased with water addition, with a yield of just 13 % found with the addition of 3 mL water (Table 4.15, Entries 13-16). Therefore, whilst the two catalysts **30** and **31** have similar catalytic activity in “neat” conditions, the incorporation of 3 mL water results in a yield disparity between the two catalysts of over 30 %. Given the established benefits of incorporating water, it is unclear why [Ru(η^6 -*p*-cymene)(PTA)Cl₂] (**31**) responded negatively to water addition. Potentially, [Ru(η^6 -*p*-cymene)(PTA)Cl₂] (**31**) degrades or converts to a less active form in the presence of water, but this was not studied further.

In all the conditions tested, the PTA complexes did not reach the yields attained with the nitrogen-bridged phosphine complexes. In the literature, complexes of PTA have displayed lesser-than-expected activity, given their small size, strong basicity and high hydrophilicity of the ligand. This has been attributed to protonation of PTA at low pH values, which reduces its electron-donating ability.³¹

Whilst the PTA complexes themselves could be optimised to reach higher yields (with [Ir(PTA)₃COD]Cl (**30**) as the most promising candidate), this again demonstrates that multidentate phosphine ligands are superior to monodentate phosphine ligands for this application.

4.5.3 Water-solubilising amine moieties

The lack of success with replacing the PCy₂ ligand with water-soluble PTA ligands demonstrates a need for retention of the nitrogen-bridged bisphosphine ligands to achieve successful LA hydrogenation. The amine substituent has been observed to have little effect on the activity of the catalysts investigated in this study. However, alteration of the catalyst structure at this point might be a route to improve the water solubility.

Chapters 2 and 3 discussed the synthesis of the ligand CH(OEt)₂CH₂N(CH₂PCy₂)₂ and its palladium complex **6** (**C4**). **C4** was found to have an improved water solubility relative to the other Pd complexes in the PNP-ligand series; however, its water solubility remained poor relative to the PTA complexes **29-31**. Its catalytic activity was also tested with volumes of water addition up to 3 mL (Table 4.15).

In the absence of water, **C4** achieved an average GVL yield of 37 % (Table 4.15, Entry 17). This is slightly lower than the other palladium complexes in the PNP-ligand series, but higher than any of the PTA complexes. Almost immediately upon heating to 100 °C, the catalytic mixtures became a dark-black colour, suggesting catalyst decomposition. However, the generation of a pressure in-line with previous reactions was observed. With addition of up to 1 mL water, the yield increased to 59 %, again

demonstrating the benefits of including water (Table 4.15, Entries 18-20). Also, the increased water solubility relative to **C2** is evident – **C2** reached a maximum conversion with addition of just 0.3 mL water before insolubility reduced the yields achieved.

Unfortunately, including water volumes of larger than 1 mL with **C4** caused a significant reduction in the yields achieved, with just 19 % yield achieved with 3 mL water (Table 4.15, Entries 21-22). This can primarily be attributed to increasing catalyst insolubility. It also demonstrates a reduced water solubility relative to [Ir(PTA)₃COD]Cl (**30**), which reached a maximum GVL yield with the addition of 3 mL water. These results indicate that the incorporation of the water-solubilising (OEt)₂ moiety into the catalyst did not cause a significant reduction in its activity and allowed for the inclusion of a larger volume of water to increase the GVL yields achieved. However, its water-solubility was not sufficiently high to allow for the attainment of quantitative LA hydrogenation. There is the potential for wider study of different water-solubilising groups at the amine position, provided that their ligands and complexes can be made effectively and that the groups do not otherwise interfere with the activity of the catalyst.

4.6 Forcing conditions

4.6.1 Increasing formic acid and temperature

The pressure limitations of the reaction vials had restricted the range of conditions which could be investigated for the transfer hydrogenation reactions. Consequently, the reactions were translated to a high-pressure reactor which offered several potential advantages. Although the reactions would need to be scaled-up and could not be run in parallel, the high-pressure reactor allowed for a sealed system which can tolerate much higher pressures. It also allowed for the detection and measurement of pressure generation on the incorporated pressure gauge.

Using **C2**, the reaction was scaled up twice and tested under the standard conditions used previously (2.1 equivalents FA, 10 mol% NEt₃, 1 mol% catalyst, 100 °C). In two hours, a GVL yield of 35 % was achieved, in line with that achieved by **C2** under the same conditions in the reaction vials (cf. 40 %) (Table 4.16, Entry 1). A pressure of ~10-15 bar was generated within a short time and maintained for the duration of the reaction. Otherwise maintaining the same conditions, the temperature was raised to 120 and 150 °C, achieving GVL yields of 53 and 70 % respectively, demonstrating that elevated temperatures have a significant effect (Table 4.16, Entries 2-3). Similar pressures were generated in each case. Maintaining a temperature of 150 °C, the FA loading was increased from two equivalents

to three or four equivalents. This generated GVL yields of 78 and 77 % respectively, demonstrating that higher FA loadings provide a small but limited benefit compared to increasing the temperature (Table 4.16, Entries 4-5). Higher pressures of ~20 and ~25 bar were generated in each case. Increasing the reaction time from two hours to six hours achieved no additional LA hydrogenation, consistent with the results described previously (Table 4.16, Entry 6). These results demonstrate that even with more forcing conditions of higher temperatures and FA loadings, non-quantitative LA hydrogenations are achieved with this catalyst system. The next sections will discuss the study of hydrogenation experiments using pressures of hydrogen gas in place of FA.

Table 4.16. Results of TH reactions performed in a high-pressure reactor under “forcing conditions”.

Entry	Temperature (°C)	FA loading (eq.)	Time (h)	GVL yield (%)
1	100	2.1	2	35
2	120	2.1	2	53
3	150	2.1	2	70
4	150	3.2	2	78
5	150	4.2	2	77
6	150	3.2	6	71

*Reactions performed using standard transfer hydrogenation conditions, with levulinic acid (6.8 mmol), **C2** (1 mol%), formic acid and triethylamine (10 mol%) at the stated temperature for the stated time. Reactions were performed in a high-pressure Asynt reactor as single runs and yields were determined by ¹H NMR spectroscopy.

4.6.2 Hydrogenation reactions under low pressures of hydrogen

Recognising that the use of FA in non-aqueous systems is unsuitable even with elevated temperatures and FA loadings, and that water-solubilising the catalysts requires significant structural modification, attempts were made to replace FA with low pressures of hydrogen gas. Initial attempts directly replaced FA for a balloon of hydrogen gas to provide a low-pressure hydrogen atmosphere. This avoids the issue of the competing decomposition routes of FA.

Maintaining the standard transfer hydrogenation conditions with **C2**, initially no conversion of LA was achieved over the full 24 hours. This remained the case with the addition of THF or 1,4-dioxane as solvents. Increasing the temperature to 150 °C gave a small improvement, achieving an average GVL yield of 23 % in 24 hours (Table 4.17, Entry 4). Both omitting triethylamine, or including 1,4-dioxane as solvent, completely inhibited the reactions. Curiously, ³¹P{¹H} NMR spectra of the reaction mixtures showed a major signal at -1 ppm, which has not been observed previously, alongside the original catalyst signals. Typically, additional signals had only been observed for the CO-bridged palladium dimers **27** and **28** which are not formed in the absence of FA. The unassigned ³¹P{¹H} NMR signal was

most significant for the reactions performed at 150 °C (Table 4.17, Entries 4-6), suggesting that the formation of this species is favourable at higher temperatures.

Encouraged by the achievement of some hydrogenation with the balloon of hydrogen gas, several NMR tube hydrogenations were performed. The NMR tubes fitted with J Young taps were filled with a pressure of ~ 4 bar H₂ gas and sealed. Maintaining the standard transfer hydrogenation reaction composition and scale with **C2** (with the omission of FA), over four hours at 100 °C just a 2 % GVL yield was determined after addition of DMSO-d₆ to the NMR tube; over four hours at 150 °C this increased to just 6 %. The results indicated that such a reaction set-up is unsuitable for this reaction. Besides the general difficulties of achieving effective mixing in an NMR tube, this is worsened by the high viscosity of LA (~30 times that of water at RT).³² Therefore the limitations of this system can be considered as inefficient mixing and the need for a higher pressure of H₂.

Table 4.17. Collected results for hydrogenation reactions under low pressures of hydrogen gas.

Entry	Hydrogen source	Temperature (°C)	Additives	Solvent	Time (h)	GVL yield (%)
1 ^a	Balloon	100	NEt ₃	-	24	nd
2 ^a	Balloon	100	NEt ₃	THF	24	nd
3 ^a	Balloon	100	NEt ₃	1,4-dioxane	24	nd
4 ^a	Balloon	150	NEt ₃	-	24	23 ^b
5 ^a	Balloon	150	-	-	24	nd
6 ^a	Balloon	150	NEt ₃	1,4-dioxane	24	nd
7 ^c	NMR tube	100	NEt ₃	-	4	2
8 ^c	NMR tube	150	NEt ₃	-	4	6

*Reactions performed using standard transfer hydrogenation conditions, with levulinic acid (3.4 mmol), **C2** (1 mol%) and triethylamine (10 mol%) at the stated temperature for the stated time. Reactions were performed as single runs and yields were determined by ¹H NMR spectroscopy. a) Reactions performed in reaction vials under balloon of hydrogen gas. b) Reaction performed in duplicate. c) Reactions performed in an NMR tube fitted with a Young's tap and filled with H₂ (~ 4 bar).

4.7 High pressure hydrogenation reactions

4.7.1 High-pressure hydrogenation of LA with palladium catalysts

The work described thus far in Chapter 4 has shown that the catalytic systems trialled have moderate activity under transfer hydrogenation conditions. However, there are some limitations surrounding a lack of water-solubility and catalyst deactivation by the products of FA dehydration which were not circumvented. Higher GVL yields could be expected using higher pressures of hydrogen gas. With the palladium catalysts trialled by Garcia et al., those with P(^tBu)₂ substituents achieved quantitative LA hydrogenation under both transfer hydrogenation and high-pressure conditions. Their PPh₂ and PCy₂

catalysts achieved zero conversion under transfer hydrogenation conditions, but these increased to GVL yields of 9 % and 34 % respectively under high pressures of hydrogen gas.¹ Therefore, excepting the decomposition of the $P(tBu)_2$ catalysts described in this work, the PCy_2 catalysts **C1** and **C2** are still highly promising.

Initial high-pressure hydrogenations were performed in a Parr reactor necessitating the addition of a large solvent volume. With **C1** and **C2** in THF, dioxane or water, at H_2 pressures up to 50 bar, zero or near-zero GVL yields were achieved. Changing to an Asynt mini-reactor which sits atop a standard hotplate stirrer allowed for hydrogenation reactions to be performed on a smaller scale (in accordance with the experiments described in Section 4.6.1). Therefore, the hydrogenation reactions could be run without an additional solvent and with the direct replacement of FA for hydrogen gas.

The reactions were scaled-up to twice the standard transfer hydrogenation scale used previously. At 100 °C and with a pressure of 10 bar H_2 , over six hours a 25 % GVL yield was achieved with **C2**. Encouraged by this, the temperature was increased to 120 and then 150 °C, achieving yields of 46 and 57 % respectively (Table 4.18, Entries 1-3). Clearly the use of 10 bar H_2 pressure was superior to both the balloon and NMR tube hydrogenations (Section 4.6.2), and capable of producing results in-line with those achieved under transfer hydrogenation conditions. At 120 °C and with an increase to 20 bar H_2 , an improved yield of 77 % was achieved (Table 4.18, Entry 4). At 150 °C and 20 bar H_2 , a GVL yield of 97 % was determined, demonstrating that quantitative hydrogenation of LA to GVL is attainable with **C2**, albeit under relatively harsh conditions (Table 4.18, Entry 5). No further improvement was achieved upon extending the reaction time to 22 hours (Table 4.18, Entry 6), and **C1** achieved a very similar 93 % GVL yield under the same conditions (Table 4.18, Entry 7).

A reduction in pressure from 20 bar to 15 bar H_2 achieved the same yield (96 %, Table 4.18, Entry 8). Therefore, to achieve quantitative LA hydrogenation with **C2** a temperature of 150 °C and a pressure of 15 bar is required. With a reduction in catalyst loading from 1 mol% to 0.5 mol%, a yield of 92 % was still achieved, and an 82 % yield was achieved with 0.1 mol% catalyst (Table 4.18, Entries 9-10). Reactions were performed with shorter reaction times. In one hour, a yield of 84 % was achieved; with the omission of NEt_3 , just a 25 % yield was achieved in one hour (Table 4.18, Entries 11-12). In three hours, a 93 % yield was achieved, demonstrating that the vast majority of LA is hydrogenated within the first three hours (Table 4.18, Entry 13). After three hours at the optimised conditions of 15 bar H_2 and 150 °C with a 0.5 mol% catalyst loading, an 85 % yield was still achieved (Table 4.18, Entry 14).

Omitting the catalyst, or using instead $[PdCl_2(COD)]$, achieved no LA hydrogenation at 20 bar H_2 and 150 °C in one hour. An in situ combination of $[PdCl_2(COD)]$ and N-Triphos^{Cy} achieved just 6 % GVL yield in the same time, demonstrating that the pre-formed catalyst is essential. As per the transfer

hydrogenation studies, the PPh₂-catalyst **C7** achieved no LA hydrogenation at 20 bar H₂ (Table 4.18, Entries 15-18).

The reaction was scaled up with **C2** to a ~10 mL scale (12 times larger than the previous reactions). At 150 °C and 20 bar H₂ with 0.5 mol% **C2**, an 85 % GVL yield was determined by ¹H NMR spectroscopy after 6 hours (Table 4.18, Entry 19). This is only slightly reduced from the 92 % yield achieved on the smaller scale. After removing the solid residue, the reaction mixture was distilled under reduced pressure to remove residual triethylamine and LA. Distilled GVL was collected as a pale-brown clear liquid in an isolated yield of 5.13 g (64 %), with product identity and purity confirmed by ¹H NMR spectroscopy. The solid residue collected from the previous reaction was reused for a subsequent reaction on the larger scale. The recovered solid residue was dark-brown/black in colour and was dried in vacuo. With the recycled catalyst, just a 5 % GVL yield was achieved, demonstrating that catalyst recycling was ineffective. This might be improved if the catalyst was recovered and stored under strict inert conditions.

Table 4.18. Collected results achieved under high-pressures of hydrogen gas with palladium catalysts.

Entry	Catalyst	Catalyst loading	Temperature (°C)	Pressure (bar)	Time (h)	GVL yield (%) ^a
1	C2	1 mol%	100	10	6	25
2	C2	1 mol%	120	10	6	46
3	C2	1 mol%	150	10	6	57
4	C2	1 mol%	120	20	6	77
5	C2	1 mol%	150	20	6	97
6	C2	1 mol%	150	20	22	93
7	C1	1 mol%	150	20	6	93
8	C2	1 mol%	150	15	6	96
9	C2	0.5 mol%	150	20	6	92
10	C2	0.1 mol%	150	20	6	82
11	C2	1 mol%	150	20	1	84
12 ^b	C2	1 mol%	150	20	1	25
13	C2	1 mol%	150	20	3	93
14	C2	0.5 mol%	150	15	3	85
15	-	n/a	150	20	1	nd
16	[PdCl ₂ (COD)]	1 mol%	150	20	1	nd
17	[PdCl ₂ (COD)] /N-Triphos ^{Cy}	1 mol%	150	20	1	6
18	C7	1 mol%	150	20	1	nd
19 ^c	C2	0.5 mol%	150	20	6	85 (64)
20 ^{cd}	C2	0.5 mol%	150	20	6	5

a) Reactions were performed using standard hydrogenation conditions in a high-pressure Asynt reactor, with levulinic acid (6.74 mmol), the stated catalyst (0.06 mmol, 1 mol%) and triethylamine (0.72 mmol, 10 mol%). GVL yields were determined by ¹H NMR spectroscopy; isolated yields in brackets. b) NEt₃ omitted. c) Reaction performed on a larger scale (81 mmol LA). d) Catalyst recycled from Entry 19.

4.7.2 High-pressure hydrogenation of LA with earth-abundant metals

*Much of the work discussed in this Section has been published in Journal of Organometallic Chemistry (2020).*³³

A wider study of high-pressure LA hydrogenation reactions was performed with in situ mixtures of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and N-Triphos ligands. This was considered as an extension of previous work performed in the Miller group, primarily with ruthenium complexes which had achieved high conversions of LA to GVL.³⁴ These systems were introduced in Chapter 1. The work performed here was also motivated by recent reports of homogeneously catalysed high-pressure hydrogenations of LA using $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ alongside the carbon-centred Triphos ligand (Chapter 1).³⁵ Chapter 5 will discuss the coordination chemistry and reactivity of first-row transition metals with N-Triphos ligands; herein will follow a brief summary of some results achieved with cobalt/N-Triphos systems under high-pressure conditions. It should be noted that a system of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ /N-Triphos^{Ph} demonstrated no catalytic activity under transfer hydrogenation conditions.

Results achieved under high-pressure conditions are collected in Table 4.19. In the first instance, a system of $[\text{Ru}(\text{acac})_3]$ (0.5 mol%) and N-Triphos (1 mol%) was trialled to establish a bench-mark result.³⁴ At 150 °C and 50 bar H_2 over six hours in THF, an 87 % GVL yield was achieved (Table 4.19, Entry 1). Directly replacing $[\text{Ru}(\text{acac})_3]$ for $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ achieved a conversion to 12 % GVL and 1 % 1,4-PDO (Table 4.19, Entry 2). Whilst the results achieved with $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ were significantly lower than for $[\text{Ru}(\text{acac})_3]$, they demonstrated that the cobalt system provides some activity for LA hydrogenation under these conditions.

The hydrogenation conditions were altered to 100 °C and 80 bar H_2 , with an increase to a 10 mol% loading of both $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and N-Triphos. These conditions were adapted from those reported by de Bruin et al.³⁵ Now, an improved LA conversion to 75 % GVL and 5 % 1,4-PDO was achieved (Table 4.19, Entry 3). Trialling conditions of 150 °C and 50 bar resulted in a GVL yield of 22 % (Table 4.19, Entry 4). This suggests that an elevated temperature above 100 °C is detrimental to the hydrogenation reaction, perhaps attributable to catalyst decomposition.

In an attempt to replicate the results reported by de Bruin et al., a system of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and the carbon-centred Triphos ligand was trialled. With a change in solvent to methanol, some issues were encountered with solubility of the ligand at RT. Yields of 60 % GVL and 21 % 1,4-PDO were achieved (Table 4.19, Entry 5). With N-Triphos in methanol, conversions to 44 % GVL and 8 % 1,4-PDO were achieved (Table 4.19, Entry 6). Therefore, by replicating the conditions reported in the literature, N-

Triphos gave lower yields than Triphos itself. However, more promising results had already been achieved in THF and this was utilised for all further reactions.

With a reduction to a 1 mol% loading of both $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and N-Triphos, reduced yields of 27 % GVL and 2 % 1,4-PDO were achieved (Table 4.19, Entry 7). However, a 5 mol% loading achieved identical yields to those achieved with a 10 mol% loading, suggesting there is no benefit to including metal or ligand above 5 mol%. (Table 4.19, Entry 8). A reduction in pressure from 80 bar to 50 bar H_2 also achieved only slightly reduced yields of 69 % GVL and 4 % 1,4-PDO (Table 4.19, Entry 9).

A change from $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ to $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ was also investigated. With an initial 1 mol% catalyst loading, yields of 28 % GVL and 5 % 1,4-PDO were achieved, similar to those achieved with the cobalt system at 1 mol% (Table 4.19, Entry 10). However, with an increase to a 5 mol% loading, a yield of just 40 % GVL was detected, significantly below that achieved with $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ under identical conditions (Table 4.19, Entry 11). These results tentatively suggest that $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ has a greater activity than $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ under these conditions.

In the absence of a ligand, $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ alone achieved no LA hydrogenation (Table 4.19, Entry 12). Trialling $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ with the monodentate ligand PPh_3 or the bidentate ligand dppe also failed to achieve any LA hydrogenation (Table 4.19, Entries 13-14). These results demonstrate that the inclusion of the tridentate ligand is essential. This could be considered as a stabilising effect achieved with tridentate metal coordination, or upon an activating effect of three phosphines bound to the metal centre. A system of $[\text{Co}(\text{acac})_2]$ with N-Triphos achieved a yield of just 7 % GVL, indicating that both choice of ligand and metal precursor are critical (Table 4.19, Entry 15). Although $[\text{Co}(\text{acac})_2]$ is a cheaper alternative to $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, it appears that $[\text{Co}(\text{acac})_2]$ inhibits the formation of the active catalytic species with N-Triphos.

Trialling $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ with the carbon-centred Triphos ligand again, but in THF at 100 °C and 80 bar H_2 achieved 82 % GVL, 15 % 1,4-PDO and 1 % 2-MTHF yields (Table 4.19, Entry 16). This again demonstrates higher yields are achieved with Triphos than for N-Triphos. Whilst it is disappointing that in a direct comparison N-Triphos is less active than Triphos, there remains several advantages with N-Triphos ligands. These are primarily their easier synthetic route and greater structural versatility. Furthermore, although the overall hydrogenation of LA is higher with Triphos than with N-Triphos, there is little difference between their GVL yields. This suggests that the Triphos ligand is better able to hydrogenate GVL into its further hydrogenation products. The greater mixture of products achieved with Triphos can also be considered as a drawback, necessitating product separation.

Therefore, the fact that N-Triphos ligands with $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ can achieve LA hydrogenations close to those achieved with Triphos is an early indication that the system under study is a promising route towards sustainable LA hydrogenation. Whilst this Chapter has focused on hydrogenations of LA to GVL using transfer hydrogenation with FA, there is clear potential for the further study of high-pressure systems based upon N-Triphos ligands with earth-abundant metals.

Table 4.19. Collected results achieved under high-pressures of hydrogen gas with Fe/Co.

Entry	Catalyst loading	Solvent	Temperature (°C)	Pressure (bar)	Yield (%)
1	$[\text{Ru}(\text{acac})_3]$ (0.5 mol%), N-Triphos (1 mol%)	THF	150	50	87 - GVL
2	$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mol%), N-Triphos (1 mol%)	THF	150	50	12 – GVL 0.5 – 1,4-PDO
3	$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, N-Triphos (both 10 mol%)	THF	100	80	75 – GVL 5 – 1,4-PDO
4	$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, N-Triphos (both 10 mol%)	THF	150	50	22 - GVL
5	$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, Triphos (both 10 mol%)	Methanol	100	80	60 – GVL 21 – 1,4-PDO
6	$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, N-Triphos (both 10 mol%)	Methanol	100	80	44 – GVL 8 – 1,4-PDO
7	$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, N-Triphos (both 1 mol%)	THF	100	80	27 – GVL 2 – 1,4-PDO
8	$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, N-Triphos (both 5 mol%)	THF	100	80	75 – GVL 5 – 1,4-PDO
9	$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, N-Triphos (both 5 mol%)	THF	100	50	69 – GVL 4 – 1,4-PDO
10	$\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, N-Triphos (both 1 mol%)	THF	100	80	28 – GVL 5 – 1,4-PDO
11	$\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, N-Triphos (both 5 mol%)	THF	100	80	40 – GVL nd – 1,4-PDO
12	$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (5 mol%)	THF	100	80	nd
13	$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (5 mol%), PPh_3 (15 mol%)	THF	100	80	nd
14	$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (5 mol%), DPPE (10 mol%)	THF	100	80	nd
15	$[\text{Co}(\text{acac})_2]$, N-Triphos (both 5 mol%)	THF	100	80	7 – GVL
16	$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, Triphos (both 5 mol%)	THF	100	80	82 - GVL 15 – 1,4-PDO 1 – 2-MTHF

*Reactions were performed in a high-pressure Parr reactor with levulinic acid (10 mmol), the stated catalyst and solvent (20 mL) and maintained at the stated temperature and pressure for 6 hours. GVL yields were determined by ^1H NMR spectroscopy. nd = not detected.

4.8 Summary and outlook

From the results described in this Chapter, several conclusions can be made. Gratifyingly, most of the catalysts tested for the transfer hydrogenation of LA showed some degree of activity under the conditions tested. The series of palladium complexes with PCy₂ substituents were identified as the most promising candidates for investigation. Their syntheses and characterisation were straightforward relative to the iridium and ruthenium analogues, as discussed in Chapter 3. Whilst some of the iridium complexes in particular showed promising activity as transfer hydrogenation catalysts, the greater difficulty and lower yields of their syntheses made them difficult to apply as candidates for the screening of a wide range of hydrogenation variables. Nonetheless, if their syntheses and characterisation could be improved, they remain as promising candidates for further study.

It should be reinstated that the transfer hydrogenation conditions trialled represent relatively mild conditions relative to many of the systems described in the literature. Under this umbrella, important variations between the palladium complexes studied were readily identified. The complexes of PPh₂-ligands showed no activity for the transfer hydrogenation of LA, whilst their PCy₂ analogues achieved modest LA hydrogenation under even the standard conditions trialled. In other work in this field, the steric bulk and electron-donating nature of the phosphine substituent have been identified as important factors affecting catalyst activity. Considering this, the P(^tBu)₂ analogue was expected to improve upon the yields achieved. In fact, significantly reduced GVL yields were achieved, attributed to catalyst decomposition. The nature of this decomposition is unknown. Coupling this with the increased difficulty of synthesising both the P(^tBu)₂ ligands and complexes relative to the PCy₂ analogues, the palladium complexes of the PCy₂ ligands were positioned as the most promising of the catalysts under study.

A wide range of variables were studied to improve upon the yields achieved, primarily with **C1** and **C2**. The selection of suitable reaction vessels must be highlighted. The most successful set-up used reaction vials running in parallel upon a single heating-block. These were carefully selected so that they provided a sealed environment for the generation and retention of a pressure whilst preventing the chance of an “over-pressure” in a controlled manner.

The majority of the reaction variables investigated failed to significantly improve the hydrogenations achieved relative to the original system. It was found that the absence of a controlled, inert atmosphere did not reduce the GVL yields achieved. Increasing the catalyst loading or the loading of FA did not provide the expected improvements. These studies were limited by the maximum pressure tolerated by the reaction vial set-up. Whilst a reduction in base loading was found to be beneficial,

triethylamine remained as the most effective base additive investigated. A reduction in temperature from 100 °C to 80 °C did not reduce the yields achieved over 24 hours. In an Asynt high-pressure reactor, an increase in temperature to 150 °C coupled with an increase in FA loading achieved the highest GVL yield of 78 % in two hours.

Although 24-hour reaction times were used as standard for the transfer hydrogenation reactions, the vast majority of the hydrogenation occurred within the first two hours. This suggested that in relatively short timescales, either the catalyst is degraded or no longer active, or that the FA supply has been exhausted. Gas evolution studies found that complete decomposition of FA was achieved within a short time, followed by no further gas evolution. The presence of CO gas was also detected.

The impact of reaction solvent was also identified. Although the benefits of using aqueous systems for transfer hydrogenations are well-established, the series of catalysts tested in this work have no water solubility, even at raised temperatures. In aqueous mixtures, no hydrogenation was achieved because of catalyst insolubility. The addition of trace volumes of water, or the use of mixed water-organic solvent systems, improved the yields achieved slightly. However, most transfer hydrogenation reactions were performed in the absence of an additional solvent. The development of water-soluble catalysts, incorporating water-soluble phosphine or amine moieties, showed some promise. This requires further optimisation, but structural modifications to increase water-solubility must be carefully balanced with maintaining, or improving upon, the catalyst activity.

The benefits of incorporating water in this system are attributed to promoting FA dehydrogenation and minimising catalyst deactivation. Correspondingly, it was found that both **C1** and **C2**, upon direct reaction with FA and triethylamine, are converted into CO-bridged palladium dimer species, considered as inactive forms of the original catalysts. It is possible to connect the observation of catalyst deactivation in non-aqueous systems to the lack of hydrogenation achieved after the first two hours, and the lack of a benefit of increasing the volume of FA or catalyst loading, if doing so promotes catalyst deactivation.

Under high-pressure hydrogenation conditions, near-quantitative GVL yields were achieved at 150 °C and 15 bar H₂. This demonstrates that the LA hydrogenations were being limited by using FA as hydrogen source, primarily attributed to the incomplete dehydrogenation of FA achieved.

In summary, the catalysts described in this study are straight-forward to synthesise, well-defined and offer the potential for a wide range of structural modifications – far beyond that attempted in this work. The benefits of transfer hydrogenations over high-pressure hydrogenation reactions are important, and all of the transfer hydrogenations described in this section showed selectivity for

hydrogenation of LA to GVL under relatively mild conditions. Whilst they show moderate catalyst activity, there appears to be a barrier towards reaching quantitative LA hydrogenation with FA, which cannot be circumvented without significant modification to the system. It is unfortunate that the catalysts lack water solubility, despite their structural similarity to catalysts in the literature, and that they were found to decompose or become deactivated. Improvements might be achieved by water-solubilisation of the catalysts, allowing for water to be used as the solvent, promoting FA dehydrogenation and minimising catalyst deactivation. Whilst increasing the temperature and FA loading gave a significant improvement, it was not until true high-pressure hydrogenation conditions were trialled that quantitative LA hydrogenation to GVL was attained. The high-pressure hydrogenations can be further optimised; however, they demonstrate a rare example of a palladium-based system for LA hydrogenation. Therefore, this work presents a rare palladium-based catalytic system able to achieve moderate but selective hydrogenation of LA to GVL using FA as hydrogen source, or near-quantitative hydrogenation under high-pressure conditions. Both the hydrogenation reactions themselves, and the design of the catalysts used, has vast potential for future investigation.

4.9 References

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Chapter 5

Coordination chemistry of tri-phosphine oxide ligands

“It isn’t faith that makes good science, Mr. Klaatu, it’s curiosity”, *The Day the Earth Stood Still* (1951)

5.1 Introduction

Phosphine oxides have been used as ligands to prepare a wide range of complexes with lanthanides, actinides, and group 13/14 elements. Such complexes often have interesting photochemical properties. Several reviews have been published covering this field.^{1–3} However, examples of complexes of phosphine oxides with transition metals are far less common. This can be attributed in part to the “hard” bonding nature of phosphine oxides, which favours bonding to “hard” metal centres. Considering this, and for relevance to the work to be discussed in this Chapter, interesting examples of the coordination chemistry of phosphine oxide ligands to transition metals will be briefly introduced.

The incorporation of a phosphine oxide moiety, either as a binding or non-binding group, is considered to impart several favourable properties to a complex. These include improved air and moisture stability^{4–7}; the modification of a phosphine ligand’s binding character (e.g. to prevent a phosphine group from binding to a metal)⁴; and catalytic activity^{6,8–14}, for reactions such as the epoxidation and hydroformylation of alkenes and the oxidation of indoles. There are examples of phosphine oxide complexes which are catalytically active, but their corresponding phosphine complexes have little or no catalytic activity – even exchanging triphenylphosphine for triphenylphosphine oxide has been found to give a promoting effect in some cases.^{6,13–16} These results challenge the assumption that phosphine oxides are poor ligands for catalysts, although they remain understudied relative to phosphines.

Most phosphine oxide ligands are of the general formula $R_3P=O$ (R = alkyl or aryl). They typically coordinate to a metal in a monodentate fashion via the oxygen atom.^{5,6,8–13,17–24} The exact nature of the phosphorus-oxygen bond is still a subject of debate. The phosphorus-oxygen bond has a multiple bond strength (that of a double bond) and has an inherently high degree of polarity (with electron density strongly skewed towards oxygen). It is thought to vary between a formal covalent double $P=O$ bond and an ionic $R_3P^+O^-$ bond depending on the metal centre it is coordinated to.^{1,21} Neither picture alone satisfyingly supports the described observations.

Most postulations for the nature of the $P=O$ bond invoke strong σ -donation supplemented by a degree of π back-bonding. The π back-bonding of oxygen’s electron lone pairs can be either bonding or antibonding in character. Several representations are illustrated in Figure 5.1.²⁵ Representation (A) is composed of a σ bond and two π back-bonds into the phosphine LUMO (σ^* type), as an example of “negative hyperconjugation”. Representation (B) is similar: beside a strong $P-O$ σ bond, each of the three equivalent oxygen lone pair orbitals is able to back-donate electron density to phosphorus.

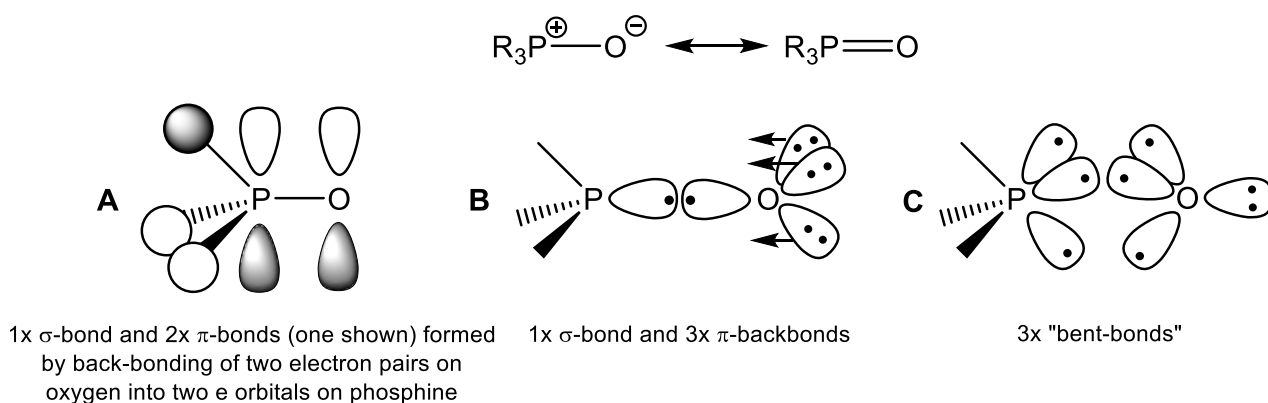


Figure 5.1. Illustrations of the nature of P-O bonding.²⁵

Representation (C) is more unorthodox, invoking three curved regions of electron density (bent multiple bonds) between phosphorus and oxygen, and is formally a triple bond. In every case, the electron density is concentrated at the oxygen atom, which can interact with metal centres through its lone pair(s) of electrons.^{26,27}

Although less common than their monodentate analogues, a range of bidentate phosphine oxide ligands have also been reported. Most of these are mixed ligands incorporating both a binding phosphine oxide moiety and one other binding group e.g. an amine^{28–30}, carbene³¹, phenol³², imine³³ or phosphine^{34,35}. The simplest of the bidentate phosphine oxide ligands are of the form $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$, where $n=1$ (BDPPM) or 2 (BDPPE) (Figure 5.2).^{6,36} Complexes of $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ with molybdenum and tungsten have been applied to catalytic epoxidation reactions. With the incorporation of phenylethynyl substituents on the phosphine oxide $\text{R}_2\text{P}(\text{O})(\text{CH}_2)_n\text{P}(\text{O})\text{R}_2$ ligands (Figure 5.2), complexes with Cd/Pb have been used as fluorescent probes.³⁷

A series of $\text{P}(\text{O})\text{NP}(\text{O})$ -type ligands are also known, with both simple amines and N-heterocycles connecting the two phosphine oxides (Figure 5.2).²⁹ This structure allows for modification of the ligand both at the nitrogen atom and along the carbon chain. Complexes of molybdenum and cobalt with $\text{EtN}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$ were reported; dependent on the choice of starting salt, octahedral or tetrahedral complexes were formed. In these, the $\text{P}(\text{O})\text{NP}(\text{O})$ ligand bound to the metal in a cis-manner, alongside chloride/oxo-/nitrate ligands.

Bidentate phosphine oxide ligands have also been found to bind through a different mode. With diphenyl ether and ferrocene linkers ($(\text{C}_6\text{H}_4\text{P}(\text{O})(\text{Ph})(\text{H}))_2\text{O}$ and $(\eta^5\text{-C}_5\text{H}_4\text{P}(\text{O})(\text{Ph})(\text{H}))_2\text{Fe}$), Figure 5.2), the phosphine oxide ligands bind through the two phosphorus atoms, instead of through the oxygen atoms as the phosphine oxide tautomerises to its phosphinous acid form. Palladium and nickel complexes of this form were reported as catalysts for cross-coupling reactions. The inclusion of phosphine oxide moieties was beneficial for long-term storage of the catalysts.^{7,38}

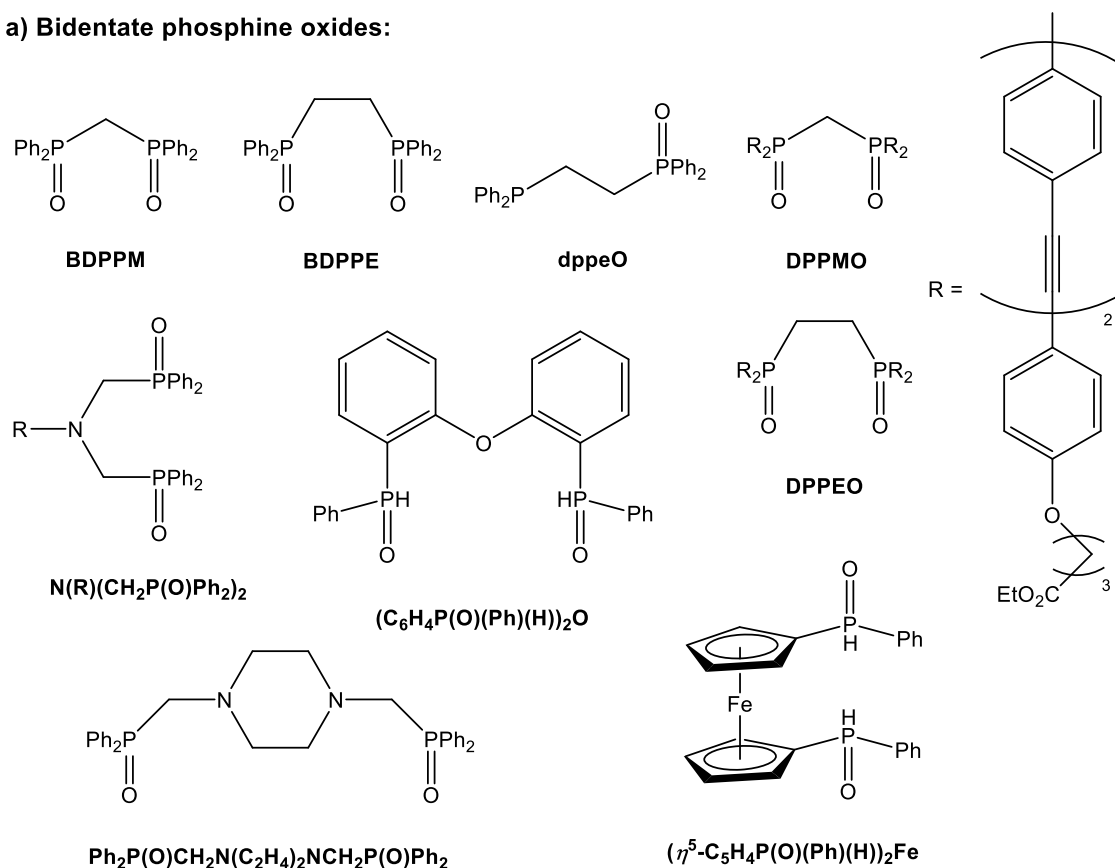
There are some mixed bidentate phosphine/phosphine oxide ligands which bind to a metal through one phosphine and one phosphine oxide group. These have been described as valuable hemilabile ligands with synthetic and catalytic applications. Some of the linkers include alkyl chains, BINAP, benzyl and ferrocene analogues.³⁴ One such example, the mixed phosphine-phosphine oxide ligand $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ (dppeO, Figure 5.2) was found to act as a bridging ligand to generate Pd-M heterobimetallic complexes, with $\text{M} = \text{Mn/Cu/Co/Zn/Hg}$.³⁵ An example of a mixed ligand with two phosphines and one phosphine oxide is $[o\text{-iPr}_2\text{P}-(\text{C}_6\text{H}_4)]_2\text{P}(\text{O})\text{Ph}$ (DPPO, Figure 5.2). DPPO displays a variety of coordination modes depending on the metal centre ($\text{M} = \text{Rh/Pd/Ag/Au}$).^{39,40} DPPO can coordinate via either one or both phosphine groups, and in some cases additionally through the phosphine oxide. This means it can adopt either mono-, bi- or tridentate modes. Further to this, the phosphine oxide of DPPO has been found to bind through either the phosphorus or oxygen atom, again dependent on the choice of metal.

Examples of tridentate phosphine oxide ligands are less common than bidentate phosphine oxide ligands. One example is $(\text{R}_\text{P}^*, \text{S}_\text{P}^*)\text{-11}$ (Figure 2)⁴¹, which contains two ortho-substituted diphenylphosphinic amides connected through a phenylphosphine oxide moiety. $(\text{R}_\text{P}^*, \text{S}_\text{P}^*)\text{-11}$ was found to coordinate to yttrium in a tridentate fashion generating complexes where either one or two of the ligands occupy metal coordination sites, alongside additional nitrate ligand(s). Further examples can be found in complexes with lanthanide elements: the ligands DPPPO (structurally similar to $(\text{R}_\text{P}^*, \text{S}_\text{P}^*)\text{-11}$) and its N/S analogues DPPYPO (Figure 5.2) and DPBTPO⁴²; and the ligand TPPM (Figure 5.2)^{43,44}, all of which adopt tridentate modes.

A relevant example is the oxide of the tridentate tripodal Triphos ligand, $\text{CH}_3\text{C}\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_3$ (P_3O_3 , Figure 5.2).⁴⁵ Complexes of P_3O_3 have been reported with ruthenium and rhodium.⁴⁶ With ruthenium, P_3O_3 coordinates in a bidentate manner through two of its three phosphine oxides. The third phosphine oxide was uncoordinated. The complex $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{P}_3\text{O}_3)]$ is octahedral, with monodentate Cl/CO ligands at the remaining four coordination sites (Figure 5.3).⁴⁷ With rhodium, a complex of the form $[\text{Rh}(\text{CO})_2\text{Cl}(\text{P}_3\text{O}_3)]$ was formed (Figure 5.3). Although its exact structure was not determined, its data was consistent with a tridentate coordination mode of P_3O_3 . The rhodium complex was studied as a catalyst for the carbonylation of methanol. From reaction with lanthanide metals, P_3O_3 formed a series of polymeric complexes with a “chelating-bridging” mode.⁴⁵

Earlier chapters of this thesis extensively described the preparation, properties and coordination chemistries of N-Triphos ligands. However, the corresponding oxide ligands $\text{N}(\text{CH}_2\text{P}(\text{O})\text{PR}_2)_3$ have received very little attention in the literature. To the best of my knowledge, there exists only a single report of a complex of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{PPh}_2)_3$ in the literature.

a) Bidentate phosphine oxides:



b) Tridentate phosphine oxides:

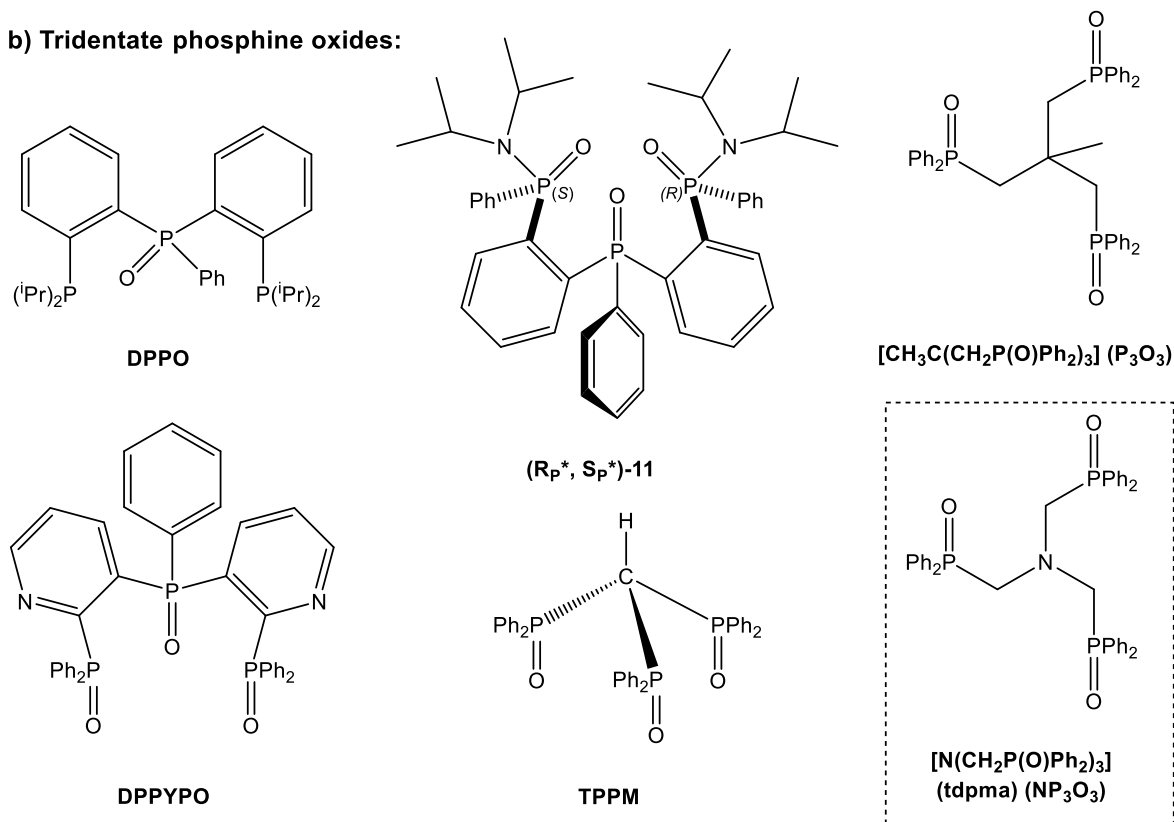


Figure 5.2. Examples of a) bidentate phosphine oxide ligands and b) tridentate phosphine oxide ligands from the literature.

In 2000, Midollini et al. described the synthesis and characterisation of the tetrahedral beryllium complex $[(N(CH_2P(O)PPh_2)_3)Be(OH_2)]^{2+}$. In that complex, the oxide ligand adopted a tridentate binding mode with coordination through the oxygen atoms (Figure 5.3).⁴⁸

Owing to the interest in N-Triphos ligands and the scarcity of knowledge regarding its oxide analogue $N(CH_2P(O)PPh_2)_3$, this was considered as an area of untapped potential. This Chapter will describe the synthesis of N-Triphos oxide ligands and their coordination chemistry with first-row transition metals, representing a significant expansion of the coordination chemistry previously described with this ligand family. Furthermore, the coordination chemistry of multidentate phosphine oxide ligands with first-row transition metals is very scarce in general.

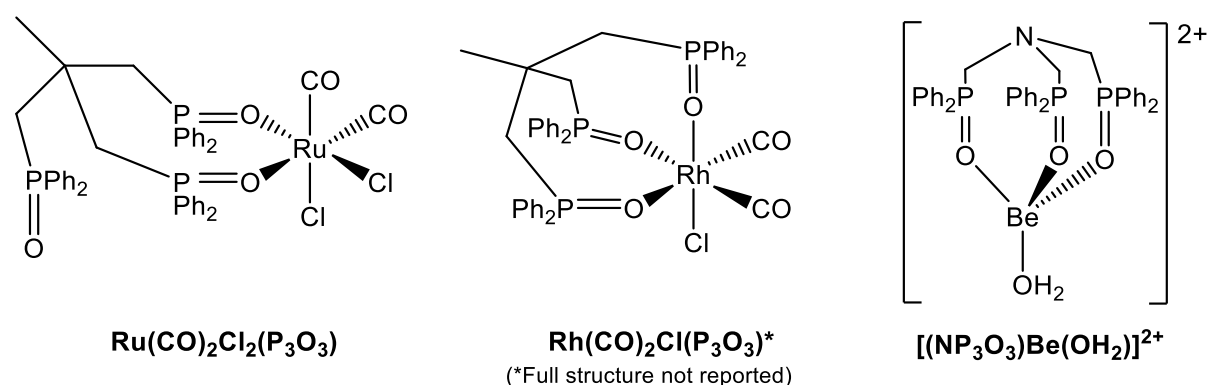
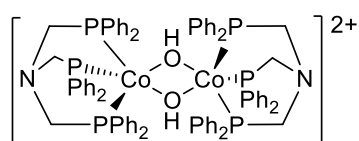


Figure 5.3. Examples of complexes formed with multidentate phosphine oxide ligands.^{45,47,48}

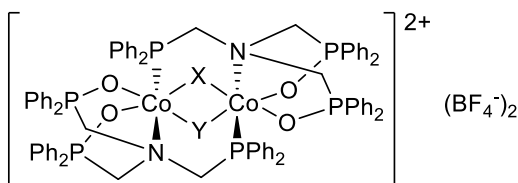
5.2 Reactions between N-Triphos^{Ph} and $Co(BF_4)_2 \cdot 6H_2O$

As context for the study of phosphine oxide ligands to be discussed in this chapter, some work performed prior to this PhD project will be briefly described.⁴⁹ The reaction between N-Triphos^{Ph} and $Co(BF_4)_2 \cdot 6H_2O$ was expected to produce a dimeric cobalt complex with an N-Triphos^{Ph} ligand bound to each cobalt centre. The expected product is shown in Figure 5.4 (a). The carbon-centered Triphos cobalt complex has been described in the literature.⁵⁰ The reaction between N-Triphos^{Ph} and $Co(BF_4)_2 \cdot 6H_2O$ was performed in THF/1-butanol, with the addition of $NaBPh_4$ to aid product isolation as a BPh_4 adduct. The products showed no $^{31}P\{^1H\}$ NMR signals and broad, undefined ^1H NMR signals. This was attributed to the paramagnetism of the product formed. Under inert conditions, liquid diffusion of diethyl ether into dichloromethane yielded single crystals suitable for X-ray crystallography.

a) Expected product from reaction of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ + N-Triphos :

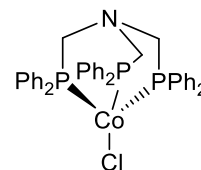


b) Obtained crystal structures:



X, Y = OH or Cl by crystallography

32



33

Figure 5.4. Structures of a) the expected product of reaction between $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and N-Triphos and b) the obtained crystal structure identities **32** and **33**.

The crystal structure of $[\text{Co}_2(\text{N}(\text{CH}_2\text{PPh}_2\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_2))_2(\mu_2\text{-OH})_2](\text{BF}_4)_2$ (**32**), shown in Figure 5.5, has both similarities and differences from the expected species (Figure 5.4). **32** is a cobalt dimer with a centre of symmetry and one N-Triphos bound to each cobalt centre. The bridging ligands were assigned as a mixture of OH and Cl ligands. Each N-Triphos ligand was partially oxidised with two phosphine oxides on each ligand, despite attempts to exclude air from the crystallisation. The phosphine oxides bind to cobalt through their oxygen atoms with the unoxidised phosphine on each N-Triphos ligand coordinating to the other cobalt centre. Additionally, the nitrogen atom of each ligand is bound to cobalt. Therefore, each N-Triphos ligand adopts a tetradentate coordination mode. Typically, metal coordination of the apical nitrogen atom is prohibited, attributed to unfavourable steric interactions. Here the nitrogen coordination can be rationalised. Binding of two N-Triphos arms through phosphine oxides positions the bulky PPh_2 groups further from the metal centre. Also, the third phosphine arm is binding to the further cobalt centre, allowing the nitrogen atom to approach the metal more closely. The dimer has the expected 2+ charge, with BF_4^- counter-ions. Incorporating nitrogen binding raises the electron count at each cobalt centre from 17 to 19 electrons. The paramagnetism of the complex is rationalised by the d^7 octahedral cobalt centres.

The bond lengths around the Co(1) centre in **32** are collected in Table 5.1. The Co-O bond lengths are the shortest at 2.108(3) and 2.051(3) Å, with a Co-N bond length of 2.296(3) Å and Co-P bond length of 2.4662(10) Å. The geometry around each cobalt centre can be described as approximately octahedral; however, the bond angles collected in Table 5.1 show that there is a high degree of variance in the angles around the cobalt centre.

Unfortunately, further characterisation was unable to support the identification of the dimer structure. In this case, the partial oxidation was unintended. Nonetheless, it demonstrated that interesting coordination modes could be accessed via the introduction of phosphine oxide moieties into N-Triphos ligands.

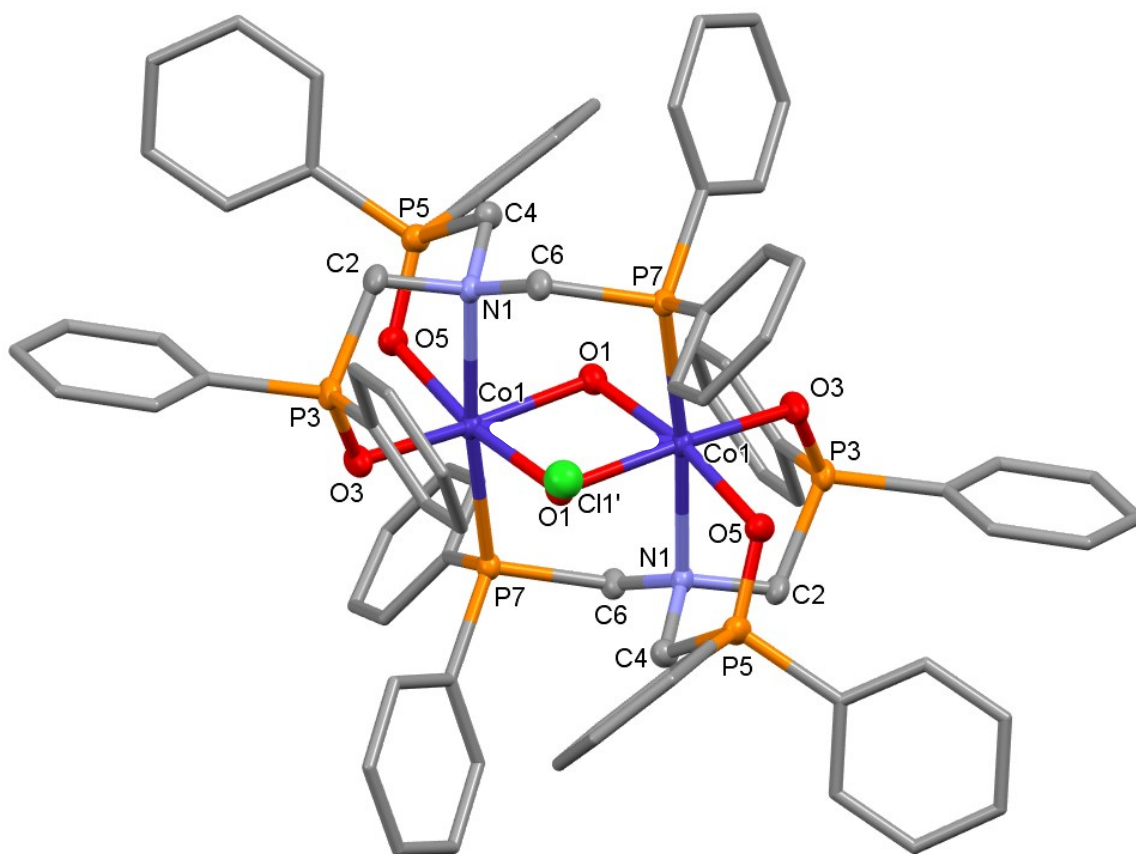


Figure 5.5. Crystal structure of $[\text{Co}_2(\text{N}(\text{CH}_2\text{PPh}_2\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_2))_2(\mu_2\text{-OH})_2](\text{BF}_4)_2$ (**32**). Hydrogen atoms, anions and solvent molecules omitted for clarity.

Table 5.1. Collected bond lengths and bond angles for **32** and **33**.

32		33	
Bond	Bond length (Å)	Bond	Bond length (Å)
Co(1)-P(7A)	2.4662(10)	Co(1)-P(8)	2.244(1)
Co(1)-O(3)	2.051(3)	Co(1)-P(12)	2.244(1)
Co(1)-O(5)	2.108(3)	Co(1)-P(14)	2.230(1)
Co(1)-N(1)	2.296(3)	Co(1)-Cl(45)	2.220(1)
P(3)-O(3)	1.505(3)		
P(5)-O(5)	1.505(3)		
Bond angle (°)		Bond angle (°)	
O(3)-Co(1)-N(1)	85.19(11)	P(8)-Co(1)-P(12)	91.97(5)
O(5)-Co(1)-N(1)	80.04(11)	P(8)-Co(1)-P(14)	90.00(5)
O(3)-Co(1)-O(5)	94.21(11)	P(12)-Co(1)-P(14)	94.57(5)
O(3)-Co(1)-P(7A)	101.42(8)	P(8)-Co(1)-Cl(45)	121.15(5)
O(5)-Co(1)-P(7A)	100.26(8)	P(12)-Co(1)-Cl(45)	124.71(5)
N(1)-Co(1)-P(7A)	173.32(8)	P(14)-Co(1)-Cl(45)	124.99(5)

The remainder of this section describes work from this PhD project. Subsequent crystallisations of the product of reacting N-Triphos^{Ph} with Co(BF₄)₂·6H₂O were set-up inside a glovebox to more rigorously avoid oxidation. Vapour diffusion of hexane into THF solutions yielded red crystals suitable for X-ray crystallography. The resulting structure was found as a monomeric cobalt mono-chloride complex with tridentate N-Triphos^{Ph} coordination, [Co(N(CH₂PPh₂)₃)Cl] (**33**) (Figure 5.6). Although the expected dimeric structure was not found, no oxidation of the N-Triphos^{Ph} ligand had occurred. An identical crystal structure was also recently determined in our group, as the product of a reaction between CoCl₂ and N-Triphos^{Ph}.⁵¹ However, in this case there is no rational explanation for the presence of the chloride ligand owing to the lack of chlorinated solvents or precursors; it is probably attributable to contamination at some stage of the reaction or crystallisation. It is also possible that the determined crystal structure does not represent the bulk product of N-Triphos^{Ph} coordination to Co(BF₄)₂·6H₂O. Potentially there is an equilibrium between the monomeric and expected dimeric form, with or without the inclusion of chloride ligands.

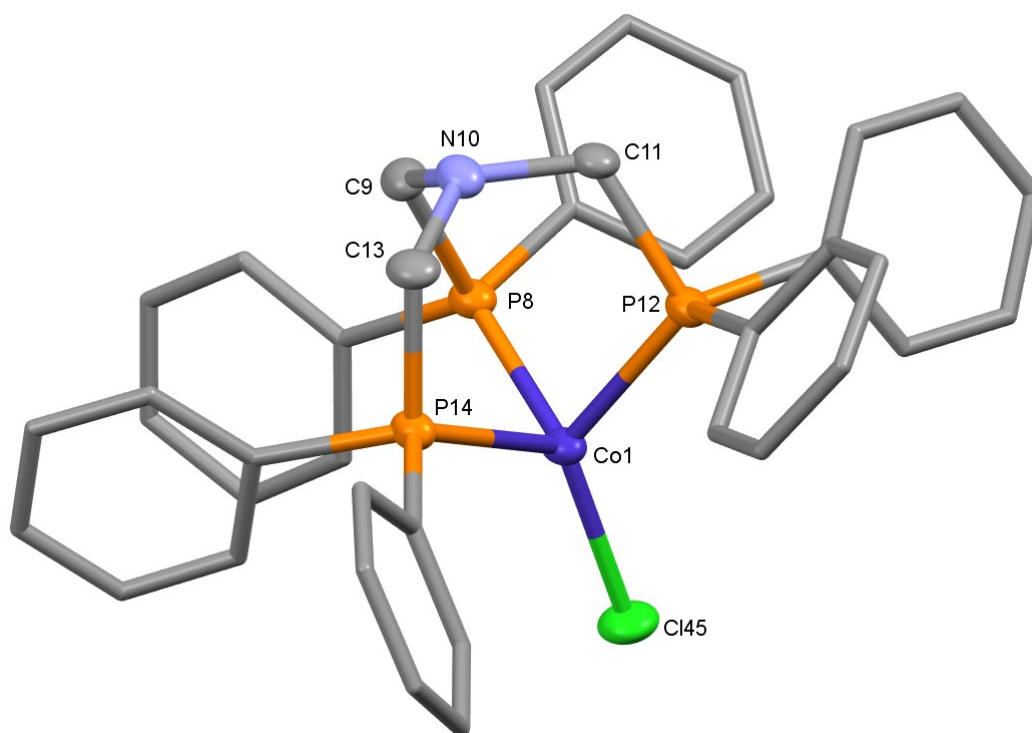


Figure 5.6. Crystal structure of [Co(N(CH₂PPh₂)₃)Cl] (**33**). Hydrogen atoms and solvent molecules omitted for clarity.

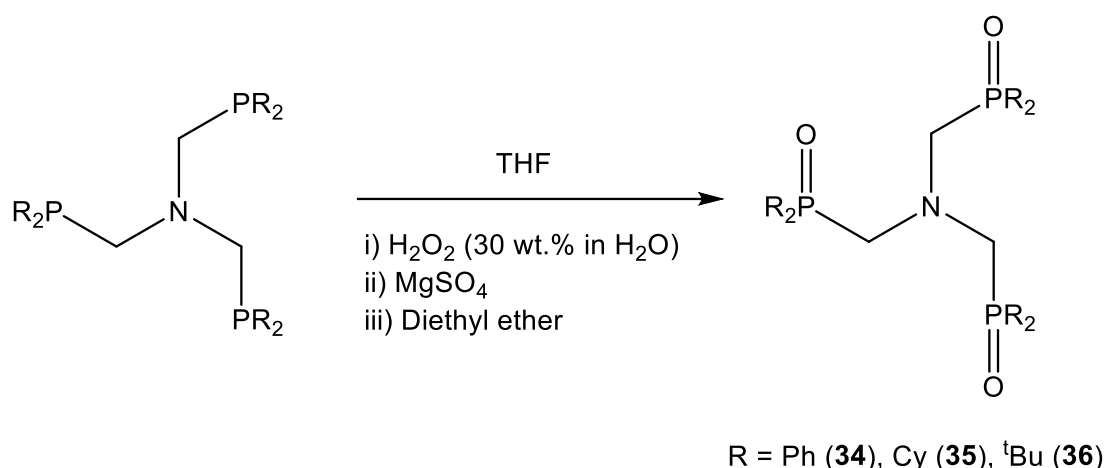
Bond lengths and bond angles for **33** are shown in Table 5.1. The Co-P bond lengths in the tetrahedral complex are in the range 2.230(1)-2.244(1) Å, slightly longer than the Co-Cl bond length (2.220(1) Å). Around the cobalt centre, the P-Co-P bond angles are in the range 90.00(5)-94.57(5) °, with P-Co-Cl bond angles in the range 121.15(5)-124.99(5) Å. Therefore, the P-Co-Cl bond angles are significantly wider than the P-Co-P bond angles, indicating a strong deviation from standard tetrahedral geometry. This reflects the tethered nature of the three phosphines. The complex has an electron count of 16 with a Co(I) d⁸ centre. Whilst this configuration would ordinarily favour a square-planar geometry, this is not accessible with tripodal N-Triphos ligands.

Therefore, the products of reactions between N-Triphos^{Ph} and Co(BF₄)₂·6H₂O were not characterised in the straight-forward manner expected. Whilst partial oxidation of the N-Triphos^{Ph} ligand accessed an unexpected coordination mode, the lack of control over the degree of oxidation precluded detailed analysis. Therefore, attention turned towards the design of full oxidation of N-Triphos ligands.

5.3 Synthesis of tridentate N-Triphos oxide ligands

Chapter 2 described the facile syntheses of symmetrical N-Triphos ligands from phosphonium chloride precursors via phosphorus-based Mannich-type reactions. Whilst the N-Triphos ligands have moderate to high air stability as a solid product, their phosphine groups are susceptible to oxidation, especially in solution. Chapter 2 also described difficulties encountered with the syntheses of mixed phosphine/phosphine oxide ligands. Therefore, attention turned to the fully oxidised N-Triphos ligands. To achieve complete oxidation of N-Triphos ligands, hydrogen peroxide was used as the oxidising agent. A similar route was described in Chapter 3 for converting uncoordinated phosphine moieties into phosphine oxides. The general route for conversion of N-Triphos ligands (R = Ph, Cy, ^tBu) into their corresponding oxide ligands is shown in Scheme 5.1.

The oxide ligand N(CH₂P(O)PPh₂)₃ (**34**) has been previously described in the literature, although only one complex of this ligand has been previously reported.^{48,52} To a solution of N-Triphos^{Ph} in THF was added hydrogen peroxide (30 wt.% in water). After stirring at RT, MgSO₄ was added and filtered off and solvent was removed under reduced pressure. The resulting white solid product was washed with diethyl ether and dried in vacuo. The product was collected in high yield (90 %) and showed a single ³¹P{¹H} NMR signal at 30.4 ppm. ¹H and ¹³C NMR spectroscopy conformed to the expected structure.



Scheme 5.1. General synthetic route for synthesis of oxide ligands **34-36** from N-Triphos ligands.

N(CH₂P(O)PPh₂)₃ (**34**) was further characterised by mass spectrometry, found as [M+H]⁺ with m/z = 660.1998 (calc. m/z = 660.1986). Unfortunately, elemental analysis failed to match the %C value (found %C = 67.08, %H = 5.82, %N = 2.27; calc. %C = 71.01, %H = 5.50, %N = 2.12), but the data was a good match if two H₂O molecules are incorporated (calc. %C = 67.33, %H = 5.80, %N = 2.01). By IR spectroscopy, the P=O stretch of **34** was found at 1167 cm⁻¹.

Single crystals of **34** were grown from vapour diffusion of diethyl ether into dichloromethane solutions. The structure determined by X-ray crystallography confirmed the expected product with a tripodal structure around the central nitrogen atom with three-fold symmetry (Figure 5.7). Slight puckering was observed at the central nitrogen. Although a crystal structure of **34** was recently published, the crystal structure obtained here is of a different crystal system and space group.⁵² Whilst the previous crystal structure lacked solvation, here the structure of **34** is solvated by hydrogen peroxide and water.

The cyclohexyl analogue N(CH₂P(O)PCy₂)₃ (**35**) has not been previously reported in the literature. After dissolving N-Triphos^{Cy} in THF and adding hydrogen peroxide (30 wt.% solution in H₂O), after 10 mins ³¹P{¹H} NMR spectroscopy found a signal peak at 49.3 ppm. After removing solvent in vacuo, a fluffy white solid was obtained. **35** was further characterised by mass spectrometry, found as [M+H]⁺ with m/z = 696.4803 (calc. m/z = 696.4803). Pleasingly, elemental analysis also supported the product identity (found %C = 67.43, %H = 10.50, %N = 2.12; calc. %C = 67.31, %H = 10.43, %N = 2.01). By IR spectroscopy, the P=O stretch was found at 1156 cm⁻¹. Single crystals of **35** were grown by vapour diffusion crystallisation from dichloromethane/hexane. Its crystal structure showed the expected tripodal structure as per **34** without solvation. The crystal structure of **35** is shown in Figure 5.7.

The tert-butyl analogue, $\text{N}(\text{CH}_2\text{P}(\text{O})\text{P}(\text{tBu})_2)_3$ (**36**), is also unreported in the literature. Small scale reactions to oxidise N-Triphos^{tBu} showed that its oxidation did not proceed cleanly, with several $^{31}\text{P}\{^1\text{H}\}$ NMR signals observed in the region 57 – 67 ppm. With the addition of further hydrogen peroxide, the number of $^{31}\text{P}\{^1\text{H}\}$ NMR signals increased, suggesting ligand degradation. However, **36** was confirmed by mass spectrometry, found as $[\text{M}+\text{H}]^+$ with $m/z = 540.3861$ (calc. $m/z = 540.3864$). Owing to the small scale and poor quality evidenced by the NMR spectra, no further work could be performed with **36**.

The $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts of all three oxide ligands **34–36** are significantly downfield relative to the original N-Triphos ligands. The $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts are collected in Table 5.2. The oxide chemical shifts are close to those observed for the palladium complexes of N-Triphos ligands **7**, **8** and **10** described in Chapter 3.

Table 5.3 collects bond lengths and bond angles for the N-Triphos oxide ligands **34** and **35**. In both **34** and **35**, all the P-O bond lengths can be considered as equivalent in length. Furthermore, the two sets of P-O bond lengths are equivalent to each other, showing that the substituent at the phosphine group does not affect the P=O bond strength. This is supported by the similarity in the P=O stretches determined by IR spectroscopy.

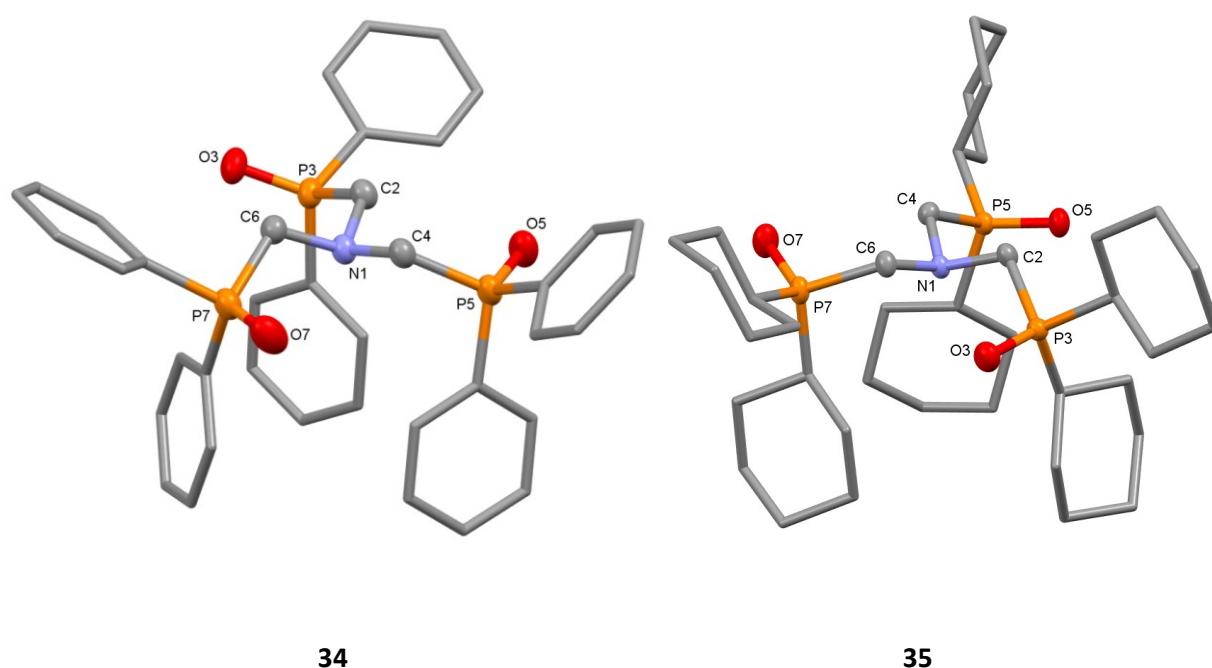


Figure 5.7. Crystal structures of a) $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$ (**34**) and b) $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Cy}_2)_3$ (**35**). Hydrogen atoms and solvent molecules omitted for clarity.

Table 5.2. Collected $^{31}\text{P}\{^1\text{H}\}$ NMR data for N-Triphos ligands and their oxide analogues **34-36**.

Substituent, R	$^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift of N-Triphos ligand (ppm)	$^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift of oxide ligand (ppm)	Change in chemical shift upon oxidation (ppm)
Ph (34)	-28.9	30.4	+59.3
Cy (35)	-17.0	49.3	+66.3
^t Bu (36)	+12.5	58.8 (*major signal)	+46.3

Table 5.3. Collected bond lengths and bond angles for N-Triphos oxide ligands **34** and **35**.

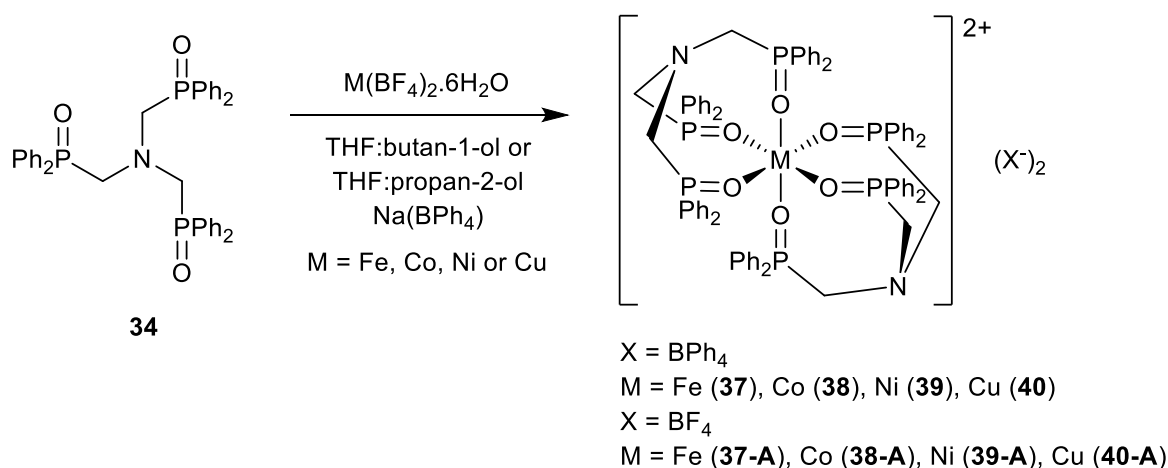
Ligand	Bond	Bond length (Å)
R = Ph (34)	P(3)-O(3)	1.485(2)
	P(5)-O(5)	1.491(2)
	P(7)-O(7)	1.477(2)
R = Cy (35)	P(3)-O(3)	1.4843(13)
	P(5)-O(5)	1.4899(13)
	P(7)-O(7)	1.4891(14)
		Bond angle (°)
R = Ph (34)	C(2)-N(1)-C(4)	109.5(3)
	C(2)-N(1)-C(6)	109.9(3)
	C(4)-N(1)-C(6)	110.3(2)
R = Cy (35)	C(2)-N(1)-C(4)	110.08(13)
	C(2)-N(1)-C(6)	108.08(13)
	C(4)-N(1)-C(6)	110.78(13)

The C-N-C bond angles around the central nitrogen of **34** are in the range 109.5(3) – 110.3(2) ° and can be considered as equivalent to each other. In **35**, two of the bond angles are equivalent to each other and to those in **34**, with one narrower bond angle (C(2)-N(1)-C(6): 108.08(13) °). The bond angles are in the expected range for a tripodal structure and are largely unaffected by the phosphine substituent. Therefore, the oxide ligands would be expected to bind to a metal centre through the typical facial coordination modes seen with N-Triphos ligands.

5.4 Coordination of N(CH₂P(O)PPh₂)₃ to first-row transition metals

Much of the work discussed in this Section has been published in Inorganica Chimica Acta (2020).⁵³

This section will discuss the coordination chemistry of **34** with first-row transition metals. The general reaction scheme is shown in Scheme 5.2. Some preliminary reactions with iron and cobalt have been reported as part of an MSci project.⁴⁹



Scheme 5.2. General scheme for reaction of N(CH₂P(O)Ph₂)₃ (**34**) with M(BF₄)₂·6H₂O (M = Fe, Co, Ni, Cu).

First-row transition metals are generally considered as “hard acids” and would be expected to form strong interactions with phosphine oxide ligands. Reaction of **34** with the commercially available precursor Co(BF₄)₂·6H₂O in a THF:1-butanol mixture at RT led to the formation of a solid precipitate within a short time (<1 h). The solvent combination was chosen to achieve full solubility of both **34** (in THF) and Co(BF₄)₂·6H₂O (in 1-butanol). The product was isolated as a pale, pink-coloured powder after washing with diethyl ether.

³¹P{¹H} NMR spectra of the solid product in both deuterated chloroform and deuterated acetonitrile showed no signals across the full spectrum range. This was attributed to the paramagnetic nature of a d⁷ cobalt complex. Therefore the nature of ligand coordination was initially unclear. The absence of a free ligand signal indicated full, tridentate coordination of **34**. The ¹H NMR spectrum of the product also showed broad, unresolved signals and ¹³C NMR signals could not be detected. When deuterated DMSO was used as a solvent, both ³¹P{¹H} and ¹H NMR spectra showed signals of the free ligand **34**. The displacement of ligands by DMSO has previously been described in the literature, and these results suggest that **34** is also readily displaced by DMSO.⁵⁴ Through IR spectroscopy, a P=O stretch

was identified at 1167 cm^{-1} ; as this is a negligible shift from the $\text{P}=\text{O}$ stretch observed for **34**, it indicates that the phosphine oxide group largely retains its double bond character upon metal coordination.

Initially, suitable crystals for X-ray diffraction could not be grown. However, with the addition of NaBPh_4 to a reaction mixture, crystals suitable for structural analysis were successfully grown from vapour diffusion crystallisation of diethyl ether into acetonitrile.

Analogous reactions with $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ were performed, both with and without NaBPh_4 , resulting in pale-orange solid products. Similar observations to those described above were found through NMR and IR spectroscopy. Suitable crystals were grown from a dichloromethane/diethyl ether combination, again from vapour diffusion crystallisation.

Reactions with $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ were performed directly with the addition of NaBPh_4 in a THF:1-propanol mixture, and yielded off-white and pale-yellow solid products respectively. Single crystals of both products were grown from a combination of acetonitrile and diethyl ether. The nickel product, however, was fully soluble only in DMSO and DMF.

Single crystal X-ray crystallography revealed the structures of the products as $[\text{Fe}(\text{N}\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_3)_2](\text{BPh}_4)_2$ (**37**), $[\text{Co}(\text{N}\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_3)_2](\text{BPh}_4)_2$ (**38**), $[\text{Ni}(\text{N}\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_3)_2](\text{BPh}_4)_2$ (**39**) and $[\text{Cu}(\text{N}\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_3)_2](\text{BF}_4)_2$ (**40-A**). Each complex was found to adopt an octahedral structure. The crystal structures are shown in Figure 5.8. In each complex, **34** binds to the metal centre in a tridentate coordination mode through all three oxygen atoms. This is the same coordination mode as observed in the previously described complex $[(\text{NP}_3\text{O}_3)\text{Be}(\text{OH}_2)]^{2+}$.⁴⁸ However, in these complexes of **34**, two ligands coordinate to each metal centre without any additional ligands. Each of the complexes **37**, **38**, **39** and **40-A** is doubly charged. Whilst the complexes with $\text{M} = \text{Fe}$, Co and Ni crystallised with two BPh_4 anions, that with $\text{M} = \text{Cu}$ crystallised instead with BF_4 anions, despite the inclusion of NaBPh_4 .

An analogous octahedral structure has not been reported for any N-Triphos ligands, with no examples of two N-Triphos ligands binding to a single metal centre. The steric bulk of N-Triphos ligands is typically considered to prohibit such a structure. The binding of **34** to the metal centre through its oxygen atoms provides additional distance between the steric bulk of the phenyl groups and the metal centre, reducing the degree of steric hindrance. Therefore, it is permitted for two oxide ligands to coordinate to a single metal to form a stable octahedral structure.

There is no binding observed between the metal centre and the nitrogen atom of **34** (as evidenced by the long M-N distances, between $3.74\text{--}3.79\text{ \AA}$). Although M-N bonding was determined in the partially oxidised cobalt dimer **32** described in Section 5.2 (with an M-N distance of $2.2961(3)\text{ \AA}$), a lack of M-N bonding is generally consistent with complexes of N-Triphos ligands.

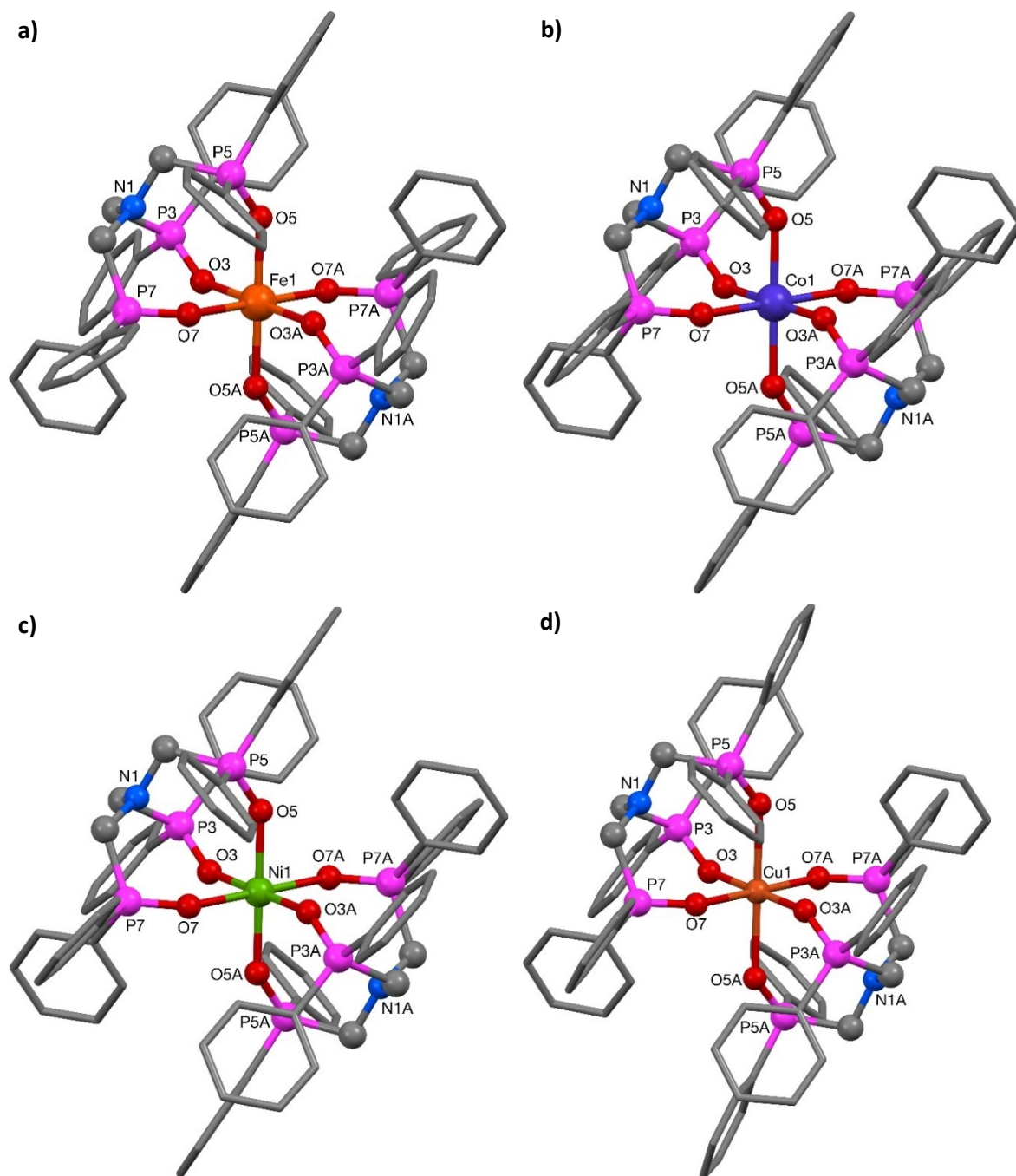


Figure 5.8. Crystal structures of a) $[\text{Fe}(\text{N}\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_3)_2](\text{BPh}_4)_2$ (**37**), b) $[\text{Co}(\text{N}\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_3)_2](\text{BPh}_4)_2$ (**38**), c) $[\text{Ni}(\text{N}\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_3)_2](\text{BPh}_4)_2$ (**39**) and d) $[\text{Cu}(\text{N}\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_3)_2](\text{BF}_4)_2$ (**40-A**). Hydrogen atoms, counter-ions and solvent molecules omitted for clarity.

Table 5.4. collects the P-O bond lengths for both **34** and the series of octahedral complexes **37**, **38**, **39** and **40-A**. In the octahedral complexes, all the P-O bonds are equivalent in length. The bond lengths confirm that the phosphine oxides retain their double bond character upon metal coordination, as the lengths are considerably shorter than would be expected for a single P-O bond and are short even for a double P=O bond.⁵⁵ The P-O bond lengths are in the same range as in the previously reported complex $[(\text{NP}_3\text{O}_3)\text{Be}(\text{OH}_2)]^{2+}$ (1.509(5)-1.517(5) Å).⁴⁸ Given that the free ligand **34** has P-O bond lengths (1.477(16)-1.491(2) Å) in the same range as for the complexes **37**, **38**, **39** and **40-A**, this indicates that the P=O bonds are not significantly altered upon coordination to the metal. This is supported by the presence of P=O bands in the range 1167-1170 cm⁻¹ in the IR spectra of $[\text{M}(\text{N}\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_3)_2](\text{BPh}_4)_2$, only a small shift from the P=O stretch at 1167 cm⁻¹ in free NP₃O₃. All P=O stretching frequencies are collected in Table 5.5. [*The P=O stretches presented are for bulk samples of products. Crystalline samples of $[\text{M}(\text{N}\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_3)_2](\text{BPh}_4)_2$ (M = Fe, Co, Ni) showed P=O stretches at 1164-1166 cm⁻¹].

The M-O bond lengths for complexes **37**, **38**, **39** and **40-A** are collected in Table 5.6. For the iron complex **37**, it was found that all the Fe-O lengths are equivalent, ranging from 2.117(2) to 2.135(3) Å, with no significant disparity between axial and equatorial bond lengths. Hence, complex **37** can be considered to have no distortion from an idealised octahedral structure.

The cobalt complex **38** features slightly compressed axial Co-O bonds (Co(1)-O(5) (2.0655(10)-2.0656(10) Å) relative to its longer equatorial Co-O bonds (Co(1)-O(3) and Co(1)-O(7)) (2.1140(11)-2.1167(11) Å). There is ~2 % difference between the two sets of bond lengths, which can be considered as a weak Jahn-Teller axial compression type distortion. The structure of the d⁸ nickel complex **39** also features equatorial Ni-O(3) and Ni-O(7) bond lengths (2.0811(12)-2.0846(11) Å) slightly longer than the axial Ni-O(5) bond lengths (2.0451(11) Å); again, there is only ~ 2% difference between the two sets of bond lengths. However, d⁸ complexes do not show Jahn-Teller type distortions.

The copper complex **40-A** shows significant distortion in its bond lengths. The axial Cu-O(5) bond lengths (2.318(3) Å) are longer than the equatorial Cu-O(3) and Cu-O(7) bond lengths (1.958(3)-2.043(3) Å). This can be attributed to a Jahn-Teller axial elongation distortion, with a difference between the two sets of bond lengths in **40-A** of ~ 15 %, indicating a significant distortion from idealised octahedral geometry in complex **40-A**. (Although each of the Cu-O bond lengths (Cu-O(3), Cu-O(5), Cu-O(7)) are statistically different from each other, the Cu-O(5) bond lengths are significantly longer than either the Cu-O(3) or Cu-O(7) bond lengths).

Table 5.4. Collected P-O bond lengths for **35** and complexes **37**, **38**, **39** and **40-A**.

N(CH₂P(O)Ph₂)₃ (34) (Å)		M = Fe (37) (Å)	Co (38) (Å)	Ni (39) (Å)	Cu (40-A) (Å)
P(3)-O(3)	1.485(2)	1.4918(11)	1.491(3)	1.4952(12)	1.504(3)
P(5)-O(5)	1.491(2)	1.4935(11)	1.492(3)	1.4957(12)	1.494(4)
P(7)-O(7)	1.477(2)	1.4901(11)	1.492(3)	1.4959(12)	1.497(3)
P(3A)-O(3A)	1.477(16)				
P(5A)-O(5A)	1.485(17)				
P(7A)-O(7A)	1.485(17)				

Table 5.5. Collected P=O infra-red stretching frequencies for NP₃O₃ (**34**) and complexes [M(N{CH₂P(O)Ph₂})₃]₂(BPh₄)₂ (**37-40**) and [M(N{CH₂P(O)Ph₂})₃](BF₄)₂ (**37-A-40-A**) (M = Fe, Co, Ni, Cu).

Compound	P=O stretch (cm⁻¹)
N(CH ₂ P(O)PPh ₂) ₃ (34)	1167
[Fe(N{CH ₂ P(O)Ph ₂ }) ₃] ₂ (BPh ₄) ₂ (37)	1167
[Co(N{CH ₂ P(O)Ph ₂ }) ₃] ₂ (BPh ₄) ₂ (38)	1167
[Ni(N{CH ₂ P(O)Ph ₂ }) ₃] ₂ (BPh ₄) ₂ (39)	1170
[Cu(N{CH ₂ P(O)Ph ₂ }) ₃] ₂ (BPh ₄) ₂ (40)	-
[Fe(N{CH ₂ P(O)Ph ₂ }) ₃](BF ₄) ₂ (37-A)	1170
[Co(N{CH ₂ P(O)Ph ₂ }) ₃](BF ₄) ₂ (38-A)	1170
[Ni(N{CH ₂ P(O)Ph ₂ }) ₃](BF ₄) ₂ (39-A)	1170
[Cu(N{CH ₂ P(O)Ph ₂ }) ₃](BF ₄) ₂ (40-A)	1174

Table 5.6. Collected M-O bond lengths for complexes **37**, **38**, **39** and **40-A**.

Bond		M = Fe (37) (Å)	M = Co (38) (Å)	M = Ni (39) (Å)	M = Cu (40-A) (Å)
Equatorial	M(1)-O(3)	2.135(3)	2.1140(11)	2.0811(12)	1.958(3)
Equatorial	M(1)-O(3A)	2.135(3)	2.1140(11)	2.0811(12)	1.958(3)
Axial	M(1)-O(5)	2.128(3)	2.0655(10)	2.0451(11)	2.318(3)
Axial	M(1)-O(5A)	2.128(3)	2.0656(10)	2.0451(11)	2.318(3)
Equatorial	M(1)-O(7)	2.117(2)	2.1166(11)	2.0846(11)	2.043(3)
Equatorial	M(1)-O(7A)	2.117(2)	2.1167(11)	2.0847(11)	2.044(3)

Across the series **37**, **38**, **39** and **40-A**, there is a general reduction in M-O bond lengths. An exception are the elongated axial Cu-O bonds in **40-A**. The axial elongation distortion might serve to relieve steric crowding around the smaller metal centre. The gradual reduction in atomic radius across the period might allow the ligand **34** to interact slightly more strongly with the metal centre moving across the series.

Table 5.7 collects O-M-O bond angles for the complexes **37**, **38**, **39** and **40-A**. All the end-to-end O-M-O bond angles are 180.0 °. Also, between axial and equatorial M-O bonds, there is only a small deviation from the idealised O-M-O bond angles of 90 °, with O-Fe-O bond angles in the range 89.19(10)-90.81(10) °, O-Co-O: 88.71(4)-91.29(4) °, O-Ni-O: 88.68(5)-91.32(5) °, O-Cu-O: 88.60(11)-91.40(11) °. Whilst this indicates a further level of small deviation from idealised octahedral geometries, it demonstrates that the presence of Jahn-Teller distortions does not significantly alter the octahedral structures of the complexes.

With the determination of the crystal structures of **37**, **38**, **39** and **40-A**, further analysis was performed. Elemental analyses on the solid products isolated from reactions with the absence of NaBPh₄ (**37-A** and **38-A**) matched closely to the expected results. However, for the reactions which used NaBPh₄, elemental analyses failed to correspond to the expected results for the BPh₄ adducts **37** - **39**. This was attributed to partial, incomplete, substitution of the BF₄ ions from M(BF₄)₂·6H₂O for the BPh₄ anions from NaBPh₄, resulting in lower than calculated values of %C for full BPh₄ substitution. However, mass spectrometry for all of **37-40** showed the expected doubly charged complex ions, along with fragmentation resulting in a major free NP₃O₃ ligand signal.

Using the structural elucidation of the M-O bond lengths in complexes **37**, **38**, **39** and **40-A**, alongside magnetic susceptibility measurements, some conclusions regarding the electronic structures of the complexes were drawn. Relevant data is presented in Table 5.8, and illustrations of the electronic energy levels are presented in Figure 5.9. Initially, Evans method calculations were attempted but these were ultimately found to be inconclusive. Although full solubility of the products could be achieved in DMSO-d₆, this was observed to degrade the products by displacement of the ligands.

Some degree of solubility was achieved for **37** and **38** in deuterated-acetonitrile, acetone and chloroform, however the values for the number of unpaired electrons from Evan's method calculations using these solvents were consistently lower than expected. This was attributed to the incomplete solubility achieved. Instead, magnetic measurements were made from solid samples using a magnetic susceptibility balance.

Table 5.7. Collected O-M-O bond angles for complexes **37**, **38**, **39** and **40-A**.

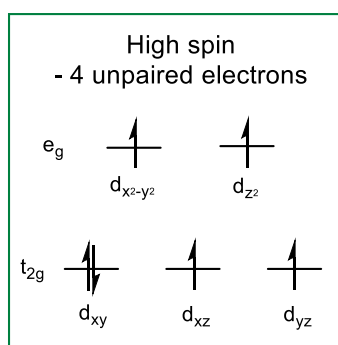
Bond	M = Fe (37) (Å)	M = Co (38) (Å)	M = Ni (39) (Å)	M = Cu (40-A) (Å)
O(3)-M(1)-O(3A)	180.0	180.0	180.0	180.0
O(5)-M(1)-O(5A)	180.0	180.0	180.0	180.0
O(7)-M(1)-O(7A)	180.00(9)	180.0	180.00(2)	180.00(14)
O(3)-M(1)-O(5)	89.37(11)	90.28(4)	90.37(5)	88.79(11)
O(3)-M(1)-O(5A)	90.63(11)	89.72(4)	89.63(5)	91.21(11)
O(3)-M(1)-O(7)	89.30(10)	89.81(4)	90.00(5)	91.40(11)
O(3)-M(1)-O(7A)	90.70(10)	90.19(4)	90.00(5)	88.60(11)
O(5)-M(1)-O(3A)	90.63(11)	89.72(4)	89.63(5)	91.20(11)
O(5)-M(1)-O(7)	89.19(10)	91.28(4)	91.32(5)	90.26(11)
O(5)-M(1)-O(7A)	90.81(10)	88.71(4)	88.68(5)	89.74(11)
O(7)-M(1)-O(3A)	90.70(10)	90.19(4)	90.00(5)	88.60(11)
O(7)-M(1)-O(5A)	90.81(10)	88.71(4)	88.68(5)	89.74(11)
O(3A)-M(1)-O(5A)	89.37(11)	90.28(4)	90.37(5)	88.79(11)
O(3A)-M(1)-O(7A)	89.30(10)	89.81(4)	90.00(5)	91.40(11)
O(5A)-M(1)-O(7A)	89.19(10)	91.29(4)	91.32(5)	90.26(11)

Table 5.8. Summary of electronic configuration data for complexes **37-40**.

Complex	37	38	39	40
d-count	d ⁶	d ⁷	d ⁸	d ⁹
Number of unpaired electrons (high-spin)	4	3	2	1
Number of unpaired electrons (low-spin)	0	1	2	1
Calculated effective magnetic moment (μ_{eff})	4.81	4.12	2.65	2.09
Calculated number of unpaired electrons (n)	3.91	3.24	1.83	1.32
Assigned number of unpaired electrons (n)	4	3	2	1

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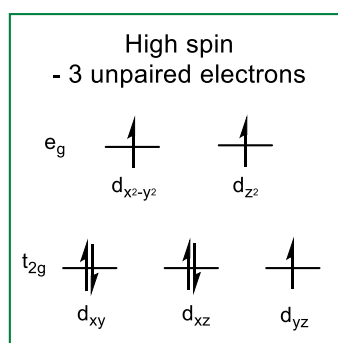
37 Fe, d^6



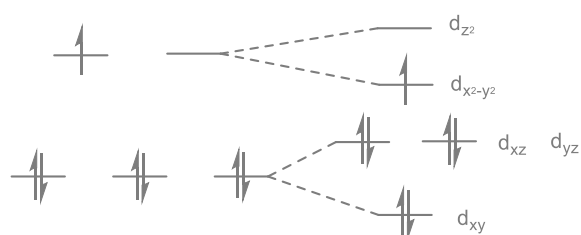
Low spin
- 0 unpaired electrons



38 Co, d^7

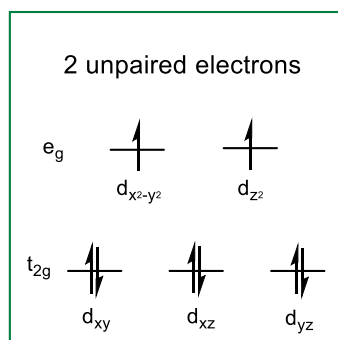


Low spin
- 1 unpaired electron



Jahn Teller axial compression
- 1 unpaired electron

39 Ni, d^8



40 Cu, d^9

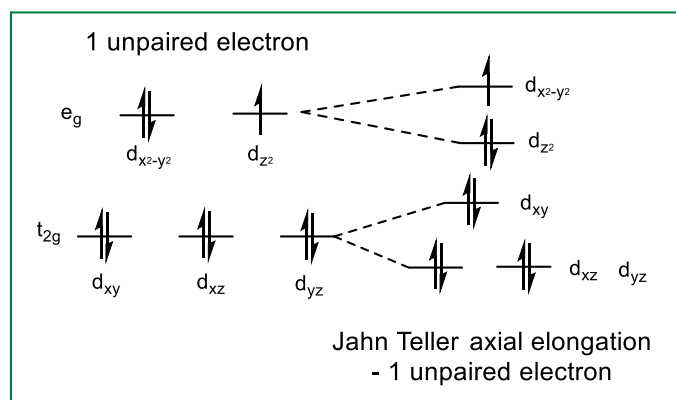


Figure 5.9. Illustration of electron configurations for complexes **37-40**.

No distortion was observed in the crystal structure of the d^6 iron complex **37**. Therefore, the standard octahedral crystal field splitting is applicable. Given that **37** was observed to be paramagnetic, it was expected to have a high-spin electronic configuration with four unpaired electrons. This was confirmed by a magnetic moment of $\mu_{\text{eff}} = 4.81$ corresponding to four unpaired electrons (Table 5.9).

For the d^7 cobalt complex **38**, applying octahedral crystal field splitting gives high-spin and low-spin configurations with three or one unpaired electrons respectively. A value of $\mu_{\text{eff}} = 4.12$ was determined, corresponding to three unpaired electrons and a high-spin electron configuration (Table 5.9). This would be expected for a first-row transition metal octahedral complex in a +2 oxidation state. Although weak Jahn-Teller distortion is accessible for high-spin d^7 complexes, and the crystal structure of **38** featured slightly compressed axial ligands, a formal Jahn-Teller axial compression would generate an electronic configuration with just one unpaired electron. This does not correspond with the magnetic measurement.

As a d^8 nickel complex, **39** features no difference between high-spin and low-spin electron configurations in the octahedral system, with two unpaired electrons. This was confirmed with a value of $\mu_{\text{eff}} = 2.65$ corresponding to two unpaired electrons (Table 5.9). A formal Jahn-Teller type distortion is not accessible; the energy stabilisation achieved by splitting the e_g levels upon axial compression does not overcome the pairing energy required.

The d^9 copper complex **40** would have one unpaired electron in both high-spin and low-spin electron configurations in the octahedral system. Again, this was confirmed by $\mu_{\text{eff}} = 2.09$ (Table 5.9). If axial elongation distortion is applied, in the t_{2g} subshell there is a lowering in energy of four electrons, and an increase in energy of only two electrons. In the e_g subshell, there is a lowering in energy of two electrons, and an increase in energy of only one electron, with no additional pairing energy involved. Therefore, there is a net reduction in energy upon axial elongation in this case. This provides a rationale for the much larger extent of axial elongation observed in **40-A** compared to the smaller bond length differences in **38** and **39**, owing to the much more favourable electronic configuration achieved for **40-A** by undergoing axial elongation.

The series of complexes $M = \text{Fe, Co, Ni and Cu}$ also exceed the standard “18-electron rule”. The Fe complex **37** has an electron count of 18 with the incorporation of 6 L-type phosphine oxide moieties. The Co, Ni and Cu complexes therefore have electron counts of 19, 20 and 21 respectively. Generally, complexes which have valence electron counts of more than 18 are attributed to the inclusion of electrostatic forces. Each of the complexes **37-40** are very pale coloured; whilst cobalt complex **38** was isolated as a pale-pink colour, the remaining complexes were an off-white colour. The lack of bright colours might be attributed to a lack of formally allowed d-d electronic transitions in the complexes.

5.4.1 Coordination of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{PPh}_2)_3$ to $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$

An analogous reaction of **34** with $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was also attempted with a 2:1 ligand:metal ratio in a solvent mixture of methanol/THF. A white solid precipitated and was collected in the usual way. In the same manner as for the complexes with $\text{M}=\text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$, the absence of $^{31}\text{P}\{^1\text{H}\}$ NMR signals indicated a paramagnetic product and IR spectroscopy showed the expected $\text{P}=\text{O}$ stretch at 1167 cm^{-1} . Unfortunately, mass spectrometry failed to identify any doubly-charged signals. However, single crystals suitable for X-ray crystallography were grown from dichloromethane and diethyl ether and identified an analogous doubly-charged octahedral Mn complex to those with $\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$, $[\text{Mn}(\text{N}\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_3)_2](\text{BPh}_4)_2$ (**41**) (Figure 5.10). The structure included BPh_4 anions and was heavily solvated by dichloromethane molecules. The Mn-O bond lengths were in the range $2.164(2)$ - $2.184(2)$ Å with no significant disparity between axial and equatorial bonds and the O-Mn-O bond angles were in the expected range. The P-O lengths were in line with those seen previously, showing no significant elongation of the P-O bond upon complexation (Table 5.9).

5.4.2 Attempted coordination of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{PPh}_2)_3$ to $\text{Zn}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$

Although the octahedral complexes obtained with $\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ and Cu had been characterised by X-ray crystallography, their paramagnetism precluded NMR analysis. To generate a diamagnetic, d^{10} Zn(II) product, a reaction between **34** and $\text{Zn}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ was also attempted. The reaction was performed as previously in THF/1-butanol with a 2:1 ligand:metal ratio. From the colourless reaction mixture, a white solid precipitated. After one hour, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed a noisy spectrum with broad, jagged signals in the region of 27-35 ppm (27.7, 30.3, 34.9 ppm). There was no change to the $^{31}\text{P}\{^1\text{H}\}$ NMR signals overnight.

After heating, the spectra remained noisy but with sharp signals at 35.3 and 29.4 ppm, potentially a mixture of free ligand plus another species. The solid product was isolated by cannula filtration, washed with 1-butanol and dried in vacuo. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the solid showed two well defined signals: a major signal at 30.0 ppm (attributed to free ligand) and a minor signal at 35.5 ppm. The filtrate produced a noisier $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum but with sharp signals at 31.5, 30.3 and 27.9 ppm. Mass spectrometry of the solid product identified a signal attributable to the ligand **34** but no other useful signals.

The observations indicate that the reaction between **34** and $\text{Zn}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ did not proceed smoothly. It is unclear why this might be. The ionic radii of M^{2+} across the first-row of the transition metals does not vary significantly, so it is unlikely to be for steric reasons. However, zinc generally adopts four or

five coordinate complexes, and therefore full coordination of two ligands would not be predicted. The analogous zinc complex would have a formal electron count of 22 valence electrons and might be prohibited.

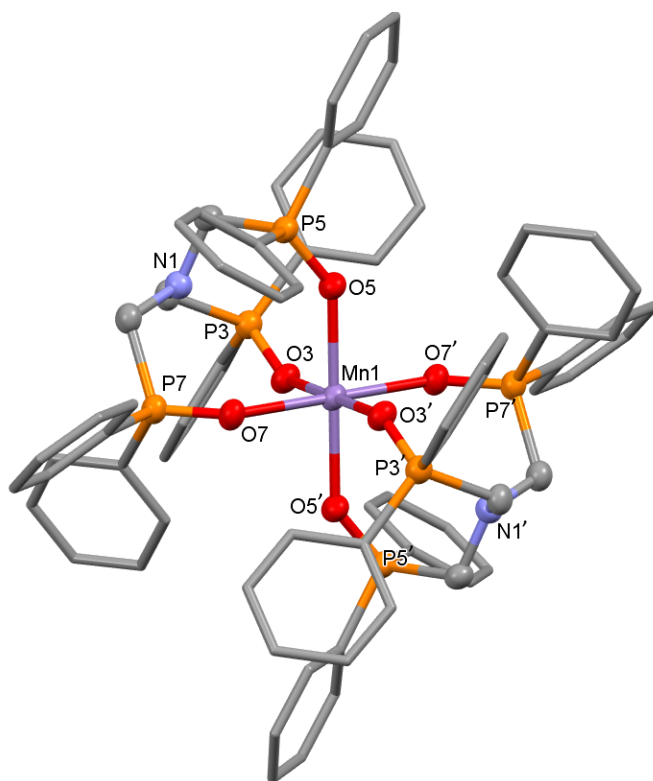


Figure 5.10. Crystal structure of $[\text{Mn}(\text{N}\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_3)_2](\text{BPh}_4)_2$ (**41**). Hydrogen atoms, counter-ions and solvent molecules omitted for clarity.

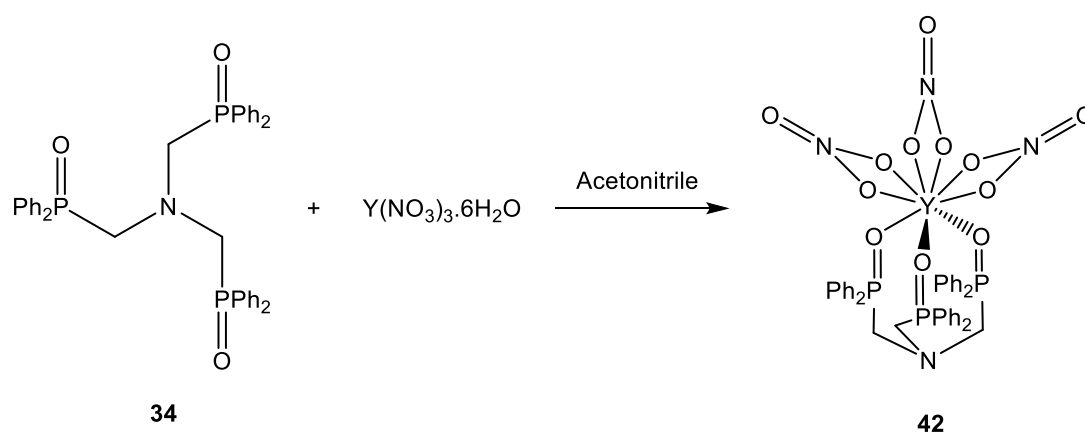
Table 5.9. Collected M-O bond lengths and O-M-O angles for $[\text{Mn}(\text{N}\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_3)_2](\text{BPh}_4)_2$ (**41**).

	Bond angle (°)		Bond length (Å)
O(3)-M(1)-O(3)'	180.00(12)	M(1)-O(3)	2.164(2)
O(5)-M(1)-O(5)'	180.0	M(1)-O(3)'	2.164(2)
O(7)-M(1)-O(7)'	180.0	M(1)-O(5)	2.168(2)
O(3)-M(1)-O(5)	91.67(8)	M(1)-O(5)'	2.168(2)
O(3)-M(1)-O(5)'	88.32(8)	M(1)-O(7)	2.184(2)
O(3)-M(1)-O(7)	92.07(8)	M(1)-O(7)'	2.184(2)
O(3)-M(1)-O(7)'	87.93(8)	P(3)-O(3)	1.494(2)
O(5)-M(1)-O(3)'	88.33(8)	P(5)-O(5)	1.497(2)
O(5)-M(1)-O(7)	92.48(8)	P(7)-O(7)	1.493(2)
O(5)-M(1)-O(7)'	87.52(8)		
O(7)-M(1)-O(3)'	87.93(8)		
O(7)-M(1)-O(5)'	87.52(8)		
O(3)'-M(1)-O(5)'	91.67(8)		
O(3)'-M(1)-O(7)'	92.07(8)		
O(5)'-M(1)-O(7)'	92.48(8)		

5.4.3 Coordination of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{PPh}_2)_3$ to $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$

In another attempt to obtain diamagnetic complexes of **34**, attention turned to yttrium. There are examples of yttrium(III) nitrate complexes of carbon-centred tripodal phosphine oxide ligands in the literature.⁵⁶ As yttrium has an electron configuration of $[\text{Kr}] 4d^1 5s^2$, yttrium(III) complexes are diamagnetic. It was hoped that this might allow for analysis by NMR spectroscopy, which was not possible for the complexes of **34** with $\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ and Cu .

$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was used as the yttrium precursor. It was expected that one equivalent of **34** would bind to yttrium with retention of the nitrate ligands (maintaining $\text{Y}(\text{III})$). The method was adapted from similar complexes of carbon-centred tripodal phosphine oxide ligands using a 1:1 ratio of ligand: metal (Scheme 5.3).⁵⁶ $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and **34** were mixed in acetonitrile, and upon heating to 70°C , a thick, white precipitate formed. Samples taken for $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy in CDCl_3 after one and two hours showed no $^{31}\text{P}\{^1\text{H}\}$ NMR signals. In this case the lack of signals observed was attributed to poor solubility. After heating was maintained overnight, the same observation was found the next day. Using instead $\text{DMSO}-d_6$ as a solvent, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed a free ligand signal at 28.8 ppm. After cooling, the white precipitate was isolated by cannula filtration, washed with diethyl ether and dried in vacuo. NMR samples in both CDCl_3 and $\text{MeCN}-d_3$ showed no $^{31}\text{P}\{^1\text{H}\}$ NMR signals. Given that **34** is fully soluble in CDCl_3 , the insolubility of the sample indicated full ligand coordination to yttrium. These observations matched those previously described in the literature, which also failed to report NMR data owing to poor solubility of yttrium oxide complexes in common NMR solvents, other than $\text{DMSO}-d_6$ which displaces the oxide ligand (as was described in Section 5.4).⁵⁶



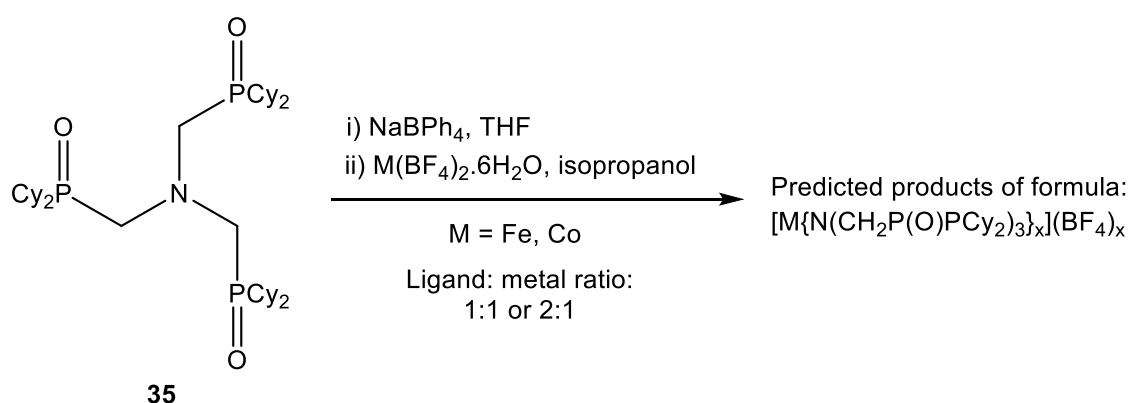
Scheme 5.3. Coordination of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{PPh}_2)_3$ (**34**) to $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

Crystallisations were attempted from vapour diffusion of diethyl ether into methanol, but also suffered from product insolubility and failed to yield viable crystals. However, mass spectrometry confirmed the identity of the expected product $[Y(N\{CH_2P(O)Ph_2\}_3)(NO_3)_3]$ (**42**), found as $[M-NO_3]^+$ with $m/z = 872.0753$ (calc. $m/z = 872.0723$). An additional signal was observed for **34** as $[M+H]^+$ at $m/z = 660.2010$ (calc. $m/z = 660.1986$). By IR spectroscopy, a P=O stretch at 1148 cm^{-1} was found, similar to those observed for the previous complexes of **34**.

A repeat reaction was performed with a 2:1 ligand: metal ratio. $^{31}P\{^1H\}$ NMR spectra of the reaction mixture showed a free ligand signal at 29.1 ppm, as did the solid product and the reaction filtrate, indicating that there was incomplete ligand coordination. Mass spectrometry found the same $[M-NO_3]^+$ signal described previously at $m/z = 872.0712$, however the major signal at $m/z = 660.1945$ corresponded to free ligand. These observations indicated that coordination of two **34** ligands to yttrium did not occur. It is uncertain if this should be attributed to sterics or to the difficulty of displacing the nitrate ligands from the yttrium centre.

5.5 Attempted coordination of $N(CH_2P(O)PCy_2)_3$ to first-row transition metals

Owing to the success achieved in forming interesting complexes of **34** with first-row transition metals, attention turned to the coordination chemistry of the cyclohexyl-analogue $N(CH_2P(O)PCy_2)_3$ (**35**) with $Fe(BF_4)_2 \cdot 6H_2O$ and $Co(BF_4)_2 \cdot 6H_2O$. There are no reports of **35** or its complexes in the literature. A general reaction is shown in Scheme 5.4. As was shown in Chapter 3, the change in phosphine substituent was expected to have an impact on the coordination chemistry achieved.



Scheme 5.4. General scheme for attempted reactions of $N(CH_2P(O)PCy_2)_3$ (**35**) with $M(BF_4)_2 \cdot 6H_2O$ ($M = Fe, Co$).

After mixing solutions of **35** and NaBPh₄ in THF and Co(BF₄)₂·6H₂O in IPA, with a 2:1 ligand: metal ratio, a purple-blue coloured mixture was formed. After stirring at RT for one hour, ³¹P{¹H} NMR spectroscopy showed a noisy spectrum with a ligand signal observed at 49 ppm. This indicated incomplete ligand coordination. After heating under reflux for two hours, a ³¹P{¹H} NMR spectrum could not be obtained. This was tentatively assigned to paramagnetism. After cooling to RT and removing solvent to dryness, a fine blue solid was collected. Its ³¹P{¹H} NMR spectrum still showed a free ligand signal and its ¹H NMR spectrum showed broad, poorly defined signals. The results suggested coordination of just one equivalent of ligand, partial coordination of one or both ligands, or no coordination at all. The colour change of the reaction mixture suggested metal coordination had occurred. Mass spectrometry found a major signal at m/z = 696.5148 attributable to the ligand **35** itself. Low abundance signals of higher mass were also found, with one doubly-charged, unassigned signal at m/z = 1073.3040.

The reaction was repeated with a 1:1 ligand: metal ratio. Every sample taken from the reaction mixture for ³¹P{¹H} NMR spectroscopy failed to run. Equally for the product collected as a purple powder, no ¹H or ³¹P{¹H} NMR spectra could be obtained. There was no difficulty in collecting NMR spectra of the free ligand itself. Therefore, the results suggest that no free ligand remained, suggesting full coordination of **35** resulting in a paramagnetic complex. Mass spectrometry found only a ligand signal at m/z = 696.5233. This suggests that if coordination of **35** to cobalt was achieved, the product readily fragments. Crystallisation attempts on each solid product collected failed to yield suitable crystals for X-ray crystallography analysis. The observations indicate that reactions of **35** with Co(BF₄)₂·6H₂O do not result in the formation of well-defined products as they do with **35**, perhaps attributed to the greater steric bulk of the PCy₂ moieties.

Reactions of **35** were also performed with Fe(BF₄)₂·6H₂O, with both 2:1 and 1:1 ligand: metal ratios. In both cases, no colour change was observed. With a 2:1 ratio, ³¹P{¹H} NMR spectra from the reaction mixture were noisy with a free ligand signal. After stirring overnight, further ³¹P{¹H} NMR samples failed to run. A pale-orange crystalline solid was collected. NMR samples from the product also failed to run. The same observations were found when using a 1:1 ligand: metal ratio, in which no NMR spectra could be obtained. Mass spectrometry again found a major signal attributable to the free ligand, with no doubly-charged signals identified. Crystallisations again failed to produce suitable single crystals.

All NMR spectra described in this Section used CDCl₃ as the solvent. Concerned that there was an issue with solubility of the products in CDCl₃, alternative NMR solvents were trialed. In DMSO-d₆, both iron products showed a free ligand signal at 47.1 ppm, again attributed to ligand displacement by

DMSO- d_6 . The product isolated from the reaction using a 2:1 ligand:metal ratio also showed a free ligand signal at 47.1 ppm in MeCN- d_3 . However, the product from the 1:1 reaction showed no $^{31}\text{P}\{^1\text{H}\}$ NMR signals in MeCN- d_3 . This might indicate that the full coordination of one equivalent of **35** to iron is possible, but the coordination of two ligands is prohibited, likely for steric reasons.

5.6 Summary and Outlook

The coordination chemistry of multidentate phosphine oxide ligands is understudied relative to their phosphine analogues, and most complexes of phosphine oxides are based upon simple monodentate ligands. The stereo-electronic and binding properties of phosphine oxides differ significantly from their corresponding phosphines, potentially allowing for the formation of previously unexplored coordination modes resulting in complexes with interesting properties. Owing to the hard bonding nature of phosphine oxides, they are generally used to form complexes with harder, less polarisable metal ions such as lanthanides or transition metals in high oxidation states.

The benefits of the tridentate N-Triphos ligands have been previously described in detail. The analogous phosphine oxide ligands retain their ease of synthesis, with ready modification of the substituent attached to the phosphine oxide. Furthermore, they adopt well-defined multidentate coordination modes. The oxides of the N-Triphos^{Ph} and N-Triphos^{Cy} ligands were produced with full oxidation achieved by hydrogen peroxide. Oxidation of the N-Triphos^{tBu} ligand did not proceed cleanly, suggesting the ligand is susceptible to degradation with oxidation.

The oxide of N-Triphos^{Ph}, $\text{N}(\text{CH}_2\text{P}(\text{O})\text{PPh}_2)_3$, was found to form a series of octahedral complexes with the general formula $[\text{M}(\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3)_2](\text{BPh}_4/\text{BF}_4)_2$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$). The structures of the complexes were determined by X-ray crystallography. These complexes feature two $\text{N}(\text{CH}_2\text{P}(\text{O})\text{PPh}_2)_3$ ligands bound to a single metal centre, with each adopting a tridentate coordination mode. Analogous complexes have not been observed with N-Triphos ligands, attributed to the steric hindrance of accommodating two N-Triphos ligands around a single metal centre. Binding through the phosphine oxide moieties appears to remove the steric bulk of each ligand sufficiently from the metal centre to accommodate the observed coordination sphere. Each of the complexes observed was paramagnetic, precluding analysis by NMR spectroscopy. Attempts at forming an analogous complex with zinc were unsuccessful. Reacting $\text{N}(\text{CH}_2\text{P}(\text{O})\text{PPh}_2)_3$ with $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ produced the complex $[\text{Y}(\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3)_3](\text{NO}_3)_3$, with a diamagnetic Y(III) centre. Unfortunately, solubility was poor in common solvents, precluding analysis by NMR spectroscopy and X-ray crystallography.

The coordination chemistry of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{PCy}_2)_3$ with $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ was also investigated. Characterisation was inconclusive but indicated that the coordination of just one $\text{N}(\text{CH}_2\text{P}(\text{O})\text{PCy}_2)_3$ ligand to a metal centre was achieved. The bis-tridentate complexes achieved with $\text{N}(\text{CH}_2\text{P}(\text{O})\text{PPh}_2)_3$ might not be accessible to $\text{N}(\text{CH}_2\text{P}(\text{O})\text{PCy}_2)_3$ owing to its greater steric bulk.

Overall, the work discussed in this chapter represents the potential for N-Triphos oxide ligands to form interesting complexes that would not be achieved with standard N-Triphos ligands. Incorporating phosphine oxide moieties with different substituents can be considered as a facile route to modify the properties of a complex; for example, its solubility and magnetic properties. Whilst the complexes described in this chapter would most likely display poor catalytic behaviour, owing to their closed coordination spheres, phosphine oxide complexes have found applications in fields such as metal sequestration, electroluminescence and as magnetic materials. Typically, those complexes use mono- or bidentate phosphine oxide ligands. The inclusion of tridentate N-Triphos oxide ligands, which are straight-forward to prepare and structurally versatile, opens up the possibilities for a wide array of new complexes.

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Chapter 6

Summary and Future work

“Everything that has a beginning has an end”, *The Matrix Revolutions* (2003)

6.1 Summary

This thesis began by highlighting the pressing need for the development of sustainable processes towards the production of chemicals, fuels and materials. Lignocellulosic biomass is widely considered as the most promising sustainable chemical feedstock, as it is renewable, low-cost and widely available. From cellulose, a wide number of chemical “building-blocks” can be derived, of which levulinic acid (LA) is one of the most important. Its two reactive functional groups enable a range of valuable chemical products to be accessed. Of these, the hydrogenation product γ -Valerolactone (GVL) was identified as an important product with applications as a green solvent, fuel-additive, chemical intermediate, and others. Over recent years, investigations into the hydrogenation of LA to GVL has been an active area of research.

Focusing upon homogeneous catalysis, Chapter 1 provided a summary of the major catalytic systems reported for LA hydrogenation using high-pressures of hydrogen gas. Most of these systems use ruthenium, although examples of iridium and palladium catalysts are also known. Many of the systems use phosphine ligands, with multidentate phosphine ligands generally providing the most active systems. This has been attributed to the formation of well-defined, robust catalysts. Whilst catalysts based upon earth-abundant metals have been reported, this area remains in its infancy.

Chapter 1 provided a summary of the catalytic systems reported for transfer hydrogenation of LA. Transfer hydrogenation reactions use an alternative source of hydrogen, and can be considered as safer, milder and more accessible than those using high-pressures of hydrogen gas. Again, most transfer hydrogenation systems use precious metals (ruthenium, iridium and palladium) with few examples based upon earth-abundant metals. The use of multidentate phosphine ligands was again highlighted.

Chapter 2 described the syntheses of nitrogen-centred tripodal N-Triphos ligands. These have been previously investigated for LA hydrogenation processes and are considered as promising candidates for further study. The syntheses of air-stable dialkyl/diaryl phosphonium chloride salts from their corresponding dialkyl/diaryl phosphine was described. A route to the diphenyl phosphonium chloride from triphenylphosphine was also described, improving the overall ease and safety of the synthesis. The syntheses of N-Triphos ligands from their corresponding phosphonium chloride (R = phenyl or cyclohexyl) are straight-forward and high-yielding. The synthesis of N-Triphos^{tBu} is less facile, largely attributed to a more difficult reaction work-up.

Attempts to synthesise unsymmetrical N-Triphos ligands of the general structures $N(CH_2PR_2)_2(CH_2PR'_2)$ and $N(CH_2PR_2)_2(CH_2P(O)R_2)$ were also performed. This was motivated by the different stereoelectronic properties provided by different phosphine substituents or functionalities. However, the syntheses of the mixed ligands were limited by the formation of multiple product species or by poor reaction progress. Then, the syntheses of bidentate nitrogen-bridged bisphosphine ligands were described. Whilst these lack the tridentate coordination offered by N-Triphos ligands, they introduce a degree of asymmetry by the choice of amine substituent. Adapting the syntheses of N-Triphos ligands from phosphonium chlorides, bidentate ligands of the form $R'-N(CH_2PR_2)_2$ were synthesised (R = phenyl, cyclohexyl; R' = methyl, benzyl). The reactions do not proceed as readily as their corresponding N-Triphos ligands and the products require air-protection. Nonetheless, they could be synthesised in good yield and purity. The tert-butyl analogues were again more difficult to synthesise, limited by poor reaction progress and a higher susceptibility to oxidation. $R'-N(CH_2PCy_2)_2$ ($R' = CH_2CH(OEt)_2$) was synthesised and collected as an oil, as a route towards improving water solubility.

Chapter 3 described the coordination chemistry of both bi- and tridentate nitrogen-centred phosphine ligands with several transition metals. Coordination of the bidentate nitrogen-bridged ligands of the formula $R'-N(CH_2PR_2)_2$ ($R' = Me, R = Cy, Ph, ^tBu$; $R' = Bn, R = ^tBu$; $R' = CH_2CH(OEt)_2, R = Cy$) to $[PdCl_2(COD)]$ formed a series of square-planar complexes. These were fully characterised with their geometry confirmed by crystallography. The distortion from an idealised square-planar geometry increased with the increasing steric bulk of the phosphine substituent. Reactions of $R'-N(CH_2PR_2)_2$ ($R' = Me, R = Cy, Ph, ^tBu$) with $[NiCl_2(PPh_3)_2]$ generated analogous square-planar complexes.

The coordination of N-Triphos ligands ($R = Ph, Cy, ^tBu$) to $[PdCl_2(COD)]$ was also performed. In each case, just two of the three phosphine arms coordinated to palladium. Addition of hydrogen peroxide oxidised the uncoordinated phosphine to a phosphine oxide without affecting the rest of the complex. Whilst product isolation was again more difficult with $R = ^tBu$, the three complexes were fully characterised, including by crystallography. The generation of palladium complexes with both the bi- and triphosphine ligands opens a scope for wider modification of the product properties and behaviour.

Reactions of both $Me-N(CH_2PCy_2)_2$ and N-Triphos^{Cy} with $[RuCl_2(p\text{-cymene})]_2$ were performed. With $Me-N(CH_2PCy_2)_2$, the expected bidentate coordination mode was obtained. The product was fully characterised, and crystallography identified a “piano-stool” type geometry. Unfortunately, reactions of N-Triphos^{Cy} with $[RuCl_2(p\text{-cymene})]_2$ were less straight-forward than those with palladium. Although two of the three phosphine arms were observed to coordinate to ruthenium, addition of hydrogen peroxide caused over-oxidation and product degradation. Omitting hydrogen peroxide, the third

phosphine was found to adopt multiple states, with a tentative assignment to the involvement of tridentate ligand coordination. The product was again susceptible to oxidation and could not be characterised by crystallography. With palladium, the reactions with N-Triphos ligands were most facile; however, with $[\text{RuCl}_2(p\text{-cymene})]_2$ the bisphosphine reactions were more straight-forward.

Initial reactions of both $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ and N-Triphos^{Cy} with $[\text{Cp}^*\text{IrCl}_2]_2$ were difficult to follow by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. It was unclear if the reaction was suffering from limited progress, or if a combination of different modes were forming. With $[\text{Ir}(\text{COD})\text{Cl}]_2$ instead, $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ adopted the expected bidentate mode. The product was fully characterised and crystallography determined an approximately square-planar geometry. A separate product from the reaction was collected, which showed an entirely different $^{31}\text{P}\{^1\text{H}\}$ NMR signal. This was assigned to an “AB quartet”, originating from two, very slightly different, $^{31}\text{P}\{^1\text{H}\}$ NMR environments with a coupling comparable to the difference in their chemical shifts. Crystallography identified this second product as an unexpected octahedral iridium complex with three chloride ligands and a water ligand in addition to the bisphosphine ligand. The route to the formation of this octahedral complex is uncertain.

Reactions of N-Triphos^{Cy} with $[\text{Ir}(\text{COD})\text{Cl}]_2$ were less straight-forward. As with $[\text{RuCl}_2(p\text{-cymene})]_2$, hydrogen peroxide addition appeared to cause over-oxidation and degradation. In the absence of hydrogen peroxide, the pendant phosphine arm was surprisingly resistant to oxidation, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy indicated a mixture of bi- and tridentate coordination modes. This was dependent on the solvent used: tridentate coordination was suppressed in the more coordinating solvent methanol, whilst the less coordination solvent dichloromethane facilitated a greater mixture of coordination modes. Unfortunately, the exact product identity could not be elucidated by crystallography. With N-Triphos^{Ph}, $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy identified all three phosphine arms coordinating to iridium in a tridentate fashion. The mixture of modes identified with N-Triphos^{Cy} could therefore be attributed to a steric effect of the three bulky PCy₂ moieties.

Reactions of both $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ and N-Triphos^{Cy} were also performed with $[\text{Rh}(\text{COD})(\text{MeCN})_2]\text{BF}_4$. The bisphosphine ligand fully coordinated to rhodium; however, the product was highly air-sensitive, limiting its characterisation. Furthermore, over the course of several days in CDCl_3 , the original product $^{31}\text{P}\{^1\text{H}\}$ NMR doublet was found to be entirely replaced by two downfield doublet of doublets. Crystallography identified this species as a tri-chloro bridged rhodium dimer, presumably generated by displacement of COD from the original product. The new rhodium dimer was fully characterised. A reaction of N-Triphos^{Cy} with $[\text{Rh}(\text{COD})(\text{MeCN})_2]\text{BF}_4$ proceeded through the expected bidentate ligand coordination, with a pendant phosphine arm. However, the high air-sensitivity of the product again limited its characterisation.

With the exception of the air-sensitive rhodium complexes, the complexes described in Chapter 3 were applied as catalysts for the transfer hydrogenation of LA. These used formic acid (FA) as the hydrogen source alongside triethylamine as a base additive. Several different reaction systems were trialled, with important factors identified as a sealed environment to maintain a pressure and a capacity to safely avoid an over-pressure. Reaction vials fitted with pressure-relief caps allowed for a high reaction throughput. Although aqueous mixtures are considered to promote transfer hydrogenation with FA, the catalysts described in this study have no water solubility. Every solvent system trialled was found to inhibit the yields achieved, therefore the reactions were generally performed without a solvent.

A wide catalyst scope was investigated. Whilst the PPh_2 -palladium complexes showed no activity, the PCy_2 -complexes achieved moderate GVL yields of 46-47 % over 24 hours. This was primarily attributed to the greater electron-donating nature of the cyclohexyl substituents. Although the $\text{P}(\text{tBu})_2$ -containing complexes were therefore expected to achieve higher GVL yields, in fact they showed very little activity. This was attributed to catalyst decomposition. The PCy_2 -ruthenium complexes achieved slightly lower yields of 26-36 %. The $\text{PPh}_2/\text{PCy}_2$ -iridium complexes gave yields in the range of 40-71 %, with an unexpectedly high variation. This was attributed at least in part to the difficulties in assigning exact coordination modes with ruthenium and iridium described in Chapter 3.

The palladium catalysts were the most straight-forward to prepare and showed the greatest consistency; therefore, they were used for the investigation of a wider range of reaction variables. Protection from air was found to be insignificant with regards to the yield achieved. Surprisingly, an increase in FA loading provided no improvement, whilst a reduction in base loading offered a small benefit. A reduction in temperature to 80 °C achieved the same maximum yields across 24 hours, albeit with a slower induction period. In fact, it was found that the vast majority of the hydrogenation achieved occurred in the first two hours. Unfortunately, the pressure tolerance of the reaction vials did not permit a full study into the effects of increasing FA loading and temperature. Through gas-evolution studies, it was found that most FA decomposition occurred within the first two hours at 100 °C, generating close to the maximum theoretical volume of gas.

Reacting the PCy_2 -palladium complexes with excess FA and triethylamine generated CO-bridged palladium dimers within short times. By $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the dimers matched signals which had been observed in $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the transfer hydrogenation reactions. The dimers were considered as inactive catalyst forms.

Collectively, these results indicated that there is a barrier towards achieving quantitative LA hydrogenation with this system, with very little additional hydrogenation or FA decomposition

occurring beyond the first two hours. With the use of 2.1 equivalents of FA, there should be sufficient hydrogen generated for quantitative LA hydrogenation. The identification of carbon monoxide production, both using a CO probe and through formation of the CO-bridged dimer species, suggested that FA dehydration is dominating over dehydrogenation, indicating that a lack of hydrogen generated was limiting hydrogenation. The palladium dimers themselves were found to be active for LA transfer hydrogenation, suggesting that their formation is not a hindrance to higher yields. This suggests that a lack of available hydrogen, rather than available catalyst, prevents higher yields. Given that the catalysts facilitate complete FA decomposition, this is attributed to a lack of hydrogen generated by FA amongst its other potential decomposition products.

Given that similar aqueous-based systems in the literature are highly active, the lack of water in the transfer hydrogenation reactions here was identified as an obstacle by limiting FA dehydrogenation. Several strategies were investigated to incorporate water into the transfer hydrogenation reactions. With the simple addition of small water volumes, addition of up to 0.3 mL had a positive effect. Trialling a set of water-soluble palladium, iridium and ruthenium complexes of the PTA ligand gave mixed results. $[\text{Ir}(\text{COD})(\text{PTA})_3]\text{Cl}$ was the most successful candidate, with GVL yield increasing with water addition up to 52 %. Trialling the palladium complex of $\text{R}'\text{-N}(\text{CH}_2\text{PCy}_2)_2$ ($\text{R}' = \text{CH}_2\text{CH}(\text{OEt})_2$) was unfortunately less successful than anticipated; with the addition of 1 mL water a 59 % conversion was achieved.

Using a high-pressure reactor, transfer hydrogenation of LA was promoted by increasing the FA loading and the temperature to 150 °C, up to a maximum 78 % GVL yield. However, it was considered that with this catalytic system traditional hydrogenation with molecular hydrogen was necessary to reach quantitative LA hydrogenation. At 150 °C and 15 bar H_2 , the PCy_2 -palladium complexes achieved 97 % GVL yields, demonstrating that their activity was being limited under transfer hydrogenation conditions. A wider study of high-pressure hydrogenations was performed with in situ systems of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and N-Triphos^{Ph}. A maximum LA conversion of 80 % was achieved at 80 bar H_2 . Given the benefits of using earth-abundant metals, this system has promise for further study.

Chapter 5 described the coordination chemistry of N-Triphos ligands with earth-abundant first-row transition metals. A barrier to the study of these products is their paramagnetism. A crystal structure of a product formed from reaction between $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and N-Triphos^{Ph} featured partial oxidation of the N-Triphos ligand. This motivated a study into the full oxide analogues of N-Triphos ligands, which have almost no presence in the literature. Reactions of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$ with $\text{M}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$) and $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ formed a series of octahedral complexes in which two tridentate oxide ligands coordinated to a single metal centre, determined by crystallography. Although the

paramagnetic complexes could not be studied by NMR spectroscopy, magnetic measurements were performed. Through reaction of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$ with $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, tridentate ligand coordination was again observed, however full characterisation was prohibited by poor solubility. Reactions of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Cy}_2)_3$ with $\text{M}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Fe}, \text{Co}$) were inconclusive, suggesting that the octahedral complexes are permitted only with the less bulky phenyl substituents. Although the complexes of the oxide ligands are unlikely to be useful candidates as hydrogenation catalysts, they could have interesting applications in other fields. They further demonstrate the effect of small modifications to N-Triphos ligands on their properties and coordination chemistry.

6.2 Evaluation of catalytic results

Table 6.1 collects some of the most effective results achieved under transfer hydrogenation conditions as discussed in Chapter 4. The catalysts **C1** and **C2** were investigated most thoroughly, generally alongside FA and NEt_3 at 100 °C in solventless conditions. The results demonstrate the moderate GVL yields which **C1** and **C2** readily achieved, with only modest improvements achieved with, for example, the addition of K_3PO_4 (Table 6.1, Entry 1) or small volumes of water (Entries 4 and 8). The highest GVL yield of 78 % was achieved with **C2** at 150 °C and 3.2 equivalents of FA in two hours (Entry 5). TON and TOF values were consistently low, attributed to the moderate yields achieved, the standard 1 mol% catalyst loading and 24-hour reaction time. A 0.5 mol% loading of **C1** achieved a slightly reduced 41 % GVL yield in 24 hours (Entry 2), whilst both **C1** and **C2** were found to achieve near-maximum GVL yields in the first two hours (Entries 3, 6-7). The iridium catalyst **C16** achieved a 71 % GVL yield (Entry 9) but was discounted from further study owing to the relative difficulty of its synthesis. Surprisingly, the palladium dimer **28** achieved a 55 % GVL yield (Entry 10), demonstrating its formation is not a barrier to higher yields.

Table 6.1 also collects some comparative results from the literature. Some of the most effective catalytic systems are based upon bipyridine, dipyridylamine or carbon-bridged bisphosphine ligands. Catalysts based upon the precious metals ruthenium, iridium and palladium are able to access high TON and TOF values (Entries 11-16), whilst those based on earth-abundant metals show much lower activity and require much higher catalyst loadings (Entries 17-18). Although several of the systems operate under solventless conditions (Entries 11, 15-16), many use aqueous systems (Entries 12-14, 17) or an alcohol solvent (Entry 18). Whilst water is considered a “green solvent”, solventless reactions can be considered as having strong green credentials. Although many systems require a base additive,

primarily triethylamine (Entries 13-15, 17), this is not always required. Whilst the results achieved in this work cannot directly compare to the most effective published results in terms of GVL yield, TON or TOF, they represent a straight-forward system which performs best in the absence of an external solvent and achieves their maximum GVL yields within a short period of time; however, achieving further hydrogenation over extended times proved difficult. Whilst the reaction conditions applied are comparable to those previously reported, the relatively high catalyst loading used (1 mol%) perhaps limits the applicability of this system; however, palladium has traditionally been considered as superior to ruthenium and iridium in natural abundance and cost. The ligand system exploited in this work is straight-forward to synthesise and modify, especially in comparison to the carbon bridged bisphosphine ligands utilised by Garcia (Entries 13-14); furthermore, their -PCy₂ catalysts failed to achieve any activity under TH conditions. Therefore, this system represents an opportunity for further improvement and investigation, given the readily accessible modification of the catalyst system, and the straight-forward, mild operating conditions.

Table 6.2 collects some of the most effective results achieved under high-pressure hydrogenation conditions, as described in Chapter 4. Both **C1** and **C2** achieved near-quantitative GVL yields at 150 °C and 15-20 bar H₂ in solventless conditions over six hours (Table 6.2, Entries 1-3). Reducing the catalyst loading from 1 mol% to 0.5 or 0.1 mol% achieved slightly reduced GVL yields (Entries 4-5), with the highest TON and TOF of 820 and 137 respectively achieved with 0.1 mol% **C2**. Trialling shorter reaction times showed that the vast majority of the hydrogenation was achieved within the first one hour, with near completion by three hours (Entries 6-8). An alternative in situ system of Fe(BF₄)₂·6H₂O or Co(BF₄)₂·6H₂O alongside N-Triphos^{Ph} was also trialled. At 100 °C and 50-80 bar H₂ in THF, high yields of GVL, alongside small yields of 1,4-PDO, were achieved with Co(BF₄)₂·6H₂O/N-Triphos^{Ph} (Entries 9-10). The cobalt system required a lower temperature than the preformed palladium catalysts, and a much higher pressure and catalyst loading. Fe(BF₄)₂·6H₂O/N-Triphos^{Ph} showed lower activity under the same conditions (Entry 11).

Table 6.2 also collects some of the most relevant, and successful, results reported in the literature for this reaction. Many of these also use multidentate phosphine ligands. The reaction conditions utilised with **C1** and **C2** compare favourably to previous systems, with a relatively low-pressure requirement, short reaction time, and effective solventless conditions (despite the requirement for NEt₃ inclusion). The standard catalyst loading of 1 mol% can again be considered as a limitation of this system; however, a 0.1 mol% loading also proved effective. Under high-pressure conditions, obtaining a mixture of hydrogenation products becomes increasingly problematic; **C1** and **C2** are entirely selective for GVL. Many of the systems reported in the literature use in situ mixtures of a commercially available metal precursor alongside a commercially available ligand (Triphos, DPPB, Tetrphos), which avoids

the requirement for synthesis of a preformed catalyst. However, the syntheses of **C1** and **C2**, in particular, are relatively inexpensive and straight-forward. More recently, examples of catalysts using earth-abundant metals (Fe, Co, Ni) for this reaction are proving highly effective. Several examples are able to achieve comparable yields of hydrogenation products under comparable conditions to earlier examples based upon precious metals. The activity of these are superior to the cobalt/N-Triphos system reported here, although N-Triphos remains as an easily accessible and versatile ligand for further study.

Table 6.1. Collection of key results achieved for the transfer hydrogenation of LA to GVL presented in this work, in addition to important and comparable previously reported results.

Entry	Catalyst	T [°C]	H source, equiv.	S/C	Time [h]	Additives	GVL yield [%]	TON	TOF [h ⁻¹]	Ref.
1	C1	100	FA, 2.1	100	24	K ₃ PO ₄	64	64	3	-
2	C1	100	FA, 2.1	200	24	NEt ₃	41	82	3	-
3	C1	100	FA, 2.1	100	4	NEt ₃	43	43	11	-
4	C2	100	FA, 2.1	100	24	NEt ₃ , 0.3 mL H ₂ O	63	63	3	-
5	C2	150	FA, 3.2	100	2	NEt ₃	78	78	39	-
6	C2	100	FA, 2.1	100	2	NEt ₃	40	40	20	-
7	C2	100	FA, 2.1	100	1	NEt ₃	31	31	31	-
8	C4	100	FA, 2.1	100	24	NEt ₃ , 1 mL H ₂ O	59	59	2	-
9	C16	100	FA, 2.1	100	24	NEt ₃	71	71	3	-
10	28	100	FA, 2.1	100	24	NEt ₃	55	55	2	-
11	Shvo's catalyst (Ar = <i>p</i> -MeOPh)	100	FA, 1.5	2400	8	-	99.9	2398	300	¹
12	[Cp*(OH ₂)Ir- bipy(OMe) ₂].SO ₄	120	FA, 2	10,000	4	-	99	9900	2475	²
13	[(dtbpe)PdCl ₂]	100	FA, 2.1	1000	1	NEt ₃	100	1000	1000	³
14	[(dtbpe)PdCl ₂]	100	FA, 2.1	3000	1	NEt ₃	70	2100	2100	³
15	[(mbdpa)(<i>p</i> - cymene)RuCl]Cl	150	FA, 2	2000	16	NEt ₃	99	1980	124	⁴
16	[(dpa)Cp*Ir(OSO ₃)]	110	FA, 2	2000	24	(H ₂ O)	100	2000	83	⁵
17	[Fe ₃ (CO) ₁₂]	180	FA, 4	25	15	Imidazole	92	23	2	⁶
18	Casey's catalyst [(CO) ₂ (MeCN)]	80	IPA, 25	25	20	-	38	10	1	⁷

Table 6.2. Collection of key results achieved for the hydrogenation of LA to GVL with H₂ presented in this work, in addition to important and comparable previously reported results.

Entry	Catalyst	T [°C]	P (bar)	S/C	Time [h]	Solvent/additives	Yield [%]	TON	TOF [h ⁻¹]	Ref
1	C1	150	20	100	6	- NEt ₃	GVL: 93	93	16	-
2	C2	150	20	100	6	- NEt ₃	GVL: 97	97	16	-
3	C2	150	15	100	6	- NEt ₃	GVL: 96	96	16	-
4	C2	150	20	200	6	- NEt ₃	GVL: 92	184	31	-
5	C2	150	20	1,000	6	- NEt ₃	GVL: 82	820	137	-
6	C2	150	20	100	1	- NEt ₃	GVL: 84	84	84	-
7	C2	150	20	100	3	- NEt ₃	GVL: 93	93	31	-
8	C2	150	15	200	3	- NEt ₃	GVL: 85	170	28	-
9	Co(BF ₄) ₂ ·6H ₂ O/ N-Triphos ^{Ph}	100	80	20	6	THF -	GVL: 75 1,4-PDO: 5	16	3	⁸
10	Co(BF ₄) ₂ ·6H ₂ O/ N-Triphos ^{Ph}	100	50	20	6	THF -	GVL: 69 1,4-PDO: 4	15	3	⁸
11	Fe(BF ₄) ₂ ·6H ₂ O/ N-Triphos ^{Ph}	100	80	20	6	THF -	GVL: 40	8	1	⁸
12	[Ru(acac) ₃]/ Triphos	160	100	1,000	18	- p-TsOH	GVL: 58 1,4-PDO: 1 2-MTHF: 39	580	32	⁹
13	[Ru(acac) ₃]/ N-Triphos	150	65	200	25	THF -	GVL: 60 1,4-PDO: 37 2-MTHF: 2	120	5	¹⁰
14	[Ru(H) ₂ (CO) (N-Triphos)]	150	65	200	25	THF NH ₄ PF ₆	GVL: 95 1,4-PDO: <1	190	8	¹⁰
15	[Ru(acac) ₃]/DPPB	160	100	12,740	0.6	-	GVL: >99.9	12,740	21,233	¹¹
16	[Ru(acac) ₃]/ Tetrachos	140	80	100,000	96	- Sc(OTf) ₃	GVL: 73	73,142	762	¹²
17	[IrH ₃ (PNP(^t Bu ₂))]	100	50	10,000	24	Ethanol KOH	GVL: 98	9,800	408	¹³
18	Cp*(OH ₂)Ir(bipy- (OMe) ₂)SO ₄	120	10	100,000	36	H ₂ O -	GVL: 78	78,000	2,167	²
19	[(dpa)Cp*Ir(OSO ₃)]	130	5	200,000	72	-	GVL: 87	174,000	2,417	⁵
20	[(dtbpe)PdCl ₂]	80	5	1,000	5	H ₂ O -	GVL: 100	1,000	200	³
21	Co(BF ₄) ₂ ·6H ₂ O/ Tetrachos	100	10	40	24	DMI -	GVL: >99	40	2	¹⁴
22	Ni(OAc) ₂ ·4H ₂ O/ Triphos	150	30	10,000	20	-	GVL: 94	9,400	470	¹⁵
23	Co(BF ₄) ₂ ·6H ₂ O/ Triphos	100	80	10	22	-	1,4-PDO: 47 2-MTHF: 14	5	-	¹⁶

6.3 Future work

Of the catalytic systems trialled for the transfer hydrogenation of LA, the palladium complexes of both N-Triphos ligands and nitrogen-centred bisphosphine ligands were identified as a promising modular framework whereby several structural modifications could be readily made. However, whilst the system demonstrated moderate catalytic activity under transfer hydrogenation conditions, there were barriers to achieving quantitative LA hydrogenation. There are several factors which could be investigated to improve this.

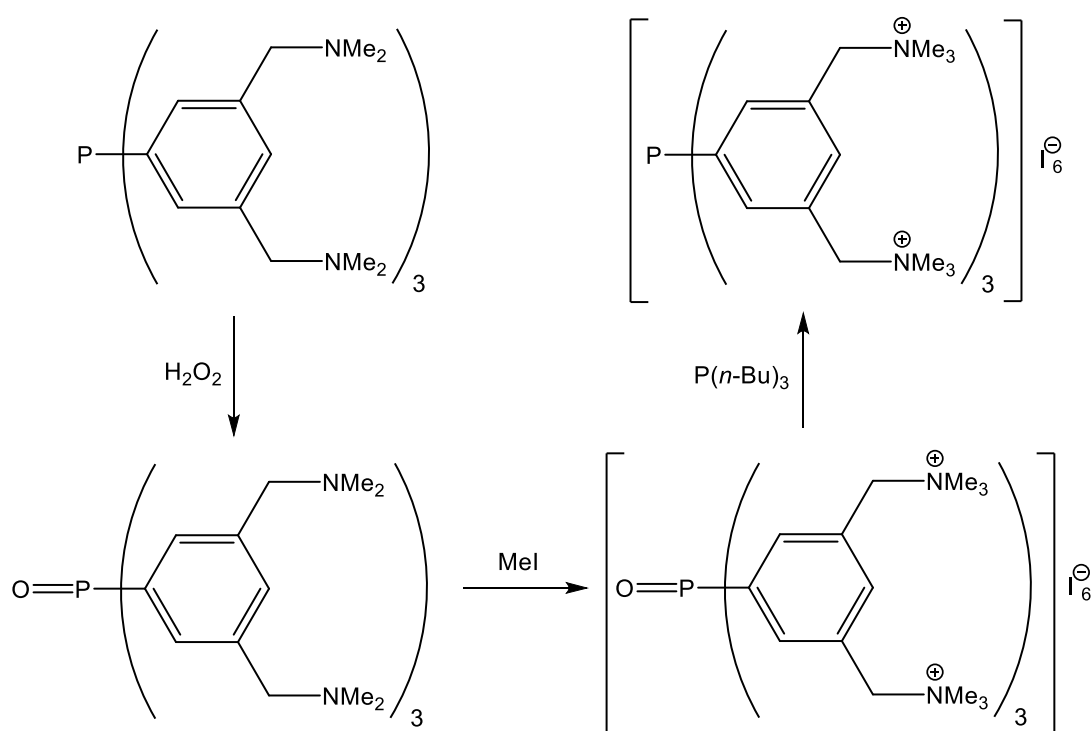
The phosphine substituent had a strong impact on the catalyst activity. Whilst bulky, electron-donating substituents promote the catalytic activity of these systems, in this work the use of tert-butyl substituents resulted in near-zero activity. This was attributed to catalyst decomposition, although the mechanism of deactivation is not understood. Study of this decomposition might enlighten further development of these catalytic systems. A wider range of bulky, electron-donating phosphine substituents could be trialled, including iso-propyl or cyclopentyl moieties. The N-Triphos analogues of these are known and they might facilitate catalysts with greater activity whilst minimising decomposition.

The lack of water-solubility was identified as a key issue with this catalytic system, with respect to FA dehydration and catalyst deactivation. Although the formation of palladium dimers was observed, they reverted readily to the original catalyst and are not a barrier towards LA hydrogenation. The full mechanistic cycle however is not understood. Whilst CO was detected both through the formation of the CO-bridged dimers and qualitatively with a CO probe, the exact composition of the gases generated in the TH reactions is unknown. However, the incorporation of water is considered as a means to avoid CO formation through FA dehydration. In this work, the incorporation of water-soluble PTA ligands showed limited success, although a wider range of water-soluble phosphines could be trialled (e.g. TPPMS, TPPTS). A more promising strategy might be the incorporation of a water-solubilising moiety at the amine position. Modification at this position was found to have little effect on catalyst activity. Whilst the incorporation of a $\text{CH}_2\text{CH}(\text{OEt})_2$ moiety was trialled, this showed only moderate water-solubility and gave little improvement to the LA hydrogenation. Therefore, the water-solubilising moiety must be able to counteract the bulky hydrophobic PCy_2 moieties. As an extension of the diethoxy substituent trialled in this work, pegylated functionalities could be trialled.

A commonly used route to enhance phosphine solubility in the literature is to introduce ionic character. Anionic phosphines containing sulfonate (SO_3^-), carboxyl or hydroxyl moieties are prevalent (e.g. TPPTS, TPPMS). Cationic examples from the literature introduce a positive charge into the

phosphine backbone using ammoniomethyl-substituents ($-\text{N}(\text{Me})_3^+$).^{17–19} A route to cationic, ammoniomethyl-substituted triarylphosphine ligands adapted from literature is shown in Scheme 6.1.

However, modification of the phosphines should be carefully tailored to avoid minimising the catalyst activity. Consequently, the use of N-Triphos ligands might play an important role. With coordination of just two phosphine arms to palladium, in this work the pendant third phosphine arm was typically converted to a phosphine oxide (with no improvement on water-solubility). However, modification of the third phosphine arm (e.g. by introduction of anionic/cationic character) could be a route to water-solubility whilst retaining the activity of the coordinated phosphines.



Scheme 6.1. Introduction of cationic ammoniomethyl-substituents to phosphine ligands.¹⁷

Whilst Chapter 2 briefly discussed the attempted syntheses of mixed, unsymmetrical N-Triphos ligands, limited success was achieved. Nonetheless, wider development of unsymmetrical N-Triphos ligands is interesting for the stereoelectronic properties, coordination behaviour and solubility such modifications would enable. This includes the choice of phosphine substituent and phosphorus moiety.

The requirement for precious metals as catalysts for transfer hydrogenation is a limit to the sustainability and applicability of these systems. If the catalysts cannot be exchanged for earth-abundant metals, a route to improving the sustainability of the processes could be to use recycled or

recovered sources of palladium. This was trialled by preparing iodo-analogues from $[\text{Pd}_2\text{I}_6](\text{TBA})_2$ recovered from spent exhaust catalysts. The new catalysts showed catalytic activity, albeit slightly lower than their chloro-analogues.

Furthermore, a wider substrate scope should be investigated to improve the usefulness of this catalytic system. An initial substrate investigation found that LA was the most successful hydrogenation candidate, attributed to its ketone and carboxylic acid functionalities. This suggests that the substrate scope is narrower than initially hoped (LA is the only of the “Top Value Added Chemicals from Biomass” selected by the U.S DoE to include a ketone). However, a fuller investigation into substrates amenable to hydrogenation in this system would be compelling.

Although the research described in this thesis was motivated by using mild transfer hydrogenation conditions, improvements were found with higher temperatures and with higher pressures of hydrogen gas. However, these more forcing conditions remove some of the advantages of transfer hydrogenation processes. Nonetheless, a wider optimisation of the high-pressure hydrogenation reactions is necessary. Of particular interest is further study of the $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}/\text{N-Triphos}$ system, owing to the activity already achieved with such a system and the greater sustainability of the earth-abundant first-row transition metals.

Furthermore, the phosphine oxide complexes described in Chapter 5 have not yet found an application. Phosphine oxide complexes, primarily with lanthanide and actinide metals, are applied as luminescent materials and metal extractants, as well as ligands for homogeneous catalysis. Therefore there is a wide scope for further study and application of N-Triphos oxide ligands, just as there is for N-Triphos ligands and nitrogen-centred phosphine ligands in general. This system remains very understudied relative to their carbon-centered analogues. The work presented in this thesis represents an advancement of the knowledge of the coordination chemistry and properties of these ligands, however the field remains in its infancy.

6.3 References

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Chapter 7

Experimental

“A thousand experiments. A thousand failures. And then, at last, the great, wonderful day”,
The Invisible Man (1933)

7.1 General considerations

7.1.1 Safety considerations

All experiments described in this thesis were undertaken only after rigorous risk assessments were reviewed and performed. Experiments with compressed gases must only be carried out using appropriate equipment under careful safety precautions by suitably trained personnel.

7.1.2 Materials and Conditions

All experiments were performed using standard Schlenk line techniques under inert atmospheres of N_2 , with strict exclusion of air and moisture, unless otherwise stated. Dry solvents were either purchased from Sigma-Aldrich or collected from departmental solvent drying towers and stored over 3 Å activated molecular sieves. All solvents were degassed prior to usage by purging with N_2 gas. Starting materials were purchased as reagent grade chemicals from Sigma-Aldrich, VWR International, Fisher Scientific or Fluorochem and used without further purification. Selected metal precursors $[PdCl_2(COD)]^1$, $[NiCl_2(PPh_3)_2]^2$, $[Cp^*IrCl_2]_2^3$ and $[Ir(COD)Cl]_2^4$ were prepared following literature procedures.

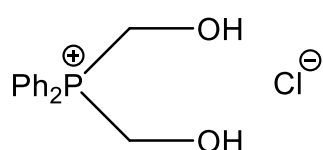
7.1.3 Instrumentation and Analysis

NMR spectra were recorded at 298 K on a Bruker AV-400 or AV-500 spectrometer operating at a frequency of 400 MHz or 500 MHz respectively for ^1H NMR, 101 MHz for $^{13}C\{^1H\}$ NMR and 162 MHz for $^{31}P\{^1H\}$ NMR spectroscopy. Chemical shifts are reported in parts per million (ppm) and referenced using the residual proton impurities in the solvents for ^1H NMR spectroscopy and the solvent for $^{13}C\{^1H\}$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR chemical shifts are reported relative to H_3PO_4 as an external standard. Specialist NMR experiments were performed by Mr. Pete Haycock of Imperial College London where stated. NMR spectra were processed and analysed using Mestrenova software. The following abbreviations are used: s (singlet), d (doublet), dd (doublet of doublets), m (multiplet), t (triplet), br (broad signal), Ph (phenyl), Cy (cyclohexyl), COD (1,5-cyclooctadiene). Mass spectrometry samples were run by Dr. Lisa Haigh of the Mass Spectrometry service at Imperial College London. Crystallographic analyses were performed by Dr. Andrew White of the Chemical Crystallography Laboratory at Imperial College London using Agilent Xcalibur 3 E and Xcalibur PX Ultra A diffractometers, and the structures were refined by full-matrix, least-squares procedures on $[F^2]$ using SHELXTL, SHELX-97 and SHELX-2013 program systems. Elemental analysis samples were run by Mr. Stephen Boyer of the Department of Health and Human Sciences at London Metropolitan University. ATR Infra-red spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer. Melting

point measurements were recorded on an OptiMelt Automated Melting Point System. Magnetic susceptibility ' χ_m ' measurements were recorded using a Sherwood Scientific Magnetic Susceptibility Balance Mark 1. Samples were first ground into a fine powder and loaded into a sample tube and the data were corrected for diamagnetism to achieve values of effective magnetic moment ' μ_{eff} '. The number of unpaired electrons was calculated from the spin-only formula. High pressure hydrogenation procedures were performed using a high-pressure stainless steel Autoclave Engineering mini-reactor fitted with a custom PTFE inner sleeve or an Asynt mini-reactor fitted with a glass inner vessel. Analysis of all hydrogenation procedures was performed using ^1H NMR spectroscopy.

7.2 Experimental details for Chapter 2

7.2.1 Preparation of diphenyl(hydroxymethyl)phosphonium chloride

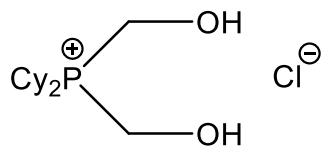


a) Method adapted from literature.⁵ To diphenylphosphine (10 g, 54 mmol) was slowly added formaldehyde (37 % aqueous solution, 9.8 mL). After stirring at RT for 30 minutes, hydrochloric acid (37 %, 5.5 mL) was added and the mixture stirred for a further hour. After

solvent removal under reduced pressure, a white crystalline solid precipitated. The solid was washed with diethyl ether and dried in vacuo. The product was collected as a white crystalline solid (14.5 g, 51 mmol, 96 %).

b) To a solution of triphenylphosphine (10 g, 38 mmol) in THF (30 mL) was added lithium (1.06 g, 153 mmol, excess). With stirring at RT for one hour, the mixture became dark-red in colour. After slow addition of degassed water (30 mL), the mixture was stirred at RT for one hour. Formaldehyde (37 % aqueous solution, 14 mL) was added and the mixture stirred for 30 minutes. After the addition of hydrochloric acid (37 %, 16 mL) the mixture was stirred for one hour. Solvent was removed in vacuo to precipitate a white solid. The solid was isolated by vacuum filtration and washed with diethyl ether. After drying in vacuo, the product was recrystallized from methanol and collected as a free-flowing white crystalline solid (9.38 g, 33.1 mmol, 87 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : 13.4 ppm (s). ^1H NMR (CDCl_3 , 400 MHz) δ : 7.2-7.9 (m, 10H, Ph), 5.08 ppm (d, $^2J_{\text{P-H}} = 7.8$ Hz, 4H).

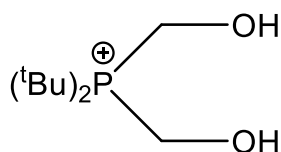
7.2.2 Preparation of dicyclohexyl(hydroxymethyl)phosphonium chloride



Method adapted from literature.⁵

With cooling in ice, formaldehyde (37 % aqueous solution, 23 mL) was added to dicyclohexylphosphine (25 g, 126 mmol). After stirring for 30 minutes at RT, hydrochloric acid (37 %, 13 mL) was added. A white precipitate formed immediately. After cooling to RT, the solid was isolated by vacuum filtration and washed with diethyl ether. After drying in vacuo, the product was collected as a free-flowing white solid (34.836 g, 118 mmol, 94 %). ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ: 27.7 ppm (s). ¹H NMR (CDCl₃, 400 MHz) δ: 6.43 (br s, 2H, OH), 4.65 (s, 4H, CH₂), 2.40 (m, 2H, Cy CH), 1.3-2.0 ppm (m, 20H, Cy CH₂).

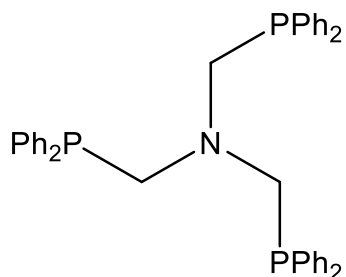
7.2.3 Preparation of ditertbutyl(hydroxymethyl)phosphonium chloride



Method adapted from literature.⁵

With cooling in ice, formaldehyde (37 % aqueous solution, 1.3 mL) was added to di-tertbutylphosphine (1 g, 6.8 mmol). After stirring for 30 minutes at RT, hydrochloric acid (37 %, 0.7 mL) was added. The mixture was stirred for 30 minutes, during which time a white solid precipitated. The mixture was cooled in ice, and the solid isolated by vacuum filtration and washed with diethyl ether. After drying in vacuo, the product was collected as a free-flowing white solid (0.948 g, 3.9 mmol, 57 %). ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ: 35.1 ppm (s).

7.2.4 Preparation of N-Triphos^{Ph}

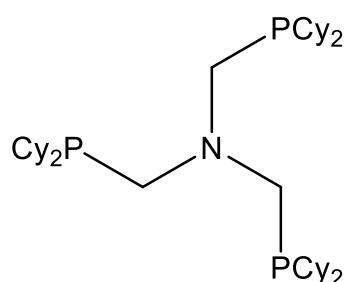


Method adapted from literature.⁶

To a solution of diphenyl(hydroxymethyl)phosphonium chloride (3.0 g, 10.6 mmol, 3 equiv.) in methanol (3 mL) was added triethylamine (4.1 mL, excess). After stirring at RT for one hour, ammonia (2M solution in methanol, 1.8 mL, 3.5 mmol, 1 equiv.) was added. The mixture was heated to reflux for two hours, during which a white solid precipitated. After cooling to

RT, the solid was isolated by cannula filtration and washed with methanol (3 x 1 mL). After drying in vacuo overnight, the product was collected as a free-flowing white solid (1.37 g, 2.2 mmol, 63 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : -29.0 ppm (s). ^1H NMR (CDCl_3 , 400 MHz) δ : 7.2-7.4 (m, 30H, Ph), 3.82 ppm (d, 6H, $^2J_{\text{P-H}} = 3.3$ Hz, CH_2).

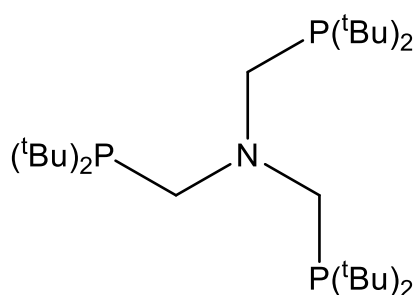
7.2.5 Preparation of N-Triphos^{Cy}



Method adapted from literature.⁶

To a solution of dicyclohexyl(hydroxymethyl)phosphonium chloride (2.0 g, 6.8 mmol, 3 equiv.) in methanol (9 mL) was added triethylamine (2.6 mL, excess). After stirring at RT for one hour, ammonia (2M solution in methanol, 1.2 mL, 2.3 mmol, 1 equiv.) was added. The mixture was heated to reflux for two hours, during which a white solid precipitated. After cooling to RT, the solid was isolated by cannula filtration and washed with methanol (3 x 1 mL). After drying in vacuo overnight, the product was collected as a free-flowing white powder (0.681 g, 1.1 mmol, 46 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : -17.0 ppm (s).

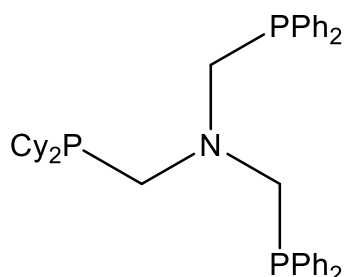
7.2.6 Preparation of N-Triphos^{tBu}



Method adapted from literature.⁶

To a solution of di-tertbutyl(hydroxymethyl)phosphonium chloride (0.486 g, 2.0 mmol, 3 equiv.) in methanol (10 mL) was added triethylamine (1.4 mL, excess). After stirring at RT for one hour, ammonia (2M solution in methanol, 0.34 mL, 0.67 mmol, 1 equiv.) was added. The mixture was heated to reflux overnight. After cooling to RT, a white solid precipitated. After reducing the solvent volume to approximately one-third in vacuo, the solid was isolated by cannula filtration and washed with methanol (3 x 1 mL). After drying in vacuo, the product was collected as a free-flowing white powder (0.110 g, 0.22 mmol, 66 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : 12.5 ppm (s). ^1H NMR (CDCl_3 , 400 MHz) δ : 2.90 (m, 6H, CH_2), 1.19 ppm (d, 54H, $J = 10.8$ Hz, CH_3).

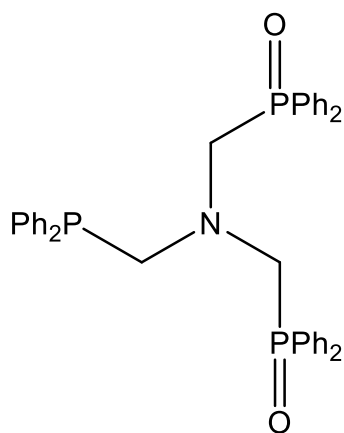
7.2.7 Attempted preparation of mixed N-Triphos ligand $N(\text{CH}_2\text{PCy}_2)(\text{CH}_2\text{PPh}_2)_2$



a) To a solution of dicyclohexyl(hydroxymethyl)phosphonium chloride (0.150 g, 0.56 mmol, 1 equiv.) in THF (20 mL) was added triethylamine (0.27 mL, excess). After stirring at RT for one hour, $H\text{-}N(\text{CH}_2\text{PPh}_2)_2$ (0.210 g, 0.51 mmol, 1 equiv.) was added and the mixture heated to reflux overnight. After cooling to RT, solvent was removed to dryness in vacuo, forming a white solid residue. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): ^{31}P NMR spectroscopy showed the presence of numerous signals across the spectrum, and several signals in the expected product regions. Signals observed at -19.3 (s, 1P, PCy_2) and -28.7 ppm (s, 2P, PPh_2) are tentatively assigned to $N(\text{CH}_2\text{PCy}_2)(\text{CH}_2\text{PPh}_2)_2$.

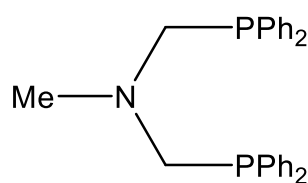
b) To a solution of dicyclohexyl(hydroxymethyl)phosphonium chloride (0.150 g, 0.56 mmol, 1 equiv.) in 1-butanol (10 mL) was added triethylamine (0.27 mL, excess). After stirring at RT for one hour, $H\text{-}N(\text{CH}_2\text{PPh}_2)_2$ (0.211 g, 0.51 mmol, 1 equiv.) was added and the mixture heated to reflux overnight. After cooling to RT, a white solid precipitated. The solid was isolated by cannula filtration and dried in vacuo (0.0447 g). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): ^{31}P NMR spectroscopy showed limited overall reaction progress. Signals observed at -18.6 (s, 1P, PCy_2) and -28.4 ppm (s, 2P, PPh_2) are tentatively assigned to $N(\text{PCy}_2)(\text{PPh}_2)_2$.

7.2.8 Attempted preparation of mixed N-Triphos ligand $N(\text{CH}_2\text{PPh}_2)(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$



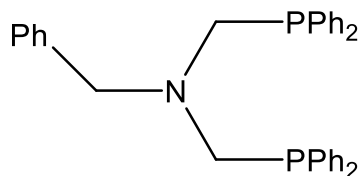
To a solution of diphenyl(hydroxymethyl)phosphonium chloride (0.115 g, 0.41 mmol, 1 equiv.) in methanol (10 mL) was added triethylamine (0.2 mL, excess). After stirring at RT for two hours, $H\text{-}N(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$ (0.180 g, 0.41 mmol, 1 equiv.) was added and the mixture heated to reflux overnight. Through ^{31}P NMR spectroscopy, no reaction progress towards the desired product was observed.

7.2.9 Preparation of Me-N(CH₂PPh₂)₂



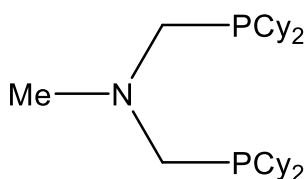
Ligand has been previously reported.^{7,8} To a solution of diphenyl(hydroxymethyl)phosphonium chloride (0.965 g, 3.4 mmol, 2 equiv.) in methanol (7 mL) and water (13 mL) was added triethylamine (1.4 mL, excess). After stirring at RT for 30 minutes, methylamine (33 wt.% solution in methanol, 0.21 mL, 1.7 mmol, 1 equiv.) was added and the mixture heated to reflux for two hours. After cooling to RT, dichloromethane (20 mL) was added. The organic layer was extracted and dried over MgSO₄. After solvent removal to dryness in vacuo, an oil remained. The product was dried in vacuo overnight and collected as a white oil (0.224 g, 0.52 mmol, 31 %). ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ: -27.4 ppm (s). ¹H NMR (CDCl₃, 400 MHz) δ: 7.5-7.2 (m, 20H, Ph), 3.49 (d, 4H, ²J_{P-H} = 2.9 Hz, N-CH₂-P), 2.66 (s, 3H, Me).

7.2.10 Preparation of Bn-N(CH₂PPh₂)₂



Ligand has been previously reported.⁹ To a solution of diphenyl(hydroxymethyl)phosphonium chloride (0.50 g, 1.8 mmol, 2 equiv.) in methanol (10 mL) and water (20 mL) was added triethylamine (0.37 mL, excess). After stirring at RT for 30 minutes, benzylamine (0.1 mL, 0.92 mmol, 1 equiv.) was added and the mixture heated to reflux for one hour. After cooling to RT, dichloromethane (2 x 20 mL) was added. The organic layer was extracted and dried over MgSO₄. With solvent removal to dryness and further drying in vacuo, the product was collected as a viscous yellow oil (0.33 g, 0.66 mmol, 74 %). ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ: -29.2 ppm (s).

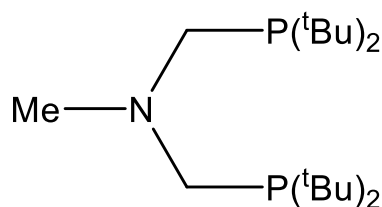
7.2.11 Preparation of Me-N(CH₂PCy₂)₂



Ligand has been previously reported.⁸ To a solution of dicyclohexyl(hydroxymethyl)phosphonium chloride (0.296 g, 1 mmol, 2 equiv.) in methanol (10 mL) was added triethylamine (0.4 mL, excess). After stirring at RT for one hour, methylamine (33 wt.% solution in methanol, 0.06 mL, 0.05 mmol, 1 equiv.) was added and the mixture heated to reflux overnight. After

cooling to RT, solvent was removed to almost completion. An oily residue remained. After cooling to -78 °C, additional methanol (10 mL) was added causing the precipitation of a white solid. The solid was isolated by cannula filtration and washed further with methanol (5 mL, 1 mL). After drying in vacuo overnight, the product was collected as a free-flowing white powder (0.0836 g, 0.19 mmol, 37 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : -16.6 ppm (s). ^1H NMR (CDCl_3 , 400 MHz) δ : 2.68 (s, 4H, CH_2), 2.40 (s, 3H, Me), 1.1-2.0 ppm (m, 44H, Cy).

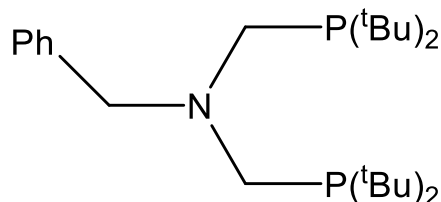
7.2.12 Preparation of $\text{Me-N}(\text{CH}_2\text{P}(\text{tBu})_2)_2$



To a solution of di-tertbutyl(hydroxymethyl)phosphonium chloride (0.90 g, 3.7 mmol, 2 equiv.) in methanol (15 mL) was added triethylamine (1.6 mL, excess). After stirring at RT for one hour, methylamine (33 wt.% solution in methanol, 0.23 mL, 1.85 mmol, 1 equiv.) was added and the mixture heated to reflux overnight. After

cooling to RT, the solvent level was reduced to approximately one-third in vacuo, causing the precipitation of a white oil/solid. The mixture was heated further overnight, and then cooled to RT and in ice. With further solvent reduction, a white solid precipitated. The solid was isolated by cannula filtration and washed with methanol (3 x 1 mL). After drying in vacuo overnight, the product was collected as a white crystalline solid (57 mg, 0.16 mmol, 9 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : 14.2 ppm (s). ^1H NMR (CDCl_3 , 400 MHz) δ : 2.67 (s, 4H, CH_2), 2.47 (s, 3H, CH_3), 1.18 ppm (d, 36H, $^2J_{\text{P-H}} = 10.9$ Hz, tBu). ES-MS (positive ion): No product signal observed.

7.2.13 Preparation of $\text{Bn-N}(\text{CH}_2\text{P}(\text{tBu})_2)_2$

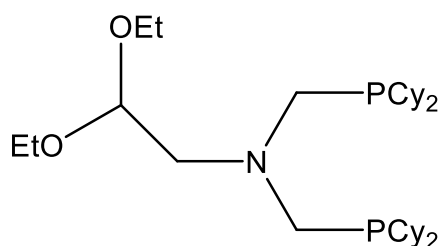


Ligand has been previously reported.¹⁰ To a solution of di-tertbutyl(hydroxymethyl)phosphonium chloride (100 mg, 0.41 mmol, 2 equiv.) in methanol (1 mL) and water (2 mL) was added triethylamine (0.06 mL, 0.41 mmol). After the addition of benzylamine (22 μL , 0.21 mmol, 1 equiv.) in toluene (3 mL)

the mixture was heated to reflux overnight. The organic layer was extracted and dried over MgSO_4 . Further methanol (7 mL) was added. After solvent removal in vacuo, a white oil formed. This was

washed with methanol (3 x 1 mL) and after drying in vacuo a white solid product was collected in trace yield. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : 13.0 ppm (s), 35.1 ppm (s, $(^t\text{Bu})_2\text{P}(\text{CH}_2\text{OH})_2\text{Cl}$).

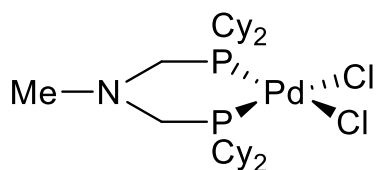
7.2.14 Preparation of $\text{CH}(\text{OEt})_2\text{CH}_2\text{-N}(\text{CH}_2\text{PCy}_2)_2$



To a solution of dicyclohexyl(hydroxymethyl)phosphonium chloride (0.50 g, 1.7 mmol, 2 equiv.) in methanol (7 mL) was added excess triethylamine (0.7 mL, 4.9 mmol). The resulting mixture was stirred at RT for one hour. After addition of 2,2-diethoxyethylamine (0.13 mL, 0.85 mmol, 1 equiv.), the mixture was heated to reflux for two hours. After cooling to RT, solvent was removed to dryness in vacuo. The resulting oil was cooled in acetone/liquid N_2 and the resultant white solid was washed with methanol (3 x 1 mL). The product remained as a white oil at RT and was not collected or analysed prior to further reaction owing to its air sensitivity. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : -17.3 ppm (s).

7.3 Experimental details for Chapter 3

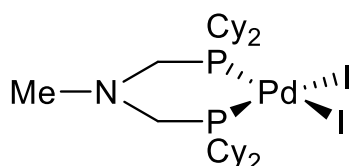
7.3.1 Preparation of $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{PdCl}_2]$ (**1**)



To a solution of $[\text{PdCl}_2(\text{COD})]$ (0.111 g, 0.38 mmol, 1 equiv.) in dichloromethane (8 mL) was added $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ (0.176 g, 0.38 mmol, 1 equiv.). After stirring at RT for one hour, diethyl ether was added (20 mL). The resulting beige-coloured precipitate was isolated by cannula filtration and washed with diethyl ether (3 x 1 mL). After drying in vacuo overnight, the product was collected as a free-flowing beige-coloured powder (0.224 g, 0.36 mmol, 94 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : 30.1 ppm (s). ^1H NMR (CDCl_3 , 400 MHz) δ : 2.62 (m, 4H, $^2J_{\text{P-H}} = 2.4$ Hz, P- $\text{CH}_2\text{-N}$), 1.2-2.5 ppm (m, 47H, Cy + N-Me). ^{13}C NMR (CDCl_3 , 101 MHz) δ : 50.2 (d, P- $\text{CH}_2\text{-N}$, $^1J_{\text{PC}} = 41.1$ Hz), 37.0 (d, Cy (P-C), $^1J_{\text{PC}} = 29.1$ Hz), 30.4 (s, Cy), 29.3 (s, Cy), 27.1 (m, N-Me), 26.0 ppm (s, Cy). ES-MS (positive ion): m/z calculated for $[\text{C}_{29}\text{H}_{57}\text{NOP}_2\text{SCl}^{105}\text{Pd}]$ ($[\text{M-Cl}+\text{DMSO}]^+$) = 669.2375, found m/z = 669.2357. Anal. Calcd.

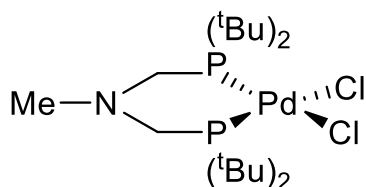
for $C_{28}H_{53}Cl_4NP_2Pd$ (inc. 1 DCM): C, 47.11; H, 7.48; N, 1.96. Found: C, 47.32; H, 6.73; N 2.09. IR (solid, cm^{-1}): 2919 (w, ν_{C-H}), 2848 (w, ν_{C-H}), 2788 (w, ν_{C-H}), 1439 (w, $\nu_{P-C \text{ asymm.}}$), 857 (w), 727 (m).

7.3.2 Preparation of $[Me-N(CH_2PCy_2)_2PdI_2]$ (**2**)



$(TBA)_2[Pd_2I_6]$ (73.1 mg, 0.05 mmol) was dissolved in acetone (5 mL) and stirred at room temperature for 10 minutes. An acetone solution (7 mL) of $Me-N(CH_2PCy_2)_2$ (45.5 mg, 0.10 mmol) was added dropwise to the black reaction mixture. The reaction mixture slowly turned to an orange-brown solution and was stirred for a further two hours. The desired orange precipitate was filtered and washed with diethyl ether (3 x 1 mL). After drying overnight in vacuo, the product was collected as a free-flowing orange powder (51.8 mg, 0.064 mmol, 64 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ : 24.5 ppm (s). ^1H NMR ($CDCl_3$, 400 MHz) δ : 2.69 (d, 4H, $^2J_{P-H} = 2.7$ Hz, P-CH₂-N), 2.50 (s, 3H, Me), 0.8-2.5 ppm (m, 44H, Cy). ^{13}C NMR ($CDCl_3$, 101 MHz) δ : 40.39 (d, $1J_{P-C} = 27.6$ Hz, P-CH₂-N), 31.0 (s, Me), 29.7 (s, Cy), 29.8 (s, Cy), 27.1 (m, Cy), 25.9 (s, Cy). ES-MS (positive ion): m/z calculated for $[C_{29}H_{54}IN_2P_2Pd]$ ($[M-Cl+CH_3CN]^+$) = 725.1842, found $m/z = 725.1862$. IR (solid, cm^{-1}): 2919 (w, ν_{C-H}), 2848 (w, ν_{C-H}), 2773 (w), 1439 (w, $\nu_{P-C \text{ asymm.}}$), 1267 (w), 1170 (w), 1096 (w), 1003 (w), 830 (w), 760 (w).

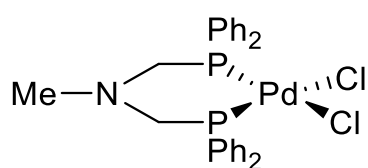
7.3.3 Preparation of $[Me-N(CH_2P(tBu)_2)_2PdCl_2]$ (**3**)



To a solution of $[PdCl_2(COD)]$ (0.050 g, 0.18 mmol, 1 equiv.) in dichloromethane (5 mL) was added $Me-N(CH_2P(tBu)_2)_2$. The resulting orange mixture was stirred at RT overnight. After addition of diethyl ether (10 mL), a yellow solid precipitated. The solid was isolated by cannula filtration and washed with diethyl ether. After drying in vacuo, the product was collected as a pale-yellow powder (41 mg, 0.078 mmol, 43 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ : 37.8 ppm (s). ^1H NMR ($CDCl_3$, 400 MHz) δ : 2.81 (d, 4H, $^2J_{P-H} = 3.1$ Hz, CH₂), 2.51 (s, 3H, Me), 1.57 ppm (d, 36H, $^3J_{P-H} = 13.9$ Hz, tBu). ^{13}C NMR ($CDCl_3$, 101 MHz) δ : 31.2 ppm (s, tBu). [Other signals not detected]. ES-MS (positive ion): m/z calculated for $[C_{19}H_{43}NP_2Cl^{108}Pd]$ ($[M-$

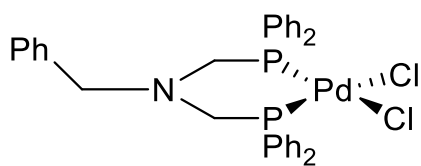
$\text{Cl}]^+ = 490.1598$, found $m/z = 490.1597$. Anal. Calcd. for $\text{C}_{20}\text{H}_{45}\text{Cl}_4\text{NP}_2\text{Pd}$ (inc. 1 DCM): C, 39.40; H, 7.44; N, 2.30. Found: C, 39.53; H, 7.79; N 2.85. IR (solid, cm^{-1}): 2948 (w, br, $\nu_{\text{C-H}}$), 2892 (w, br, $\nu_{\text{C-H}}$), 2788 (w, br, $\nu_{\text{C-H}}$), 1461 (w, $\nu_{\text{P-C asymm.}}$), 1394 (w), 1170 (w), 1018 (w), 809 (w).

7.3.4 Preparation of $[\text{Me-N}(\text{CH}_2\text{PPh}_2)_2\text{PdCl}_2]$ (**4**)



4 has been previously reported.^{7,11} A mixture of $\text{Me-N}(\text{CH}_2\text{PPh}_2)_2$ (1.06 g, 2.48 mmol, 1 equiv.) and $[\text{PdCl}_2(\text{COD})]$ (0.53 g, 1.86 mmol, 1 equiv.) in dichloromethane (6 mL) was stirred for one hour at RT. After reducing the solvent level in vacuo, the addition of diethyl ether (55 mL) caused the precipitation of an orange solid. The solid was isolated by cannula filtration and washed with diethyl ether. After drying in vacuo, the product was collected as an orange powder (0.991 g, 1.64 mmol, 88 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : 8.0 ppm (s). ^1H NMR (CDCl_3 , 400 MHz) δ : 7.90-7.40 (m, 2H, Ph), 3.25 (s, 4H, P- CH_2 -N), 2.56 ppm (s, 3H, N-Me). ^{13}C NMR (CDCl_3 , 101 MHz) δ : 128.7-133.9 (m, Ph), 57.9 ppm (d, $^1J_{\text{CP}} = 45.3$ Hz, P- CH_2 -N). ES-MS (positive ion): m/z calculated for $[\text{C}_{29}\text{H}_{30}\text{N}_2\text{Cl}^{106}\text{PdP}_2]$ ($[\text{M-Cl}+\text{CH}_3\text{CN}]^+$) = 609.0608, found $m/z = 609.0635$.

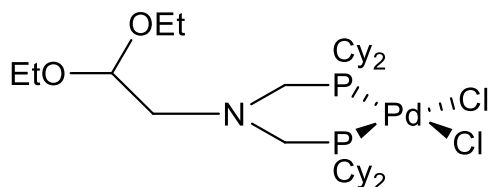
7.3.5 Preparation of $[\text{Bn-N}(\text{CH}_2\text{PPh}_2)_2\text{PdCl}_2]$ (**5**)



A mixture of $\text{Bn-N}(\text{CH}_2\text{PPh}_2)_2$ (0.405 g, 0.81 mmol, 1 equiv.) and $[\text{PdCl}_2(\text{COD})]$ (0.15 g, 0.52 mmol, 1 equiv.) in dichloromethane (15 mL) was stirred for one hour at RT. After reducing the solvent level in vacuo, the addition of diethyl ether (15 mL) caused the precipitation of an off-white solid. The solid was isolated by cannula filtration and washed with diethyl ether. After drying in vacuo, the product was collected as an off-white powder (0.266 g, 0.39 mmol, 75 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : 8.5 ppm (s). ^1H NMR (CDCl_3 , 400 MHz) δ : 7.80-6.97 (m, 25H, Ph), 3.68 (s, 2H, Ph- CH_2 -N), 3.40 ppm (s, 4H, P- CH_2 -N). ^{13}C NMR (CDCl_3 , 101 MHz) δ : 128.2-134.0 (m, Ph), 66.9 (s, N- CH_2 -Ph), 56.2 ppm (d, $^1J_{\text{CP}} = 48.2$ Hz, N- CH_2 -P). ES-MS (positive ion): m/z calculated for $[\text{C}_{35}\text{H}_{34}\text{N}_2\text{P}_2\text{Cl}^{106}\text{Pd}]$ ($[\text{M-Cl}+\text{CH}_3\text{CN}]^+$) = 685.0921,

found m/z = 685.0911. Anal. Calcd. for $C_{33}H_{31}Cl_2NP_2Pd$: C, 58.21; H, 4.59; N, 2.06. Found: C, 57.82; H, 4.39; N 2.07. IR (solid, cm^{-1}): 1435 (w, ν_{P-C} asym.), 1103 (w), 738 (w), 690 (w).

7.3.6 Preparation of $[CH(OEt)_2CH_2-N(CH_2PCy_2)_2PdCl_2]$ (6)

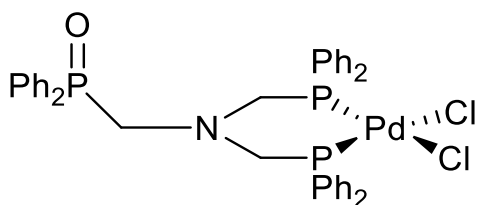


To a solution of $C(OEt)_2HCH_2-N(CH_2PCy_2)_2$ (unweighed) in dichloromethane (8 mL) was added $[PdCl_2(COD)]$ (0.243 g, 0.85 mmol). After stirring at RT for two hours, diethyl ether (40 mL) was added, resulting in the precipitation of a pale-yellow solid. After isolation by cannula filtration

and washing with diethyl ether (3 x 1 mL), the product was dried in vacuo overnight and collected as a free-flowing pale-yellow powder (0.357 g, 0.49 mmol, 57 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ : 28.4 ppm (s). ^1H NMR ($CDCl_3$, 400 MHz) δ : 6.31 (br s, 4H, $O-CH_2-CH_3$), 4.62 (m, 1H, $O-CH-CH_2$), 2.79 (d, 2H, $HC-CH_2-N$), 2.63 (m, 4H, $N-CH_2-P$), 1.2-2.5 ppm (m, Cy + CH_3). ^{13}C NMR ($CDCl_3$, 101 MHz) δ : 117.0 (s, $CH(O)_2$), 101.0 (s, CH_2O), 62.3 (s, $N-CH_2-CH$), 46.0 (s, $N-CH_2-P$), 25.9-31.1 (m, Cy), 15.4 ppm (s, CH_3). ES-MS (positive ion): m/z calculated for $[C_{34}H_{64}N_2O_2P_2Cl^{106}Pd]$ ($[M-Cl+CH_3CN]^+$) = 735.3166, found m/z = 735.3181. IR (solid, cm^{-1}): 2851 (w, ν_{C-H}), 2922 (w, ν_{C-H}), 1446 (w, ν_{P-C} asym.), 1059 (w).

Additional single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into an acetonitrile solution. The identity of the crystal was determined as $[C_{27}H_{53}N_2O_4P](PdCl_4)$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ : 11.2 ppm (s). ^1H NMR ($CDCl_3$, 400 MHz) δ : 4.20 (m, 2H, $H_2C-CH-O$), 3.52 (s, 2H, $N-CH_2-N$), 3.1-3.3 (m, 4H, $N-CH_2-CH$), 2.81 (m, 8H, $O-CH_2-CH_3$), 2.4-2.6 (m, 4H, $N-CH_2-P$), 1.04 (t, 12H, CH_3), 0.8-1.7 ppm (m, 22H, Cy). ES-MS (positive ion): m/z calculated for $[C_{27}H_{54}N_2O_4P]$ ($[M]^+$) = 501.3821, found m/z = 501.3824.

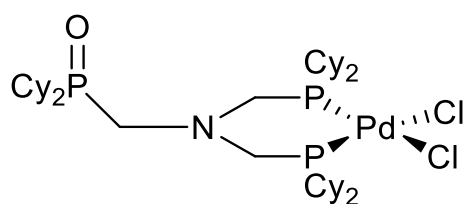
7.3.7 Preparation of $[P(O)Ph_2CH_2-N(CH_2PPh_2)_2PdCl_2]$ (7)



A solution of N-Triphos^{Ph} (0.30 g, 0.49 mmol, 1 equiv.) in dichloromethane (5 mL) was added to a solution of $[PdCl_2(COD)]$ (0.140 g, 0.49 mmol, 1 equiv.) in dichloromethane (8 mL). The pale-yellow reaction mixture was stirred at RT for 20 minutes. After addition

of hydrogen peroxide (30 wt.% solution in water, 0.05 mL, 0.49 mmol, 1 equiv.), the mixture was stirred for a further 10 minutes. With the addition of diethyl ether (25 mL), a pale-yellow solid precipitated. The solid was isolated by cannula filtration and washed with diethyl ether (3 x 2 mL). After drying in vacuo overnight, the product was collected as free-flowing pale-yellow powder (0.231 g, 0.29 mmol, 59 %). Single crystals suitable for X-ray diffraction formed directly from the filtrate of the reaction mixture (dichloromethane/diethyl ether). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : 27.0 (1P, s, $\text{P}(\text{O})\text{Ph}_2$), 8.90 ppm (2P, s, P-Pd). ^1H NMR (CDCl_3 , 162 MHz) δ : 7.2-7.9 (m, 30H, Ph), 3.72 (d, 4H, $^2J_{\text{P-H}} = 2.1$ Hz, NCH_2P), 3.41 ppm (d, 2H, $^2J_{\text{P-H}} = 5.4$ Hz, $\text{NCH}_2\text{P}(\text{O})$). ^{13}C NMR (CDCl_3 , 101 MHz) δ : 127.5-134.1 (m, Ph), 57.7 (d, $^1J_{\text{CP}} = 7.4$ Hz, CH_2), 57.2 (d, $^1J_{\text{CP}} = 6.9$ Hz, CH_2). ES-MS (positive ion): m/z calculated for $[\text{C}_{41}\text{H}_{39}\text{N}_2\text{OP}_3\text{Cl}^{106}\text{Pd}]$ ($[\text{M-Cl}+\text{CH}_3\text{CN}]^+$) = 809.0975, found m/z = 809.1007. Anal. Calcd. for $\text{C}_{44}\text{H}_{48}\text{Cl}_4\text{NO}_2\text{P}_3\text{Pd}$ (inc. 1 DCM + 1 DEE): C, 54.82; H, 5.02; N, 1.45. Found: C, 54.42; H, 4.74; N 1.75. IR (solid, cm^{-1}): 1435 (w, $\nu_{\text{P-C asymm.}}$), 1100 (w, $\nu_{\text{P=O}}$), 738 (w), 690 (w).

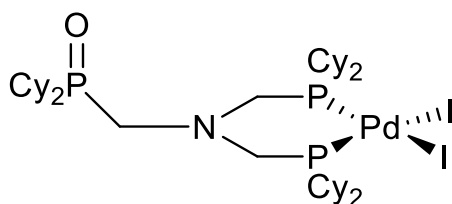
7.3.8 Preparation of $[\text{P}(\text{O})\text{Cy}_2\text{CH}_2\text{-N}(\text{CH}_2\text{PCy}_2)_2\text{PdCl}_2]$ (**8**)



A solution of N-Triphos^{Cy} (0.632 g, 0.98 mmol, 1 equiv.) in dichloromethane (7 mL) was added to a solution of $[\text{PdCl}_2(\text{COD})]$ (0.278 g, 0.97 mmol, 1 equiv.) in dichloromethane (15 mL). The resulting pale-yellow mixture was stirred at RT for 30 minutes. After addition of

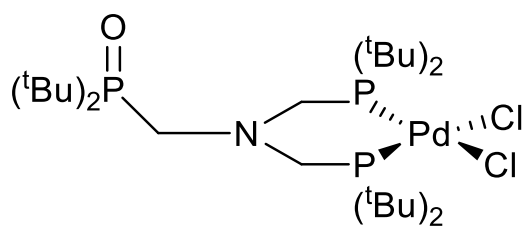
hydrogen peroxide (30 wt.% solution in water, 0.05 mL, 1 equiv.), the mixture was stirred for a further 10 minutes. After addition of diethyl ether (30 mL), a pale-yellow solid precipitated. The solid was isolated by cannula filtration and washed with diethyl ether (3 x 2 mL). After drying in vacuo overnight, the product was collected as a free-flowing pale-yellow powder (0.484 g, 0.58 mmol, 60 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : 46.7 (1P, s, $\text{P}(\text{O})\text{Ph}_2$), 29.1 ppm (2P, s, P-Pd). ^1H NMR (CDCl_3 , 162 MHz) δ : 2.94 (br s, 4H, CH_2P), 2.83 (br s, 2H, $\text{CH}_2\text{P}(\text{O})$), 0.9-3.5 ppm (m, Cy). ^{13}C NMR (CDCl_3 , 101 MHz) δ : 65.9 (s, $\text{N-CH}_2\text{-P}(\text{O})$), 36.9 (d, $^1J_{\text{CP}} = 28.7$ Hz, $\text{N-CH}_2\text{-PCy}_2$), 36.0 (s, Cy (CH)), 30.0 (s, Cy), 29.6 (s, Cy), 27.0 (m, Cy), 26.6 (m, Cy), 26.1 (s, Cy), 25.9 ppm (s, Cy). ES-MS (positive ion): m/z calculated for $[\text{C}_{41}\text{H}_{75}\text{N}_2\text{OP}_3\text{Cl}^{106}\text{Pd}]$ ($[\text{M-Cl}+\text{CH}_3\text{CN}]^+$) = 845.3816, found m/z = 845.3830. Anal. Calcd. for $\text{C}_{39}\text{H}_{72}\text{Cl}_2\text{NOP}_3\text{Pd}$: C, 55.68; H, 8.63; N, 1.67. Found: C, 55.73; H, 8.58; N 1.69. IR (solid, cm^{-1}): 2919 (m, $\nu_{\text{C-H}}$), 2848 (m, $\nu_{\text{C-H}}$), 1737 (w), 1443 (w, $\nu_{\text{P-C asymm.}}$), 1148 (w, $\nu_{\text{P=O}}$), 1006 (w), 850 (w).

7.3.9 Preparation of [P(O)Cy₂CH₂-N(CH₂PCy₂)₂PdI₂] (**9**)



(TBA)₂[Pd₂I₆] (58 mg, 0.04 mmol, 1 equiv.) was dissolved in acetone (5 mL) and stirred at room temperature for 10 minutes. An acetone solution (9 mL) of N-Triphos^{Cy} (52 mg, 0.08 mmol, 2 equiv.) was added dropwise to the black reaction mixture. The reaction mixture slowly turned to an orange-brown solution and was stirred for a further two hours. After addition of hydrogen peroxide (30 wt.% solution in water, 0.01 mL), solvent was removed to completion in vacuo. The resulting orange-precipitate was washed with diethyl ether (3 x 1 mL) and dried in vacuo. The product was recrystallized from dichloromethane/diethyl ether and dried further in vacuo. Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution, however the collected data could not be resolved. ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ: 46.6 (s, 1P, P(O)Cy₂), 23.1 ppm (s, 2P, P-Pd). ES-MS (positive ion): m/z calculated for [C₃₉H₇₃NOP₃¹⁰⁶PdI₂] ([M+H]⁺) = 1024.2029, found m/z = 1024.2061. m/z calculated for [C₄₁H₇₅N₂ONaP₃¹⁰⁶PdI₂] ([M+Na+CH₃CN]⁺) = 1087.2114, found m/z = 1087.2144. IR (solid, cm⁻¹): 2922 (m, ν_{C-H}), 2851 (m, ν_{C-H}), 1670 (w), 1446 (m, ν_{P-C asym.}), 1264 (w), 1152 (w, ν_{P=O}), 1115 (w), 891 (w), 854 (w), 801 (w), 738 (w).

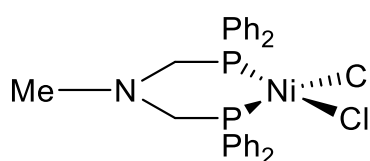
7.3.10 Preparation of [P(O)(^tBu)₂CH₂-N(CH₂P(^tBu)₂)₂PdCl₂] (**10**)



A solution of N-Triphos^{tBu} (0.107 g, 0.22 mmol, 1 equiv.) in dichloromethane (5 mL) was added to a solution of [PdCl₂(COD)] (0.062 g, 0.22 mmol, 1 equiv.) in dichloromethane (5 mL). The dark-orange reaction mixture was stirred at RT for one hour. After addition of hydrogen peroxide (30 wt.% solution in water, 0.03 mL, 0.22 mmol, 1 equiv.), the mixture was stirred for a further 10 minutes. After the addition of diethyl ether (40 mL), a solid was observed to precipitate. After cannula filtration, only a trace amount of solid was collected. After removal of solvent in vacuo, a gummy yellow solid precipitated. After drying in vacuo overnight, the solid was washed with diethyl ether (3 x 3 mL) and dried further in vacuo. The product was collected as a pale-yellow powder (32 mg, 0.047 mmol, 21 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution. ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ: 58.8 (1P, s, P(O)Ph₂), 36.1 ppm (2P, s, P-Pd). ES-MS (positive ion): m/z calculated for

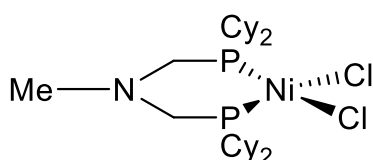
$[\text{C}_{27}\text{H}_{60}\text{NOP}_3\text{Cl}^{106}\text{Pd}] ([\text{M}-\text{Cl}]^+) = 648.2611$, found $m/z = 648.2626$. Anal. Calcd. for $\text{C}_{27}\text{H}_{64}\text{Cl}_2\text{NO}_3\text{P}_3\text{Pd}$ (inc. $2\text{H}_2\text{O}$): C, 44.98; H, 8.95; N, 1.94. Found: C, 44.82; H, 8.94; N 2.49. IR (solid, cm^{-1}): 2948 (w, br, $\nu_{\text{C-H}}$), 2900 (w, br, $\nu_{\text{C-H}}$), 1673 (w, $\nu_{\text{P=O}}$), 1469 (w, $\nu_{\text{P-C asymm.}}$), 1394 (w), 1174 (w, $\nu_{\text{P=O}}$), 1021 (w), 809 (w).

7.3.11 Preparation of $[\text{Me-N}(\text{CH}_2\text{PPh}_2)_2\text{NiCl}_2]$ (**11**)



11 has been previously reported.^{11–14} A solution of $\text{Me-N}(\text{CH}_2\text{PPh}_2)_2$ (0.224 g, 0.52 mmol, 1 equiv.) in dichloromethane (5 mL) was added to a solution of $[\text{NiCl}_2(\text{PPh}_3)_2]$ (0.342 g, 0.52 mmol, 1 equiv.) in dichloromethane (15 mL). The resulting deep-red mixture was stirred at RT overnight. After addition of diethyl ether (32 mL), a red-orange solid precipitated. The solid was isolated by cannula filtration and washed with diethyl ether (3 x 1 mL). After drying in vacuo, the product was collected as an orange-red powder (0.155 g, 0.28 mmol, 54 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): No signals observed; attributed to paramagnetism. ^1H NMR (CDCl_3 , 162 MHz) δ : 7.3–7.9 (m, 20H, Ph), 2.45 (s, 3H, Me), 1.2–1.6 ppm (m, 4H, N- CH_2 -P). ^{13}C NMR (CDCl_3 , 101 MHz) δ : 131.8 (s, Ph), 128.7 (s, Ph), 50.4 ppm (s, N- CH_2 -P). [No other signals detected]. ES-MS (positive ion): m/z calculated for $[\text{C}_{29}\text{H}_{31}\text{N}_2\text{P}_2\text{Cl}^{58}\text{Ni}] ([\text{M}-\text{Cl}+\text{CH}_3\text{CN}+\text{H}]^+) = 562.1005$, found $m/z = 562.1017$. Anal. Calcd. for $\text{C}_{54}\text{H}_{60}\text{Cl}_4\text{N}_2\text{Ni}_2\text{O}_3\text{P}_4$ (inc. $1.5\text{xH}_2\text{O}$): C, 55.52; H, 5.18; N, 2.40. Found: C, 55.39; H, 5.25; N 2.39. IR (solid, cm^{-1}): 1625 (w), 1480 (w), 1435 (w, $\nu_{\text{P-C asymm.}}$), 1096 (m), 880 (w), 846 (w), 738 (m), 690 (m).

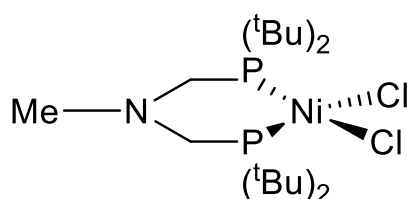
7.3.12 Preparation of $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{NiCl}_2]$ (**12**)



12 has been previously reported.^{11–14} To a solution of $[\text{NiCl}_2(\text{PPh}_3)_2]$ (0.145 g, 0.22 mmol, 1 equiv.) in dichloromethane (15 mL) was added $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ (0.10 g, 0.22 mmol, 1 equiv.). The resulting red-coloured mixture was stirred at RT overnight. After addition of diethyl ether (26 mL), an orange solid precipitated. The solid was isolated by cannula filtration and washed with diethyl ether (3 x 1 mL). After drying in vacuo, the product was collected as an orange powder (0.0752 g, 0.12 mmol, 58 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : 17.4 ppm (br s). ^1H NMR (CDCl_3 , 400 MHz) δ : 2.87 (d, 4H, $J = 12.3$ Hz, N- CH_2 -P), 1.2–2.1 ppm (m, 47H,

Cy + Me). ^{13}C NMR (CDCl_3 , 101 MHz) δ : 30.7 (s, Cy), 29.2 (s), 27.2 (d, $J = 27.2$ Hz, Cy), 26.1 (s, Cy). [No other signals detected]. ES-MS (positive ion): m/z calculated for $[\text{C}_{29}\text{H}_{54}\text{N}_2\text{P}_2\text{Cl}^{58}\text{Ni}]$ ($[\text{M}-\text{Cl}+\text{CH}_3\text{CN}]^+$) = 585.2804, found $m/z = 585.2811$. Anal. Calcd. for $\text{C}_{27}\text{H}_{51}\text{Cl}_2\text{NNiP}_2$: C, 55.79; H, 8.84; N, 2.41. Found: C, 55.99; H, 9.15; N 2.29. IR (solid, cm^{-1}): 2919 (m, $\nu_{\text{C-H}}$), 2848 (m, $\nu_{\text{C-H}}$), 2784 (w, $\nu_{\text{C-H}}$), 1737 (w), 1443 (m, $\nu_{\text{P-C asymm.}}$), 1230 (w), 1003 (w).

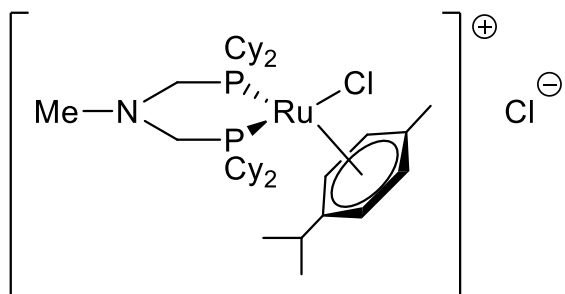
7.3.13 Attempted preparation of $[\text{Me}-\text{N}(\text{CH}_2\text{P}(\text{tBu})_2)_2\text{NiCl}_2]$



To a solution of $[\text{NiCl}_2(\text{PPh}_3)_2]$ (0.145 g, 0.22 mmol, 1 equiv.) in dichloromethane (15 mL) was added $\text{Me}-\text{N}(\text{CH}_2\text{P}(\text{tBu})_2)_2$ (0.0694 g, 0.20 mmol, 1 equiv.). The resulting dark-blue mixture was stirred at RT overnight. After addition of diethyl ether (36 mL), a pale-blue solid precipitated. After cannula filtration, a

trace amount of solid was collected. Solvent was removed from the filtrate in vacuo, forming a dark blue solid. After washing with diethyl ether, the solid was dried in vacuo and collected as a blue powder (0.0398 g). Attempts to grow single crystals for X-ray diffraction by vapour diffusion of diethyl ether or hexane into dichloromethane solutions were unsuccessful. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : 36.7 ppm (s) [-5.3 ppm (s, PPh_3)]. ^1H NMR (CDCl_3 , 162 MHz): Signals are intractable. ES-MS (positive ion): No product signal observed.

7.3.14 Preparation of $[\text{Me}-\text{N}(\text{CH}_2\text{PCy}_2)_2\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}]\text{Cl}$ (**13**)

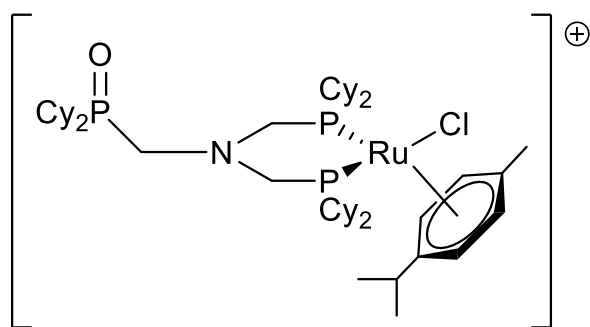


To a solution of $[\text{RuCl}_2(p\text{-cymene})]_2$ (0.100 g, 0.16 mmol, 1 equiv.) in methanol (15 mL) was added $\text{Me}-\text{N}(\text{CH}_2\text{PCy}_2)_2$ (0.148 g, 0.33 mmol, 2 equiv.). The reaction mixture was heated to 50 °C and stirred overnight. After cooling to RT, solvent was removed in vacuo, forming an orange-yellow solid

residue. After addition of diethyl ether (6 mL) and cannula filtration, the solid was further washed with diethyl ether (2 x 6 mL). After drying in vacuo, the product was collected as a yellow powder (0.142 g, 0.19 mmol, 57 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : 27.6 ppm (s). ^1H NMR

(CDCl₃, 400 MHz) δ : 6.91 (br s, 2H, ring CH), 5.85 (d, 2H, J = 5.2 Hz, ring CH), 2.8-3.1 (m, 4H, N-CH₂-P), 2.59-2.66 (m, 1H, J = 7.0 Hz, ⁱPr CH), 2.35 (s, 3H, N-Me), 2.10 (s, 3H, *p*-cymene CH₃), 1.30 (d, 6H, J = 7.0 Hz, ⁱPr CH₃), 0.9-2.0 ppm (m, Cy). ¹³C NMR (CDCl₃, 101 MHz) δ : 30.7 (s), 30.2 (s), 29.9 (s), 29.4 (s), 27.4 (m), 26.2 (s), 26.1 (s), 21.5 ppm (s). ES-MS (positive ion): m/z calculated for [C₃₇H₆₅NP₂Cl¹⁰²Ru] ([M]⁺) = 722.3324, found m/z = 722.3342. Anal. Calcd. for C₃₇H₆₉Cl₂NO₂P₂Ru (inc. 2H₂O): C, 55.98; H, 8.76; N, 1.76. Found: C, 55.70; H, 9.12; N 1.95. IR (solid, cm⁻¹): 3373 (w, br), 2922 (w, ν_{C-H}), 2848 (w, ν_{C-H}), 1443 (w, $\nu_{P-C \text{ asym.}}$), 1170 (w), 1003 (w), 876 (w).

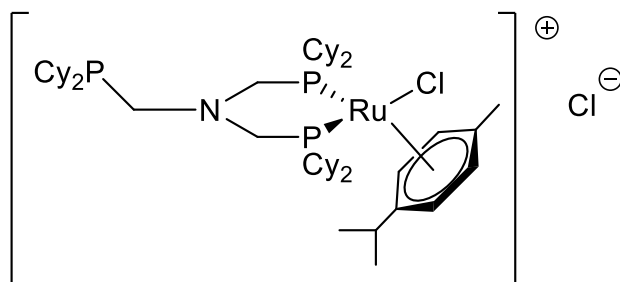
7.3.15 Preparation of [P(O)Cy₂CH₂-N(CH₂PCy₂)₂Ru(η^6 -*p*-cymene)Cl]Cl (**14**)



To a solution of [RuCl₂(*p*-cymene)]₂ (0.061 g, 0.10 mmol, 1 equiv.) in methanol (10 mL) was added N-Triphos^{Cy} (0.130 g, 0.20 mmol, 2 equiv.). The mixture was heated to 50 °C for 90 minutes. After addition of hydrogen peroxide (30 wt.% solution in water, 0.03 mL), the mixture was stirred for a further

hour. After cooling to RT, solvent was removed to dryness in vacuo resulting in an orange-yellow oily residue. After addition of diethyl ether (2 mL), a solid precipitated and this was washed with diethyl ether (2 x 2 mL). After drying in vacuo, the product was collected as an orange-brown powder (0.137 g, 0.14 mmol, 71 %). Attempts to grow single crystals for X-ray diffraction by vapour diffusion of diethyl ether into dichloromethane solutions were unsuccessful. ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ : 40.4 (s, 1P, P(O)Cy₂), 26.6 ppm (s, 2P, P-Ru). ¹H NMR (CDCl₃, 162 MHz) δ : 5.5-7.1 (m, 4H, ring CH), 3.1-3.5 (m, 6H, N-CH₂-P), 2.65 (m, 1H, ⁱPr CH), 2.09 (s, 3H, Me), 0.9-2.5 ppm (m, Cy + ⁱPr CH₃). ES-MS (positive ion): m/z calculated for [C₄₉H₈₆NOP₃Cl¹⁰²Ru] ([M]⁺) = 934.4654, found m/z = 934.4679. IR (solid, cm⁻¹): 2919 (w, ν_{C-H}), 2848 (w, ν_{C-H}), 1446 (w, $\nu_{P-C \text{ asym.}}$), 1003 (w), 850 (w).

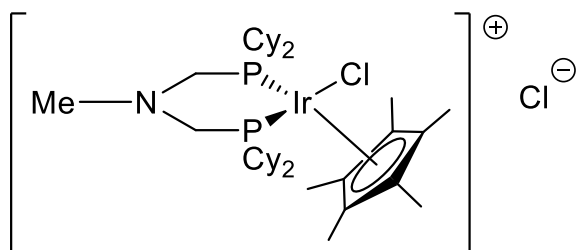
7.3.16 Preparation of [PCy₂CH₂-N(CH₂PCy₂)₂Ru(η⁶-*p*-cymene)Cl]Cl (**15**)



To a solution of [RuCl₂(*p*-cymene)]₂ (0.059 g, 0.10 mmol, 1 equiv.) in methanol (10 mL) was added N-Triphos^{Cy} (0.124 g, 0.19 mmol, 2 equiv.). After heating the mixture at 50 °C for 90 minutes, the mixture was cooled to RT. Solvent was removed to dryness in vacuo, resulting in the formation of an orange-

yellow residue. With the addition of diethyl ether (5 mL), a solid precipitated. The solid was washed with diethyl ether (2 x 2 mL) and dried in vacuo overnight. The product was collected as a free-flowing orange powder (0.12 g, 0.12 mmol, 62 %). The product was recrystallized from dichloromethane/diethyl ether, filtered and dried further in vacuo. Attempts to grow single crystals for X-ray diffraction by vapour diffusion of diethyl ether into dichloromethane solutions were unsuccessful. ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ: 26.5 ppm (s). ¹H NMR (CDCl₃, 162 MHz) δ: 6.35 (m, 2H, ring CH), 5.70 (m, 2H, ring CH), 3.13 (m, 6H, N-CH₂-P), 2.67 (m, 1H, ⁱPr CH), 2.63 (s, 3H, Me), 0.88 (br d, 6H, ⁱPr CH₃), 0.5-2.2 ppm (m, Cy). ES-MS (positive ion): m/z calculated for [C₄₉H₈₆ClNP₃¹⁰²Ru] ([M]⁺) = 918.4660, found m/z = 918.4720. IR (solid, cm⁻¹): 2917 (w, ν_{C-H}), 2847 (w, ν_{C-H}), 1443 (w, ν_{P-C} asym.), 1003 (w), 850 (w).

7.3.17 Preparation of [Me-N(CH₂PCy₂)₂Ir(Cp*)Cl]Cl (**16**)

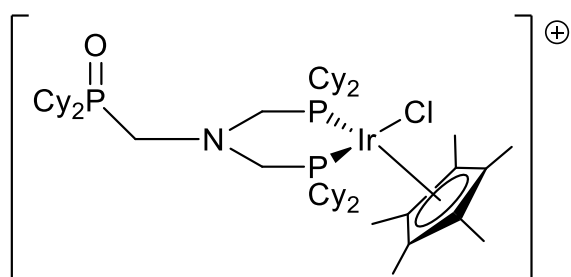


To a solution of [Cp*IrCl₂]₂ (0.05 g, 0.063 mmol, 1 equiv.) in methanol (18 mL) was added Me-N(CH₂PCy₂)₂ (0.057 g, 0.126 mmol, 2 equiv.). The resulting yellow mixture was heated at 50 °C overnight. After full solvent removal in vacuo, a yellow oil residue was formed. With the addition

of diethyl ether (2 mL), a yellow solid precipitated. The solid was isolated by cannula filtration and washed with further diethyl ether (2 x 2 mL). After drying in vacuo, the product was collected as a free-flowing yellow powder (48 mg, 0.056 mmol, 45 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution; however the identity of the crystal was determined as triethylammonium chloride. ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ: -3.7

ppm (s). [-16.8 ppm (s, Me-N(CH₂PCy₂)₂)]. ¹H NMR (CDCl₃, 400 MHz) δ: 3.15 (s, 3H, N-CH₃), 1.87 (s, 15H, Cp* CH₃), 1.2-3.0 ppm (m, Cy). ES-MS (positive ion): m/z calculated for [C₃₇H₆₆NP₂Cl¹⁹³Ir] ([M]⁺) = 814.3988, found m/z = 814.3990. IR (solid, cm⁻¹): 2919 (w, ν_{C-H}), 2848 (w, ν_{C-H}), 2601 (w), 2497 (w), 1446 (w, ν_{P-C asym.}), 1170 (w), 1003 (w), 1036 (w).

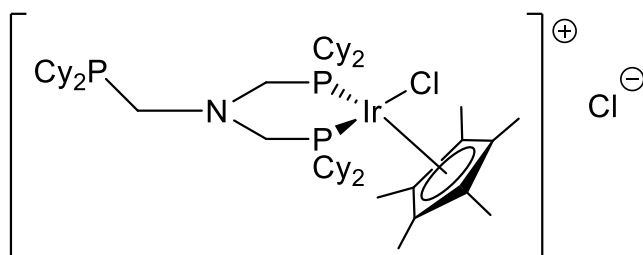
7.3.18 Preparation of [P(O)Cy₂CH₂-N(CH₂PCy₂)₂Ir(Cp*)Cl]Cl (**17**)



To a solution of [Cp*IrCl₂]₂ (0.0365 g, 0.046 mmol, 1 equiv.) in methanol (10 mL) was added N-Triphos^{Cy} (0.054 g, 0.092 mmol, 2 equiv.). The resulting mixture was heated to 50 °C overnight. After addition of hydrogen peroxide (30 wt.% solution in

water, 0.02 mL), the mixture was cooled to RT. After removing solvent to dryness, an orange-yellow residue formed. With the addition of diethyl ether, a solid precipitated. After drying in vacuo, the product was collected as a yellow-brown free-flowing powder (0.0214 g, 0.020 mmol, 21 %). Attempts to grow single crystals for X-ray diffraction by vapour diffusion of diethyl ether into acetonitrile or dichloromethane solutions were unsuccessful. ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ: 49.3 (s, 1P, P(O)Cy₂), -3.6 ppm (s, 2P, P-Ir). ¹H NMR (CDCl₃, 400 MHz) δ: 3.13 (m, 2H, N-CH₂-P(O)), 2.34 (m, 4H, N-CH₂-P), 1.28 ppm (s, 15H, Cp* CH₃), 0.9-2.2 ppm (m, Cy). ES-MS (positive ion): m/z calculated for [C₄₉H₈₇NOCl¹⁹³IrP₃] ([M]⁺) = 1026.5319, found m/z = 1026.5319. IR (solid, cm⁻¹): 2922 (w, ν_{C-H}), 2851 (w, ν_{C-H}), 1737 (w), 1670 (w), 1446 (w, ν_{P-C asym.}).

7.3.19 Preparation of [PCy₂CH₂-N(CH₂PCy₂)₂Ir(Cp*)Cl]Cl (**18**)

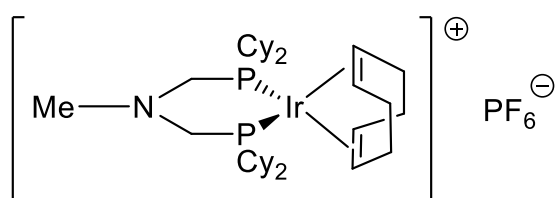


A solution of [Cp*IrCl₂]₂ (0.05 g, 0.063 mmol, 1 equiv.) in methanol (6 mL) was added to a solution of N-Triphos^{Cy} (0.0813 g, 0.126 mmol, 2 equiv.) in methanol (10 mL). The resulting orange mixture was heated to 50 °C for two hours. After the addition of

hydrogen peroxide (30 wt.% solution in water, 0.01 mL), the reaction was continued overnight. After

solvent removal to dryness in vacuo, a yellow oil residue was formed. This was washed with diethyl ether (3 x 2 mL) and dried overnight in vacuo. The product was collected as a free-flowing yellow powder (80 mg, 0.076 mmol, 60 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : -3.5 (s, 2P, P-Ir), -15.2 ppm (s, 1P, PCy_2). Also: 49.4 ppm (s, $\text{P}(\text{O})\text{Cy}_2$). ES-MS (positive ion): No product signal observed; only the oxidised analogue $[\text{P}(\text{O})\text{Cy}_2\text{CH}_2\text{-N}(\text{CH}_2\text{PCy}_2)_2\text{Ir}(\text{Cp}^*)\text{Cl}]\text{Cl}$ identified. Attempts to grow single crystals for X-ray diffraction by vapour diffusion of diethyl ether into acetonitrile or dichloromethane solutions were unsuccessful.

7.3.20 Preparation of $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{Ir}(\text{COD})]\text{PF}_6$ (**19**)



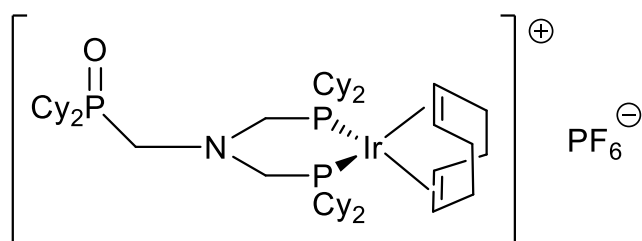
$\text{Me-N}(\text{CH}_2\text{PCy}_2)_2$ (0.114 g, 0.253 mmol, 2 equiv.) was added to a solution of $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.085 g, 0.127 mmol, 1 equiv.) in methanol (13 mL). The dark-red mixture was heated to 50 °C for one hour. After addition of NH_4PF_6 (0.0412 g, 0.253 mmol, 2 equiv.)

in methanol (5 mL), the mixture was heated for a further hour. After reduction of the solvent in vacuo to $\sim 1/3$, diethyl ether (30 mL) was added. After cooling at 5 °C overnight, a dark-red solid precipitated. The solid was isolated by cannula filtration, washed with diethyl ether (3 x 1 mL) and dried in vacuo. The product was collected as a free-flowing dark-red powder (0.099 g, 0.11 mmol, 44 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : -1.64 (s, 2P, PCy_2), -144.2 ppm (m, 1P, PF_6^-). ^1H NMR (CDCl_3 , 400 MHz) δ : 4.69 (br s, 4H, COD C=CH), 2.93 (s, 4H, NCH_2), 2.48 (s, 3H, NCH_3), 1.2-2.1 ppm (m, 52H, Cy + COD CH_2). ^{13}C NMR (CDCl_3 , 101 MHz) δ : 81.7 (m), 37.7 (m), 31.4 (s), 30.3 (s), 28.9 (s), 27.4 (s), 27.0 (m), 26.1 (s). ES-MS (positive ion): m/z calculated for $[\text{C}_{35}\text{H}_{63}\text{NP}_2^{193}\text{Ir}]$ ($[\text{M}]^+$) = 752.4065, found m/z = 752.4074. Anal. Calcd. for $\text{C}_{35}\text{H}_{63}\text{F}_6\text{IrNP}_3$: C, 46.86; H, 7.08; N, 1.56. Found: C, 46.55; H, 6.95; N 1.67. IR (solid, cm^{-1}): 2922 (w, $\nu_{\text{C-H}}$), 2848 (w, $\nu_{\text{C-H}}$), 1439 (w, $\nu_{\text{P-C asym.}}$), 1409 (w), 831 (s).

A pale-yellow crystalline material was also observed to precipitate from the filtrate of the synthesis of $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{Ir}(\text{COD})]\text{PF}_6$. After discarding the solvent and drying in vacuo, single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a chloroform solution, identifying the material as $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{Ir}(\text{Cl})_3(\text{OH}_2)]$ (**20**). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : -31.7 ppm (AB quartet): -31.6 (d, 1P, $^2J_{\text{P-P}} = 22.7$ Hz), -31.8 ppm (d, 1P, $^2J_{\text{P-P}} = 22.7$ Hz). ^1H NMR (CDCl_3 , 162 MHz) δ : 3.03 (m, 4H, CH_2), 2.36 (s, 3H, Me), 1.58 (s, 2H, OH_2), 0.8-3.7 ppm (m, 44H, Cy). No ^{13}C NMR

signals detected. ES-MS (positive ion): m/z calculated for $[C_{29}H_{54}N_2P_2Cl_2^{193}Ir]$ ($[M-Cl-H_2O+MeCN]^+$) = 755.2769, found m/z = 755.2783. Anal. Calcd. for $C_{27}H_{53}Cl_3IrNOP_2$: C, 42.21; H, 6.95; N, 1.82. Found: C, 41.87; H, 7.05; N 2.09. IR (solid, cm^{-1}): 3336 (w, ν_{O-H}), 3258 (w, ν_{O-H}), 2922 (w, ν_{C-H}), 2848 (w, ν_{C-H}), 1438 (w, $\nu_{P-C\text{ asym.}}$), 1226 (w), 842 (m).

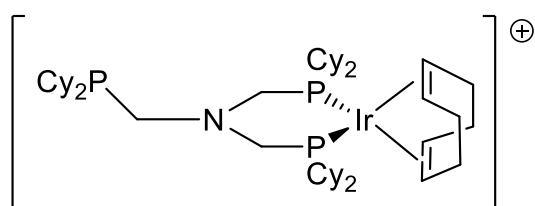
7.3.21 Preparation of $[P(O)Cy_2CH_2-N(CH_2PCy_2)_2Ir(COD)]PF_6$ (**21**)



To a solution of $[Ir(COD)Cl]_2$ (0.0775 g, 0.12 mmol, 1 equiv.) in methanol (13 mL) was added N-Triphos^{Cy} (0.150 g, 0.23 mmol, 2 equiv.). The resulting dark-red mixture was heated to 50 °C for one hour. After the

addition of hydrogen peroxide (30 wt.% solution in water, 0.03 mL, 0.23 mmol, 2 equiv.), the mixture was stirred for a further hour. After the addition of NH_4PF_6 (0.038 g, 0.23 mmol, 2 equiv.) in methanol (4 mL), the mixture was stirred for a further hour. The solvent level was reduced to approximately one third in vacuo. After the addition of diethyl ether (15 mL), the mixture was stored at 5 °C overnight. With the addition of further diethyl ether (20 mL), an orange solid precipitated and was isolated by cannula filtration. After washing the solid with diethyl ether (3 x 1 mL), the product was collected as a free-flowing red-brown powder (0.157 g, 0.14 mmol, 61 %). Attempts to grow single crystals for X-ray diffraction by vapour diffusion of diethyl ether into dichloromethane solutions were unsuccessful. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ : 49.2 (s, 3P, $P(O)Cy_2$), -2.31 (s, 1P, P-Ir), -144.2 ppm (m, 1P, PF_6^-). ^1H NMR data collected only for $[PCy_2CH_2-N(CH_2PCy_2)_2Ir(COD)]PF_6$. ES-MS (positive ion): m/z calculated for $[C_{47}H_{84}NOP_3^{193}Ir]$ ($[M]^+$) = 964.5395, found m/z = 964.5410. Anal. Calcd. for $C_{47}H_{84}F_6IrNOP_4$: C, 50.89; H, 7.63; N, 1.26. Found: C, 34.27; H, 4.88; N 3.34. IR (solid, cm^{-1}): 2924 (w, ν_{C-H}), 2851 (w, ν_{C-H}), 1446 (w, $\nu_{P-C\text{ asym.}}$), 1407 (w), 837 (m).

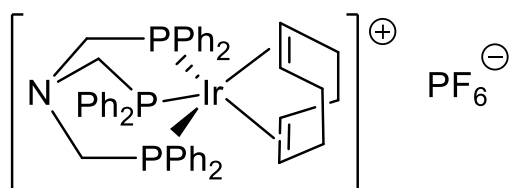
7.3.22 Preparation of $[PCy_2CH_2-N(CH_2PCy_2)_2Ir(COD)]PF_6$ (**22**)



To a solution of $[Ir(COD)Cl]_2$ (0.050 g, 0.074 mmol, 1 equiv.) in dichloromethane (8 mL) was added N-Triphos^{Cy} (0.090 g, 0.15 mmol, 2 equiv.). After heating the mixture at 50 °C

overnight, NH_4PF_6 (0.0243 g, 0.15 mmol, 2 equiv.) in dichloromethane (4 mL) was added. After further heating overnight, the mixture was cooled to RT and the solvent level reduced to approximately one-third in vacuo. After addition of diethyl ether (15 mL), the mixture was cooled at 5 °C overnight. An orange-red solid was observed to precipitate. The solid was isolated by cannula filtration and washed with cold diethyl ether (3 x 1 mL). After drying in vacuo overnight, the product was collected as a dark orange-red powder (0.11 g, 0.098 mmol, 65 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : -2.2 (s, 2P, η^2 -P-Ir), -16.0 (s, 1P, PCy_2), -52.6 (s, 1P, η^3 -P-Ir), -144.3 ppm (m, 2P, PF_6^-). ^1H NMR (CDCl_3 , 400 MHz) δ : 4.72 (br s, 4H, COD C=CH), 3.20 (m, 6H, PCH_2), 0.8-3.0 ppm (m, Cy + COD CH_2). ES-MS (positive ion): m/z calculated for $[\text{C}_{47}\text{H}_{84}\text{NP}_3^{193}\text{Ir}]$ ($[\text{M}]^+$) = 948.5446, found m/z = 948.5458. Anal. Calcd. for $\text{C}_{47}\text{H}_{84}\text{F}_6\text{IrNP}_4$: C, 51.63; H, 7.74; N, 1.28. Found: C, 40.56; H, 6.82; N 3.81. IR (solid, cm^{-1}): 2919 (w, $\nu_{\text{C-H}}$), 2848 (w, $\nu_{\text{C-H}}$), 1444 (w, $\nu_{\text{P-C asym.}}$), 1405 (w), 835 (m).

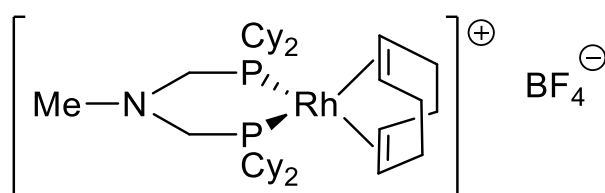
7.3.23 Preparation of $[\text{N}(\text{CH}_2\text{PPh}_2)_3\text{Ir}(\text{COD})]\text{PF}_6$ (**23**)



A mixture of $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.0425 g, 0.063 mmol, 1 equiv.) and N-Triphos^{Ph} (0.0775 g, 0.127 mmol, 2 equiv.) in methanol (10 mL) was heated to 50 °C for one hour. After addition of NH_4PF_6 (0.0205 g, 0.122 mmol, 2 equiv.), the mixture was heated for a further

hour. After reducing the solvent in vacuo, a yellow solid residue precipitated. After addition of diethyl ether (20 mL), the mixture was cooled at 5 °C overnight. The solid was isolated by cannula filtration and washed with diethyl ether (3 x 1 mL). After drying in vacuo overnight, the product was collected as a beige-coloured powder (0.103 g, 0.095 mmol, 75 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : -49.8 (s, 3P, PPh_2), -144.3 ppm (m, 1P, PF_6^-). ^1H NMR (CDCl_3 , 162 MHz) δ : 6.9-7.3 (m, 30H, Ph), 4.37 (s, 6H, NCH_2), 3.96 (s, 4H, COD CH=C), 2.5-2.7 ppm (m, 8H, COD CH_2). ^{13}C NMR (CDCl_3 , 101 MHz) δ : 132.4 (m, Ph), 130.3 (s, Ph), 128.6 (br s, Ph), 72.0 (m, N- CH_2 -P), 34.5 ppm (br s, COD CH_2). ES-MS (positive ion): m/z calculated for $[\text{C}_{47}\text{H}_{48}\text{NP}_3^{193}\text{Ir}]$ ($[\text{M}]^+$) = 912.2629, found m/z = 912.2635. IR (solid, cm^{-1}): 3142 (w, br, $\nu_{\text{C-H}}$), 3049 (w, br, $\nu_{\text{C-H}}$), 1409 (w, $\nu_{\text{P-C asym.}}$), 1088 (w), 835 (s), 693 (m). Anal. Calcd. for $\text{C}_{49}\text{H}_{54}\text{Cl}_4\text{F}_6\text{IrNOP}_4$ (inc. 2 x DCM + 1 x H_2O): C, 47.28; H, 4.37; N, 1.13. Found: C, 47.56; H, 4.52; N 2.85. Attempts to grow single crystals for X-ray diffraction by vapour diffusion of diethyl ether or hexane into dichloromethane or acetonitrile solutions, or by liquid-liquid diffusion of diethyl ether or hexane into dichloromethane solutions were unsuccessful.

7.3.24 Preparation of [Me-N(CH₂PCy₂)₂Rh(COD)]BF₄ (**24**)

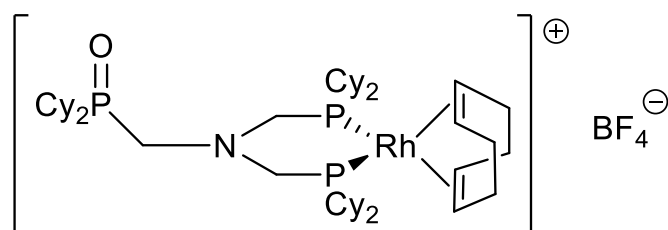


To a solution of [Rh(COD)(MeCN)₂]BF₄ (0.032 g, 0.083 mmol, 1 equiv.) in dichloromethane (5 mL) was added Me-N(CH₂PCy₂)₂ (0.037 g, 0.083 mmol, 1 equiv.). The resulting dark-orange mixture was heated at 30 °C for one hour. After

reducing the solvent volume to approximately one-third in vacuo, a yellow solid residue precipitated. With the addition of diethyl ether (15 mL), the mixture became cloudy, without a solid precipitate. With full solvent removal in vacuo, an orange solid precipitated and was dried in vacuo overnight. The product was collected as a crystalline orange powder (30 mg, 0.040 mmol, 48 %). Attempts to grow single crystals for X-ray diffraction by liquid-liquid diffusion of diethyl ether or hexane into acetonitrile solutions (sealed in a Young's tap NMR tube) were unsuccessful. ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ: 10.6 ppm (d, ¹J_{P-Rh} = 134.9 Hz). ¹H NMR (CDCl₃, 162 MHz) δ: 5.15 (s, 4H, COD C=CH), 2.73 (s, 4H, NCH₂), 2.49 (s, 3H, NCH₃), 0.8-3.5 ppm (m, Cy + COD CH₂). ES-MS (positive ion): m/z calculated for [C₃₅H₆₆NP₂Rh] ([M+3H]⁺) = 665.3726, found m/z = 665.3740. IR (solid, cm⁻¹): 2922 (m, ν_{C-H}), 2848 (w, ν_{C-H}), 1446 (w, ν_{P-C} asym.), 1047 (m, br). EA was untried owing to the high air sensitivity of the product. ¹³C NMR spectroscopy was unsuccessful as the product was found to degrade in solution.

Through ³¹P{¹H} NMR spectroscopy, a solution of [Me-N(CH₂PCy₂)₂Rh(COD)]BF₄ in deuterated-chloroform was observed to convert to a distinct species over the course of several days. Single crystals suitable for X-ray diffraction were grown by liquid-liquid diffusion of hexane into the deuterated-chloroform solution, identifying the material as [{Rh(Cl)(Me-N(CH₂PCy₂)₂)₂(μ-Cl)₃]BF₄ (**25**). ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ: 47.7 (2P, dd, ²J_{P-P} = 22.1 Hz, ¹J_{P-Rh} = 112.3 Hz), 38.6 (2P, dd, ²J_{P-P} = 22.0 Hz, ¹J_{P-Rh} = 110.1 Hz). ¹H NMR (CDCl₃, 162 MHz) δ: 3.27 (m, 8H, CH₂), 0.9-3.0 ppm (m, 94 H, Cy + Me). ¹³C NMR (CDCl₃, 101 MHz) δ: 47.5 (s, CH₃), 25-31 (m, Cy, N-CH₂-P), 9.0 ppm (s, Cy (CH)). ES-MS (positive ion): m/z calculated for [C₅₄H₁₀₂N₂P₄³⁵Cl₄³⁷Cl¹⁰³Rh₂] ([M]⁺) = 1285.3517, found m/z = 1285.3544. Anal. Calcd. for C₅₄H₁₀₂BCl₅F₄N₂P₄Rh₂: C, 47.23; H, 7.49; N, 2.04. Found: C, 47.07; H, 7.61; N 2.16. IR (solid, cm⁻¹): 2922 (w, ν_{C-H}), 2848 (w, ν_{C-H}), 1446 (w, ν_{P-C} asym.), 1259 (w), 1021 (m, br), 798 (m).

7.3.25 Preparation of [P(O)Cy₂CH₂-N(CH₂PCy₂)₂Rh(COD)]BF₄ (**26**)



To a solution of [Rh(COD)(MeCN)₂]BF₄ (0.096 g, 0.25 mmol, 1 equiv.) in dichloromethane (10 mL) was added N-Triphos^{Cy} (0.164 g, 0.25 mmol, 1 equiv.). The resulting mixture was heated to 30 °C

for one hour. After cooling to RT, the solvent volume was reduced to approximately one-third in vacuo. After addition of diethyl ether (15 mL), the mixture was cooled at 5 °C overnight. During this time, an orange solid precipitated. The solid was isolated by cannula filtration and washed with diethyl ether (3 x 1 mL). After drying in vacuo overnight, the product was collected as a red-orange crystalline solid (86 mg, 0.088 mmol, 35 %). ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ: 10.8 (2P, d, ¹J_{P-Rh} = 139.4 Hz), -16.7 (1P, s). ¹H NMR (CD₃CN, 162 MHz) δ: 5.58 (s, 4H, COD C=CH), 3.15 (m, 6H, P-CH₂), 1.3-2.9 ppm (m, Cy + COD CH₂). ES-MS (positive ion): m/z calculated for [C₄₇H₈₂NOP₃Rh] ([M-2H]⁺) = 872.9837, found m/z = 872.4420. IR (solid, cm⁻¹): 2922 (w, ν_{C-H}), 2848 (w, ν_{C-H}), 1446 (w, ν_{P-C} asym.), 1047 (w). EA was untried owing to the high air sensitivity of the product. ¹³C NMR spectroscopy was unsuccessful as the product was found to degrade in solution.

7.4 Experimental details for Chapter 4

7.4.1 General procedure for transfer hydrogenation reactions

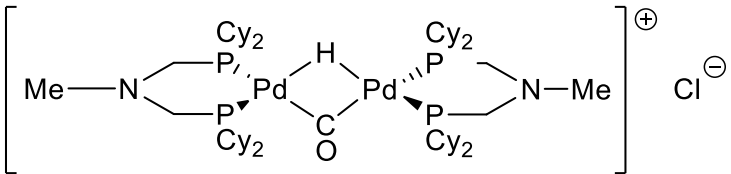
A solution of levulinic acid (0.34 mL, 3.37 mmol), catalyst (1 mol%), formic acid (0.27 mL, 7.2 mmol, 2.1 equiv.) and triethylamine (0.05 mL, 0.36 mmol, 10 mol%) was prepared in a reaction vial (Chemglass Item number CG-4912-06, Vial, 40 mL, 28 x 95 mm, 24-414 thread) under nitrogen. After sealing with a pressure relief cap, the mixture was heated to 100 °C and stirred at RT for 24 hours. The mixture was then cooled to room temperature and a sample was prepared for ¹H NMR spectroscopy from DMSO-d₆. Where a solid precipitate was observed, the mixture was passed through a plug of silica to remove the precipitate. The products and unreacted substrates were identified by their characteristic methyl signals using ¹H NMR spectroscopy. Methyl protons of LA are identified by the characteristic singlet at 2.10 ppm, while GVL displays a doublets at 1.33 ppm.

7.4.2 General procedure for high pressure hydrogenation reactions

a) *Hydrogenation reactions with palladium catalysts.* In a typical experiment, a solution of levulinic acid (0.68 mL, 6.8 mmol), triethylamine (0.1 mL, 0.72 mmol) and 1 mol% catalyst was prepared in the reactor vessel and attached to the main reactor (Asynt reactor). After flushing with nitrogen (x3), the atmosphere was changed to hydrogen by repeatedly pressurising to 10 bar and depressurising (x3) before the pressure was raised to the designated pressure and the reactor was sealed. The reactor was heated to the stated temperature and stirred, causing a small increase in internal pressure once the reaction temperature was reached. The reaction mixture was stirred at 1000 rpm at the stated temperature and pressure for the stated time duration, and then the reactor was allowed to cool to RT before slowly depressurising. The reaction mixture was analysed by ^1H NMR spectroscopy in DMSO-d_6 .

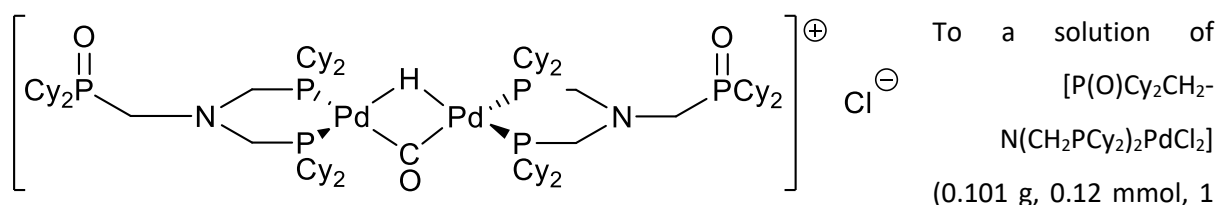
b) *Hydrogenation reactions with iron/cobalt catalysts.* In a typical experiment, a solution of levulinic acid (1.16 g, 10 mmol) and catalyst in solvent (methanol or THF, 20 mL) was injected into a pre-purged high-pressure stainless-steel Autoclave Engineering mini-reactor fitted with a PTFE inner sleeve under a positive flow of nitrogen. The atmosphere was changed to hydrogen by repeatedly pressurising to 10 bar and depressurising (x3) before the pressure was raised to the designated pressure and the reactor was sealed. Reactions were heated to the required temperature and were run for six hours with stirring at 4000 rpm. Then the vessel was cooled to room temperature and depressurised. The crude reaction mixture was passed through a plug of silica. The products and unreacted substrates were identified by their characteristic methyl signals using ^1H NMR spectroscopy.

7.4.3 Preparation of $[\{\text{Pd}(\text{Me-N}(\text{CH}_2\text{PCy}_2)_2)_2(\mu\text{-H})(\mu\text{-CO})\}]\text{Cl}$ (**27**)

 To a solution of $[\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{PdCl}_2]$ (0.075 g, 0.12 mmol, 1 equiv.) in dichloromethane (3 mL) was added formic acid (0.023 mL, 0.6 mmol, 5 equiv.) and triethylamine (0.05 mL, 0.36 mmol, 3 equiv). With heating to 40 °C, the mixture became a deep red colour within a short time. After heating overnight, the mixture was cooled to RT. After solvent removal in vacuo, a red solid precipitated. After drying in vacuo overnight, the product was collected as a free-flowing red powder (0.061 g, 0.052 mmol, 87 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : 12.3 (s). Signal attributable to $\text{Me-N}(\text{CH}_2\text{PCy}_2)_2\text{PdCl}_2$ observed at 30.6 ppm (s). ^1H NMR

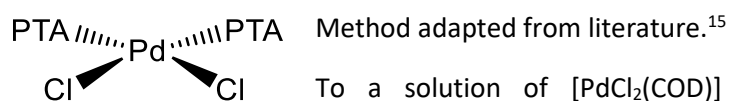
(CDCl₃, 162 MHz) δ : 2.79 (s, 4H, P-CH₂-N), 2.43 (s, 4H, P-CH₂-N), 1.96 (s, 6H, Me), 0.8-2.3 (m, Cy), -5.20 ppm (quin., 1H, $^2J_{\text{H-P}} = 42$ Hz, $\mu\text{-H}$). ^{13}C NMR (CDCl₃, 101 MHz) δ : 170.0-173.2 (m, CO), 74.3 (s, CH₃), 68.8 (m, N-CH₂-P), 62.1 (m, N-CH₂-P), 20.6-34.0 (m, Cy), 14.0 ppm (s, Cy CH). ES-MS (positive ion): m/z calculated for [C₅₅H₁₀₃N₂OP₄¹⁰⁶Pd¹⁰⁸Pd] ([M]⁺) = 1145.5095, found m/z = 1145.5104. IR (solid, cm⁻¹): 2922 (m, $\nu_{\text{C-H}}$), 2851 (m, $\nu_{\text{C-H}}$), 2602 (w), 2494 (w), 1741 (m, $\nu_{\text{P=O}}$), 1446 (m, $\nu_{\text{P-C asymm.}}$), 1372 (m), 1219 (m), 1170 (m), 1036 (m). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution; however the identity of the crystals was determined as [Me-N(CH₂PCy₂)₂PdCl₂] (**1**).

7.4.4 Preparation of [{Pd(P(O)Cy₂CH₂-N(CH₂PCy₂)₂)}₂($\mu\text{-H}$)($\mu\text{-CO}$)]Cl (**28**)



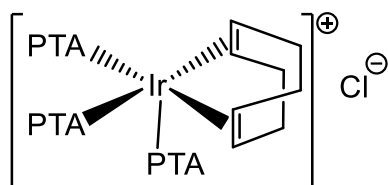
equiv.) in dichloromethane (3 mL) was added formic acid (0.023 mL, 0.6 mmol, 5 equiv.) and triethylamine (0.05 mL, 0.36 mmol, 3 equiv). With heating to 40 °C, the mixture became a deep red colour within a short time. After heating for 66 hours, and with addition of further formic acid (0.046 mL) and triethylamine (0.10 mL), the mixture was cooled to RT. After removing solvent in vacuo, a red oil formed. The product remained as an oil even with extended drying in vacuo. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃, 162 MHz) δ : 12.3 (s, 2P, P-Pd), 48.7 ppm (s, 1P, P(O)Cy₂). Signals attributable to [P(O)Cy₂CH₂-N(CH₂PCy₂)₂PdCl₂] also observed at 30.1 (s, 2P) and 48.8 ppm (s, 1P). ^1H NMR (CDCl₃, 162 MHz) δ : 4.7-5.2 (m, 4H, N-CH₂-P(O)), 4.0-4.3 (m, 4H, N-CH₂-P), 0.7-2.3 (m, Cy), -5.02 ppm (quin., 1H, $^2J_{\text{H-P}} = 42$ Hz, $\mu\text{-H}$). ^{13}C NMR (CDCl₃, 101 MHz) δ : 170.0-173.2 (m, CO), 74.3 (s, CH₃), 68.9 (m, N-CH₂-P), 62.1 (m, N-CH₂-P), 20.5-34.0 (m, Cy), 14.0 ppm (s, Cy CH). ES-MS (positive ion): m/z calculated for [C₇₉H₁₄₅N₂O₃¹⁰⁶Pd¹⁰⁸PdP₆] ([M]⁺) = 1569.7755, found m/z = 1569.7804. IR (solid, cm⁻¹): 2926 (w, $\nu_{\text{C-H}}$), 2855 (w, $\nu_{\text{C-H}}$), 2602 (w), 2494 (w), 1737 (m, $\nu_{\text{C=O}}$), 1443 (w, $\nu_{\text{P-C asymm.}}$), 1372 (w), 1219 (m), 1170 (m, $\nu_{\text{P=O}}$), 1036 (m). Attempts to grow single crystals for X-ray diffraction by vapour diffusion of diethyl ether into dichloromethane solutions were unsuccessful.

7.4.5 Preparation of [Pd(PTA)₂Cl₂] (**29**)



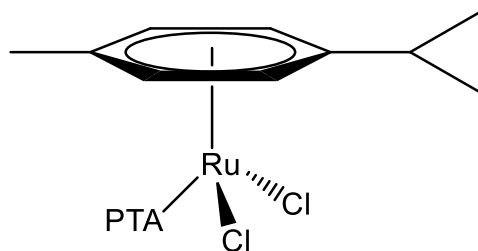
To a solution of [PdCl₂(COD)] (0.32 g, 1.12 mmol, 1 equiv.) in dichloromethane (13 mL) was added PTA (0.354 g, 2.26 mmol, 2 equiv.). The mixture was stirred at RT overnight, during which time a pale-yellow solid had precipitated. The solid was isolated by cannula filtration and washed with dichloromethane (3 x 1 mL). After drying in vacuo overnight, the product was collected as a free-flowing yellow powder (0.352 g, 0.72 mmol, 64 %). NMR spectra conformed to literature values. ³¹P{¹H} NMR (DMSO-d₆, 162 MHz) δ: -24.3 ppm (s). ¹H NMR (D₂O, 400 MHz) δ: 4.56 (d, 6H, J = 13.0 Hz, NCH₂N), 4.47 (s, 12H, NCH₂P), 4.43 ppm (d, 6H, J = 13.8 Hz, NCH₂N). ES-MS (positive ion): m/z calculated for [C₁₄H₂₇N₇P₂Cl¹⁰⁸Pd] ([M-Cl+CH₃CN]⁺) = 498.0531, found m/z = 498.0521. IR (solid, cm⁻¹): 2930 (w, ν_{C-H}), 2907 (w, ν_{C-H}), 1283 (w, ν_{C-N}), 1241 (w, ν_{C-N}), 1100 (w), 1014 (w), 969 (m), 939 (w), 902 (w), 805 (w), 742 (w).

7.4.6 Preparation of [Ir(PTA)₃(COD)]Cl (**30**)



To a solution of [Ir(COD)Cl]₂ (0.19 g, 0.28 mmol, 1 equiv.) in dichloromethane (10 mL) was added PTA (0.27 g, 1.70 mmol, 6 equiv.). An off-white solid precipitated within a short time. The solid was isolated by cannula filtration and washed with dichloromethane (3 x 1 mL). After drying in vacuo overnight, the product was collected as a free-flowing beige-coloured powder (0.32 g, 0.40 mmol, 71 %). NMR spectra conformed to literature values. ³¹P{¹H} NMR (D₂O, 162 MHz) δ: -87.5 ppm (s). ¹H NMR (D₂O, 400 MHz) δ: 4.51 (br s, 18H, NCH₂N), 4.04 (br s, 18H, PCH₂N), 3.64 (br s, 4H, CH=CHCH₂), 2.31 ppm (br dd, 8H, CHCH₂CH₂). ES-MS (positive ion): m/z calculated for [C₂₆H₄₈N₉P₃¹⁹³Ir] ([M]⁺) = 772.2875, found m/z = 772.2868. IR (solid, cm⁻¹): 2878 (w, br, ν_{C-H}), 1241 (w, ν_{C-N}), 1103 (w), 1014 (w), 969 (w), 895 (w), 805 (w), 742 (w).

7.4.7 Preparation of $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{PTA})\text{Cl}_2]$ (**31**)

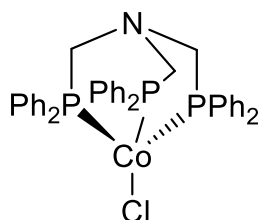
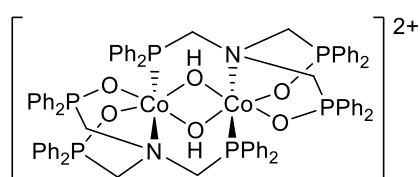


Method adapted from literature.¹⁷

A solution of PTA (103 mg, 0.66 mmol, 2 equiv.) in methanol (10 mL) was added to a solution of $[\text{RuCl}_2(p\text{-cymene})]_2$ (200 mg, 0.33 mmol, 1 equiv.) in methanol (20 mL). The deep-red mixture was heated to reflux overnight. After cooling to RT, solvent was removed to dryness in vacuo, causing the precipitation of an orange-red solid. After drying in vacuo, the product was collected as a free-flowing orange-red powder (0.31 g, 0.66 mmol, 97 %). NMR spectra conformed to literature values. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : -36.7 ppm (s). ^1H NMR (CDCl_3 , 400 MHz) δ : 5.50 (m, 4H, *p*-cymene), 4.56 (s, 6H, NCH_2N), 4.34 (s, 6H, PCH_2N), 2.80 (sept, 1H, CH), 2.10 (s, 3H, CH_3), 1.23 ppm (d, 6H, $J = 6.7$ Hz, CH_3). ES-MS (positive ion): m/z calculated for $[\text{C}_{18}\text{H}_{29}\text{N}_4\text{Cl}^{102}\text{RuP}]$ ($[\text{M-Cl}+\text{CH}_3\text{CN}]^+$) = 469.0862, found $m/z = 469.0869$. IR (solid, cm^{-1}): 2922 (w, $\nu_{\text{C-H}}$), 2855 (w, $\nu_{\text{C-H}}$), 1737 (w), 1238 (m, $\nu_{\text{C-N}}$), 1014 (m), 969 (m), 947 (m), 798 (w), 742 (w).

7.5 Experimental details for Chapter 5

7.5.1 Coordination of N-Triphos^{Ph} to $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$



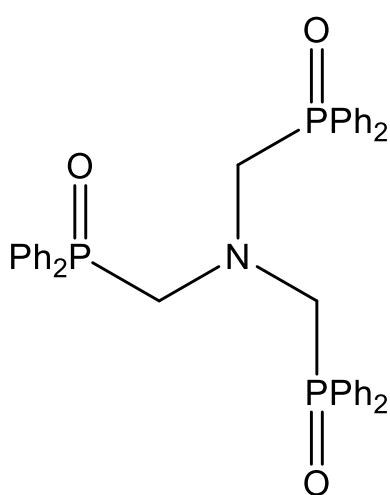
a) A solution of N-Triphos^{Ph} (0.3 g, 0.49 mmol) and NaBPh_4 (0.168 g, 0.49 mmol) in THF (8 mL) was added to a solution of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.167 g, 0.49 mmol) in 1-butanol (10 mL) dropwise. The resulting mixture became

dark-brown in colour with full addition. After stirring the mixture at RT overnight, full solvent removal in vacuo yielded a pale brown solid. After washing with 1-butanol (2 x 2 mL) and hexane (3 x 2 mL) and drying in vacuo, a free-flowing red-brown powder was collected. The product showed no signals by $^{31}\text{P}\{^1\text{H}\}$ or ^1H NMR spectroscopy. Single crystals

suitable for X-ray diffraction were grown by liquid diffusion of diethyl ether into a dichloromethane solution, in an NMR fitted with a J Young tap. The identity of the crystal was found as $[\text{Co}_2(\text{N}(\text{CH}_2\text{PPh}_2(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2))_2(\mu_2\text{-OH})_2](\text{BF}_4)_2$ (**32**). b) The reaction was repeated as above. Single

crystals suitable for X-ray diffraction were grown by vapour diffusion of hexane into a THF solution, inside a glovebox. The identity of the crystal was found as $[\text{Co}(\text{N}(\text{CH}_2\text{PPh}_2)_3)\text{Cl}]$ (**33**).¹⁸

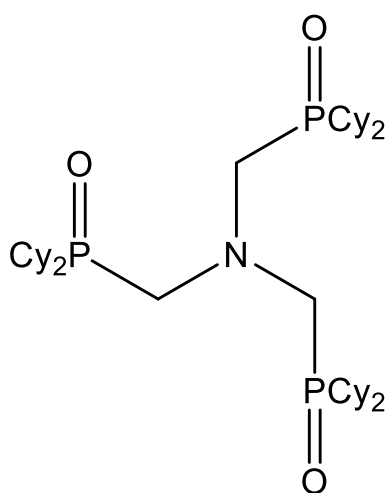
7.5.2 Preparation of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$ (**34**)



A crystal structure of **34** has previously been reported.¹⁹ To a solution of N-Triphos^{Ph} (0.5 g, 0.817 mmol) in THF (10 mL), was added hydrogen peroxide (30 % solution in water) (0.25 mL, 2.45 mmol) and the resulting colourless solution was stirred at RT for two hours. The mixture was then dried over MgSO_4 , filtered and the solvent removed under reduced pressure to yield a white solid. The solid was washed with diethyl ether, dried *in vacuo* and collected as a white powder (0.44 g, 0.67 mmol, 82 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution. $^{31}\text{P}\{^1\text{H}\}$

NMR (CDCl_3 , 162 MHz) δ : 30.4 ppm (s). ^1H NMR (CDCl_3 , 162 MHz) δ : 7.2–7.9 (m, 30H, Ph), 4.23 ppm (d, 6H, $^2J_{\text{P-H}} = 6.4$ Hz, CH_2). ^{13}C NMR (CDCl_3 , 101 MHz) δ : 128.4–131.6 (m, Ph), 58.1 ppm (dt, $^1J_{\text{PC}} = 84.2$ Hz, $^3J_{\text{PC}} = 7.4$ Hz, CH_2). ES-MS (positive ion): m/z calcd. for $[\text{C}_{39}\text{H}_{37}\text{NO}_3\text{P}_3]$ ($[\text{M}+\text{H}]^+$) = 660.1981, found m/z = 660.1998. Anal. Calcd. for $\text{C}_{39}\text{H}_{40}\text{NO}_5\text{P}_3$ (inc. $2 \times \text{H}_2\text{O}$): C, 67.33; H, 5.80; N, 2.01. Found: C, 67.08; H, 5.82; N, 2.27. IR (solid, cm^{-1}): 1435 (w, $\nu_{\text{P-C asymm.}}$), 1167 (w, $\nu_{\text{P=O}}$), 1118 (w), 857 (w), 716 (w), 693 (w).

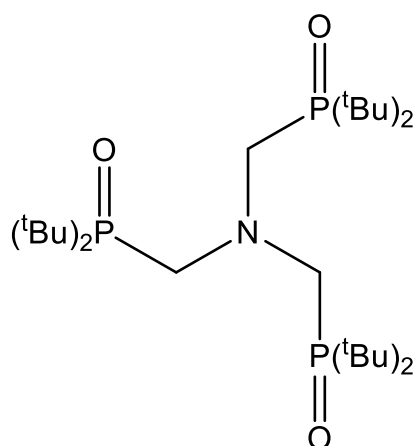
7.5.3 Preparation of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Cy}_2)_3$ (**35**)



To a solution of N-Triphos^{Cy} (0.379 g, 0.58 mmol) in THF (20 mL) was added hydrogen peroxide (30 wt.% solution in water, 0.05 mL). After stirring at RT for 10 minutes, solvent was removed *in vacuo*, forming a white oil, and with further drying *in vacuo* overnight a fluffy white solid (0.245 g, 0.35 mmol, 61 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of hexane into a dichloromethane solution. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : 49.3 ppm (s). ^1H NMR (CDCl_3 , 162 MHz) δ : 3.32 (d, 6H, CH_2 , $^2J_{\text{P-H}} = 4.8$ Hz), 1.2–2.2 ppm (m, 66H, Cy). ^1H NMR (CDCl_3 , 400 MHz) δ : 3.32 (d, 6H, $^2J_{\text{P-H}} = 4.8$ Hz, CH_2), 1.2–2.2 ppm (m, Cy). ^{13}C NMR (CDCl_3 , 101 MHz)

δ : 35.7 (d, $^1J_{\text{PC}} = 63.2$ Hz, N-CH₂-P), 25.5-26.8 ppm (m, Cy). ES-MS (positive ion): m/z calculated for [C₃₉H₇₃NO₃P₃] ([M+H]⁺) = 696.4803, found m/z = 696.4803. Anal. Calcd. for C₃₉H₇₂NO₃P₃: C, 67.31; H, 10.43; N, 2.01. Found: C, 67.43; H, 10.50; N 2.12. IR (solid, cm⁻¹): 2922 (w, $\nu_{\text{C-H}}$), 2848 (w, $\nu_{\text{C-H}}$), 1446 (w, $\nu_{\text{P-C asym.}}$), 1156 (w, $\nu_{\text{P=O}}$).

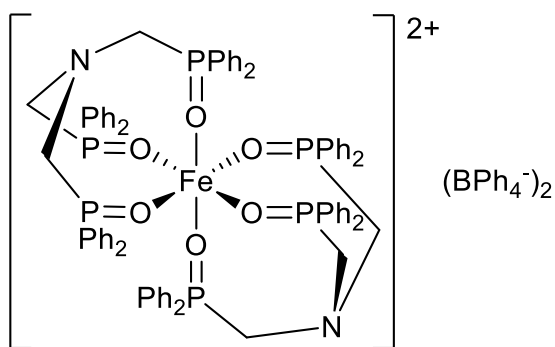
7.5.4 Preparation of N(CH₂P(O)(^tBu)₂)₃ (**36**)



To a solution of di-tert-butyl(hydroxymethyl)phosphonium chloride (0.0586 g, 0.24 mmol, 3 equiv.) in methanol (3 mL) was added triethylamine (0.17 mL, 1.22 mmol). After stirring at RT for one hour, ammonium chloride (0.0043 g, 0.081 mmol, 1 equiv.) was added. The mixture was heated at reflux overnight. After cooling to RT, the solvent level was reduced to approximately one-third in vacuo, precipitating a white solid. The solid was isolated by cannula filtration and washed with methanol. After addition of further methanol (2 mL), hydrogen peroxide (30 wt.%

solution in water, 0.01 mL) was added and the mixture stirred at RT. After removing the solvent to dryness, the white solid precipitate was dried in vacuo overnight. The product was collected as a trace amount of white powder. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃, 162 MHz) δ : 58.8 ppm (s). ^1H NMR (CDCl₃, 400 MHz) δ : 3.13 (m, CH₂), 1.44 ppm (m, ^tBu). ES-MS (positive ion): m/z calculated for [C₂₇H₆₁NO₃P₃] ([M+H]⁺) = 540.3864, found m/z = 540.3866. Insufficient quantity was collected for further analysis.

7.5.5 Preparation of [Fe{N(CH₂P(O)Ph₂)₃}₂](BPh₄)₂ (**37**)

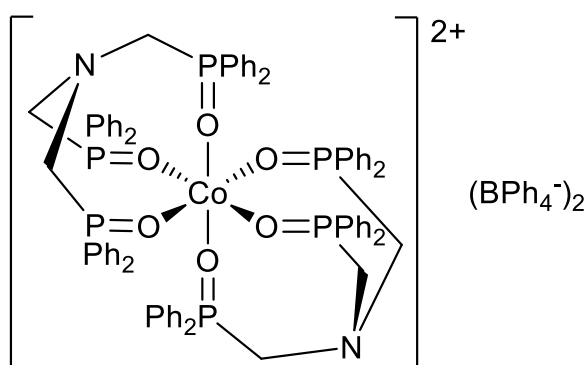


To a solution of N(CH₂P(O)Ph₂)₃ (0.15 g, 0.227 mmol, 2 equiv.) and NaBPh₄ (0.078 g, 0.227 mmol, 2 equiv.) in THF (5 mL) was added Fe(BF₄)₂·6H₂O (0.0385 g, 0.114 mmol, 1 equiv.) in isopropanol (6 mL) and stirred at room temperature for one hour. The resulting pale-orange precipitate was isolated by cannula filtration, washed with diethyl ether (3 x 1.5

mL) and dried in vacuo (0.120 g, 0.06 mmol, 52 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): No signals observed; attributed to paramagnetism. ^1H NMR (CDCl_3 , 400 MHz): Broad, poorly resolved signals observed, attributed to paramagnetism. ES-MS (positive ion): m/z calcd. for $[\text{C}_{78}\text{H}_{72}\text{FeN}_2\text{O}_6\text{P}_6]^{2+}$ ($[\text{M}]^{2+}$) = 687.1583, found m/z = 687.1609. Anal. Calcd. for $\text{C}_{126}\text{H}_{112}\text{B}_2\text{FeN}_2\text{O}_6\text{P}_6$: C, 75.16; H, 5.61; N, 1.39. Found: C, 64.67; H, 5.12; N 1.33. X. IR (solid, cm^{-1}): 3049 (w, $\nu_{\text{C-H}}$), 2982 (w, $\nu_{\text{C-H}}$), 1435 (w, $\nu_{\text{P-C asymm.}}$), 1167 (w, $\nu_{\text{P=O}}$), 1129 (w), 857 (w), 693 (w).

The reaction was also repeated with the omission of NaBPh_4 to produce the BF_4 analogue $[\text{Fe}\{\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3\}_2](\text{BF}_4)_2$ (**37-A**) (0.050 g, 0.0323 mmol, 28 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): No signals observed. Anal. Calcd. for $\text{C}_{78}\text{H}_{72}\text{B}_2\text{F}_8\text{FeN}_2\text{O}_6\text{P}_6$: C, 60.49; H, 4.69; N, 1.81. Found: C, 59.14; H, 4.64; N 1.88. IR (solid, cm^{-1}): 1439 (w, $\nu_{\text{P-C asymm.}}$), 1170 (w, $\nu_{\text{P=O}}$), 1118 (w), 1055 (w), 857 (w), 716 (w).

7.5.6 Preparation of $[\text{Co}\{\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3\}_2](\text{BPh}_4)_2$ (**38**)



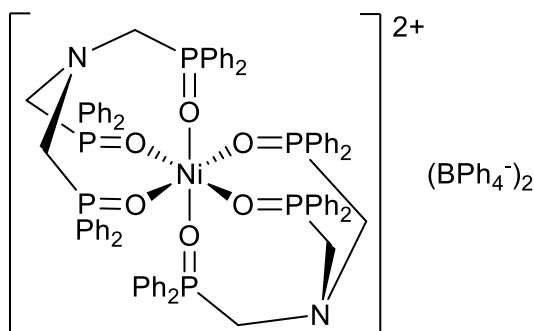
To a solution of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$ (0.15 g, 0.227 mmol, 2 equiv.) and NaBPh_4 (0.078 g, 0.227 mmol, 2 equiv.) in THF (5 mL) was added $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0390 g, 0.114 mmol, 1 equiv.) in isopropanol (5 mL) and stirred at room temperature for one hour. The resulting pale-pink precipitate was isolated by cannula filtration, washed with diethyl ether (3 x 1.5 mL) and dried in vacuo (0.172 g,

0.085 mmol, 75 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into an acetonitrile solution. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): No signals observed; attributed to paramagnetism. ^1H NMR (CDCl_3 , 400 MHz): Broad, poorly resolved signals observed, attributed to paramagnetism. ES-MS (positive ion): m/z calcd. for $[\text{C}_{78}\text{H}_{72}\text{CoN}_2\text{O}_6\text{P}_6]^{2+}$ ($[\text{M}]^{2+}$) = 688.6574, found m/z = 688.6606. Anal. Calcd. for $\text{C}_{126}\text{H}_{112}\text{B}_2\text{CoN}_2\text{O}_6\text{P}_6$: C, 75.04; H, 5.60; N, 1.39. Found: C, 66.11; H, 5.20; N 1.39. IR (solid, cm^{-1}): 3041 (w, $\nu_{\text{C-H}}$), 2986 (w, $\nu_{\text{C-H}}$), 1435 (w, $\nu_{\text{P-C asymm.}}$), 1167 (w, $\nu_{\text{P=O}}$), 1118 (w), 857 (w), 693 (w).

The reaction was also repeated with the omission of NaBPh_4 to produce the BF_4 analogue $[\text{Co}\{\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3\}_2](\text{BF}_4)_2$ (**38-A**) (0.0641 g, 0.041 mmol, 36 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): No signals observed. Anal. Calcd. for $\text{C}_{78}\text{H}_{72}\text{B}_2\text{F}_8\text{CoN}_2\text{O}_6\text{P}_6$: C, 60.37; H, 4.68; N, 1.81. Found: C, 60.28; H,

4.51; N 1.91. IR (solid, cm^{-1}): 3056 (vw, $\nu_{\text{C-H}}$), 1439 (w, $\nu_{\text{P-C asym.}}$), 1170 (w, $\nu_{\text{P=O}}$), 1118 (w), 1059 (w), 861 (w), 716 (w).

7.5.7 Preparation of $[\text{Ni}\{\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3\}_2](\text{BPh}_4)_2$ (**39**)

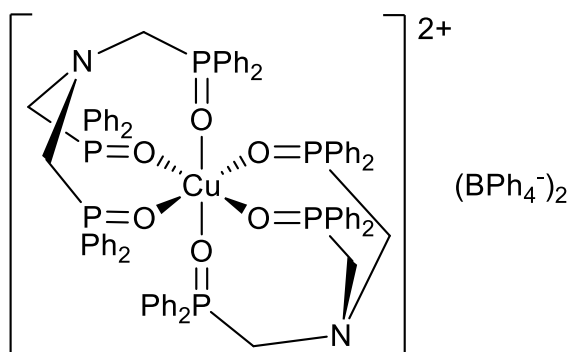


To a solution of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$ (0.15 g, 0.227 mmol, 2 equiv.) and NaBPh_4 (0.078 g, 0.227 mmol, 2 equiv.) in THF (5 mL) was added $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0388 g, 0.114 mmol, 1 equiv.) in isopropanol (5 mL) and stirred at room temperature for one hour. The resulting pale-yellow precipitate was isolated by cannula filtration, washed with diethyl ether (3 x 1.5

mL) and dried in vacuo (0.160 g, 0.079 mmol, 69 %). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into an acetonitrile solution. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): No signals observed; attributed to paramagnetism. ^1H NMR (CDCl_3 , 400 MHz): Broad, poorly resolved signals observed, attributed to paramagnetism. ES-MS (positive ion): m/z calcd. for $[\text{C}_{78}\text{H}_{72}\text{CoN}_2\text{O}_6\text{P}_6]^{2+}$ ($[\text{M}]^{2+}$) = 688.1585, found m/z = 688.160. Anal. Calcd. for $\text{C}_{126}\text{H}_{112}\text{B}_2\text{NiN}_2\text{O}_6\text{P}_6$: C, 75.05; H, 5.60; N, 1.39. Found: C, 66.80; H, 6.15; N 1.35. IR (solid, cm^{-1}): 3049 (vw, $\nu_{\text{C-H}}$), 2986 (vw, $\nu_{\text{C-H}}$), 2848 (vw, $\nu_{\text{C-H}}$), 1435 (w, $\nu_{\text{P-C asym.}}$), 1170 (w, $\nu_{\text{P=O}}$), 857 (w), 693 (w).

The reaction was also repeated with the omission of NaBPh_4 to produce the BF_4 analogue $[\text{Ni}\{\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3\}_2](\text{BF}_4)_2$ (**39-A**) (0.0422 g, 0.027 mmol, 24 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): No signals observed. IR (solid, cm^{-1}): 3056 (vw, $\nu_{\text{C-H}}$), 1439 (w, $\nu_{\text{P-C asym.}}$), 1170 (w, $\nu_{\text{P=O}}$), 1118 (w), 1059 (w), 857 (w), 716 (w).

7.5.8 Preparation of $[\text{Cu}\{\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3\}_2](\text{BPh}_4)_2$ (**40**)



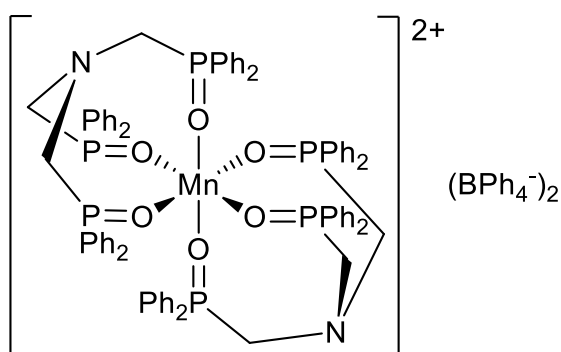
To a solution of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$ (0.15 g, 0.227 mmol, 2 equiv.) and NaBPh_4 (0.078 g, 0.227 mmol, 2 equiv.) in THF (5 mL) was added $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0394 g, 0.114 mmol, 1 equiv.) in isopropanol (5 mL) and stirred at room temperature for one hour. The resulting yellow precipitate was isolated by cannula filtration, washed with diethyl ether (3 x

1.5 mL) and dried in vacuo (0.0363 g, 0.026 mmol, 23 %). Single crystals suitable for X-ray diffraction

were grown by vapour diffusion of diethyl ether into an acetonitrile solution; the identity of the crystal was found as $[\text{Cu}\{\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3\}_2](\text{BF}_4)_2$. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): No signals observed; attributed to paramagnetism. ^1H NMR (CDCl_3 , 400 MHz): Broad, poorly resolved signals observed, attributed to paramagnetism. ES-MS (positive ion): m/z calcd. for $[\text{C}_{78}\text{H}_{72}\text{CuN}_2\text{O}_6\text{P}_6]^{2+}$ ($[\text{M}]^{2+}$) = 690.6556, found m/z = 690.6541. IR (solid, cm^{-1}): 1070 (w, br), 1021 (w), 697 (vw).

The reaction was also repeated with the omission of NaBPh_4 to produce $[\text{Cu}\{\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3\}_2](\text{BF}_4)_2$ (**40-A**) (0.0215 g, 0.014 mmol, 12 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): No signals observed. IR (solid, cm^{-1}): 3053 (w), 2878 (vw, $\nu_{\text{C-H}}$), 1439 (w, $\nu_{\text{P-C asym.}}$), 1174 (w, $\nu_{\text{P=O}}$), 1118 (w), 861 (w), 738 (w), 689 (w).

7.5.9 Preparation of $[\text{Mn}\{\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3\}_2](\text{BPh}_4)_2$ (**41**)



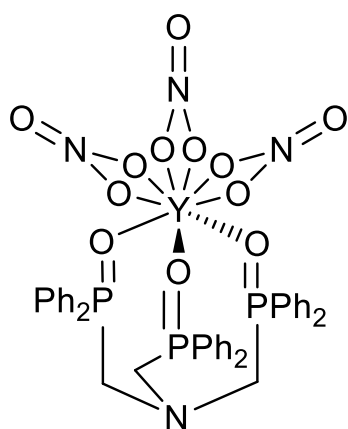
A solution of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$ (0.065 g, 0.1 mmol, 2 equiv.) in THF (5 mL) was added to a solution of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.121 g, 0.05 mmol, 1 equiv.) in methanol (6 mL) and stirred at room temperature. A white precipitate formed within a short time. The solid was isolated by cannula filtration, washed with diethyl ether (3 x 1 mL) and dried in vacuo overnight

(0.0278 g). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): No signals observed; attributed to paramagnetism. ^1H NMR (CDCl_3 , 400 MHz): Broad, poorly resolved signals observed, attributed to paramagnetism. Mass spectrometry failed to identify any doubly-charged signals. IR (solid, cm^{-1}): 3045 (vw, $\nu_{\text{C-H}}$), 2986 (vw, $\nu_{\text{C-H}}$), 1435 (w, $\nu_{\text{P-C asym.}}$), 1167 (m, $\nu_{\text{P=O}}$), 1126 (w), 857 (w), 693 (m).

7.5.10 Attempted coordination of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$ to $\text{Zn}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$

A solution of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$ (0.25 g, 0.38 mmol, 2 equiv.) in THF (8 mL) was added to a solution of $\text{Zn}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.065 g, 0.19 mmol, 1 equiv.) in 1-butanol (5 mL). The resulting mixture was stirred at RT and a white solid precipitated within a short time. After 48 hours, the solid was isolated by cannula filtration and washed with 1-butanol (2 x 2 mL) and dried in vacuo overnight. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ : 35.5 ppm (s), 30.0 ppm ($\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$). No ^1H NMR spectroscopy. ES-MS (positive ion): No product signal observed; m/z = 659.8961 ($\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$).

7.5.11 Preparation of $[Y\{N(CH_2P(O)Ph_2)_3\}(NO_3)_3]$ (**42**)



A solution of $N(CH_2P(O)Ph_2)_3$ (0.105 g, 0.16 mmol, 1 equiv.) in acetonitrile (4 mL) was added to a solution of $Y(NO_3)_3 \cdot 6H_2O$ (0.061 g, 0.16 mmol, 1 equiv.) in acetonitrile (1 mL). A white solid formed within a short time. The reaction mixture was heated to reflux overnight. After cooling to RT, the solid was isolated by cannula filtration and washed with diethyl ether (3 x 1 mL). After drying in vacuo overnight, the product was collected as a white powder (0.0674 g, 0.072 mmol, 45 %). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): No signals observed; attributed to insolubility in common NMR

solvents. $^{31}P\{^1H\}$ NMR ($DMSO-d_6$, 162 MHz) δ : 28.8 ppm (s, $N(CH_2P(O)Ph_2)_3$). ^1H NMR ($CDCl_3$, 400 MHz): No product signals observed. ES-MS (positive ion): m/z calcd. for $[C_{39}H_{36}N_3O_9P_3Y]^+$ ($[M-NO_3]^+$) = 872.0723, found m/z = 872.0712. IR (solid, cm^{-1}): 3056 (w, ν_{C-H}), 2878 (w, ν_{C-H}), 1461 (w, $\nu_{P-C_{asym}}$), 1312 (w), 1182 (w), 1148 (w, $\nu_{P=O}$), 1126 (w), 869 (w), 719 (w). Attempts to grow single crystals for X-ray diffraction by vapour diffusion of diethyl ether into methanol or acetonitrile solutions were unsuccessful, attributed to poor solubility. Further attempts to grow single crystals from in situ mixtures of $Y(NO_3)_3 \cdot 6H_2O$ and $N(CH_2P(O)Ph_2)_3$ by vapour diffusion of diethyl ether into methanol, acetonitrile or dichloromethane solutions were also unsuccessful.

7.5.12 Attempted coordination of $N(CH_2P(O)Cy_2)_3$ to $Fe(BF_4)_2 \cdot 6H_2O$

Solutions of $N(CH_2P(O)Cy_2)_3$ (0.125 g, 0.18 mmol, 2 equiv.) and $NaBPh_4$ (0.062 g, 0.18 mmol, 2 equiv.) in THF (7 mL) were added to solutions of $Fe(BF_4)_2 \cdot 6H_2O$ (0.03 g, 0.09 mmol, 1 equiv. or 0.061 g, 0.18 mmol, 2 equiv.) in isopropanol (3 or 5 mL). After stirring at RT overnight, pale-orange crystalline solids (0.0628 g) were isolated by full solvent removal in vacuo. Attempts to grow single crystals for X-ray diffraction by vapour diffusion of diethyl ether into dichloromethane or acetonitrile solutions were unsuccessful. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): No signals observed; attributed to paramagnetism. ^1H NMR ($CDCl_3$, 400 MHz): Broad, poorly resolved signals observed, attributed to paramagnetism. ES-MS (positive ion): No product signal observed; m/z = 696.4547 ($N(CH_2P(O)Cy_2)_3$). IR (solid, cm^{-1}): 2929 (m), 2855 (w), 1446 (w), 1059 (m, br), 857 (w), 701 (m).

7.5.13 Attempted coordination of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Cy}_2)_3$ to $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$

A solution of $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Cy}_2)_3$ (0.109 g, 0.16 mmol, 1 equiv.) and NaBPh_4 (0.054 g, 0.16 mmol, 1 equiv.) in THF (10 mL) was added to a solution of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.054 g, 0.16 mmol, 1 equiv.) in isopropanol (10 mL). The resulting purple-coloured mixture was stirred at RT overnight. After full solvent removal in vacuo, a purple-coloured powder was collected (0.0872 g). Single crystals were grown by vapour diffusion of diethyl ether into a dichloromethane solution; these were found not to diffract successfully or had grown as a collection of crystals rather than single crystals. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): No signals observed; attributed to paramagnetism. ^1H NMR (CDCl_3 , 400 MHz): Broad, poorly resolved signals observed, attributed to paramagnetism. ES-MS (positive ion): No product signal observed; $m/z = 696.5148$ ($\text{N}(\text{CH}_2\text{P}(\text{O})\text{Cy}_2)_3$). IR (solid, cm^{-1}): 2930 (w), 2855 (w), 1446 (w), 1070 (m, br), 869 (w), 734 (w), 701 (m).

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Appendix A

Supplementary Information: Crystallographic Data

This appendix contains crystallographic data and geometric parameters of compounds which have had their crystal structures determined by single crystal X-ray diffraction.

Table A1 – Crystallographic data for 1 and 2	A2
Table A2 – Crystallographic data for 3 , 4 and 5	A3
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Table A1. Crystallographic data for [Me-N(CH₂PCy₂)₂PdCl₂] (**1**) (A) and (B) and [Me-N(CH₂PCy₂)₂PdI₂] (**2**).

Compound	[Me-N(CH ₂ PCy ₂) ₂ PdCl ₂] (1)	[Me-N(CH ₂ PCy ₂) ₂ PdCl ₂] (1)	[Me-N(CH ₂ PCy ₂) ₂ PdI ₂] (2)
Identification code	PWM1701	PWM2002	PWM2006
Formula	C ₂₇ H ₅₁ Cl ₂ NP ₂ Pd, CH ₂ Cl ₂	C ₂₇ H ₅₁ Cl ₂ NP ₂ Pd	C ₂₇ H ₅₁ I ₂ NP ₂ Pd
Formula weight	713.85	628.92	811.83
Temperature (K)	173(2)	173(2)	173(2)
Diffractometer	Agilent Xcalibur 3 E	Agilent Xcalibur 3 E	Agilent Xcalibur 3 E,
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P2 ₁	P2 ₁ /n	P1
Unit cell dimensions			
a (Å)	9.4685(3)	11.6371(3)	9.6270(4)
b (Å)	17.3688(5)	17.9594(4)	9.7726(4)
c (Å)	10.4064(3)	14.8740(4)	10.0851(4)
α (°)	90	90	101.050(3)
β (°)	103.102(3)	110.216(3)	101.912(4)
γ (°)	90	90	117.706(4)
Volume (Å ³)	1666.84(9)	2917.09(14)	775.31(6)
Z	2	4	1
Density (calculated) (Mg/m ³)	1.422	1.432	1.739
Absorption coefficient (mm ⁻¹)	0.992	0.946	2.709
F(000)	744	1320	402
Crystal colour / morphology	Colourless blocky needles	Brown blocks	Orange needles
Crystal size (mm ³)	0.53 x 0.29 x 0.23	0.666 x 0.523 x 0.275	0.441 x 0.232 x 0.077
θ range for data collection (°)	2.628 to 28.301	2.697 to 28.244°	2.454 to 28.342
Index ranges	-12<=h<=8, -23<=k<=20, -11<=l<=13	-13<=h<=14, -23<=k<=23, -16<=l<=19	-12<=h<=12, -11<=k<=11, -12<=l<=12
Reflns collected / unique	6265 / 4966 [R(int) = 0.0135]	9886 / 5842 [R(int) = 0.0145]	10280 / 6146 [R(int) = 0.0238]
Reflns observed [F>4σ(F)]	4845	4995	5932
Absorption correction	Analytical	Analytical	Analytical
Max. and min. transmission	0.810 and 0.691	0.774 and 0.659	0.829 and 0.480
Data / restraints / parameters	4966 / 1 / 326	5842 / 0 / 300	6146 / 3 / 299
Goodness-of-fit on F ²	1.050	1.068	1.024
Final R indices [F>4σ(F)]	R1 = 0.0244, wR2 = 0.0574	R1 = 0.0267, wR2 = 0.0573	R1 = 0.0243, wR2 = 0.0493
R indices (all data)	R1 = 0.0255, wR2 = 0.0582	R1 = 0.0358, wR2 = 0.0613	R1 = 0.0261, wR2 = 0.0503
Absolute structure parameter	-0.016(17)		-0.024(11)
Largest diff. peak, hole	0.735, -0.557 eÅ ⁻³	0.521, -0.467 eÅ ⁻³	0.413, -0.573 eÅ ⁻³
Mean and maximum shift/error	0.000 and 0.000	0.000 and 0.001	0.000 and 0.000

Table A2. Crystallographic data for [Me-N(CH₂P(^tBu)₂)₂PdCl₂] (**3**), [Me-N(CH₂PPh₂)₂PdCl₂] (**4**) and [Bn-N(CH₂PPh₂)₂PdCl₂] (**5**).

Compound	[Me-N(CH ₂ P(^t Bu) ₂) ₂ PdCl ₂] (3)	[Me-N(CH ₂ PPh ₂) ₂ PdCl ₂] (4)	[Bn-N(CH ₂ PPh ₂) ₂ PdCl ₂] (5)
Identification code	PWM1708	PWM1702	PWM1704
Formula	C ₁₉ H ₄₃ Cl ₂ NP ₂ Pd, CH ₂ Cl ₂	C ₂₇ H ₂₇ Cl ₂ NP ₂ Pd	C ₃₃ H ₃₁ Cl ₂ NP ₂ Pd, CH ₂ Cl ₂
Formula weight	609.71	604.73	765.75
Temperature (K)	173(2)	173(2)	173(2)
Diffractometer	Agilent Xcalibur 3 E	Agilent Xcalibur 3 E	Agilent Xcalibur PX Ultra A
Wavelength (Å)	0.71073	0.71073	1.54184
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	P2 ₁ /n	Pnma	P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions			
a (Å)	12.5489(10)	17.0286(5)	8.07065(15)
b (Å)	15.0943(11)	20.7914(6)	19.9466(4)
c (Å)	15.4650(16)	7.2598(2)	21.0591(4)
α (°)	90	90	90
β (°)	90.442(8)	90	90
γ (°)	90	90	90
Volume (Å ³)	2929.3(4)	2570.33(13)	3390.12(12)
Z	4	4	4
Density (calculated) (Mg/m ³)	1.383	1.563	1.500
Absorption coefficient (mm ⁻¹)	1.116	1.071	8.397
F(000)	1264	1224	1552
Crystal colour / morphology	Pale yellow blocky needles	Colourless blocks	Colourless thin needles
Crystal size (mm ³)	0.598 x 0.323 x 0.230	0.33 x 0.18 x 0.10	0.34 x 0.02 x 0.01
θ range for data collection (°)	2.481 to 28.292	2.972 to 28.339	4.199 to 73.695
Index ranges	-16 ≤ h ≤ 14, -18 ≤ k ≤ 15, -19 ≤ l ≤ 14	-22 ≤ h ≤ 14, -26 ≤ k ≤ 23, -4 ≤ l ≤ 8	-8 ≤ h ≤ 9, -24 ≤ k ≤ 22, -14 ≤ l ≤ 25
Reflns collected / unique	16842 / 5928 [R(int) = 0.0511]	6019 / 2695 [R(int) = 0.0321]	7083 / 5432 [R(int) = 0.0471]
Reflns observed [F > 4σ(F)]	5197	2288	4718
Absorption correction	Analytical	Analytical	Analytical
Max. and min. transmission	0.827 and 0.576	0.885 and 0.758	0.888 and 0.346
Data / restraints / parameters	5928 / 98 / 294	2695 / 0 / 156	5432 / 49 / 380
Goodness-of-fit on F ²	1.065	1.033	0.997
Final R indices [F > 4σ(F)]	R1 = 0.0487, wR2 = 0.1192	R1 = 0.0308, wR2 = 0.0665	R1 = 0.0378, wR2 = 0.0784
R indices (all data)	R1 = 0.0594, wR2 = 0.1304	R1 = 0.0400, wR2 = 0.0713	R1 = 0.0481, wR2 = 0.0839
Absolute structure parameter			-0.016(10)
Largest diff. peak, hole	1.134, -1.531 eÅ ⁻³	0.450, -0.491 eÅ ⁻³	0.441, -0.683 eÅ ⁻³
Mean and maximum shift/error	0.000 and 0.002	0.000 and 0.001	0.000 and 0.001

Table A3. Crystallographic data for [C(OEt)₂HCH₂-N(CH₂PCy₂)₂PdCl₂] (**6**), [C₂₇H₅₃N₂O₄P](PdCl₄) and [P(O)Ph₂CH₂-N(CH₂PPh₂)₂PdCl₂] (**7**).

Compound	[C(OEt) ₂ HCH ₂ -N(CH ₂ PCy ₂) ₂ PdCl ₂] (6)	[C ₂₇ H ₅₃ N ₂ O ₄ P](PdCl ₄)	[P(O)Ph ₂ CH ₂ -N(CH ₂ PPh ₂) ₂ PdCl ₂] (7)
Identification code	PWM2004	PWM2003	PWM1810
Formula	C ₃₂ H ₆₁ Cl ₂ NO ₂ P ₂ Pd, 0.5(C ₄ H ₁₀ O), 0.5(CH ₂ Cl ₂)	C ₂₇ H ₅₃ N ₂ O ₄ P, Cl ₄ Pd	C ₃₉ H ₃₆ Cl ₂ NOP ₃ Pd, 1.375(CH ₂ Cl ₂)
Formula weight	810.58	748.88	921.67
Temperature (K)	173(2)	173(2)	173(2)
Diffractometer	Agilent Xcalibur 3 E	Agilent Xcalibur 3 E	Agilent Xcalibur 3 E
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	P-1	Pbca	P2 ₁ /c
Unit cell dimensions			
a (Å)	11.5616(4)	15.2225(5)	19.5979(5)
b (Å)	14.8519(5)	15.0861(6)	23.5321(5)
c (Å)	23.8031(9)	29.6899(13)	17.6809(4)
α (°)	98.694(3)	90	90
β (°)	94.603(3)	90	91.0387(18)
γ (°)	92.635(3)	90	90
Volume (Å ³)	4020.3(3)	6818.2(5)	8152.8(3)
Z	4	8	8
Density (calculated) (Mg/m ³)	1.339	1.459	1.502
Absorption coefficient (mm ⁻¹)	0.771	0.938	0.918
F(000)	1712	3120	3742
Crystal colour /morphology	Colourless tablets	Pale brown plates	Pale yellow blocks
Crystal size (mm ³)	0.479 x 0.174 x 0.107	0.664 x 0.475 x 0.015	0.608 x 0.258 x 0.163
θ range for data collection (°)	2.314 to 28.240	2.700 to 28.178	2.461 to 28.280
Index ranges	-10<=h<=15, -18<=k<=19, -29<=l<=31	-11<=h<=20, -10<=k<=18, -37<=l<=34	-24<=h<=19, -30<=k<=20, -15<=l<=22
Reflns collected / unique	23324 / 15807 [R(int) = 0.0263]	15731 / 6931 [R(int) = 0.0313]	27875 / 16255 [R(int) = 0.0244]
Reflns observed [F>4σ(F)]	12356	5153	12406
Absorption correction	Analytical	Analytical	Analytical
Max. and min. transmission	0.933 and 0.780	0.982 and 0.660	0.883 and 0.772
Data / restraints / parameters	15807 / 144 / 857	6931 / 60 / 383	16255 / 37 / 848
Goodness-of-fit on F ²	1.145	1.142	1.034
Final R indices [F>4σ(F)]	R1 = 0.0591, wR2 = 0.1170	R1 = 0.0468, wR2 = 0.0781	R1 = 0.0393, wR2 = 0.0792
R indices (all data)	R1 = 0.0793, wR2 = 0.1246	R1 = 0.0753, wR2 = 0.0879	R1 = 0.0612, wR2 = 0.0889
Absolute structure parameter			
Largest diff. peak, hole	0.750, -0.656 eÅ ⁻³	0.817, -0.745 eÅ ⁻³	0.557, -0.465 eÅ ⁻³
Mean and maximum shift/error	0.000 and 0.003	0.000 and 0.002	0.000 and 0.002

Table A4. Crystallographic data for [P(O)Cy₂CH₂-N(CH₂PCy₂)₂PdCl₂] (**8**), [P(O)(^tBu)₂CH₂-N(CH₂P(^tBu)₂)₂PdCl₂] (**10**) and [Me-N(CH₂PPh₂)₂NiCl₂] (**11**).

Compound	[P(O)Cy ₂ CH ₂ -N(CH ₂ PCy ₂) ₂ PdCl ₂] (8)	[P(O)(^t Bu) ₂ CH ₂ -N(CH ₂ P(^t Bu) ₂) ₂ PdCl ₂] (10)	[Me-N(CH ₂ PPh ₂) ₂ NiCl ₂] (11)
Identification code	PWM1809	PWM1812	PWM1803
Formula	C ₃₉ H ₇₂ Cl ₂ NOP ₃ Pd, 2.5(CH ₂ Cl ₂)	C ₂₇ H ₆₀ Cl ₂ NOP ₃ Pd	C ₂₇ H ₂₇ Cl ₂ NNiP ₂
Formula weight	1053.50	684.97	557.04
Temperature (K)	173(2)	173(2)	173(2)
Diffractometer	Agilent Xcalibur 3 E	Agilent Xcalibur PX Ultra A	Agilent Xcalibur 3 E
Wavelength (Å)	0.71073	1.54184	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	P2 ₁ /c	P2 ₁ /c	Pnma
Unit cell dimensions			
a (Å)	21.0724(6)	18.0522(7)	16.8548(5)
b (Å)	14.5876(4)	12.4552(4)	20.6576(8)
c (Å)	18.1270(8)	15.3171(6)	7.2794(2)
α (°)	90	90	90
β (°)	106.492(4)	99.703(4)	90
γ (°)	90	90	90
Volume (Å ³)	5342.9(3)	3394.7(2)	2534.53(15)
Z	4	4	4
Density (calculated) (Mg/m ³)	1.310	1.340	1.460
Absorption coefficient (mm ⁻¹)	0.817	7.337	1.119
F(000)	2204	1448	1152
Crystal colour /morphology	Colourless blocks	Yellow shards	Orange plates
Crystal size (mm ³)	0.524 x 0.269 x 0.182	0.124 x 0.115 x 0.061	0.412 x 0.236 x 0.055
Θ range for data collection (°)	2.459 to 28.322	4.333 to 73.271	2.967 to 28.215
Index ranges	-27<=h<=25, -18<=k<=18, -13<=l<=23	-17<=h<=22, -10<=k<=14, -18<=l<=9	-12<=h<=21, -27<=k<=17, -9<=l<=6
Reflns collected / unique	18696 / 10683 [R(int) = 0.0356]	10619 / 6475 [R(int) = 0.0491]	5709 / 2652 [R(int) = 0.0264]
Reflns observed [F>4σ(F)]	7463	4719	2193
Absorption correction	Analytical	Analytical	Analytical
Max. and min. transmission	0.900 and 0.752	0.676 and 0.515	0.933 and 0.782
Data / restraints / parameters	10683 / 699 / 600	6475 / 0 / 334	2652 / 0 / 155
Goodness-of-fit on F ²	1.069	1.038	1.041
Final R indices [F>4σ(F)]	R1 = 0.0618, wR2 = 0.1416	R1 = 0.0515, wR2 = 0.1268	R1 = 0.0326, wR2 = 0.0695
R indices (all data)	R1 = 0.1014, wR2 = 0.1708	R1 = 0.0766, wR2 = 0.1466	R1 = 0.0442, wR2 = 0.0756
Absolute structure parameter			
Largest diff. peak, hole	1.224, -0.826 eÅ ⁻³	1.372, -0.717 eÅ ⁻³	0.346, -0.333 eÅ ⁻³
Mean and maximum shift/error	0.000 and 0.008	0.000 and 0.000	0.000 and 0.001

Table A5. Crystallographic data for [Me-N(CH₂PCy₂)₂NiCl₂] (**12**), [Me-N(CH₂PCy₂)₂Ru(η⁶-*p*-cymene)Cl]Cl (**13**) and [MeN(CH₂PCy₂)₂Ir(COD)]PF₆ (**19**).

Compound	[Me-N(CH ₂ PCy ₂) ₂ NiCl ₂] (12)	[Me-N(CH ₂ PCy ₂) ₂ Ru(η ⁶ - <i>p</i> -cymene)Cl]Cl (13)	[MeN(CH ₂ PCy ₂) ₂ Ir(COD)]PF ₆ (19)
Identification code	PWM1802	PWM1807	PWM1904
Formula	C ₂₇ H ₅₁ Cl ₂ NNiP ₂ , CH ₂ Cl ₂	C ₃₇ H ₆₅ ClNP ₂ Ru, Cl, 0.8125(H ₂ O), 0.625(C ₄ H ₁₀ O)	C ₃₅ H ₆₃ IrNP ₂ , F ₆ P
Formula weight	666.16	818.77	896.97
Temperature (K)	173(2)	173(2)	173(2)
Diffractionmeter	Agilent Xcalibur 3 E	Agilent Xcalibur PX Ultra A	Agilent Xcalibur PX Ultra A
Wavelength (Å)	0.71073	1.54184	1.54184
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P2 ₁	Pbcn	P2 ₁ /c
Unit cell dimensions			
a (Å)	9.4993(5)	31.7445(3)	9.7774(3)
b (Å)	17.1082(8)	18.42095(14)	19.2840(5)
c (Å)	10.3607(5)	29.0505(3)	20.0076(5)
α (°)	90	90	90
β (°)	102.226(5)	90	100.178(3)
γ (°)	90	90	90
Volume (Å ³)	1645.60(14)	16987.7(3)	3713.01(18)
Z	2	16	4
Density (calculated) (Mg/m ³)	1.344	1.281	1.605
Absorption coefficient (mm ⁻¹)	1.030	5.081	8.660
F(000)	708	6982	1824
Crystal colour / morphology	Orange blocky needles	Orange blocky needles	Red needles
Crystal size (mm ³)	0.782 x 0.197 x 0.136	0.391 x 0.105 x 0.104	0.164 x 0.050 x 0.050
Θ range for data collection (°)	2.337 to 28.257	3.346 to 73.853	4.491 to 73.407
Index ranges	-12<=h<=7, -11<=k<=22, -10<=l<=13	-38<=h<=18, -22<=k<=21, -20<=l<=35	-11<=h<=10, -14<=k<=23, -24<=l<=20
Reflns collected / unique	6005 / 4130 [R(int) = 0.0274]	35040 / 16601 [R(int) = 0.0322]	11469 / 7090 [R(int) = 0.0561]
Reflns observed [F>4σ(F)]	3730	13579	4948
Absorption correction	Analytical	Analytical	Analytical
Max. and min. transmission	0.916 and 0.563	0.685 and 0.388	0.692 and 0.425
Data / restraints / parameters	4130 / 26 / 340	16601 / 3 / 811	7090 / 384 / 445
Goodness-of-fit on F ²	1.021	1.017	0.975
Final R indices [F>4σ(F)]	R1 = 0.0350, wR2 = 0.0719	R1 = 0.0356, wR2 = 0.0889	R1 = 0.0465, wR2 = 0.1024
R indices (all data)	R1 = 0.0419, wR2 = 0.0757	R1 = 0.0473, wR2 = 0.0977	R1 = 0.0767, wR2 = 0.1172
Absolute structure parameter	-0.018(16)		
Largest diff. peak, hole	0.391, -0.344 eÅ ⁻³	0.931, -0.732 eÅ ⁻³	1.858, -1.049 eÅ ⁻³
Mean and maximum shift/error	0.000 and 0.001	0.000 and 0.003	0.000 and 0.000

Table A6. Crystallographic data for [Me-N(CH₂PCy₂)₂Ir(Cl)₃(OH₂)] (**20**), [{Rh(Cl)(Me-N(CH₂PCy₂)₂)₂(μ-Cl)₃]BF₄ (**25**) and [Co₂(N(CH₂PPh₂{CH₂P(O)Ph₂})₂)(μ²-OH)₂](BF₄)₂ (**32**).

Compound	[Me-N(CH ₂ PCy ₂) ₂ Ir(Cl) ₃ (OH ₂)] (20)	[[Rh(Cl)(Me-N(CH ₂ PCy ₂) ₂) ₂ (μ-Cl) ₃]BF ₄ (25)	[Co ₂ (N(CH ₂ PPh ₂ {CH ₂ P(O)Ph ₂ }) ₂)(μ ² -OH) ₂](BF ₄) ₂ (32)
Identification code	PWM1906	PWM1905	PWM1602
Formula	C ₂₇ H ₅₃ Cl ₃ IrNOP ₂ , 0.75(C ₄ H ₁₀ O), 0.5(CHCl ₃)	C ₅₄ H ₁₀₂ Cl ₅ N ₂ P ₄ Rh ₂ , BF ₄ , 3(CHCl ₃)	C ₇₈ H _{73.5} Cl _{0.5} Co ₂ N ₂ O _{5.5} P ₆ , 2(BF ₄), 4(CH ₂ Cl ₂)
Formula weight	883.46	1731.23	1961.61
Temperature (K)	173(2)	173(2)	173(2)
Diffractometer	Agilent Xcalibur 3 E	Agilent Xcalibur 3 E	Agilent Xcalibur 3 E
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P2 ₁ /c
Unit cell dimensions			
a (Å)	13.1097(4)	13.4291(4)	13.06410(19)
b (Å)	17.9464(5)	17.0216(4)	14.2006(3)
c (Å)	18.9091(7)	19.0365(6)	23.5346(4)
α (°)	63.501(3)	75.982(2)	90
β (°)	76.082(3)	70.008(3)	96.6137(15)
γ (°)	74.072(3)	74.546(2)	90
Volume (Å ³)	3792.3(2)	3886.1(2)	4337.04(12)
Z	4	2	2
Density (calculated) (Mg/m ³)	1.547	1.480	1.502
Absorption coefficient (mm ⁻¹)	3.949	1.034	0.825
F(000)	1794	1780	2004
Crystal colour / morphology	Colourless blocks	Yellow blocks	Pale pink-dark pink dichroic blocks
Crystal size (mm ³)	0.251 x 0.202 x 0.120	0.354 x 0.212 x 0.156	0.24 x 0.23 x 0.13
θ range for data collection (°)	2.267 to 28.347	2.360 to 28.284	2.257 to 28.150
Index ranges	-16 ≤ h ≤ 17, -21 ≤ k ≤ 16, -22 ≤ l ≤ 15	-17 ≤ h ≤ 17, -21 ≤ k ≤ 20, -22 ≤ l ≤ 23	-11 ≤ h ≤ 17, -18 ≤ k ≤ 13, -29 ≤ l ≤ 31
Reflns collected / unique	22367 / 15041 [R(int) = 0.0235]	22646 / 15327 [R(int) = 0.0210]	15685 / 8638 [R(int) = 0.0196]
Reflns observed [F > 4σ(F)]	11395	12060	7017
Absorption correction	Analytical	Analytical	Analytical
Max. and min. transmission	0.697 and 0.484	0.892 and 0.806	0.916 and 0.866
Data / restraints / parameters	15041 / 137 / 780	15327 / 298 / 831	8638 / 303 / 559
Goodness-of-fit on F ²	1.050	1.013	1.044
Final R indices [F > 4σ(F)]	R1 = 0.0397, wR2 = 0.0806	R1 = 0.0383, wR2 = 0.0830	R1 = 0.0644, wR2 = 0.1592
R indices (all data)	R1 = 0.0652, wR2 = 0.0920	R1 = 0.0562, wR2 = 0.0920	R1 = 0.0800, wR2 = 0.1703
Largest diff. peak, hole	1.672, -1.148 eÅ ⁻³	0.902, -0.654 eÅ ⁻³	1.043, -1.101 eÅ ⁻³
Mean and maximum shift/error	0.000 and 0.001	0.000 and 0.002	0.000 and 0.002

Table A7. Crystallographic data for $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$ (**34**), $\text{N}(\text{CH}_2\text{P}(\text{O})\text{Cy}_2)_3$ (**35**) and $[\text{Fe}\{\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3\}_2](\text{BPh}_4)_2$ (**37**).

Compound	$\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$ (34)	$\text{N}(\text{CH}_2\text{P}(\text{O})\text{Cy}_2)_3$ (35)	$[\text{Fe}\{\text{N}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3\}_2](\text{BPh}_4)_2$ (37)
Identification code	PWM1709	PWM1811	PWM1604
Formula	$\text{C}_{39}\text{H}_{36}\text{NO}_3\text{P}_3$, H_2O_2 , $0.5(\text{H}_2\text{O})$	$\text{C}_{39}\text{H}_{72}\text{NO}_3\text{P}_3$	$\text{C}_{78}\text{H}_{72}\text{FeN}_2\text{O}_6\text{P}_6$, $2(\text{C}_{24}\text{H}_{20}\text{B})$, $1.5(\text{CH}_2\text{Cl}_2)$
Formula weight	702.62	695.88	2140.85
Temperature (K)	173(2)	173(2)	173(2)
Diffractometer	Agilent Xcalibur 3 E	Agilent Xcalibur 3 E	Agilent Xcalibur 3 E
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pbcn	$\text{P}2_1/\text{c}$	$\text{C}2/\text{c}$
Unit cell dimensions			
a (Å)	13.6336(4)	10.3044(2)	20.8796(7)
b (Å)	19.7591(7)	19.2321(4)	18.2086(6)
c (Å)	26.8567(11)	19.8514(4)	28.8297(9)
α (°)	90	90	90
β (°)	90	90.0732(18)	90.896(3)
γ (°)	90	90	90
Volume (Å ³)	7234.9(4)	3934.06(14)	10959.4(6)
Z	8	4	4
Density (calculated) (Mg/m ³)	1.290	1.175	1.298
Absorption coefficient (mm ⁻¹)	0.210	0.187	0.357
F(000)	2952	1528	4476
Crystal colour / morphology	Colourless tablets	Colourless blocks	Colourless blocks
Crystal size (mm ³)	0.602 x 0.385 x 0.174	0.555 x 0.457 x 0.414	0.22 x 0.14 x 0.08
Θ range for data collection (°)	2.559 to 28.288	2.465 to 28.225	2.391 to 28.299
Index ranges	-17<= h <=11, -26<= k <=13, -32<= l <=28	-13<= h <=9, -24<= k <=24, -20<= l <=26	-25<= h <=27, -23<= k <=14, -20<= l <=38
Reflns collected / unique	16332 / 7399 [R(int) = 0.0272]	21496 / 8117 [R(int) = 0.0251]	19055 / 10885 [R(int) = 0.0404]
Reflns observed [$F > 4\sigma(F)$]	5476	6469	6733
Absorption correction	Analytical	Analytical	Analytical
Max. and min. transmission	0.967 and 0.933	0.942 and 0.925	0.976 and 0.945
Data / restraints / parameters	7399 / 593 / 563	8117 / 0 / 415	10885 / 11 / 685
Goodness-of-fit on F^2	1.073	1.028	1.042
Final R indices [$F > 4\sigma(F)$]	R1 = 0.0555, wR2 = 0.1363	R1 = 0.0429, wR2 = 0.0970	R1 = 0.0730, wR2 = 0.1420
R indices (all data)	R1 = 0.0811, wR2 = 0.1514	R1 = 0.0594, wR2 = 0.1066	R1 = 0.1277, wR2 = 0.1700
Absolute structure parameter			
Largest diff. peak, hole	0.657, -0.270 eÅ ⁻³	0.497, -0.414 eÅ ⁻³	0.487, -0.583 eÅ ⁻³
Mean and maximum shift/error	0.000 and 0.001	0.000 and 0.000	0.000 and 0.001

Table A8. Crystallographic data for [Co{N(CH₂P(O)Ph₂)₃}₂](BPh₄)₂ (**38**) (A) and (B) and [Ni{N(CH₂P(O)Ph₂)₃}₂](BPh₄)₂ (**39**).

Compound	[Co{N(CH ₂ P(O)Ph ₂) ₃ } ₂](BPh ₄) ₂ (38)	[Co{N(CH ₂ P(O)Ph ₂) ₃ } ₂](BPh ₄) ₂ (38)	[Ni{N(CH ₂ P(O)Ph ₂) ₃ } ₂](BPh ₄) ₂ (39)
Identification code	PWM1603	PWM1605	PWM1804b
Formula	C ₇₈ H ₇₂ CoN ₂ O ₆ P ₆ , 2(C ₂₄ H ₂₀ B), 4(C ₂ H ₃ N)	C ₇₈ H ₇₂ CoN ₂ O ₆ P ₆ , 2(C ₂₄ H ₂₀ B), 4(C ₂ H ₃ N)	C ₇₈ H ₇₂ NiN ₂ O ₆ P ₆ , 2(C ₂₄ H ₂₀ B), 4(C ₂ H ₃ N)
Formula weight	2180.75	2180.75	2180.53
Temperature (K)	173(2)	173(2)	173(2)
Diffractometer	Agilent Xcalibur PX Ultra A	Agilent Xcalibur PX Ultra A	Agilent Xcalibur PX Ultra A
Wavelength (Å)	1.54184	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
Unit cell dimensions			
a (Å)	13.45423(11)	13.45476(8)	13.47027(12)
b (Å)	20.01419(18)	20.00475(14)	19.9660(2)
c (Å)	21.7089(2)	21.70642(16)	21.70578(19)
α (°)	90	90	90
β (°)	96.5768(8)	96.5856(6)	96.6359(8)
γ (°)	90	90	90
Volume (Å ³)	5807.21(9)	5803.93(7)	5798.59(9)
Z	2	2	2
Density (calculated) (Mg/m ³)	1.247	1.248	1.249
Absorption coefficient (mm ⁻¹)	2.402	2.404	1.487
F(000)	2290	2290	2292
Crystal colour / morphology	Colourless needles	Colourless needles	Colourless needles
Crystal size (mm ³)	0.30 x 0.03 x 0.02	0.33 x 0.07 x 0.07	0.316 x 0.062 x 0.036
θ range for data collection (°)	3.307 to 73.827	3.307 to 73.861	3.303 to 73.909
Index ranges	-16<=h<=15, -13<=k<=24, -21<=l<=26	-15<=h<=16, -17<=k<=23, -24<=l<=26	-12<=h<=15, -21<=k<=24, -24<=l<=26
Reflns collected / unique	19750 / 11151 [R(int) = 0.0275]	19829 / 11166 [R(int) = 0.0244]	19073 / 11172 [R(int) = 0.0320]
Reflns observed [F>4σ(F)]	8861	9450	9013
Absorption correction	Analytical	Analytical	Analytical
Max. and min. transmission	0.954 and 0.707	0.862 and 0.605	0.952 and 0.792
Data / restraints / parameters	11151 / 0 / 703	11166 / 0 / 702	11172 / 0 / 702
Goodness-of-fit on F ²	1.059	1.038	1.010
Final R indices [F>4σ(F)]	R1 = 0.0369, wR2 = 0.0922	R1 = 0.0347, wR2 = 0.0851	R1 = 0.0372, wR2 = 0.0889
R indices (all data)	R1 = 0.0504, wR2 = 0.0962	R1 = 0.0440, wR2 = 0.0901	R1 = 0.0513, wR2 = 0.0987
Absolute structure parameter			
Largest diff. peak, hole	0.304, -0.297 eÅ ⁻³	0.372, -0.280 eÅ ⁻³	0.366, -0.300 eÅ ⁻³
Mean and maximum shift/error	0.000 and 0.001	0.000 and 0.002	0.000 and 0.001

Table A9. Crystallographic data for [Cu{N(CH₂P(O)Ph₂)₃}₂](BF₄)₂ (**40-A**) and [Mn{N(CH₂P(O)Ph₂)₃}₂](BPh₄)₂ (**41**).

Compound	[Cu{N(CH ₂ P(O)Ph ₂) ₃ } ₂](BF ₄) ₂ (40-A)	[Mn{N(CH ₂ P(O)Ph ₂) ₃ } ₂](BPh ₄) ₂ (41)
Identification code	PWM1801	PWM2005
Formula	C ₇₈ H ₇₂ CuN ₂ O ₆ P ₆ , 2(BF ₄), 4(C ₂ H ₃ N)	C ₇₈ H ₇₂ MnN ₂ O ₆ P ₆ , 2(C ₂₄ H ₂₀ B), 5.5(CH ₂ Cl ₂)
Formula weight	1720.57	2479.64
Temperature (K)	173(2)	173(2)
Diffractometer	Agilent Xcalibur PX Ultra A	Agilent Xcalibur PX Ultra A
Wavelength (Å)	1.54184	1.54184
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2 ₁ /n
Unit cell dimensions		
a (Å)	12.3925(9)	13.4993(3)
b (Å)	13.0398(10)	16.5259(3)
c (Å)	13.8009(10)	28.4839(6)
α (°)	72.638(7)	90
β (°)	89.866(6)	93.818(2)
γ (°)	79.572(6)	90
Volume (Å ³)	2090.2(3)	6340.3(2)
Z	1	2
Density (calculated) (Mg/m ³)	1.367	1.299
Absorption coefficient (mm ⁻¹)	2.079	4.122
F(000)	891	2572
Crystal colour / morphology	Colourless blocks	Colourless blocks
Crystal size (mm ³)	0.140 x 0.107 x 0.101	0.277 x 0.157 x 0.076
Θ range for data collection (°)	3.360 to 73.785	4.103 to 73.446
Index ranges	-12<=h<=15, -15<=k<=16, -17<=l<=12	-16<=h<=15, -11<=k<=20, -30<=l<=35
Reflns collected / unique	12006 / 7969 [R(int) = 0.0609]	21017 / 12177 [R(int) = 0.0574]
Reflns observed [F>4σ(F)]	5191	7994
Absorption correction	Analytical	Analytical
Max. and min. transmission	0.853 and 0.818	0.740 and 0.414
Data / restraints / parameters	7969 / 43 / 523	12177 / 0 / 646
Goodness-of-fit on F ²	0.986	0.977
Final R indices [F>4σ(F)]	R1 = 0.0676, wR2 = 0.1638	R1 = 0.0541, wR2 = 0.1217
R indices (all data)	R1 = 0.1051, wR2 = 0.2031	R1 = 0.0886, wR2 = 0.1442
Absolute structure parameter		
Largest diff. peak, hole	0.988, -0.558 eÅ ⁻³	0.467, -0.433 eÅ ⁻³
Mean and maximum shift/error	0.000 and 0.000	0.000 and 0.001

Table A10. Geometric parameters of [Me-N(CH₂PCy₂)₂PdCl₂] (**1**) (A).

Bond lengths (Å)		Bond angles (°)			
Pd(1)-P(5)	2.2385(11)	P(5)-Pd(1)-P(3)	95.35(4)	C(23)-C(24)-C(19)	109.8(4)
Pd(1)-P(3)	2.2493(10)	P(5)-Pd(1)-Cl(1)	86.94(4)	C(26)-C(25)-C(30)	111.1(3)
Pd(1)-Cl(1)	2.3472(10)	P(3)-Pd(1)-Cl(1)	177.61(4)	C(26)-C(25)-P(5)	115.9(3)
Pd(1)-Cl(2)	2.3554(10)	P(5)-Pd(1)-Cl(2)	173.55(4)	C(30)-C(25)-P(5)	110.5(3)
N(1)-C(2)	1.464(5)	P(3)-Pd(1)-Cl(2)	88.40(4)	C(25)-C(26)-C(27)	109.3(4)
N(1)-C(4)	1.466(5)	Cl(1)-Pd(1)-Cl(2)	89.26(4)	C(28)-C(27)-C(26)	111.7(4)
N(1)-C(6)	1.468(5)	C(2)-N(1)-C(4)	110.8(3)	C(27)-C(28)-C(29)	111.4(4)
C(2)-P(3)	1.842(4)	C(2)-N(1)-C(6)	109.8(3)	C(28)-C(29)-C(30)	111.3(4)
P(3)-C(7)	1.845(4)	C(4)-N(1)-C(6)	110.3(3)	C(25)-C(30)-C(29)	110.5(4)
P(3)-C(13)	1.845(4)	N(1)-C(2)-P(3)	114.5(3)	Cl(42)-C(40)-Cl(41)	113.6(3)
C(4)-P(5)	1.826(4)	C(2)-P(3)-C(7)	100.7(2)		
P(5)-C(19)	1.828(4)	C(2)-P(3)-C(13)	103.58(19)		
P(5)-C(25)	1.841(4)	C(7)-P(3)-C(13)	106.66(19)		
C(7)-C(8)	1.530(6)	C(2)-P(3)-Pd(1)	118.39(13)		
C(7)-C(12)	1.533(7)	C(7)-P(3)-Pd(1)	115.84(12)		
C(8)-C(9)	1.535(6)	C(13)-P(3)-Pd(1)	110.33(14)		
C(9)-C(10)	1.523(7)	N(1)-C(4)-P(5)	114.2(3)		
C(10)-C(11)	1.523(7)	C(4)-P(5)-C(19)	102.81(19)		
C(11)-C(12)	1.526(6)	C(4)-P(5)-C(25)	102.77(19)		
C(13)-C(14)	1.529(6)	C(19)-P(5)-C(25)	106.79(18)		
C(13)-C(18)	1.534(6)	C(4)-P(5)-Pd(1)	117.31(14)		
C(14)-C(15)	1.536(6)	C(19)-P(5)-Pd(1)	110.02(14)		
C(15)-C(16)	1.519(8)	C(25)-P(5)-Pd(1)	115.87(13)		
C(16)-C(17)	1.507(7)	C(8)-C(7)-C(12)	110.5(4)		
C(17)-C(18)	1.535(6)	C(8)-C(7)-P(3)	111.3(3)		
C(19)-C(20)	1.533(6)	C(12)-C(7)-P(3)	115.7(3)		
C(19)-C(24)	1.540(6)	C(7)-C(8)-C(9)	109.7(4)		
C(20)-C(21)	1.538(6)	C(10)-C(9)-C(8)	112.0(4)		
C(21)-C(22)	1.509(8)	C(9)-C(10)-C(11)	110.8(4)		
C(22)-C(23)	1.508(7)	C(10)-C(11)-C(12)	111.8(4)		
C(23)-C(24)	1.537(6)	C(11)-C(12)-C(7)	109.3(4)		
C(25)-C(26)	1.527(5)	C(14)-C(13)-C(18)	111.7(4)		
C(25)-C(30)	1.532(6)	C(14)-C(13)-P(3)	114.3(3)		
C(26)-C(27)	1.532(6)	C(18)-C(13)-P(3)	110.6(3)		
C(27)-C(28)	1.504(7)	C(13)-C(14)-C(15)	110.1(4)		
C(28)-C(29)	1.515(7)	C(16)-C(15)-C(14)	111.5(4)		
C(29)-C(30)	1.540(6)	C(17)-C(16)-C(15)	111.7(4)		
C(40)-Cl(42)	1.737(7)	C(16)-C(17)-C(18)	112.0(4)		
C(40)-Cl(41)	1.760(7)	C(13)-C(18)-C(17)	111.2(4)		
		C(20)-C(19)-C(24)	110.2(3)		
		C(20)-C(19)-P(5)	112.6(3)		
		C(24)-C(19)-P(5)	114.7(3)		
		C(19)-C(20)-C(21)	109.6(4)		
		C(22)-C(21)-C(20)	111.5(4)		
		C(23)-C(22)-C(21)	111.4(4)		
		C(22)-C(23)-C(24)	111.3(4)		

Table A11. Geometric parameters of [Me-N(CH₂PCy₂)₂PdCl₂] (**1**) (B).

Bond lengths (Å)		Bond angles (°)			
Pd(1)-P(5)	2.2483(6)	P(5)-Pd(1)-P(3)	95.08(2)	C(23)-C(24)-C(19)	110.14(19)
Pd(1)-P(3)	2.2503(6)	P(5)-Pd(1)-Cl(1)	87.04(2)	C(26)-C(25)-C(30)	109.96(19)
Pd(1)-Cl(1)	2.3543(6)	P(3)-Pd(1)-Cl(1)	177.05(2)	C(26)-C(25)-P(5)	117.06(16)
Pd(1)-Cl(2)	2.3584(6)	P(5)-Pd(1)-Cl(2)	175.93(2)	C(30)-C(25)-P(5)	110.01(15)
N(1)-C(2)	1.458(3)	P(3)-Pd(1)-Cl(2)	87.73(2)	C(27)-C(26)-C(25)	110.0(2)
N(1)-C(4)	1.465(3)	Cl(1)-Pd(1)-Cl(2)	90.26(2)	C(26)-C(27)-C(28)	111.5(2)
N(1)-C(6)	1.470(3)	C(2)-N(1)-C(4)	109.70(19)	C(29)-C(28)-C(27)	110.3(2)
C(2)-P(3)	1.840(2)	C(2)-N(1)-C(6)	109.63(18)	C(28)-C(29)-C(30)	111.2(2)
P(3)-C(7)	1.838(2)	C(4)-N(1)-C(6)	109.76(18)	C(29)-C(30)-C(25)	111.2(2)
P(3)-C(13)	1.845(2)	N(1)-C(2)-P(3)	115.00(15)		
C(4)-P(5)	1.833(2)	C(7)-P(3)-C(2)	104.31(11)		
P(5)-C(19)	1.838(2)	C(7)-P(3)-C(13)	107.56(10)		
P(5)-C(25)	1.851(2)	C(2)-P(3)-C(13)	99.85(11)		
C(7)-C(8)	1.530(3)	C(7)-P(3)-Pd(1)	110.37(7)		
C(7)-C(12)	1.531(3)	C(2)-P(3)-Pd(1)	118.47(8)		
C(8)-C(9)	1.529(3)	C(13)-P(3)-Pd(1)	115.09(8)		
C(9)-C(10)	1.524(3)	N(1)-C(4)-P(5)	112.73(15)		
C(10)-C(11)	1.516(3)	C(4)-P(5)-C(19)	103.35(10)		
C(11)-C(12)	1.523(3)	C(4)-P(5)-C(25)	101.37(11)		
C(13)-C(18)	1.530(3)	C(19)-P(5)-C(25)	107.27(10)		
C(13)-C(14)	1.533(3)	C(4)-P(5)-Pd(1)	116.81(8)		
C(14)-C(15)	1.524(4)	C(19)-P(5)-Pd(1)	112.61(7)		
C(15)-C(16)	1.518(4)	C(25)-P(5)-Pd(1)	114.18(7)		
C(16)-C(17)	1.517(4)	C(8)-C(7)-C(12)	110.84(19)		
C(17)-C(18)	1.527(4)	C(8)-C(7)-P(3)	109.90(15)		
C(19)-C(20)	1.526(3)	C(12)-C(7)-P(3)	114.99(15)		
C(19)-C(24)	1.539(3)	C(9)-C(8)-C(7)	111.98(19)		
C(20)-C(21)	1.529(3)	C(10)-C(9)-C(8)	112.1(2)		
C(21)-C(22)	1.525(3)	C(11)-C(10)-C(9)	111.6(2)		
C(22)-C(23)	1.512(3)	C(10)-C(11)-C(12)	111.2(2)		
C(23)-C(24)	1.531(3)	C(11)-C(12)-C(7)	110.53(19)		
C(25)-C(26)	1.530(3)	C(18)-C(13)-C(14)	109.7(2)		
C(25)-C(30)	1.536(3)	C(18)-C(13)-P(3)	110.66(16)		
C(26)-C(27)	1.521(3)	C(14)-C(13)-P(3)	116.05(16)		
C(27)-C(28)	1.521(4)	C(15)-C(14)-C(13)	110.3(2)		
C(28)-C(29)	1.520(4)	C(16)-C(15)-C(14)	111.3(2)		
C(29)-C(30)	1.521(3)	C(17)-C(16)-C(15)	111.2(2)		
		C(16)-C(17)-C(18)	111.7(2)		
		C(17)-C(18)-C(13)	110.8(2)		
		C(20)-C(19)-C(24)	110.61(18)		
		C(20)-C(19)-P(5)	111.24(15)		
		C(24)-C(19)-P(5)	113.40(16)		
		C(19)-C(20)-C(21)	111.26(19)		
		C(22)-C(21)-C(20)	111.0(2)		
		C(23)-C(22)-C(21)	110.34(19)		
		C(22)-C(23)-C(24)	111.4(2)		

Table A12. Geometric parameters of [Me-N(CH₂PCy₂)₂PdI₂] (**2**).

Bond lengths (Å)		Bond angles (°)			
Pd(1)-P(3)	2.2670(14)	P(3)-Pd(1)-P(5)	94.32(5)	C(16)-C(17)-C(18)	111.6(5)
Pd(1)-P(5)	2.2793(14)	P(3)-Pd(1)-I(2)	87.87(4)	C(13)-C(18)-C(17)	110.7(5)
Pd(1)-I(2)	2.6385(5)	P(5)-Pd(1)-I(2)	174.95(4)	C(24)-C(19)-C(20)	110.4(5)
Pd(1)-I(1)	2.6704(5)	P(3)-Pd(1)-I(1)	173.12(4)	C(24)-C(19)-P(5)	116.7(4)
N(1)-C(4)	1.457(7)	P(5)-Pd(1)-I(1)	90.80(4)	C(20)-C(19)-P(5)	109.3(4)
N(1)-C(2)	1.458(7)	I(2)-Pd(1)-I(1)	87.400(16)	C(21)-C(20)-C(19)	111.3(5)
N(1)-C(6)	1.471(7)	C(4)-N(1)-C(2)	110.9(4)	C(22)-C(21)-C(20)	112.1(5)
C(2)-P(3)	1.835(5)	C(4)-N(1)-C(6)	109.6(4)	C(21)-C(22)-C(23)	111.4(5)
P(3)-C(13)	1.846(5)	C(2)-N(1)-C(6)	110.6(4)	C(24)-C(23)-C(22)	111.2(5)
P(3)-C(7)	1.859(5)	N(1)-C(2)-P(3)	112.4(3)	C(23)-C(24)-C(19)	110.3(5)
C(4)-P(5)	1.852(5)	C(2)-P(3)-C(13)	102.8(2)	C(30)-C(25)-C(26)	111.4(5)
P(5)-C(25)	1.838(5)	C(2)-P(3)-C(7)	100.5(3)	C(27)-C(26)-C(25)	110.4(5)
P(5)-C(19)	1.844(5)	C(13)-P(3)-C(7)	107.6(2)	C(26)-C(27)-C(28)	110.7(5)
C(7)-C(12)	1.523(7)	C(2)-P(3)-Pd(1)	116.17(18)	C(30)-C(25)-P(5)	109.4(3)
C(7)-C(8)	1.528(7)	C(13)-P(3)-Pd(1)	113.18(18)	C(26)-C(25)-P(5)	115.9(4)
C(8)-C(9)	1.534(8)	C(7)-P(3)-Pd(1)	115.08(17)	C(29)-C(28)-C(27)	111.7(6)
C(9)-C(10)	1.516(8)	N(1)-C(4)-P(5)	116.5(3)	C(28)-C(29)-C(30)	111.4(5)
C(10)-C(11)	1.511(8)	C(25)-P(5)-C(19)	107.1(2)	C(29)-C(30)-C(25)	110.9(5)
C(11)-C(12)	1.535(8)	C(25)-P(5)-C(4)	104.5(3)		
C(13)-C(18)	1.509(8)	C(19)-P(5)-C(4)	99.1(2)		
C(13)-C(14)	1.531(7)	C(25)-P(5)-Pd(1)	111.72(17)		
C(14)-C(15)	1.533(8)	C(19)-P(5)-Pd(1)	114.04(19)		
C(15)-C(16)	1.510(9)	C(4)-P(5)-Pd(1)	119.02(17)		
C(16)-C(17)	1.501(8)	C(12)-C(7)-C(8)	109.1(4)		
C(17)-C(18)	1.523(8)	C(12)-C(7)-P(3)	115.7(4)		
C(19)-C(24)	1.521(8)	C(8)-C(7)-P(3)	111.3(4)		
C(19)-C(20)	1.534(8)	C(7)-C(8)-C(9)	110.9(5)		
C(20)-C(21)	1.532(8)	C(10)-C(9)-C(8)	111.3(5)		
C(21)-C(22)	1.497(9)	C(11)-C(10)-C(9)	111.1(5)		
C(22)-C(23)	1.526(9)	C(10)-C(11)-C(12)	111.1(4)		
C(23)-C(24)	1.514(8)	C(7)-C(12)-C(11)	110.0(5)		
C(25)-C(30)	1.526(8)	C(18)-C(13)-C(14)	111.2(4)		
C(25)-C(26)	1.528(7)	C(18)-C(13)-P(3)	112.7(4)		
C(26)-C(27)	1.521(7)	C(14)-C(13)-P(3)	113.8(4)		
C(27)-C(28)	1.539(9)	C(13)-C(14)-C(15)	108.5(5)		
C(28)-C(29)	1.513(9)	C(16)-C(15)-C(14)	111.5(5)		
C(29)-C(30)	1.520(7)	C(17)-C(16)-C(15)	111.9(5)		

Table A13. Geometric parameters of [Me-N(CH₂P(^tBu)₂)₂PdCl₂] (**3**).

Bond lengths (Å)		Bond angles (°)			
Pd(1)-P(3)	2.2893(15)	P(3)-Pd(1)-P(5)	97.04(5)	C(22)-C(19)-P(5)	105.9(5)
Pd(1)-P(5)	2.2931(16)	P(3)-Pd(1)-Cl(2)	169.67(6)	Cl(3)-C(30)-Cl(4)	117.6(14)
Pd(1)-Cl(2)	2.3444(16)	P(5)-Pd(1)-Cl(2)	88.20(6)	Cl(3')-C(30')-Cl(4')	118(2)
Pd(1)-Cl(1)	2.3585(17)	P(3)-Pd(1)-Cl(1)	90.81(6)	Cl(4'')-C(30'')-Cl(3'')	117(2)
N(1)-C(4)	1.439(8)	P(5)-Pd(1)-Cl(1)	169.23(6)		
N(1)-C(2)	1.478(8)	Cl(2)-Pd(1)-Cl(1)	85.24(6)		
N(1)-C(6)	1.480(6)	C(4)-N(1)-C(2)	109.5(4)		
C(2)-P(3)	1.839(6)	C(4)-N(1)-C(6)	110.0(5)		
P(3)-C(7)	1.882(6)	C(2)-N(1)-C(6)	108.6(5)		
P(3)-C(11)	1.908(7)	N(1)-C(2)-P(3)	116.4(4)		
C(4)-P(5)	1.848(6)	C(2)-P(3)-C(7)	102.1(3)		
P(5)-C(15)	1.884(6)	C(2)-P(3)-C(11)	100.8(3)		
P(5)-C(19)	1.922(7)	C(7)-P(3)-C(11)	111.3(3)		
C(7)-C(8)	1.529(10)	C(2)-P(3)-Pd(1)	115.0(2)		
C(7)-C(9)	1.539(10)	C(7)-P(3)-Pd(1)	110.95(19)		
C(7)-C(10)	1.553(9)	C(11)-P(3)-Pd(1)	115.6(2)		
C(11)-C(12)	1.523(9)	N(1)-C(4)-P(5)	111.2(4)		
C(11)-C(13)	1.530(9)	C(4)-P(5)-C(15)	99.4(3)		
C(11)-C(14)	1.536(9)	C(4)-P(5)-C(19)	103.1(3)		
C(15)-C(16)	1.536(10)	C(15)-P(5)-C(19)	113.2(3)		
C(15)-C(17)	1.540(9)	C(4)-P(5)-Pd(1)	114.4(2)		
C(15)-C(18)	1.548(9)	C(15)-P(5)-Pd(1)	111.3(2)		
C(19)-C(20)	1.527(10)	C(19)-P(5)-Pd(1)	114.3(2)		
C(19)-C(21)	1.532(9)	C(8)-C(7)-C(9)	109.3(6)		
C(19)-C(22)	1.536(10)	C(8)-C(7)-C(10)	108.6(6)		
C(30)-Cl(3)	1.707(16)	C(9)-C(7)-C(10)	107.6(6)		
C(30)-Cl(4)	1.752(15)	C(8)-C(7)-P(3)	107.4(5)		
C(30')-Cl(3')	1.74(2)	C(9)-C(7)-P(3)	111.8(4)		
C(30')-Cl(4')	1.74(2)	C(10)-C(7)-P(3)	112.0(5)		
C(30'')-Cl(4'')	1.74(2)	C(12)-C(11)-C(13)	108.9(6)		
C(30'')-Cl(3'')	1.74(2)	C(12)-C(11)-C(14)	107.6(5)		
		C(13)-C(11)-C(14)	109.3(6)		
		C(12)-C(11)-P(3)	113.4(5)		
		C(13)-C(11)-P(3)	112.6(4)		
		C(14)-C(11)-P(3)	104.8(4)		
		C(16)-C(15)-C(17)	106.7(6)		
		C(16)-C(15)-C(18)	109.9(5)		
		C(17)-C(15)-C(18)	108.0(6)		
		C(16)-C(15)-P(5)	107.6(5)		
		C(17)-C(15)-P(5)	114.6(5)		
		C(18)-C(15)-P(5)	109.9(5)		
		C(20)-C(19)-C(21)	108.3(6)		
		C(20)-C(19)-C(22)	109.6(5)		
		C(21)-C(19)-C(22)	107.5(7)		
		C(20)-C(19)-P(5)	113.1(5)		
		C(21)-C(19)-P(5)	112.3(4)		

Table A14. Geometric parameters of [Me-N(CH₂PPh₂)₂PdCl₂] (**4**).

Bond lengths (Å)		Bond angles (°)	
Pd(1)-P(3)	2.2341(7)	P(3)-Pd(1)-P(3)#1	92.25(4)
Pd(1)-P(3)#1	2.2341(7)	P(3)-Pd(1)-Cl(1)#1	176.91(3)
Pd(1)-Cl(1)#1	2.3537(7)	P(3)#1-Pd(1)-Cl(1)#1	87.99(2)
Pd(1)-Cl(1)	2.3537(7)	P(3)-Pd(1)-Cl(1)	87.99(2)
N(1)-C(2)	1.459(3)	P(3)#1-Pd(1)-Cl(1)	176.91(3)
N(1)-C(2)#1	1.459(3)	Cl(1)#1-Pd(1)-Cl(1)	91.60(3)
N(1)-C(4)	1.465(5)	C(2)-N(1)-C(2)#1	110.9(3)
C(2)-P(3)	1.833(3)	C(2)-N(1)-C(4)	110.18(19)
P(3)-C(5)	1.814(3)	C(2)#1-N(1)-C(4)	110.18(19)
P(3)-C(11)	1.821(3)	N(1)-C(2)-P(3)	114.9(2)
C(5)-C(6)	1.389(4)	C(5)-P(3)-C(11)	107.54(12)
C(5)-C(10)	1.392(4)	C(5)-P(3)-C(2)	105.45(12)
C(6)-C(7)	1.386(4)	C(11)-P(3)-C(2)	98.15(12)
C(7)-C(8)	1.367(4)	C(5)-P(3)-Pd(1)	111.11(8)
C(8)-C(9)	1.383(4)	C(11)-P(3)-Pd(1)	114.93(9)
C(9)-C(10)	1.383(4)	C(2)-P(3)-Pd(1)	118.38(9)
C(11)-C(12)	1.388(3)	C(6)-C(5)-C(10)	119.5(3)
C(11)-C(16)	1.392(4)	C(6)-C(5)-P(3)	120.9(2)
C(12)-C(13)	1.387(4)	C(10)-C(5)-P(3)	119.6(2)
C(13)-C(14)	1.388(4)	C(7)-C(6)-C(5)	119.8(3)
C(14)-C(15)	1.383(4)	C(8)-C(7)-C(6)	120.5(3)
C(15)-C(16)	1.379(4)	C(7)-C(8)-C(9)	120.2(3)
		C(10)-C(9)-C(8)	120.1(3)
		C(9)-C(10)-C(5)	119.9(3)
		C(12)-C(11)-C(16)	119.2(2)
		C(12)-C(11)-P(3)	122.5(2)
		C(16)-C(11)-P(3)	117.89(19)
		C(13)-C(12)-C(11)	120.3(3)
		C(12)-C(13)-C(14)	119.9(3)
		C(15)-C(14)-C(13)	119.9(3)
		C(16)-C(15)-C(14)	120.2(3)
		C(15)-C(16)-C(11)	120.4(3)

Table A15. Geometric parameters of [Bn-N(CH₂PPh₂)₂PdCl₂] (**5**).

Bond lengths (Å)					
Pd(1)-P(3)	2.2405(17)	C(34)-C(35)	1.363(13)	C(13)-C(14)-C(15)	121.3(9)
Pd(1)-P(5)	2.2422(17)	C(35)-C(36)	1.399(10)	C(16)-C(15)-C(14)	119.5(10)
Pd(1)-Cl(2)	2.3520(16)	C(40)-Cl(41)	1.747(12)	C(15)-C(16)-C(17)	119.7(8)
Pd(1)-Cl(1)	2.3613(16)	C(40)-Cl(42)	1.751(12)	C(18)-C(17)-C(16)	120.8(9)
N(1)-C(2)	1.460(9)	Bond angles (°)		C(17)-C(18)-C(13)	120.5(9)
N(1)-C(4)	1.468(9)	P(3)-Pd(1)-P(5)	94.61(6)	C(20)-C(19)-C(24)	119.0(7)
N(1)-C(6)	1.483(9)	P(3)-Pd(1)-Cl(2)	87.11(6)	C(20)-C(19)-P(3)	121.1(6)
C(2)-P(3)	1.844(8)	P(5)-Pd(1)-Cl(2)	176.60(6)	C(24)-C(19)-P(3)	119.7(5)
P(3)-C(13)	1.801(7)	P(3)-Pd(1)-Cl(1)	174.00(7)	C(19)-C(20)-C(21)	119.7(7)
P(3)-C(19)	1.815(7)	P(5)-Pd(1)-Cl(1)	86.10(6)	C(22)-C(21)-C(20)	120.7(7)
C(4)-P(5)	1.849(7)	Cl(2)-Pd(1)-Cl(1)	92.49(6)	C(23)-C(22)-C(21)	119.2(7)
P(5)-C(25)	1.814(7)	C(2)-N(1)-C(4)	110.4(6)	C(22)-C(23)-C(24)	120.6(8)
P(5)-C(31)	1.823(7)	C(2)-N(1)-C(6)	112.1(6)	C(23)-C(24)-C(19)	120.8(7)
C(6)-C(7')	1.474(13)	C(4)-N(1)-C(6)	110.8(6)	C(26)-C(25)-C(30)	120.1(7)
C(6)-C(7)	1.512(10)	N(1)-C(2)-P(3)	109.2(5)	C(26)-C(25)-P(5)	117.8(5)
C(7)-C(8)	1.3900	C(13)-P(3)-C(19)	108.7(3)	C(30)-C(25)-P(5)	122.0(5)
C(7)-C(12)	1.3900	C(13)-P(3)-C(2)	102.0(3)	C(27)-C(26)-C(25)	119.6(8)
C(8)-C(9)	1.3900	C(19)-P(3)-C(2)	102.0(3)	C(26)-C(27)-C(28)	120.4(8)
C(9)-C(10)	1.3900	C(13)-P(3)-Pd(1)	115.2(2)	C(29)-C(28)-C(27)	120.1(7)
C(10)-C(11)	1.3900	C(19)-P(3)-Pd(1)	110.3(2)	C(28)-C(29)-C(30)	119.8(8)
C(11)-C(12)	1.3900	C(2)-P(3)-Pd(1)	117.5(2)	C(29)-C(30)-C(25)	120.0(7)
C(7')-C(8')	1.3900	N(1)-C(4)-P(5)	113.2(5)	C(36)-C(31)-C(32)	121.4(7)
C(7')-C(12')	1.3900	C(25)-P(5)-C(31)	107.7(3)	C(36)-C(31)-P(5)	120.8(6)
C(8')-C(9')	1.3900	C(25)-P(5)-C(4)	103.3(3)	C(32)-C(31)-P(5)	117.8(6)
C(9')-C(10')	1.3900	C(31)-P(5)-C(4)	101.4(3)	C(31)-C(32)-C(33)	117.4(8)
C(10')-C(11')	1.3900	C(25)-P(5)-Pd(1)	113.1(2)	C(34)-C(33)-C(32)	120.3(9)
C(11')-C(12')	1.3900	C(31)-P(5)-Pd(1)	111.1(2)	C(33)-C(34)-C(35)	121.5(8)
C(13)-C(14)	1.392(11)	C(4)-P(5)-Pd(1)	119.0(2)	C(34)-C(35)-C(36)	119.9(9)
C(13)-C(18)	1.393(11)	C(7')-C(6)-N(1)	109.5(12)	C(31)-C(36)-C(35)	119.5(8)
C(14)-C(15)	1.394(11)	N(1)-C(6)-C(7)	113.6(7)	Cl(41)-C(40)-Cl(42)	111.6(5)
C(15)-C(16)	1.370(15)	C(8)-C(7)-C(12)	120.0		
C(16)-C(17)	1.389(14)	C(8)-C(7)-C(6)	118.5(7)		
C(17)-C(18)	1.374(12)	C(12)-C(7)-C(6)	121.5(7)		
C(19)-C(20)	1.387(9)	C(7)-C(8)-C(9)	120.0		
C(19)-C(24)	1.388(11)	C(10)-C(9)-C(8)	120.0		
C(20)-C(21)	1.395(11)	C(11)-C(10)-C(9)	120.0		
C(21)-C(22)	1.387(13)	C(12)-C(11)-C(10)	120.0		
C(22)-C(23)	1.372(12)	C(11)-C(12)-C(7)	120.0		
C(23)-C(24)	1.380(10)	C(8')-C(7')-C(12')	120.0		
C(25)-C(26)	1.384(10)	C(8')-C(7')-C(6)	120.4(13)		
C(25)-C(30)	1.389(10)	C(12')-C(7')-C(6)	119.5(13)		
C(26)-C(27)	1.381(11)	C(7')-C(8')-C(9')	120.0		
C(27)-C(28)	1.386(12)	C(8')-C(9')-C(10')	120.0		
C(28)-C(29)	1.381(12)	C(11')-C(10')-C(9')	120.0		
C(29)-C(30)	1.385(10)	C(12')-C(11')-C(10')	120.0		
C(31)-C(36)	1.365(10)	C(11')-C(12')-C(7')	120.0		
C(31)-C(32)	1.395(11)	C(14)-C(13)-C(18)	118.1(7)		
C(32)-C(33)	1.427(11)	C(14)-C(13)-P(3)	118.1(6)		
C(33)-C(34)	1.350(13)	C(18)-C(13)-P(3)	123.8(6)		

Table A16. Geometric parameters of [C(OEt)₂HCH₂-N(CH₂PCy₂)₂PdCl₂] (**6**).

Bond lengths (Å)					
Pd(1A)-P(5A)	2.2450(13)	O(50)-C(51)	1.378(17)	C(21A)-C(20A)-C(25A)	110.9(5)
Pd(1A)-P(3A)	2.2514(14)	C(51)-C(52)	1.454(18)	C(21A)-C(20A)-P(3A)	115.0(4)
Pd(1A)-Cl(2A)	2.3595(13)	C(53)-C(54)	1.524(19)	C(25A)-C(20A)-P(3A)	112.1(4)
Pd(1A)-Cl(1A)	2.3689(14)	O(50')-C(53')	1.376(19)	C(22A)-C(21A)-C(20A)	109.9(5)
N(1A)-C(4A)	1.458(6)	O(50')-C(51')	1.393(19)	C(21A)-C(22A)-C(23A)	110.7(5)
N(1A)-C(6A)	1.472(6)	C(51')-C(52')	1.498(19)	C(24A)-C(23A)-C(22A)	112.4(6)
N(1A)-C(2A)	1.474(6)	C(53')-C(54')	1.509(19)	C(23A)-C(24A)-C(25A)	110.9(5)
C(2A)-P(3A)	1.835(5)	O(50'')-C(53'')	1.330(19)	C(20A)-C(25A)-C(24A)	110.2(5)
P(3A)-C(20A)	1.835(5)	O(50'')-C(51'')	1.354(18)	O(11D)-C(7D)-C(6B)	126.5(18)
P(3A)-C(14A)	1.848(5)	C(51'')-C(52'')	1.476(19)	O(8B)-C(7E)-O(11E)	122.3(16)
C(4A)-P(5A)	1.836(5)	C(53'')-C(54'')	1.573(19)	O(8B)-C(7E)-C(6B)	109.1(10)
P(5A)-C(32A)	1.830(5)	Bond angles (°)		O(11E)-C(7E)-C(6B)	100.4(11)
P(5A)-C(26A)	1.851(6)	P(5A)-Pd(1A)-P(3A)	94.29(5)	C(31A)-C(26A)-C(27A)	110.7(4)
C(6A)-C(7A)	1.525(8)	P(5A)-Pd(1A)-Cl(2A)	172.56(6)	C(31A)-C(26A)-P(5A)	116.3(4)
C(7A)-O(11A)	1.414(7)	P(3A)-Pd(1A)-Cl(2A)	88.65(5)	C(27A)-C(26A)-P(5A)	110.8(4)
C(7A)-O(8A)	1.417(7)	P(5A)-Pd(1A)-Cl(1A)	87.79(5)	C(26A)-C(27A)-C(28A)	111.0(5)
O(8A)-C(9A)	1.422(8)	P(3A)-Pd(1A)-Cl(1A)	173.46(6)	C(29A)-C(28A)-C(27A)	111.5(6)
C(9A)-C(10A)	1.495(10)	Cl(2A)-Pd(1A)-Cl(1A)	90.04(5)	C(30A)-C(29A)-C(28A)	110.7(5)
O(11A)-C(12A)	1.370(8)	C(4A)-N(1A)-C(6A)	110.5(4)	C(29A)-C(30A)-C(31A)	112.8(5)
C(12A)-C(13A)	1.459(9)	C(4A)-N(1A)-C(2A)	110.2(4)	C(26A)-C(31A)-C(30A)	109.6(5)
C(14A)-C(15A)	1.523(7)	C(6A)-N(1A)-C(2A)	113.3(4)	C(37A)-C(32A)-C(33A)	110.4(5)
C(14A)-C(19A)	1.526(7)	N(1A)-C(2A)-P(3A)	113.8(4)	C(37A)-C(32A)-P(5A)	113.6(4)
C(15A)-C(16A)	1.527(8)	C(2A)-P(3A)-C(20A)	101.9(2)	C(33A)-C(32A)-P(5A)	115.1(4)
C(16A)-C(17A)	1.515(9)	C(2A)-P(3A)-C(14A)	103.3(2)	C(34A)-C(33A)-C(32A)	108.9(5)
C(17A)-C(18A)	1.532(9)	C(20A)-P(3A)-C(14A)	105.7(2)	C(35A)-C(34A)-C(33A)	111.3(5)
C(18A)-C(19A)	1.546(8)	C(2A)-P(3A)-Pd(1A)	118.87(18)	C(34A)-C(35A)-C(36A)	111.8(5)
C(20A)-C(21A)	1.526(8)	C(20A)-P(3A)-Pd(1A)	112.33(18)	C(35A)-C(36A)-C(37A)	112.4(6)
C(20A)-C(25A)	1.535(8)	C(14A)-P(3A)-Pd(1A)	113.26(19)	C(36A)-C(37A)-C(32A)	109.0(5)
C(21A)-C(22A)	1.521(8)	N(1A)-C(4A)-P(5A)	116.3(3)	P(3B)-Pd(1B)-P(5B)	96.13(5)
C(22A)-C(23A)	1.523(9)	C(32A)-P(5A)-C(4A)	108.7(2)	P(3B)-Pd(1B)-Cl(1B)	173.53(5)
C(23A)-C(24A)	1.510(9)	C(32A)-P(5A)-C(26A)	106.2(2)	P(5B)-Pd(1B)-Cl(1B)	87.72(5)
C(24A)-C(25A)	1.536(8)	C(4A)-P(5A)-C(26A)	98.1(2)	P(3B)-Pd(1B)-Cl(2B)	85.29(5)
C(26A)-C(31A)	1.526(8)	C(32A)-P(5A)-Pd(1A)	111.26(18)	P(5B)-Pd(1B)-Cl(2B)	177.25(5)
C(26A)-C(27A)	1.530(7)	C(4A)-P(5A)-Pd(1A)	118.10(17)	Cl(1B)-Pd(1B)-Cl(2B)	91.08(5)
C(27A)-C(28A)	1.538(8)	C(26A)-P(5A)-Pd(1A)	113.19(17)	C(6B)-N(1B)-C(2B)	114.0(4)
C(28A)-C(29A)	1.516(8)	N(1A)-C(6A)-C(7A)	117.0(5)	C(6B)-N(1B)-C(4B)	113.2(4)
C(29A)-C(30A)	1.514(9)	O(11A)-C(7A)-O(8A)	110.0(5)	C(2B)-N(1B)-C(4B)	111.1(4)
C(30A)-C(31A)	1.531(8)	O(11A)-C(7A)-C(6A)	108.2(5)	N(1B)-C(2B)-P(3B)	111.1(4)
C(32A)-C(37A)	1.537(8)	O(8A)-C(7A)-C(6A)	107.2(5)	C(2B)-P(3B)-C(14B)	106.1(3)
C(32A)-C(33A)	1.538(7)	C(7A)-O(8A)-C(9A)	115.9(5)	C(2B)-P(3B)-C(20B)	103.7(2)
C(33A)-C(34A)	1.536(8)	O(8A)-C(9A)-C(10A)	109.3(6)	C(14B)-P(3B)-C(20B)	108.2(3)
C(34A)-C(35A)	1.509(9)	C(12A)-O(11A)-C(7A)	115.8(5)	C(2B)-P(3B)-Pd(1B)	117.48(18)
C(35A)-C(36A)	1.515(10)	O(11A)-C(12A)-C(13A)	113.2(6)	C(14B)-P(3B)-Pd(1B)	110.20(19)
C(36A)-C(37A)	1.531(8)	C(15A)-C(14A)-C(19A)	109.6(5)	C(20B)-P(3B)-Pd(1B)	110.61(18)
Pd(1B)-P(3B)	2.2518(15)	C(15A)-C(14A)-P(3A)	112.1(4)	N(1B)-C(4B)-P(5B)	112.5(4)
Pd(1B)-P(5B)	2.2549(14)	C(19A)-C(14A)-P(3A)	115.2(4)	C(4B)-P(5B)-C(26B)	104.4(2)
Pd(1B)-Cl(1B)	2.3552(14)	C(14A)-C(15A)-C(16A)	111.8(5)	C(4B)-P(5B)-C(32B)	101.7(3)
Pd(1B)-Cl(2B)	2.3819(13)	C(17A)-C(16A)-C(15A)	111.3(5)	C(26B)-P(5B)-C(32B)	105.5(3)
N(1B)-C(6B)	1.457(7)	C(16A)-C(17A)-C(18A)	111.1(5)	C(4B)-P(5B)-Pd(1B)	116.62(18)
N(1B)-C(2B)	1.460(7)	C(17A)-C(18A)-C(19A)	110.9(5)	C(26B)-P(5B)-Pd(1B)	112.65(18)
N(1B)-C(4B)	1.467(6)	C(14A)-C(19A)-C(18A)	109.9(5)	C(32B)-P(5B)-Pd(1B)	114.61(18)

C(2B)-P(3B)	1.837(5)	N(1B)-C(6B)-C(7E)	124.5(9)	C(21B)-C(20B)-P(3B)	115.3(4)
P(3B)-C(14B)	1.846(5)	N(1B)-C(6B)-C(7D)	116.2(11)	C(25B)-C(20B)-P(3B)	110.0(4)
P(3B)-C(20B)	1.856(6)	N(1B)-C(6B)-C(7B)	113.4(8)	C(22B)-C(21B)-C(20B)	111.6(5)
C(4B)-P(5B)	1.837(6)	O(8B)-C(7B)-O(11B)	105.1(12)	C(23B)-C(22B)-C(21B)	110.7(5)
P(5B)-C(26B)	1.841(5)	O(8B)-C(7B)-C(6B)	106.2(8)	C(27B)-C(26B)-P(5B)	110.9(4)
P(5B)-C(32B)	1.848(6)	O(11B)-C(7B)-C(6B)	106.0(13)	C(31B)-C(26B)-P(5B)	113.0(4)
C(6B)-C(7E)	1.487(14)	O(8B)-C(7D)-O(11D)	107.5(15)	C(28B)-C(27B)-C(26B)	110.9(5)
C(6B)-C(7D)	1.526(15)	O(8B)-C(7D)-C(6B)	107.0(10)	C(27B)-C(28B)-C(29B)	111.6(6)
C(6B)-C(7B)	1.547(13)	C(22B)-C(23B)-C(24B)	111.1(5)	C(30B)-C(29B)-C(28B)	112.5(6)
C(7B)-O(8B)	1.411(12)	C(23B)-C(24B)-C(25B)	111.1(5)	C(29B)-C(30B)-C(31B)	110.7(6)
C(7B)-O(11B)	1.440(13)	C(20B)-C(25B)-C(24B)	111.5(5)	C(30B)-C(31B)-C(26B)	110.0(5)
C(7D)-O(8B)	1.418(14)	C(27B)-C(26B)-C(31B)	111.0(5)	C(33B)-C(32B)-C(37B)	109.6(5)
C(7D)-O(11D)	1.426(14)	C(7B)-O(8B)-C(9B)	111.7(7)	C(33B)-C(32B)-P(5B)	115.8(4)
C(7E)-O(8B)	1.419(13)	C(7D)-O(8B)-C(9B)	113.7(10)	C(37B)-C(32B)-P(5B)	111.6(4)
C(7E)-O(11E)	1.443(14)	C(7E)-O(8B)-C(9B)	119.9(9)	C(34B)-C(33B)-C(32B)	110.4(6)
O(8B)-C(9B)	1.427(8)	O(8B)-C(9B)-C(10B)	108.8(6)	C(27B)-C(26B)-P(5B)	110.9(4)
C(9B)-C(10B)	1.480(10)	C(7B)-O(11B)-C(12B)	109.8(14)	C(31B)-C(26B)-P(5B)	113.0(4)
O(11B)-C(12B)	1.45(2)	C(13B)-C(12B)-O(11B)	114.3(18)	C(28B)-C(27B)-C(26B)	110.9(5)
C(12B)-C(13B)	1.39(2)	C(7D)-O(11D)-C(12D)	112.3(17)	C(27B)-C(28B)-C(29B)	111.6(6)
O(11D)-C(12D)	1.44(2)	C(13D)-C(12D)-O(11D)	116(2)	C(30B)-C(29B)-C(28B)	112.5(6)
C(12D)-C(13D)	1.42(2)	C(7E)-O(11E)-C(12E)	109.3(13)	C(29B)-C(30B)-C(31B)	110.7(6)
O(11E)-C(12E)	1.458(19)	C(13E)-C(12E)-O(11E)	110.5(17)	C(30B)-C(31B)-C(26B)	110.0(5)
C(12E)-C(13E)	1.42(2)	C(15B)-C(14B)-C(19B)	111.2(5)	C(33B)-C(32B)-C(37B)	109.6(5)
C(14B)-C(15B)	1.518(8)	O(11D)-C(7D)-C(6B)	126.5(18)	C(33B)-C(32B)-P(5B)	115.8(4)
C(14B)-C(19B)	1.547(8)	O(8B)-C(7E)-O(11E)	122.3(16)	C(37B)-C(32B)-P(5B)	111.6(4)
C(15B)-C(16B)	1.548(8)	O(8B)-C(7E)-C(6B)	109.1(10)	C(34B)-C(33B)-C(32B)	110.4(6)
C(16B)-C(17B)	1.516(9)	O(11E)-C(7E)-C(6B)	100.4(11)	C(35B)-C(34B)-C(33B)	110.7(6)
C(17B)-C(18B)	1.517(10)	C(7B)-O(8B)-C(9B)	111.7(7)	C(36B)-C(35B)-C(34B)	112.4(6)
C(18B)-C(19B)	1.525(8)	C(7D)-O(8B)-C(9B)	113.7(10)	C(35B)-C(36B)-C(37B)	112.1(6)
C(20B)-C(21B)	1.529(8)	C(7E)-O(8B)-C(9B)	119.9(9)	C(36B)-C(37B)-C(32B)	110.8(5)
C(20B)-C(25B)	1.534(8)	O(8B)-C(9B)-C(10B)	108.8(6)	Cl(3)-C(40)-Cl(4)	120.4(11)
C(21B)-C(22B)	1.524(8)	C(7B)-O(11B)-C(12B)	109.8(14)	Cl(3')-C(40')-Cl(4')	118.7(17)
C(22B)-C(23B)	1.514(9)	C(13B)-C(12B)-O(11B)	114.3(18)	Cl(4'')-C(40'')-Cl(3'')	118(2)
C(23B)-C(24B)	1.525(9)	C(7D)-O(11D)-C(12D)	112.3(17)	C(53)-O(50)-C(51)	118(2)
C(24B)-C(25B)	1.545(8)	C(13D)-C(12D)-O(11D)	116(2)	O(50)-C(51)-C(52)	120(2)
C(26B)-C(27B)	1.533(7)	C(7E)-O(11E)-C(12E)	109.3(13)	O(50)-C(53)-C(54)	104(2)
C(26B)-C(31B)	1.541(7)	C(13E)-C(12E)-O(11E)	110.5(17)	C(53')-O(50')-C(51')	108(2)
C(27B)-C(28B)	1.518(8)	C(15B)-C(14B)-C(19B)	111.2(5)	O(50')-C(51')-C(52')	112(3)
C(28B)-C(29B)	1.519(10)	C(15B)-C(14B)-P(3B)	109.7(4)	O(50'')-C(53'')-C(54'')	103(2)
C(29B)-C(30B)	1.493(10)	C(19B)-C(14B)-P(3B)	115.5(4)	C(53'')-O(50'')-C(51'')	144(3)
C(30B)-C(31B)	1.541(8)	C(14B)-C(15B)-C(16B)	112.1(5)	O(50'')-C(51'')-C(52'')	112(2)
C(32B)-C(33B)	1.534(8)	C(17B)-C(16B)-C(15B)	111.3(5)	O(50'')-C(53'')-C(54'')	111(3)
C(32B)-C(37B)	1.541(8)	C(16B)-C(17B)-C(18B)	110.9(6)		
C(33B)-C(34B)	1.529(9)	C(17B)-C(18B)-C(19B)	111.1(6)		
C(34B)-C(35B)	1.526(10)	C(18B)-C(19B)-C(14B)	111.7(5)		
C(35B)-C(36B)	1.497(10)	C(21B)-C(20B)-C(25B)	110.2(5)		
C(36B)-C(37B)	1.535(9)	C(15B)-C(14B)-P(3B)	109.7(4)		
C(40)-Cl(3)	1.695(11)	C(19B)-C(14B)-P(3B)	115.5(4)		
C(40)-Cl(4)	1.694(15)	C(14B)-C(15B)-C(16B)	112.1(5)		
C(40')-Cl(3')	1.694(16)	C(17B)-C(16B)-C(15B)	111.3(5)		
C(40')-Cl(4')	1.699(18)	C(16B)-C(17B)-C(18B)	110.9(6)		
C(40'')-Cl(4'')	1.695(18)	C(17B)-C(18B)-C(19B)	111.1(6)		
C(40'')-Cl(3'')	1.697(18)	C(18B)-C(19B)-C(14B)	111.7(5)		
O(50)-C(53)	1.359(18)	C(21B)-C(20B)-C(25B)	110.2(5)		

Table A17. Geometric parameters of [C₂₇H₅₃N₂O₄P](PdCl₄).

Bond lengths (Å)		Bond angles (°)			
Pd(1)-Cl(3)	2.2866(10)	Cl(3)-Pd(1)-Cl(2)	89.07(4)	O(32)-C(28)-O(29)	111.1(6)
Pd(1)-Cl(2)	2.2930(10)	Cl(3)-Pd(1)-Cl(4)	89.51(4)	O(32)-C(28)-C(27)	106.9(5)
Pd(1)-Cl(4)	2.3047(10)	Cl(2)-Pd(1)-Cl(4)	178.58(4)	O(29)-C(28)-C(27)	114.0(7)
Pd(1)-Cl(1)	2.3246(10)	Cl(3)-Pd(1)-Cl(1)	179.67(4)	C(28)-O(29)-C(30)	114.6(6)
P(1)-C(13)	1.801(4)	Cl(2)-Pd(1)-Cl(1)	90.95(4)	C(31)-C(30)-O(29)	111.0(7)
P(1)-C(2)	1.805(4)	Cl(4)-Pd(1)-Cl(1)	90.47(4)	C(28)-O(32)-C(33)	114.3(4)
P(1)-C(6)	1.811(4)	C(13)-P(1)-C(2)	109.07(17)	O(32)-C(33)-C(34)	110.4(5)
P(1)-C(7)	1.815(4)	C(13)-P(1)-C(6)	112.86(17)	O(32')-C(28')-O(29')	112(3)
C(2)-N(3)	1.461(5)	C(2)-P(1)-C(6)	100.31(17)	O(32')-C(28')-C(27)	101.1(16)
N(3)-C(4)	1.310(5)	C(13)-P(1)-C(7)	110.76(18)	O(29')-C(28')-C(27)	110(3)
N(3)-C(19)	1.478(4)	C(2)-P(1)-C(7)	112.39(18)	C(28')-O(29')-C(30')	109(2)
C(4)-N(5)	1.319(4)	C(6)-P(1)-C(7)	111.07(18)	C(31')-C(30')-O(29')	108(3)
N(5)-C(6)	1.465(4)	N(3)-C(2)-P(1)	112.4(2)	C(28')-O(32')-C(33')	113.4(18)
N(5)-C(27)	1.474(5)	C(4)-N(3)-C(2)	125.6(3)	O(32')-C(33')-C(34')	113(2)
C(7)-C(8)	1.531(5)	C(4)-N(3)-C(19)	117.6(3)		
C(7)-C(12)	1.538(5)	C(2)-N(3)-C(19)	116.6(3)		
C(8)-C(9)	1.518(5)	N(3)-C(4)-N(5)	127.1(4)		
C(9)-C(10)	1.515(6)	C(4)-N(5)-C(6)	122.8(3)		
C(10)-C(11)	1.524(6)	C(4)-N(5)-C(27)	118.5(3)		
C(11)-C(12)	1.522(5)	C(6)-N(5)-C(27)	117.6(3)		
C(13)-C(18)	1.534(5)	N(5)-C(6)-P(1)	109.6(2)		
C(13)-C(14)	1.542(5)	C(8)-C(7)-C(12)	111.5(3)		
C(14)-C(15)	1.519(5)	C(8)-C(7)-P(1)	114.7(3)		
C(15)-C(16)	1.515(6)	C(12)-C(7)-P(1)	111.2(3)		
C(16)-C(17)	1.520(6)	C(9)-C(8)-C(7)	109.9(3)		
C(17)-C(18)	1.526(5)	C(10)-C(9)-C(8)	111.6(4)		
C(19)-C(20)	1.521(5)	C(9)-C(10)-C(11)	111.1(4)		
C(20)-O(24)	1.390(5)	C(12)-C(11)-C(10)	112.1(3)		
C(20)-O(21)	1.418(4)	C(11)-C(12)-C(7)	109.6(3)		
O(21)-C(22)	1.431(5)	C(18)-C(13)-C(14)	111.1(3)		
C(22)-C(23)	1.507(6)	C(18)-C(13)-P(1)	113.1(3)		
O(24)-C(25)	1.438(6)	C(14)-C(13)-P(1)	110.0(3)		
C(25)-C(26)	1.451(7)	C(15)-C(14)-C(13)	110.6(3)		
C(27)-C(28')	1.516(18)	C(16)-C(15)-C(14)	111.5(4)		
C(27)-C(28)	1.523(6)	C(15)-C(16)-C(17)	111.7(4)		
C(28)-O(32)	1.394(8)	C(16)-C(17)-C(18)	111.8(4)		
C(28)-O(29)	1.412(6)	C(17)-C(18)-C(13)	110.1(3)		
O(29)-C(30)	1.447(8)	N(3)-C(19)-C(20)	112.2(3)		
C(30)-C(31)	1.434(8)	O(24)-C(20)-O(21)	113.1(3)		
O(32)-C(33)	1.455(7)	O(24)-C(20)-C(19)	107.3(3)		
C(33)-C(34)	1.502(8)	O(21)-C(20)-C(19)	109.9(3)		
C(28')-O(32')	1.37(2)	C(20)-O(21)-C(22)	115.9(3)		
C(28')-O(29')	1.413(18)	O(21)-C(22)-C(23)	106.6(4)		
O(29')-C(30')	1.457(19)	C(20)-O(24)-C(25)	115.5(4)		
C(30')-C(31')	1.437(19)	O(24)-C(25)-C(26)	113.3(5)		
O(32')-C(33')	1.470(17)	N(5)-C(27)-C(28')	119.5(18)		
C(33')-C(34')	1.486(19)	N(5)-C(27)-C(28)	110.4(4)		

Table A18. Geometric parameters of [P(O)Ph₂CH₂-N(CH₂PPh₂)₂PdCl₂] (**7**).

Bond lengths (Å)					
Pd(1A)-P(5A)	2.2291(8)	C(36B)-C(37B)	1.384(6)	C(16A)-C(17A)-C(18A)	119.9(4)
Pd(1A)-P(3A)	2.2358(8)	C(38B)-C(43B)	1.377(5)	C(17A)-C(18A)-C(19A)	120.7(4)
Pd(1A)-Cl(2A)	2.3384(8)	C(38B)-C(39B)	1.389(5)	C(14A)-C(19A)-C(18A)	119.6(4)
Pd(1A)-Cl(1A)	2.3612(8)	C(39B)-C(40B)	1.386(5)	C(25A)-C(20A)-C(21A)	119.0(3)
N(1A)-C(4A)	1.475(4)	C(40B)-C(41B)	1.371(6)	N(1B)-C(4B)-P(5B)	115.5(2)
N(1A)-C(2A)	1.477(4)	C(41B)-C(42B)	1.361(6)	C(20B)-P(5B)-C(26B)	110.99(18)
N(1A)-C(6A)	1.485(4)	C(42B)-C(43B)	1.379(5)	C(20")-P(5B)-C(26B)	107.6(3)
C(2A)-P(3A)	1.837(3)	Bond angles (°)		C(20B)-P(5B)-C(4B)	107.25(17)
P(3A)-C(14A)	1.804(3)	P(5A)-Pd(1A)-P(3A)	93.80(3)	C(25A)-C(20A)-P(5A)	119.6(2)
P(3A)-C(8A)	1.811(3)	P(5A)-Pd(1A)-Cl(2A)	176.38(3)	C(21A)-C(20A)-P(5A)	121.2(2)
C(4A)-P(5A)	1.842(3)	P(3A)-Pd(1A)-Cl(2A)	88.61(3)	C(22A)-C(21A)-C(20A)	120.1(3)
P(5A)-C(20A)	1.809(3)	P(5A)-Pd(1A)-Cl(1A)	87.09(3)	C(23A)-C(22A)-C(21A)	120.4(3)
P(5A)-C(26A)	1.821(3)	P(3A)-Pd(1A)-Cl(1A)	175.37(3)	C(22A)-C(23A)-C(24A)	119.9(3)
C(6A)-P(7A)	1.816(3)	Cl(2A)-Pd(1A)-Cl(1A)	90.72(3)	C(25A)-C(24A)-C(23A)	120.3(3)
O(7A)-P(7A)	1.488(2)	C(4A)-N(1A)-C(2A)	110.1(2)	C(24A)-C(25A)-C(20A)	120.3(3)
P(7A)-C(32A)	1.804(4)	C(4A)-N(1A)-C(6A)	109.9(2)	C(27A)-C(26A)-C(31A)	119.2(3)
P(7A)-C(38A)	1.810(3)	C(2A)-N(1A)-C(6A)	106.2(2)	C(27A)-C(26A)-P(5A)	119.1(2)
C(8A)-C(13A)	1.382(5)	N(1A)-C(2A)-P(3A)	118.6(2)	C(31A)-C(26A)-P(5A)	121.7(3)
C(8A)-C(9A)	1.384(4)	C(14A)-P(3A)-C(8A)	107.93(15)	C(26A)-C(27A)-C(28A)	120.7(4)
C(9A)-C(10A)	1.394(5)	C(14A)-P(3A)-C(2A)	105.74(15)	C(29A)-C(28A)-C(27A)	119.5(4)
C(10A)-C(11A)	1.376(6)	C(8A)-P(3A)-C(2A)	98.27(14)	C(30A)-C(29A)-C(28A)	120.6(4)
C(11A)-C(12A)	1.368(5)	C(14A)-P(3A)-Pd(1A)	111.03(10)	C(29A)-C(30A)-C(31A)	120.5(4)
C(12A)-C(13A)	1.377(5)	C(8A)-P(3A)-Pd(1A)	113.52(10)	C(26A)-C(31A)-C(30A)	119.6(4)
C(14A)-C(19A)	1.389(4)	C(2A)-P(3A)-Pd(1A)	119.18(10)	C(33A)-C(32A)-C(37A)	119.3(3)
C(14A)-C(15A)	1.405(5)	N(1A)-C(4A)-P(5A)	115.5(2)	C(33A)-C(32A)-P(7A)	124.4(3)
C(15A)-C(16A)	1.378(5)	C(20A)-P(5A)-C(26A)	107.95(14)	C(37A)-C(32A)-P(7A)	116.1(3)
C(16A)-C(17A)	1.372(5)	C(20A)-P(5A)-C(4A)	106.09(14)	C(34A)-C(33A)-C(32A)	120.4(3)
C(17A)-C(18A)	1.382(6)	C(26A)-P(5A)-C(4A)	99.92(14)	C(33A)-C(34A)-C(35A)	119.6(4)
C(18A)-C(19A)	1.391(5)	C(20A)-P(5A)-Pd(1A)	112.96(10)	C(36A)-C(35A)-C(34A)	120.5(4)
C(20A)-C(25A)	1.388(4)	C(26A)-P(5A)-Pd(1A)	110.71(11)	C(35A)-C(36A)-C(37A)	120.7(3)
C(20A)-C(21A)	1.398(4)	C(4A)-P(5A)-Pd(1A)	118.10(10)	C(36A)-C(37A)-C(32A)	119.4(3)
C(21A)-C(22A)	1.385(5)	N(1A)-C(6A)-P(7A)	118.9(2)	C(43A)-C(38A)-C(39A)	119.4(3)
C(22A)-C(23A)	1.371(5)	O(7A)-P(7A)-C(32A)	112.27(14)	C(43A)-C(38A)-P(7A)	118.4(3)
C(23A)-C(24A)	1.386(5)	O(7A)-P(7A)-C(38A)	112.30(15)	C(39A)-C(38A)-P(7A)	122.0(3)
C(24A)-C(25A)	1.382(5)	C(32A)-P(7A)-C(38A)	105.93(15)	C(40A)-C(39A)-C(38A)	120.0(4)
C(26A)-C(27A)	1.383(5)	O(7A)-P(7A)-C(6A)	113.54(14)	C(41A)-C(40A)-C(39A)	120.3(4)
C(26A)-C(31A)	1.389(5)	C(32A)-P(7A)-C(6A)	109.63(15)	C(40A)-C(41A)-C(42A)	120.4(4)
C(27A)-C(28A)	1.389(5)	C(38A)-P(7A)-C(6A)	102.50(14)	C(41A)-C(42A)-C(43A)	119.7(4)
C(28A)-C(29A)	1.372(6)	C(13A)-C(8A)-C(9A)	118.7(3)	C(38A)-C(43A)-C(42A)	120.2(4)
C(29A)-C(30A)	1.365(6)	C(13A)-C(8A)-P(3A)	119.4(2)	P(5B)-Pd(1B)-P(3B)	89.14(3)
C(30A)-C(31A)	1.391(5)	C(9A)-C(8A)-P(3A)	121.6(3)	P(5B)-Pd(1B)-Cl(2B)	177.28(3)
C(32A)-C(33A)	1.389(5)	C(8A)-C(9A)-C(10A)	120.0(3)	P(3B)-Pd(1B)-Cl(2B)	93.48(3)
C(32A)-C(37A)	1.404(4)	C(11A)-C(10A)-C(9A)	120.1(3)	P(5B)-Pd(1B)-Cl(1B)	86.41(3)
C(33A)-C(34A)	1.382(5)	C(12A)-C(11A)-C(10A)	120.0(3)	P(3B)-Pd(1B)-Cl(1B)	166.94(3)
C(34A)-C(35A)	1.387(5)	C(11A)-C(12A)-C(13A)	120.0(4)	Cl(2B)-Pd(1B)-Cl(1B)	91.18(3)
C(35A)-C(36A)	1.367(5)	C(12A)-C(13A)-C(8A)	121.2(3)	C(4B)-N(1B)-C(6B)	111.1(2)
C(36A)-C(37A)	1.381(5)	C(19A)-C(14A)-C(15A)	119.1(3)	C(4B)-N(1B)-C(2B)	111.9(2)
C(38A)-C(43A)	1.373(5)	C(19A)-C(14A)-P(3A)	120.9(3)	C(6B)-N(1B)-C(2B)	106.9(2)
C(38A)-C(39A)	1.393(5)	C(15A)-C(14A)-P(3A)	119.9(3)	N(1B)-C(2B)-P(3B)	116.8(2)
C(39A)-C(40A)	1.378(5)	C(16A)-C(15A)-C(14A)	120.4(3)	C(14B)-P(3B)-C(8B)	106.27(15)
C(40A)-C(41A)	1.367(6)	C(17A)-C(16A)-C(15A)	120.4(4)	C(14B)-P(3B)-C(2B)	107.37(15)

C(41A)-C(42A)	1.376(6)	C(8B)-P(3B)-C(2B)	98.40(14)	C(28B)-C(29B)-C(30B)	120.4(4)
C(42A)-C(43A)	1.393(5)	C(14B)-P(3B)-Pd(1B)	105.57(10)	C(29B)-C(30B)-C(31B)	120.2(4)
Pd(1B)-P(5B)	2.2356(9)	C(8B)-P(3B)-Pd(1B)	119.53(11)	C(26B)-C(31B)-C(30B)	119.7(4)
Pd(1B)-P(3B)	2.2358(8)	C(2B)-P(3B)-Pd(1B)	118.72(10)	C(33B)-C(32B)-C(37B)	119.0(4)
Pd(1B)-Cl(2B)	2.3426(9)	C(27B)-C(26B)-P(5B)	118.8(3)	C(33B)-C(32B)-P(7B)	123.7(3)
Pd(1B)-Cl(1B)	2.3608(8)	C(31B)-C(26B)-P(5B)	121.9(3)	C(37B)-C(32B)-P(7B)	117.3(3)
N(1B)-C(4B)	1.459(4)	C(26B)-C(27B)-C(28B)	120.3(4)	C(32B)-C(33B)-C(34B)	120.2(4)
N(1B)-C(6B)	1.472(4)	C(29B)-C(28B)-C(27B)	120.2(4)	C(35B)-C(34B)-C(33B)	120.6(4)
N(1B)-C(2B)	1.476(4)	C(20'')-P(5B)-C(4B)	109.4(3)	C(34B)-C(35B)-C(36B)	119.7(4)
C(2B)-P(3B)	1.832(3)	C(26B)-P(5B)-C(4B)	98.85(14)	C(35B)-C(36B)-C(37B)	120.5(4)
P(3B)-C(14B)	1.804(3)	C(20B)-P(5B)-Pd(1B)	110.66(13)	C(36B)-C(37B)-C(32B)	120.0(4)
P(3B)-C(8B)	1.820(3)	C(20'')-P(5B)-Pd(1B)	111.6(3)	C(43B)-C(38B)-C(39B)	119.0(3)
C(4B)-P(5B)	1.830(3)	C(26B)-P(5B)-Pd(1B)	112.11(11)	C(43B)-C(38B)-P(7B)	118.7(3)
P(5B)-C(20B)	1.806(3)	C(4B)-P(5B)-Pd(1B)	116.37(11)	C(39B)-C(38B)-P(7B)	122.3(3)
P(5B)-C(20'')	1.815(7)	N(1B)-C(6B)-P(7B)	117.4(2)	C(40B)-C(39B)-C(38B)	119.8(4)
P(5B)-C(26B)	1.815(3)	O(7B)-P(7B)-C(32B)	111.50(16)	C(41B)-C(40B)-C(39B)	119.9(4)
C(6B)-P(7B)	1.815(3)	O(7B)-P(7B)-C(38B)	112.36(16)	C(42B)-C(41B)-C(40B)	120.6(4)
O(7B)-P(7B)	1.493(2)	C(32B)-P(7B)-C(38B)	108.32(16)	C(41B)-C(42B)-C(43B)	119.8(4)
P(7B)-C(32B)	1.802(4)	O(7B)-P(7B)-C(6B)	114.19(14)	C(38B)-C(43B)-C(42B)	120.8(4)
P(7B)-C(38B)	1.811(3)	C(32B)-P(7B)-C(6B)	109.66(16)		
C(8B)-C(13B)	1.382(5)	C(38B)-P(7B)-C(6B)	100.16(15)		
C(8B)-C(9B)	1.394(5)	C(13B)-C(8B)-C(9B)	119.6(3)		
C(9B)-C(10B)	1.388(5)	C(13B)-C(8B)-P(3B)	121.0(3)		
C(10B)-C(11B)	1.370(6)	C(9B)-C(8B)-P(3B)	119.3(3)		
C(11B)-C(12B)	1.372(6)	C(10B)-C(9B)-C(8B)	119.4(4)		
C(12B)-C(13B)	1.387(5)	C(11B)-C(10B)-C(9B)	120.1(4)		
C(14B)-C(15B)	1.387(5)	C(10B)-C(11B)-C(12B)	121.1(4)		
C(14B)-C(19B)	1.387(4)	C(11B)-C(12B)-C(13B)	119.3(4)		
C(15B)-C(16B)	1.378(5)	C(8B)-C(13B)-C(12B)	120.5(4)		
C(16B)-C(17B)	1.373(5)	C(15B)-C(14B)-C(19B)	119.4(3)		
C(17B)-C(18B)	1.384(5)	C(15B)-C(14B)-P(3B)	117.8(2)		
C(18B)-C(19B)	1.378(5)	C(19B)-C(14B)-P(3B)	122.8(3)		
C(20B)-C(21B)	1.3900	C(16B)-C(15B)-C(14B)	119.9(3)		
C(20B)-C(25B)	1.3900	C(17B)-C(16B)-C(15B)	120.8(4)		
C(21B)-C(22B)	1.3900	C(16B)-C(17B)-C(18B)	119.4(4)		
C(22B)-C(23B)	1.3900	C(19B)-C(18B)-C(17B)	120.3(4)		
C(23B)-C(24B)	1.3900	C(18B)-C(19B)-C(14B)	120.2(3)		
C(24B)-C(25B)	1.3900	C(21B)-C(20B)-C(25B)	120.0		
C(20'')-C(21'')	1.3900	C(21B)-C(20B)-P(5B)	119.5(2)		
C(20'')-C(25'')	1.3900	C(25B)-C(20B)-P(5B)	120.5(2)		
C(21'')-C(22'')	1.3900	C(20B)-C(21B)-C(22B)	120.0		
C(22'')-C(23'')	1.3900	C(23B)-C(22B)-C(21B)	120.0		
C(23'')-C(24'')	1.3900	C(22B)-C(23B)-C(24B)	120.0		
C(26B)-C(27B)	1.382(5)	C(25B)-C(24B)-C(23B)	120.0		
C(26B)-C(31B)	1.383(5)	C(24B)-C(25B)-C(20B)	120.0		
C(27B)-C(28B)	1.388(5)	C(21'')-C(20'')-C(25'')	120.0		
C(28B)-C(29B)	1.364(6)	C(21'')-C(20'')-P(5B)	119.1(5)		
C(29B)-C(30B)	1.365(6)	C(25'')-C(20'')-P(5B)	120.8(5)		
C(30B)-C(31B)	1.398(5)	C(22'')-C(21'')-C(20'')	120.0		
C(32B)-C(33B)	1.377(5)	C(23'')-C(22'')-C(21'')	120.0		
C(32B)-C(37B)	1.394(5)	C(22'')-C(23'')-C(24'')	120.0		
C(33B)-C(34B)	1.388(6)	C(25'')-C(24'')-C(23'')	120.0		
C(34B)-C(35B)	1.367(6)	C(24'')-C(25'')-C(20'')	120.0		
C(35B)-C(36B)	1.369(6)	C(27B)-C(26B)-C(31B)	119.3(3)		

Table A19. Geometric parameters of [P(O)Cy₂CH₂-N(CH₂PCy₂)₂PdCl₂] (**8**).

Bond lengths (Å)		Bond angles (°)			
Pd(1)-P(3)	2.2447(13)	P(3)-Pd(1)-P(5)	94.84(5)	C(15)-C(16)-C(17)	110.3(5)
Pd(1)-P(5)	2.2519(13)	P(3)-Pd(1)-Cl(2)	88.13(5)	C(18)-C(17)-C(16)	111.6(5)
Pd(1)-Cl(2)	2.3643(13)	P(5)-Pd(1)-Cl(2)	176.62(5)	C(19)-C(18)-C(17)	111.3(5)
Pd(1)-Cl(1)	2.3751(14)	P(3)-Pd(1)-Cl(1)	178.93(5)	C(18)-C(19)-C(14)	110.4(4)
N(1)-C(4)	1.458(6)	P(5)-Pd(1)-Cl(1)	85.33(5)	C(25)-C(20)-C(21)	111.1(4)
N(1)-C(2)	1.471(6)	Cl(2)-Pd(1)-Cl(1)	91.67(5)	C(25)-C(20)-P(5)	111.0(4)
N(1)-C(6)	1.479(6)	C(4)-N(1)-C(2)	110.4(4)	C(21)-C(20)-P(5)	115.3(3)
C(2)-P(3)	1.842(5)	C(4)-N(1)-C(6)	108.9(4)	C(22)-C(21)-C(20)	110.6(5)
P(3)-C(8)	1.841(5)	C(2)-N(1)-C(6)	108.8(4)	C(23)-C(22)-C(21)	112.6(5)
P(3)-C(14)	1.842(5)	N(1)-C(2)-P(3)	114.8(3)	C(22)-C(23)-C(24)	111.0(5)
C(4)-P(5)	1.820(5)	C(8)-P(3)-C(2)	102.1(2)	C(25)-C(24)-C(23)	111.8(5)
P(5)-C(20)	1.844(5)	C(8)-P(3)-C(14)	106.1(2)	C(24)-C(25)-C(20)	111.2(5)
P(5)-C(26)	1.865(5)	C(2)-P(3)-C(14)	102.4(2)	C(31)-C(26)-C(27)	110.1(5)
C(6)-P(7)	1.821(6)	C(8)-P(3)-Pd(1)	116.63(17)	C(31)-C(26)-P(5)	115.3(4)
O(7)-P(7)	1.489(4)	C(2)-P(3)-Pd(1)	117.24(17)	C(27)-C(26)-P(5)	112.2(4)
P(7)-C(32')	1.691(12)	C(14)-P(3)-Pd(1)	110.91(17)	C(26)-C(27)-C(28)	109.5(5)
P(7)-C(38')	1.819(16)	N(1)-C(4)-P(5)	115.1(3)	C(29)-C(28)-C(27)	111.2(6)
P(7)-C(38)	1.829(7)	C(4)-P(5)-C(20)	101.8(2)	C(28)-C(29)-C(30)	111.7(6)
P(7)-C(32)	1.878(7)	C(4)-P(5)-C(26)	108.1(2)	C(29)-C(30)-C(31)	111.7(6)
C(8)-C(13)	1.514(7)	C(20)-P(5)-C(26)	108.1(2)	C(26)-C(31)-C(30)	110.6(5)
C(8)-C(9)	1.537(7)	C(4)-P(5)-Pd(1)	118.40(16)	C(33)-C(32)-C(37)	110.5(6)
C(9)-C(10)	1.536(7)	C(20)-P(5)-Pd(1)	109.66(16)	C(33)-C(32)-P(7)	112.4(5)
C(10)-C(11)	1.510(9)	C(26)-P(5)-Pd(1)	110.20(17)	C(37)-C(32)-P(7)	114.8(5)
C(11)-C(12)	1.525(9)	N(1)-C(6)-P(7)	114.0(4)	C(34)-C(33)-C(32)	112.3(6)
C(12)-C(13)	1.530(7)	O(7)-P(7)-C(32')	111.4(6)	C(35)-C(34)-C(33)	111.9(6)
C(14)-C(19)	1.525(7)	O(7)-P(7)-C(38')	108.5(18)	C(34)-C(35)-C(36)	111.3(7)
C(14)-C(15)	1.533(8)	C(32')-P(7)-C(38')	122(2)	C(35)-C(36)-C(37)	111.5(7)
C(15)-C(16)	1.522(8)	O(7)-P(7)-C(6)	113.4(2)	C(36)-C(37)-C(32)	112.5(6)
C(16)-C(17)	1.533(8)	C(32')-P(7)-C(6)	93.8(7)	C(33')-C(32')-C(37')	111.2(11)
C(17)-C(18)	1.531(9)	C(38')-P(7)-C(6)	107.5(17)	C(33')-C(32')-P(7)	105.5(10)
C(18)-C(19)	1.517(7)	O(7)-P(7)-C(38)	115.6(5)	C(37')-C(32')-P(7)	115.6(12)
C(20)-C(25)	1.527(7)	C(6)-P(7)-C(38)	102.9(5)	C(32')-C(33')-C(34')	107.8(10)
C(20)-C(21)	1.527(7)	O(7)-P(7)-C(32)	110.9(3)	C(35')-C(34')-C(33')	110.4(11)
C(21)-C(22)	1.525(7)	C(6)-P(7)-C(32)	108.9(4)	C(34')-C(35')-C(36')	112.9(11)
C(22)-C(23)	1.507(10)	C(38)-P(7)-C(32)	104.4(5)	C(35')-C(36')-C(37')	110.0(11)
C(23)-C(24)	1.522(9)	C(13)-C(8)-C(9)	110.2(4)	C(32')-C(37')-C(36')	108.0(10)
C(24)-C(25)	1.520(8)	C(13)-C(8)-P(3)	111.6(4)	C(43)-C(38)-C(39)	110.2(6)
C(26)-C(31)	1.510(7)	C(9)-C(8)-P(3)	115.8(3)	C(43)-C(38)-P(7)	110.4(8)
C(26)-C(27)	1.530(7)	C(10)-C(9)-C(8)	109.4(4)	C(39)-C(38)-P(7)	111.9(8)
C(27)-C(28)	1.549(9)	C(11)-C(10)-C(9)	111.7(5)	C(40)-C(39)-C(38)	111.7(6)
C(28)-C(29)	1.482(10)	C(10)-C(11)-C(12)	111.6(5)	C(41)-C(40)-C(39)	112.1(7)
C(29)-C(30)	1.502(10)	C(11)-C(12)-C(13)	111.3(5)	C(40)-C(41)-C(42)	110.8(7)
C(30)-C(31)	1.535(9)	C(8)-C(13)-C(12)	111.0(5)	C(43)-C(42)-C(41)	111.4(7)
C(32)-C(33)	1.529(9)	C(19)-C(14)-C(15)	111.0(4)	C(42)-C(43)-C(38)	111.9(7)
C(32)-C(37)	1.531(9)	C(19)-C(14)-P(3)	112.6(3)	C(39')-C(38')-C(43')	111.0(15)
C(33)-C(34)	1.522(9)	C(15)-C(14)-P(3)	113.4(4)	C(39')-C(38')-P(7)	112(3)
C(34)-C(35)	1.510(10)	C(16)-C(15)-C(14)	110.4(5)	C(43')-C(38')-P(7)	107(3)
C(35)-C(36)	1.511(10)	C(40')-C(39')-C(38')	111.5(15)		
C(36)-C(37)	1.529(9)	C(41')-C(40')-C(39')	111.8(14)		
C(32')-C(33')	1.524(13)	C(40')-C(41')-C(42')	111.3(14)		
C(32')-C(37')	1.526(13)	C(43')-C(42')-C(41')	111.2(15)		

C(33')-C(34')	1.541(13)	C(42')-C(43')-C(38')	111.1(14)		
C(34')-C(35')	1.519(13)	Cl(52)-C(50)-Cl(51)	113.5(6)		
C(35')-C(36')	1.522(13)	Cl(53)-C(50')-Cl(54)	113.8(17)		
C(36')-C(37')	1.533(13)	Cl(62)-C(60)-Cl(61)	119.6(13)		
C(38)-C(43)	1.529(9)	Cl(63)-C(60')-Cl(64)	119.9(18)		
C(38)-C(39)	1.529(8)	Cl(65)-C(60'')-Cl(66)	119.8(16)		
C(39)-C(40)	1.515(9)	Cl(71)-C(70)-Cl(72)	116.3(12)		
C(40)-C(41)	1.507(9)	Cl(73)-C(70')-Cl(74)	114.0(18)		
C(41)-C(42)	1.528(9)				
C(42)-C(43)	1.513(10)				
C(38')-C(39')	1.522(15)				
C(38')-C(43')	1.524(15)				
C(39')-C(40')	1.517(15)				
C(40')-C(41')	1.517(15)				
C(41')-C(42')	1.523(15)				
C(42')-C(43')	1.519(15)				
C(50)-Cl(52)	1.721(9)				
C(50)-Cl(51)	1.733(10)				
C(50')-Cl(53)	1.732(17)				
C(50')-Cl(54)	1.735(17)				
C(60)-Cl(62)	1.630(14)				
C(60)-Cl(61)	1.657(13)				
C(60')-Cl(63)	1.622(17)				
C(60')-Cl(64)	1.627(17)				
C(60'')-Cl(65)	1.626(16)				
C(60'')-Cl(66)	1.638(15)				
C(70)-Cl(71)	1.668(14)				
C(70)-Cl(72)	1.711(15)				
C(70')-Cl(73)	1.692(18)				
C(70')-Cl(74)	1.702(18)				

Table A20. Geometric parameters of $[P(O)(^tBu)_2CH_2-N(CH_2P(^tBu)_2)_2PdCl_2]$ (**10**).

Bond lengths (Å)		Bond angles (°)			
Pd(1)-P(3)	2.2884(12)	P(3)-Pd(1)-P(5)	96.57(5)	C(17)-C(16)-P(5)	112.4(4)
Pd(1)-P(5)	2.2970(14)	P(3)-Pd(1)-Cl(1)	171.20(6)	C(19)-C(16)-P(5)	112.7(5)
Pd(1)-Cl(1)	2.3519(13)	P(5)-Pd(1)-Cl(1)	90.35(5)	C(23)-C(20)-C(21)	109.2(5)
Pd(1)-Cl(2)	2.3524(16)	P(3)-Pd(1)-Cl(2)	89.14(5)	C(23)-C(20)-C(22)	109.0(5)
N(1)-C(2)	1.469(6)	P(5)-Pd(1)-Cl(2)	171.75(6)	C(21)-C(20)-C(22)	106.1(5)
N(1)-C(4)	1.473(7)	Cl(1)-Pd(1)-Cl(2)	84.58(6)	C(23)-C(20)-P(5)	111.4(4)
N(1)-C(6)	1.491(7)	C(2)-N(1)-C(4)	108.8(4)	C(21)-C(20)-P(5)	113.5(4)
C(2)-P(3)	1.849(5)	C(2)-N(1)-C(6)	107.0(4)	C(22)-C(20)-P(5)	107.3(4)
P(3)-C(12)	1.889(6)	C(4)-N(1)-C(6)	106.6(4)	C(27)-C(24)-C(26)	111.4(6)
P(3)-C(8)	1.906(5)	N(1)-C(2)-P(3)	117.9(3)	C(27)-C(24)-C(25)	110.9(7)
C(4)-P(5)	1.853(5)	C(2)-P(3)-C(12)	103.6(3)	C(26)-C(24)-C(25)	107.6(7)
P(5)-C(20)	1.901(6)	C(2)-P(3)-C(8)	100.4(2)	C(27)-C(24)-P(7)	113.2(5)
P(5)-C(16)	1.904(6)	C(12)-P(3)-C(8)	111.1(3)	C(26)-C(24)-P(7)	108.2(5)
C(6)-P(7)	1.850(6)	C(2)-P(3)-Pd(1)	115.53(17)	C(25)-C(24)-P(7)	105.2(4)
P(7)-O(7)	1.495(5)	C(12)-P(3)-Pd(1)	111.26(18)	C(31)-C(28)-C(29)	109.3(5)
P(7)-C(28)	1.865(6)	C(8)-P(3)-Pd(1)	114.08(18)	C(31)-C(28)-C(30)	109.6(6)
P(7)-C(24)	1.872(6)	N(1)-C(4)-P(5)	115.2(4)	C(29)-C(28)-C(30)	110.2(5)
C(8)-C(11)	1.527(9)	C(4)-P(5)-C(20)	98.8(2)	C(31)-C(28)-P(7)	105.2(4)
C(8)-C(10)	1.533(9)	C(4)-P(5)-C(16)	103.6(3)	C(29)-C(28)-P(7)	107.9(5)
C(8)-C(9)	1.547(8)	C(20)-P(5)-C(16)	112.3(3)	C(30)-C(28)-P(7)	114.4(4)
C(12)-C(14)	1.534(9)	C(4)-P(5)-Pd(1)	115.36(18)		
C(12)-C(13)	1.541(9)	C(20)-P(5)-Pd(1)	112.16(19)		
C(12)-C(15)	1.544(8)	C(16)-P(5)-Pd(1)	113.4(2)		
C(16)-C(18)	1.523(10)	N(1)-C(6)-P(7)	116.0(4)		
C(16)-C(17)	1.539(9)	O(7)-P(7)-C(6)	114.3(3)		
C(16)-C(19)	1.541(9)	O(7)-P(7)-C(28)	109.6(3)		
C(20)-C(23)	1.520(9)	C(6)-P(7)-C(28)	103.8(3)		
C(20)-C(21)	1.535(8)	O(7)-P(7)-C(24)	108.7(3)		
C(20)-C(22)	1.545(8)	C(6)-P(7)-C(24)	106.1(3)		
C(24)-C(27)	1.529(11)	C(28)-P(7)-C(24)	114.5(3)		
C(24)-C(26)	1.540(10)	C(11)-C(8)-C(10)	109.8(5)		
C(24)-C(25)	1.545(10)	C(11)-C(8)-C(9)	107.9(5)		
C(28)-C(31)	1.529(9)	C(10)-C(8)-C(9)	108.0(5)		
C(28)-C(29)	1.535(9)	C(11)-C(8)-P(3)	112.9(4)		
C(28)-C(30)	1.538(10)	C(10)-C(8)-P(3)	106.3(4)		
		C(9)-C(8)-P(3)	111.9(4)		
		C(14)-C(12)-C(13)	107.7(5)		
		C(14)-C(12)-C(15)	110.4(5)		
		C(13)-C(12)-C(15)	107.0(5)		
		C(14)-C(12)-P(3)	105.7(4)		
		C(13)-C(12)-P(3)	114.4(4)		
		C(15)-C(12)-P(3)	111.6(4)		
		C(18)-C(16)-C(17)	107.6(6)		
		C(18)-C(16)-C(19)	109.6(6)		
		C(17)-C(16)-C(19)	108.0(6)		
		C(18)-C(16)-P(5)	106.4(4)		

Table A21. Geometric parameters of [Me-N(CH₂PPh₂)₂NiCl₂] (**11**).

Bond lengths (Å)		Bond angles (°)	
Ni(1)-P(3)	2.1585(6)	P(3)-Ni(1)-P(3)#1	93.19(3)
Ni(1)-P(3)#1	2.1585(6)	P(3)-Ni(1)-Cl(1)	87.09(2)
Ni(1)-Cl(1)	2.2026(6)	P(3)#1-Ni(1)-Cl(1)	176.87(3)
Ni(1)-Cl(1)#1	2.2026(6)	P(3)-Ni(1)-Cl(1)#1	176.87(3)
N(1)-C(2)#1	1.452(2)	P(3)#1-Ni(1)-Cl(1)#1	87.09(2)
N(1)-C(2)	1.453(2)	Cl(1)-Ni(1)-Cl(1)#1	92.46(3)
N(1)-C(4)	1.478(4)	C(2)#1-N(1)-C(2)	110.9(2)
C(2)-P(3)	1.840(2)	C(2)#1-N(1)-C(4)	110.59(15)
P(3)-C(5)	1.816(2)	C(2)-N(1)-C(4)	110.59(15)
P(3)-C(11)	1.820(2)	N(1)-C(2)-P(3)	114.86(15)
C(5)-C(6)	1.397(3)	C(5)-P(3)-C(11)	107.58(10)
C(5)-C(10)	1.398(3)	C(5)-P(3)-C(2)	104.28(10)
C(6)-C(7)	1.388(3)	C(11)-P(3)-C(2)	97.32(9)
C(7)-C(8)	1.376(3)	C(5)-P(3)-Ni(1)	111.07(7)
C(8)-C(9)	1.384(3)	C(11)-P(3)-Ni(1)	115.65(7)
C(9)-C(10)	1.382(3)	C(2)-P(3)-Ni(1)	119.41(7)
C(11)-C(16)	1.395(3)	C(6)-C(5)-C(10)	119.1(2)
C(11)-C(12)	1.397(3)	C(6)-C(5)-P(3)	120.55(16)
C(12)-C(13)	1.386(3)	C(10)-C(5)-P(3)	120.40(17)
C(13)-C(14)	1.389(3)	C(7)-C(6)-C(5)	119.9(2)
C(14)-C(15)	1.384(3)	C(8)-C(7)-C(6)	120.4(2)
C(15)-C(16)	1.381(3)	C(7)-C(8)-C(9)	120.2(2)
		C(10)-C(9)-C(8)	120.1(2)
		C(9)-C(10)-C(5)	120.3(2)
		C(16)-C(11)-C(12)	118.8(2)
		C(16)-C(11)-P(3)	118.03(16)
		C(12)-C(11)-P(3)	122.76(17)
		C(13)-C(12)-C(11)	120.3(2)
		C(12)-C(13)-C(14)	120.2(2)
		C(15)-C(14)-C(13)	119.6(2)
		C(16)-C(15)-C(14)	120.4(2)
		C(15)-C(16)-C(11)	120.5(2)

Table A22. Geometric parameters of [Me-N(CH₂PCy₂)₂NiCl₂] (**12**).

Bond lengths (Å)		Bond angles (°)			
Ni(1)-P(5)	2.1673(14)	P(5)-Ni(1)-P(3)	96.37(5)	C(22)-C(23)-C(24)	111.6(4)
Ni(1)-P(3)	2.1772(11)	P(5)-Ni(1)-Cl(1)	85.99(5)	C(19)-C(24)-C(23)	109.9(4)
Ni(1)-Cl(1)	2.1998(11)	P(3)-Ni(1)-Cl(1)	177.53(6)	C(26)-C(25)-C(30)	110.7(4)
Ni(1)-Cl(2)	2.2066(13)	P(5)-Ni(1)-Cl(2)	173.86(5)	C(26)-C(25)-P(5)	116.7(3)
N(1)-C(4)	1.460(5)	P(3)-Ni(1)-Cl(2)	87.22(5)	C(30)-C(25)-P(5)	110.7(3)
N(1)-C(6)	1.461(6)	Cl(1)-Ni(1)-Cl(2)	90.48(5)	C(27)-C(26)-C(25)	110.1(4)
N(1)-C(2)	1.467(6)	C(4)-N(1)-C(6)	110.1(4)	C(28)-C(27)-C(26)	111.3(4)
C(2)-P(3)	1.844(5)	C(4)-N(1)-C(2)	110.0(3)	C(27)-C(28)-C(29)	111.2(4)
P(3)-C(13)	1.849(4)	C(6)-N(1)-C(2)	109.7(3)	C(28)-C(29)-C(30)	111.3(4)
P(3)-C(7)	1.858(4)	N(1)-C(2)-P(3)	114.7(3)	C(29)-C(30)-C(25)	110.9(4)
C(4)-P(5)	1.838(4)	C(2)-P(3)-C(13)	102.8(2)	Cl(42)-C(40)-Cl(41)	115.4(5)
P(5)-C(19)	1.840(4)	C(2)-P(3)-C(7)	99.7(2)	Cl(52)-C(50)-Cl(51)	106.4(16)
P(5)-C(25)	1.845(4)	C(13)-P(3)-C(7)	106.6(2)		
C(7)-C(12)	1.528(7)	C(2)-P(3)-Ni(1)	118.90(14)		
C(7)-C(8)	1.534(6)	C(13)-P(3)-Ni(1)	111.03(14)		
C(8)-C(9)	1.537(7)	C(7)-P(3)-Ni(1)	116.23(14)		
C(9)-C(10)	1.517(8)	N(1)-C(4)-P(5)	113.5(3)		
C(10)-C(11)	1.517(7)	C(4)-P(5)-C(19)	101.6(2)		
C(11)-C(12)	1.537(6)	C(4)-P(5)-C(25)	101.7(2)		
C(13)-C(18)	1.521(6)	C(19)-P(5)-C(25)	106.09(19)		
C(13)-C(14)	1.537(6)	C(4)-P(5)-Ni(1)	118.08(15)		
C(14)-C(15)	1.535(7)	C(19)-P(5)-Ni(1)	111.35(17)		
C(15)-C(16)	1.516(8)	C(25)-P(5)-Ni(1)	116.29(15)		
C(16)-C(17)	1.527(7)	C(12)-C(7)-C(8)	110.9(4)		
C(17)-C(18)	1.529(7)	C(12)-C(7)-P(3)	116.7(3)		
C(19)-C(24)	1.528(7)	C(8)-C(7)-P(3)	111.2(3)		
C(19)-C(20)	1.531(6)	C(7)-C(8)-C(9)	109.3(4)		
C(20)-C(21)	1.535(6)	C(10)-C(9)-C(8)	112.7(5)		
C(21)-C(22)	1.516(8)	C(9)-C(10)-C(11)	111.0(4)		
C(22)-C(23)	1.511(7)	C(10)-C(11)-C(12)	111.7(4)		
C(23)-C(24)	1.531(6)	C(7)-C(12)-C(11)	109.1(4)		
C(25)-C(26)	1.530(6)	C(18)-C(13)-C(14)	111.4(4)		
C(25)-C(30)	1.533(6)	C(18)-C(13)-P(3)	110.9(3)		
C(26)-C(27)	1.528(6)	C(14)-C(13)-P(3)	114.2(3)		
C(27)-C(28)	1.504(6)	C(15)-C(14)-C(13)	109.8(4)		
C(28)-C(29)	1.524(7)	C(16)-C(15)-C(14)	111.6(5)		
C(29)-C(30)	1.529(7)	C(15)-C(16)-C(17)	110.9(4)		
C(40)-Cl(42)	1.743(10)	C(16)-C(17)-C(18)	111.5(4)		
C(40)-Cl(41)	1.765(8)	C(13)-C(18)-C(17)	111.6(4)		
C(50)-Cl(52)	1.749(19)	C(24)-C(19)-C(20)	110.3(4)		
C(50)-Cl(51)	1.751(19)	C(24)-C(19)-P(5)	115.5(3)		
		C(20)-C(19)-P(5)	111.8(3)		
		C(19)-C(20)-C(21)	109.7(4)		
		C(22)-C(21)-C(20)	111.6(5)		
		C(23)-C(22)-C(21)	111.3(5)		

Table A23. Geometric parameters of [Me-N(CH₂PCy₂)₂Ru(η⁶-*p*-cymene)Cl]Cl (**13**).

Bond lengths (Å)		Bond angles (°)			
Ru(1A)-C(33A)	2.220(3)	C(33A)-Ru(1A)-C(35A)	65.44(11)	C(4A)-P(5A)-C(19A)	105.83(14)
Ru(1A)-C(35A)	2.257(3)	C(33A)-Ru(1A)-C(36A)	77.49(11)	C(4A)-P(5A)-C(25A)	101.71(14)
Ru(1A)-C(36A)	2.266(3)	C(35A)-Ru(1A)-C(36A)	36.24(11)	C(19A)-P(5A)-C(25A)	104.29(14)
Ru(1A)-C(32A)	2.267(3)	C(33A)-Ru(1A)-C(32A)	37.01(11)	C(4A)-P(5A)-Ru(1A)	113.92(10)
Ru(1A)-C(34A)	2.291(3)	C(35A)-Ru(1A)-C(32A)	76.93(12)	C(19A)-P(5A)-Ru(1A)	119.08(10)
Ru(1A)-C(31A)	2.309(3)	C(36A)-Ru(1A)-C(32A)	65.06(11)	C(25A)-P(5A)-Ru(1A)	110.22(10)
Ru(1A)-P(3A)	2.3482(7)	C(33A)-Ru(1A)-C(34A)	36.28(12)	C(8A)-C(7A)-C(12A)	109.4(2)
Ru(1A)-P(5A)	2.3511(7)	C(35A)-Ru(1A)-C(34A)	36.31(11)	C(8A)-C(7A)-P(3A)	114.0(2)
Ru(1A)-Cl(1A)	2.4040(7)	C(36A)-Ru(1A)-C(34A)	65.36(11)	C(12A)-C(7A)-P(3A)	113.3(2)
N(1A)-C(4A)	1.456(4)	C(32A)-Ru(1A)-C(34A)	65.54(12)	C(9A)-C(8A)-C(7A)	110.9(3)
N(1A)-C(6A)	1.462(4)	C(33A)-Ru(1A)-C(31A)	65.64(11)	C(10A)-C(9A)-C(8A)	112.1(3)
N(1A)-C(2A)	1.467(4)	C(35A)-Ru(1A)-C(31A)	65.03(12)	C(9A)-C(10A)-C(11A)	110.4(3)
C(2A)-P(3A)	1.840(3)	C(36A)-Ru(1A)-C(31A)	36.19(11)	C(10A)-C(11A)-C(12A)	110.4(3)
P(3A)-C(7A)	1.870(3)	C(32A)-Ru(1A)-C(31A)	35.90(10)	C(11A)-C(12A)-C(7A)	110.6(3)
P(3A)-C(13A)	1.879(3)	C(34A)-Ru(1A)-C(31A)	76.94(12)	C(14A)-C(13A)-C(18A)	110.3(3)
C(4A)-P(5A)	1.844(3)	C(33A)-Ru(1A)-P(3A)	133.45(9)	C(14A)-C(13A)-P(3A)	114.1(2)
P(5A)-C(19A)	1.853(3)	C(35A)-Ru(1A)-P(3A)	91.20(8)	C(18A)-C(13A)-P(3A)	116.0(2)
P(5A)-C(25A)	1.877(3)	C(36A)-Ru(1A)-P(3A)	107.62(8)	C(15A)-C(14A)-C(13A)	110.5(3)
C(7A)-C(8A)	1.536(4)	C(32A)-Ru(1A)-P(3A)	167.36(8)	C(16A)-C(15A)-C(14A)	111.9(4)
C(7A)-C(12A)	1.538(4)	C(34A)-Ru(1A)-P(3A)	102.29(9)	C(17A)-C(16A)-C(15A)	110.7(3)
C(8A)-C(9A)	1.528(4)	C(31A)-Ru(1A)-P(3A)	141.32(8)	C(16A)-C(17A)-C(18A)	111.4(3)
C(9A)-C(10A)	1.514(4)	C(33A)-Ru(1A)-P(5A)	92.23(8)	C(17A)-C(18A)-C(13A)	111.1(3)
C(10A)-C(11A)	1.522(4)	C(35A)-Ru(1A)-P(5A)	149.66(8)	C(20A)-C(19A)-C(24A)	109.2(3)
C(11A)-C(12A)	1.531(4)	C(36A)-Ru(1A)-P(5A)	162.01(8)	C(20A)-C(19A)-P(5A)	113.6(2)
C(13A)-C(14A)	1.532(4)	C(32A)-Ru(1A)-P(5A)	97.87(8)	C(24A)-C(19A)-P(5A)	114.5(2)
C(13A)-C(18A)	1.535(5)	C(34A)-Ru(1A)-P(5A)	114.16(8)	C(19A)-C(20A)-C(21A)	109.7(3)
C(14A)-C(15A)	1.526(5)	C(31A)-Ru(1A)-P(5A)	125.98(8)	C(22A)-C(21A)-C(20A)	110.5(3)
C(15A)-C(16A)	1.511(7)	P(3A)-Ru(1A)-P(5A)	90.20(2)	C(21A)-C(22A)-C(23A)	110.8(3)
C(16A)-C(17A)	1.507(6)	C(33A)-Ru(1A)-Cl(1A)	139.18(9)	C(22A)-C(23A)-C(24A)	110.5(3)
C(17A)-C(18A)	1.525(5)	C(35A)-Ru(1A)-Cl(1A)	129.34(8)	C(19A)-C(24A)-C(23A)	109.5(3)
C(19A)-C(20A)	1.525(4)	C(36A)-Ru(1A)-Cl(1A)	97.04(8)	C(26A)-C(25A)-C(30A)	109.4(3)
C(19A)-C(24A)	1.534(4)	C(32A)-Ru(1A)-Cl(1A)	103.76(8)	C(26A)-C(25A)-P(5A)	116.0(2)
C(20A)-C(21A)	1.548(5)	C(34A)-Ru(1A)-Cl(1A)	161.79(8)	C(30A)-C(25A)-P(5A)	113.1(2)
C(21A)-C(22A)	1.527(5)	C(31A)-Ru(1A)-Cl(1A)	85.99(8)	C(27A)-C(26A)-C(25A)	110.4(3)
C(22A)-C(23A)	1.529(6)	P(3A)-Ru(1A)-Cl(1A)	87.05(2)	C(28A)-C(27A)-C(26A)	112.1(3)
C(23A)-C(24A)	1.535(5)	P(5A)-Ru(1A)-Cl(1A)	81.00(2)	C(27A)-C(28A)-C(29A)	109.9(3)
C(25A)-C(26A)	1.541(4)	C(4A)-N(1A)-C(6A)	109.3(3)	C(28A)-C(29A)-C(30A)	110.3(3)
C(25A)-C(30A)	1.542(4)	C(4A)-N(1A)-C(2A)	110.9(2)	C(29A)-C(30A)-C(25A)	109.9(3)
C(26A)-C(27A)	1.516(5)	C(6A)-N(1A)-C(2A)	109.4(3)	C(32A)-C(31A)-C(36A)	118.8(3)
C(27A)-C(28A)	1.515(5)	N(1A)-C(2A)-P(3A)	113.3(2)	C(32A)-C(31A)-C(37A)	122.8(3)
C(28A)-C(29A)	1.528(5)	C(2A)-P(3A)-C(7A)	101.66(13)	C(36A)-C(31A)-C(37A)	118.4(3)
C(29A)-C(30A)	1.538(5)	C(2A)-P(3A)-C(13A)	103.73(14)	C(32A)-C(31A)-Ru(1A)	70.42(16)
C(31A)-C(32A)	1.411(4)	C(7A)-P(3A)-C(13A)	105.11(13)	C(36A)-C(31A)-Ru(1A)	70.26(16)
C(31A)-C(36A)	1.422(4)	C(2A)-P(3A)-Ru(1A)	114.06(10)	C(37A)-C(31A)-Ru(1A)	132.5(2)
C(31A)-C(37A)	1.513(4)	C(7A)-P(3A)-Ru(1A)	115.35(9)	C(31A)-C(32A)-C(33A)	120.0(3)
C(32A)-C(33A)	1.425(4)	C(13A)-P(3A)-Ru(1A)	115.32(11)	C(31A)-C(32A)-Ru(1A)	73.69(16)
C(33A)-C(34A)	1.406(5)	N(1A)-C(4A)-P(5A)	113.3(2)	C(33A)-C(32A)-Ru(1A)	69.71(16)
C(34A)-C(35A)	1.417(4)	C(34A)-C(33A)-C(32A)	121.3(3)	C(36B)-Ru(1B)-Cl(1B)	100.76(7)
C(34A)-C(40A)	1.505(4)	C(34A)-C(33A)-Ru(1A)	74.60(17)	C(31B)-Ru(1B)-Cl(1B)	86.22(7)
C(35A)-C(36A)	1.407(4)	C(32A)-C(33A)-Ru(1A)	73.28(16)	P(3B)-Ru(1B)-Cl(1B)	84.89(2)
C(37A)-C(39A)	1.527(5)	C(33A)-C(34A)-C(35A)	118.0(3)	P(5B)-Ru(1B)-Cl(1B)	85.22(2)

C(37A)-C(38A)	1.532(5)	C(33A)-C(34A)-C(40A)	120.8(3)	C(4B)-N(1B)-C(2B)	114.3(2)
Ru(1B)-C(33B)	2.226(3)	C(35A)-C(34A)-C(40A)	120.9(3)	C(4B)-N(1B)-C(6B)	110.0(2)
Ru(1B)-C(35B)	2.235(3)	C(33A)-C(34A)-Ru(1A)	69.12(16)	C(2B)-N(1B)-C(6B)	109.7(2)
Ru(1B)-C(34B)	2.263(2)	C(35A)-C(34A)-Ru(1A)	70.56(16)	N(1B)-C(2B)-P(3B)	113.11(18)
Ru(1B)-C(32B)	2.275(3)	C(40A)-C(34A)-Ru(1A)	137.2(2)	C(2B)-P(3B)-C(7B)	103.11(12)
Ru(1B)-C(36B)	2.285(3)	C(36A)-C(35A)-C(34A)	121.2(3)	C(2B)-P(3B)-C(13B)	104.99(13)
Ru(1B)-C(31B)	2.304(3)	C(36A)-C(35A)-Ru(1A)	72.23(16)	C(7B)-P(3B)-C(13B)	105.42(13)
Ru(1B)-P(3B)	2.3295(7)	C(34A)-C(35A)-Ru(1A)	73.13(16)	C(2B)-P(3B)-Ru(1B)	113.51(9)
Ru(1B)-P(5B)	2.3477(7)	C(35A)-C(36A)-C(31A)	120.4(3)	C(7B)-P(3B)-Ru(1B)	113.37(10)
Ru(1B)-Cl(1B)	2.3976(6)	C(35A)-C(36A)-Ru(1A)	71.53(16)	C(13B)-P(3B)-Ru(1B)	115.28(9)
N(1B)-C(4B)	1.457(4)	C(31A)-C(36A)-Ru(1A)	73.55(16)	N(1B)-C(4B)-P(5B)	111.80(18)
N(1B)-C(2B)	1.470(3)	C(31A)-C(37A)-C(39A)	115.1(3)	C(4B)-P(5B)-C(25B)	104.69(13)
N(1B)-C(6B)	1.476(3)	C(31A)-C(37A)-C(38A)	108.4(3)	C(4B)-P(5B)-C(19B)	103.30(13)
C(2B)-P(3B)	1.842(3)	C(39A)-C(37A)-C(38A)	111.3(3)	C(25B)-P(5B)-C(19B)	105.23(13)
P(3B)-C(7B)	1.860(3)	C(33B)-Ru(1B)-C(35B)	65.29(11)	C(4B)-P(5B)-Ru(1B)	112.74(9)
P(3B)-C(13B)	1.877(3)	C(33B)-Ru(1B)-C(34B)	36.56(11)	C(25B)-P(5B)-Ru(1B)	113.06(10)
C(4B)-P(5B)	1.840(3)	C(35B)-Ru(1B)-C(34B)	36.74(10)	C(19B)-P(5B)-Ru(1B)	116.64(9)
P(5B)-C(25B)	1.852(3)	C(33B)-Ru(1B)-C(32B)	36.73(10)	C(12B)-C(7B)-C(8B)	108.5(2)
P(5B)-C(19B)	1.868(3)	C(35B)-Ru(1B)-C(32B)	76.96(11)	C(12B)-C(7B)-P(3B)	113.8(2)
C(7B)-C(12B)	1.525(4)	C(34B)-Ru(1B)-C(32B)	66.15(11)	C(8B)-C(7B)-P(3B)	115.0(2)
C(7B)-C(8B)	1.533(4)	C(33B)-Ru(1B)-C(36B)	76.66(10)	C(9B)-C(8B)-C(7B)	110.2(3)
C(8B)-C(9B)	1.529(4)	C(35B)-Ru(1B)-C(36B)	36.45(10)	C(10B)-C(9B)-C(8B)	111.6(3)
C(9B)-C(10B)	1.508(5)	C(34B)-Ru(1B)-C(36B)	65.93(10)	C(9B)-C(10B)-C(11B)	111.4(3)
C(10B)-C(11B)	1.520(5)	C(32B)-Ru(1B)-C(36B)	64.39(10)	C(10B)-C(11B)-C(12B)	111.1(3)
C(11B)-C(12B)	1.528(4)	C(33B)-Ru(1B)-C(31B)	65.54(10)	C(7B)-C(12B)-C(11B)	110.0(3)
C(13B)-C(18B)	1.531(4)	C(35B)-Ru(1B)-C(31B)	65.43(11)	C(18B)-C(13B)-C(14B)	110.2(3)
C(13B)-C(14B)	1.534(4)	C(34B)-Ru(1B)-C(31B)	78.14(10)	C(18B)-C(13B)-P(3B)	115.5(2)
C(14B)-C(15B)	1.528(5)	C(32B)-Ru(1B)-C(31B)	35.96(10)	C(14B)-C(13B)-P(3B)	114.3(2)
C(15B)-C(16B)	1.517(6)	C(36B)-Ru(1B)-C(31B)	35.84(11)	C(15B)-C(14B)-C(13B)	111.3(3)
C(16B)-C(17B)	1.512(6)	C(33B)-Ru(1B)-P(3B)	139.62(8)	C(16B)-C(15B)-C(14B)	112.0(3)
C(17B)-C(18B)	1.523(5)	C(35B)-Ru(1B)-P(3B)	90.45(8)	C(17B)-C(16B)-C(15B)	110.7(3)
C(19B)-C(20B)	1.531(4)	C(34B)-Ru(1B)-P(3B)	105.65(8)	C(16B)-C(17B)-C(18B)	112.4(3)
C(19B)-C(24B)	1.539(4)	C(32B)-Ru(1B)-P(3B)	166.93(8)	C(17B)-C(18B)-C(13B)	110.2(3)
C(20B)-C(21B)	1.525(4)	C(36B)-Ru(1B)-P(3B)	103.30(8)	C(20B)-C(19B)-C(24B)	110.6(2)
C(21B)-C(22B)	1.528(5)	C(31B)-Ru(1B)-P(3B)	134.67(8)	C(20B)-C(19B)-P(5B)	113.2(2)
C(22B)-C(23B)	1.518(5)	C(33B)-Ru(1B)-P(5B)	91.81(7)	C(24B)-C(19B)-P(5B)	116.22(19)
C(23B)-C(24B)	1.528(4)	C(35B)-Ru(1B)-P(5B)	140.21(8)	C(21B)-C(20B)-C(19B)	110.7(3)
C(25B)-C(26B)	1.534(4)	C(34B)-Ru(1B)-P(5B)	106.44(7)	C(20B)-C(21B)-C(22B)	110.6(3)
C(25B)-C(30B)	1.534(4)	C(32B)-Ru(1B)-P(5B)	104.49(8)	C(23B)-C(22B)-C(21B)	110.8(3)
C(26B)-C(27B)	1.525(5)	C(36B)-Ru(1B)-P(5B)	168.08(7)	C(22B)-C(23B)-C(24B)	112.4(3)
C(27B)-C(28B)	1.511(6)	C(31B)-Ru(1B)-P(5B)	135.89(8)	C(23B)-C(24B)-C(19B)	110.7(2)
C(28B)-C(29B)	1.518(5)	P(3B)-Ru(1B)-P(5B)	87.40(2)	C(26B)-C(25B)-C(30B)	108.6(2)
C(29B)-C(30B)	1.529(5)	C(33B)-Ru(1B)-Cl(1B)	135.30(8)	C(26B)-C(25B)-P(5B)	115.1(2)
C(31B)-C(36B)	1.412(4)	C(35B)-Ru(1B)-Cl(1B)	134.15(8)	C(30B)-C(25B)-P(5B)	114.1(2)
C(31B)-C(32B)	1.414(4)	C(34B)-Ru(1B)-Cl(1B)	164.35(8)	C(27B)-C(26B)-C(25B)	110.8(3)
C(31B)-C(37B)	1.525(4)	C(32B)-Ru(1B)-Cl(1B)	101.25(7)	C(28B)-C(27B)-C(26B)	111.2(3)
C(32B)-C(33B)	1.419(4)	C(27B)-C(28B)-C(29B)	110.7(3)	C(33B)-C(34B)-C(35B)	116.8(3)
C(33B)-C(34B)	1.408(4)	C(28B)-C(29B)-C(30B)	111.2(3)	C(33B)-C(34B)-C(40B)	121.8(3)
C(34B)-C(35B)	1.418(4)	C(29B)-C(30B)-C(25B)	110.5(3)	C(35B)-C(34B)-C(40B)	121.4(3)
C(34B)-C(40B)	1.509(4)	C(36B)-C(31B)-C(32B)	118.6(3)	C(33B)-C(34B)-Ru(1B)	70.30(15)
C(35B)-C(36B)	1.414(4)	C(36B)-C(31B)-C(37B)	118.0(3)	C(35B)-C(34B)-Ru(1B)	70.56(15)
C(37B)-C(39B)	1.520(5)	C(32B)-C(31B)-C(37B)	123.4(3)	C(40B)-C(34B)-Ru(1B)	132.4(2)
C(37B)-C(38B)	1.523(4)	C(36B)-C(31B)-Ru(1B)	71.37(16)	C(36B)-C(35B)-C(34B)	121.8(3)
		C(32B)-C(31B)-Ru(1B)	70.91(16)	C(36B)-C(35B)-Ru(1B)	73.73(15)

		C(37B)-C(31B)-Ru(1B)	131.12(19)	C(34B)-C(35B)-Ru(1B)	72.70(15)
		C(31B)-C(32B)-C(33B)	120.0(3)	C(31B)-C(36B)-C(35B)	120.5(3)
		C(31B)-C(32B)-Ru(1B)	73.13(16)	C(31B)-C(36B)-Ru(1B)	72.79(15)
		C(33B)-C(32B)-Ru(1B)	69.76(16)	C(35B)-C(36B)-Ru(1B)	69.83(15)
		C(34B)-C(33B)-C(32B)	122.3(3)	C(39B)-C(37B)-C(38B)	111.0(3)
		C(34B)-C(33B)-Ru(1B)	73.14(15)	C(39B)-C(37B)-C(31B)	115.0(3)
		C(32B)-C(33B)-Ru(1B)	73.51(15)	C(38B)-C(37B)-C(31B)	107.4(3)

Table A24. Geometric parameters of [Me-N(CH₂PCy₂)₂Ir(COD)]PF₆ (**19**).

Bond lengths (Å)		Bond angles (°)			
Ir(1)-C(35)	2.165(7)	C(35)-Ir(1)-C(31)	95.2(3)	C(13)-C(18)-C(17)	109.4(6)
Ir(1)-C(31)	2.179(8)	C(35)-Ir(1)-C(32)	79.2(3)	C(24)-C(19)-C(20)	111.2(6)
Ir(1)-C(32)	2.240(7)	C(31)-Ir(1)-C(32)	37.1(3)	C(24)-C(19)-P(5)	114.8(6)
Ir(1)-C(36)	2.242(8)	C(35)-Ir(1)-C(36)	37.2(3)	C(20)-C(19)-P(5)	108.9(5)
Ir(1)-P(5)	2.3052(19)	C(31)-Ir(1)-C(36)	79.5(3)	C(21)-C(20)-C(19)	110.5(6)
Ir(1)-P(3)	2.3114(17)	C(32)-Ir(1)-C(36)	86.6(3)	C(22)-C(21)-C(20)	111.4(7)
N(1)-C(4)	1.457(9)	C(35)-Ir(1)-P(5)	138.9(2)	C(21)-C(22)-C(23)	111.4(7)
N(1)-C(2)	1.468(10)	C(31)-Ir(1)-P(5)	99.1(2)	C(22)-C(23)-C(24)	110.2(6)
N(1)-C(6)	1.500(9)	C(32)-Ir(1)-P(5)	89.5(2)	C(19)-C(24)-C(23)	111.7(6)
C(2)-P(3)	1.838(8)	C(36)-Ir(1)-P(5)	175.08(19)	C(26)-C(25)-C(30)	109.3(6)
P(3)-C(7)	1.849(7)	C(35)-Ir(1)-P(3)	97.2(2)	C(26)-C(25)-P(5)	115.0(5)
P(3)-C(13)	1.866(7)	C(31)-Ir(1)-P(3)	144.3(2)	C(30)-C(25)-P(5)	110.0(5)
C(4)-P(5)	1.857(7)	C(32)-Ir(1)-P(3)	176.4(2)	C(25)-C(26)-C(27)	109.5(6)
P(5)-C(19)	1.847(7)	C(36)-Ir(1)-P(3)	90.57(19)	C(28)-C(27)-C(26)	110.4(6)
P(5)-C(25)	1.873(7)	P(5)-Ir(1)-P(3)	93.22(6)	C(29)-C(28)-C(27)	111.8(6)
C(7)-C(12)	1.523(9)	C(4)-N(1)-C(2)	111.7(6)	C(30)-C(29)-C(28)	111.5(7)
C(7)-C(8)	1.543(10)	C(4)-N(1)-C(6)	107.5(6)	C(29)-C(30)-C(25)	110.8(6)
C(8)-C(9)	1.537(10)	C(2)-N(1)-C(6)	110.4(6)	C(32)-C(31)-C(38)	125.3(7)
C(9)-C(10)	1.513(11)	N(1)-C(2)-P(3)	109.6(5)	C(32)-C(31)-Ir(1)	73.8(4)
C(10)-C(11)	1.514(11)	C(2)-P(3)-C(7)	105.0(4)	C(38)-C(31)-Ir(1)	108.9(5)
C(11)-C(12)	1.530(10)	C(2)-P(3)-C(13)	104.6(3)	C(31)-C(32)-C(33)	125.8(7)
C(13)-C(18)	1.529(10)	C(7)-P(3)-C(13)	104.8(3)	C(31)-C(32)-Ir(1)	69.1(4)
C(13)-C(14)	1.542(9)	C(2)-P(3)-Ir(1)	116.8(2)	C(33)-C(32)-Ir(1)	112.5(5)
C(14)-C(15)	1.538(10)	C(7)-P(3)-Ir(1)	115.8(2)	C(34)-C(33)-C(32)	110.2(6)
C(15)-C(16)	1.535(12)	C(13)-P(3)-Ir(1)	108.7(2)	C(35)-C(34)-C(33)	114.3(7)
C(16)-C(17)	1.515(12)	N(1)-C(4)-P(5)	116.7(5)	C(36)-C(35)-C(34)	127.6(7)
C(17)-C(18)	1.543(10)	C(19)-P(5)-C(4)	102.4(3)	C(36)-C(35)-Ir(1)	74.4(4)
C(19)-C(24)	1.523(10)	C(19)-P(5)-C(25)	105.8(3)	C(34)-C(35)-Ir(1)	109.6(5)
C(19)-C(20)	1.550(9)	C(4)-P(5)-C(25)	99.0(3)	C(35)-C(36)-C(37)	124.6(7)
C(20)-C(21)	1.548(11)	C(19)-P(5)-Ir(1)	117.0(3)	C(35)-C(36)-Ir(1)	68.4(4)
C(21)-C(22)	1.516(11)	C(4)-P(5)-Ir(1)	119.0(2)	C(37)-C(36)-Ir(1)	112.1(5)
C(22)-C(23)	1.517(11)	C(25)-P(5)-Ir(1)	111.5(2)	C(38)-C(37)-C(36)	111.5(7)
C(23)-C(24)	1.551(10)	C(12)-C(7)-C(8)	110.4(6)	C(31)-C(38)-C(37)	115.1(7)
C(25)-C(26)	1.530(10)	C(12)-C(7)-P(3)	116.1(5)	F(3)-P(1)-F(4)	90.8(5)
C(25)-C(30)	1.547(10)	C(8)-C(7)-P(3)	110.8(5)	F(3)-P(1)-F(1)	91.1(5)
C(26)-C(27)	1.541(10)	C(9)-C(8)-C(7)	109.9(6)	F(4)-P(1)-F(1)	89.9(4)
C(27)-C(28)	1.527(11)	C(10)-C(9)-C(8)	110.6(6)	F(3)-P(1)-F(6)	91.3(5)
C(28)-C(29)	1.523(10)	C(9)-C(10)-C(11)	110.6(7)	F(4)-P(1)-F(6)	90.3(4)
C(29)-C(30)	1.518(10)	C(10)-C(11)-C(12)	111.6(7)	F(1)-P(1)-F(6)	177.6(5)
C(31)-C(32)	1.408(10)	C(7)-C(12)-C(11)	110.7(6)	F(3)-P(1)-F(5)	178.7(6)
C(31)-C(38)	1.492(11)	C(18)-C(13)-C(14)	108.9(6)	F(4)-P(1)-F(5)	90.5(5)
C(32)-C(33)	1.533(10)	C(18)-C(13)-P(3)	113.2(5)	F(1)-P(1)-F(5)	89.1(4)
C(33)-C(34)	1.530(11)	C(14)-C(13)-P(3)	114.7(5)	F(6)-P(1)-F(5)	88.5(5)
C(34)-C(35)	1.485(10)	C(15)-C(14)-C(13)	109.9(7)	F(3)-P(1)-F(2)	89.6(5)
C(35)-C(36)	1.407(11)	C(16)-C(15)-C(14)	111.1(7)	F(4)-P(1)-F(2)	179.5(6)
C(36)-C(37)	1.517(11)	C(17)-C(16)-C(15)	110.5(7)	F(1)-P(1)-F(2)	89.7(4)
C(37)-C(38)	1.511(11)	C(16)-C(17)-C(18)	111.6(7)	F(6)-P(1)-F(2)	90.1(5)
P(1)-F(3)	1.550(7)	F(5)-P(1)-F(2)	89.1(5)	F(3')-P(1')-F(5')	179.9(12)
P(1)-F(4)	1.566(7)	F(3')-P(1')-F(2')	90.3(8)	F(2')-P(1')-F(5')	89.7(8)
P(1)-F(1)	1.579(7)	F(3')-P(1')-F(4')	90.6(8)	F(4')-P(1')-F(5')	89.5(8)
P(1)-F(6)	1.583(7)	F(2')-P(1')-F(4')	179.2(11)	F(1')-P(1')-F(5')	90.0(8)

P(1)-F(5)	1.588(7)	F(3')-P(1')-F(1')	90.2(8)		
P(1)-F(2)	1.589(7)	F(2')-P(1')-F(1')	90.1(8)		
P(1')-F(3')	1.571(12)	F(4')-P(1')-F(1')	89.9(8)		
P(1')-F(2')	1.574(13)	F(3')-P(1')-F(6')	90.2(8)		
P(1')-F(4')	1.575(12)	F(2')-P(1')-F(6')	90.1(8)		
P(1')-F(1')	1.577(12)	F(5)-P(1)-F(2)	89.1(5)		
P(1')-F(6')	1.579(12)	F(4')-P(1')-F(6')	89.9(8)		
P(1')-F(5')	1.580(13)	F(1')-P(1')-F(6')	179.6(11)		

Table A25. Geometric parameters of [Me-N(CH₂PCy₂)₂Ir(Cl)₃(OH₂)] (**20**).

Bond lengths (Å)		Bond angles (°)			
Ir(1A)-O(40A)	2.117(4)	O(40A)-Ir(1A)-P(3A)	97.58(14)	C(17A)-C(18A)-C(13A)	111.1(6)
Ir(1A)-P(3A)	2.2746(17)	O(40A)-Ir(1A)-P(5A)	95.65(13)	C(24A)-C(19A)-C(20A)	109.6(5)
Ir(1A)-P(5A)	2.2821(15)	P(3A)-Ir(1A)-P(5A)	91.26(5)	C(24A)-C(19A)-P(5A)	113.7(4)
Ir(1A)-Cl(3A)	2.3797(16)	O(40A)-Ir(1A)-Cl(3A)	172.37(13)	C(20A)-C(19A)-P(5A)	117.9(4)
Ir(1A)-Cl(2A)	2.4192(15)	P(3A)-Ir(1A)-Cl(3A)	88.67(6)	C(21A)-C(20A)-C(19A)	109.4(5)
Ir(1A)-Cl(1A)	2.4333(16)	P(5A)-Ir(1A)-Cl(3A)	88.56(5)	C(22A)-C(21A)-C(20A)	111.5(6)
N(1A)-C(4A)	1.460(8)	O(40A)-Ir(1A)-Cl(2A)	83.62(13)	C(21A)-C(22A)-C(23A)	111.9(5)
N(1A)-C(6A)	1.469(7)	P(3A)-Ir(1A)-Cl(2A)	90.63(6)	C(24A)-C(23A)-C(22A)	111.0(5)
N(1A)-C(2A)	1.474(7)	P(5A)-Ir(1A)-Cl(2A)	178.05(5)	C(23A)-C(24A)-C(19A)	111.4(5)
C(2A)-P(3A)	1.832(6)	Cl(3A)-Ir(1A)-Cl(2A)	91.97(6)	C(30A)-C(25A)-C(26A)	108.1(5)
P(3A)-C(13A)	1.854(7)	O(40A)-Ir(1A)-Cl(1A)	82.67(14)	C(30A)-C(25A)-P(5A)	115.3(4)
P(3A)-C(7A)	1.859(6)	P(3A)-Ir(1A)-Cl(1A)	177.01(5)	C(26A)-C(25A)-P(5A)	114.8(5)
C(4A)-P(5A)	1.832(5)	P(5A)-Ir(1A)-Cl(1A)	91.68(5)	C(27A)-C(26A)-C(25A)	109.6(5)
P(5A)-C(19A)	1.844(6)	Cl(3A)-Ir(1A)-Cl(1A)	90.86(6)	C(28A)-C(27A)-C(26A)	112.7(6)
P(5A)-C(25A)	1.847(6)	Cl(2A)-Ir(1A)-Cl(1A)	86.43(6)	C(27A)-C(28A)-C(29A)	112.2(6)
C(7A)-C(12A)	1.531(9)	C(4A)-N(1A)-C(6A)	109.1(5)	C(30A)-C(29A)-C(28A)	110.9(6)
C(7A)-C(8A)	1.536(10)	C(4A)-N(1A)-C(2A)	113.4(5)	C(29A)-C(30A)-C(25A)	110.1(5)
C(8A)-C(9A)	1.526(9)	C(6A)-N(1A)-C(2A)	108.7(4)	O(40B)-Ir(1B)-P(5B)	92.82(13)
C(9A)-C(10A)	1.516(12)	N(1A)-C(2A)-P(3A)	113.9(4)	O(40B)-Ir(1B)-P(3B)	91.87(13)
C(10A)-C(11A)	1.508(13)	C(2A)-P(3A)-C(13A)	105.9(3)	P(5B)-Ir(1B)-P(3B)	91.76(5)
C(11A)-C(12A)	1.538(10)	C(2A)-P(3A)-C(7A)	102.3(3)	O(40B)-Ir(1B)-Cl(3B)	170.16(13)
C(13A)-C(14A)	1.534(8)	C(13A)-P(3A)-C(7A)	105.7(3)	P(5B)-Ir(1B)-Cl(3B)	93.94(5)
C(13A)-C(18A)	1.535(8)	C(2A)-P(3A)-Ir(1A)	113.2(2)	P(3B)-Ir(1B)-Cl(3B)	95.05(5)
C(14A)-C(15A)	1.510(9)	C(13A)-P(3A)-Ir(1A)	112.12(19)	O(40B)-Ir(1B)-Cl(1B)	86.30(12)
C(15A)-C(16A)	1.517(10)	C(7A)-P(3A)-Ir(1A)	116.6(2)	P(5B)-Ir(1B)-Cl(1B)	89.40(5)
C(16A)-C(17A)	1.510(10)	N(1A)-C(4A)-P(5A)	112.4(4)	P(3B)-Ir(1B)-Cl(1B)	177.89(5)
C(17A)-C(18A)	1.522(10)	C(4A)-P(5A)-C(19A)	105.5(3)	Cl(3B)-Ir(1B)-Cl(1B)	86.63(5)
C(19A)-C(24A)	1.536(7)	C(4A)-P(5A)-C(25A)	103.9(3)	O(40B)-Ir(1B)-Cl(2B)	87.61(13)
C(19A)-C(20A)	1.537(8)	C(19A)-P(5A)-C(25A)	105.8(3)	P(5B)-Ir(1B)-Cl(2B)	177.21(5)
C(20A)-C(21A)	1.526(9)	C(4A)-P(5A)-Ir(1A)	112.35(19)	P(3B)-Ir(1B)-Cl(2B)	90.98(5)
C(21A)-C(22A)	1.525(9)	C(19A)-P(5A)-Ir(1A)	112.81(19)	Cl(3B)-Ir(1B)-Cl(2B)	85.30(5)
C(22A)-C(23A)	1.525(9)	C(25A)-P(5A)-Ir(1A)	115.6(2)	Cl(1B)-Ir(1B)-Cl(2B)	87.88(5)
C(23A)-C(24A)	1.507(9)	C(12A)-C(7A)-C(8A)	109.6(5)	C(4B)-N(1B)-C(2B)	113.3(5)
C(25A)-C(30A)	1.520(9)	C(12A)-C(7A)-P(3A)	114.0(5)	C(4B)-N(1B)-C(6B)	109.5(5)
C(25A)-C(26A)	1.538(8)	C(8A)-C(7A)-P(3A)	114.2(5)	C(2B)-N(1B)-C(6B)	109.7(5)
C(26A)-C(27A)	1.524(9)	C(9A)-C(8A)-C(7A)	111.2(7)	N(1B)-C(2B)-P(3B)	114.0(4)
C(27A)-C(28A)	1.514(11)	C(10A)-C(9A)-C(8A)	111.1(7)	C(2B)-P(3B)-C(13B)	104.8(3)
C(28A)-C(29A)	1.528(10)	C(11A)-C(10A)-C(9A)	110.9(7)	C(2B)-P(3B)-C(7B)	101.7(2)
C(29A)-C(30A)	1.515(9)	C(10A)-C(11A)-C(12A)	111.9(7)	C(13B)-P(3B)-C(7B)	106.1(3)
Ir(1B)-O(40B)	2.118(4)	C(7A)-C(12A)-C(11A)	110.9(6)	C(2B)-P(3B)-Ir(1B)	113.46(18)
Ir(1B)-P(5B)	2.2904(15)	C(14A)-C(13A)-C(18A)	111.2(5)	C(13B)-P(3B)-Ir(1B)	112.02(18)
Ir(1B)-P(3B)	2.2974(14)	C(14A)-C(13A)-P(3A)	118.6(4)	C(7B)-P(3B)-Ir(1B)	117.52(19)
Ir(1B)-Cl(3B)	2.3840(13)	C(18A)-C(13A)-P(3A)	111.5(5)	N(1B)-C(4B)-P(5B)	113.9(4)
Ir(1B)-Cl(1B)	2.4280(13)	C(15A)-C(14A)-C(13A)	111.0(5)	C(4B)-P(5B)-C(19B)	104.4(3)
Ir(1B)-Cl(2B)	2.4403(14)	C(14A)-C(15A)-C(16A)	112.6(6)	C(4B)-P(5B)-C(25B)	101.2(3)
N(1B)-C(4B)	1.455(7)	C(17A)-C(16A)-C(15A)	111.8(6)	C(19B)-P(5B)-C(25B)	106.3(3)
N(1B)-C(2B)	1.458(7)	C(16A)-C(17A)-C(18A)	110.3(5)	C(4B)-P(5B)-Ir(1B)	114.0(2)
N(1B)-C(6B)	1.467(8)	C(19B)-P(5B)-Ir(1B)	112.2(2)		
C(2B)-P(3B)	1.833(5)	C(25B)-P(5B)-Ir(1B)	117.4(2)		
P(3B)-C(13B)	1.847(6)	C(8B)-C(7B)-C(12B)	110.1(5)		
P(3B)-C(7B)	1.870(6)	C(8B)-C(7B)-P(3B)	113.1(4)		

C(4B)-P(5B)	1.827(5)	C(12B)-C(7B)-P(3B)	112.8(4)		
P(5B)-C(19B)	1.856(6)	C(9B)-C(8B)-C(7B)	111.1(5)		
P(5B)-C(25B)	1.864(6)	C(10B)-C(9B)-C(8B)	112.6(5)		
C(7B)-C(8B)	1.529(8)	C(9B)-C(10B)-C(11B)	110.2(5)		
C(7B)-C(12B)	1.541(8)	C(10B)-C(11B)-C(12B)	111.1(5)		
C(8B)-C(9B)	1.528(8)	C(11B)-C(12B)-C(7B)	111.6(5)		
C(9B)-C(10B)	1.502(8)	C(14B)-C(13B)-C(18B)	110.9(5)		
C(10B)-C(11B)	1.529(9)	C(14B)-C(13B)-P(3B)	119.6(4)		
C(11B)-C(12B)	1.532(8)	C(18B)-C(13B)-P(3B)	109.9(4)		
C(13B)-C(14B)	1.522(8)	C(13B)-C(14B)-C(15B)	109.9(5)		
C(13B)-C(18B)	1.543(8)	C(16B)-C(15B)-C(14B)	111.4(6)		
C(14B)-C(15B)	1.529(9)	C(15B)-C(16B)-C(17B)	111.3(6)		
C(15B)-C(16B)	1.515(10)	C(18B)-C(17B)-C(16B)	111.0(5)		
C(16B)-C(17B)	1.516(10)	C(17B)-C(18B)-C(13B)	110.4(5)		
C(17B)-C(18B)	1.509(8)	C(20B)-C(19B)-C(24B)	112.2(5)		
C(19B)-C(20B)	1.529(8)	C(20B)-C(19B)-P(5B)	117.5(4)		
C(19B)-C(24B)	1.541(8)	C(24B)-C(19B)-P(5B)	111.9(4)		
C(20B)-C(21B)	1.514(9)	C(21B)-C(20B)-C(19B)	109.8(5)		
C(21B)-C(22B)	1.526(10)	C(20B)-C(21B)-C(22B)	111.3(6)		
C(22B)-C(23B)	1.514(10)	C(23B)-C(22B)-C(21B)	111.4(6)		
C(23B)-C(24B)	1.523(9)	C(22B)-C(23B)-C(24B)	111.4(6)		
C(25B)-C(30B)	1.515(8)	C(23B)-C(24B)-C(19B)	109.7(5)		
C(25B)-C(26B)	1.537(8)	C(30B)-C(25B)-C(26B)	109.4(5)		
C(26B)-C(27B)	1.523(8)	C(30B)-C(25B)-P(5B)	114.9(4)		
C(27B)-C(28B)	1.519(11)	C(26B)-C(25B)-P(5B)	112.7(4)		
C(28B)-C(29B)	1.509(10)	C(27B)-C(26B)-C(25B)	111.0(6)		
C(29B)-C(30B)	1.526(8)	C(28B)-C(27B)-C(26B)	110.1(6)		
C(50)-Cl(51)	1.712(10)	C(29B)-C(28B)-C(27B)	110.8(6)		
C(50)-Cl(53)	1.716(10)	C(28B)-C(29B)-C(30B)	111.8(6)		
C(50)-Cl(52)	1.731(9)	C(25B)-C(30B)-C(29B)	111.8(5)		
O(60)-C(61)	1.375(9)	Cl(51)-C(50)-Cl(53)	109.7(5)		
O(60)-C(63)	1.385(9)	Cl(51)-C(50)-Cl(52)	111.7(5)		
C(61)-C(62)	1.499(10)	Cl(53)-C(50)-Cl(52)	108.9(6)		
C(63)-C(64)	1.500(10)	C(61)-O(60)-C(63)	113.2(12)		
O(60')-C(61')	1.380(10)	O(60)-C(61)-C(62)	109.6(13)		
O(60')-C(63')	1.383(10)	O(60)-C(63)-C(64)	108.3(12)		
C(61')-C(62')	1.503(10)	C(61')-O(60')-C(63')	116.8(16)		
C(63')-C(64')	1.499(10)	O(60')-C(61')-C(62')	111.7(15)		
O(70)-C(73)	1.378(10)	O(60')-C(63')-C(64')	107.9(14)		
O(70)-C(71)	1.394(10)	C(73)-O(70)-C(71)	116.2(14)		
C(71)-C(72)	1.509(10)	O(70)-C(71)-C(72)	109.5(14)		
C(73)-C(74)	1.501(10)	O(70)-C(73)-C(74)	112.7(15)		

Table A26. Geometric parameters of $[\{\text{Rh}(\text{Cl})(\text{Me}-\text{N}(\text{CH}_2\text{PCy}_2)_2\}_2(\mu\text{-Cl})_3]\text{BF}_4$ (**25**).

Bond lengths (Å)		Bond angles (°)			
Rh(1)-P(3)	2.2662(8)	P(3)-Rh(1)-P(5)	90.67(3)	C(4)-P(5)-Rh(1)	112.36(12)
Rh(1)-P(5)	2.2810(8)	P(3)-Rh(1)-Cl(1)	88.63(3)	C(25)-P(5)-Rh(1)	113.77(11)
Rh(1)-Cl(1)	2.3165(8)	P(5)-Rh(1)-Cl(1)	88.78(3)	C(19)-P(5)-Rh(1)	112.23(10)
Rh(1)-Cl(3)	2.3711(8)	P(3)-Rh(1)-Cl(3)	96.54(3)	C(8)-C(7)-C(12)	109.0(3)
Rh(1)-Cl(5)	2.4931(8)	P(5)-Rh(1)-Cl(3)	94.55(3)	C(8)-C(7)-P(3)	114.7(2)
Rh(1)-Cl(4)	2.5042(8)	Cl(1)-Rh(1)-Cl(3)	173.81(3)	C(12)-C(7)-P(3)	112.6(2)
Rh(2)-P(33)	2.2786(8)	P(3)-Rh(1)-Cl(5)	94.19(3)	C(9)-C(8)-C(7)	111.0(3)
Rh(2)-P(35)	2.2876(8)	P(5)-Rh(1)-Cl(5)	174.64(3)	C(10)-C(9)-C(8)	112.2(3)
Rh(2)-Cl(2)	2.3326(9)	Cl(1)-Rh(1)-Cl(5)	93.60(3)	C(11)-C(10)-C(9)	110.9(3)
Rh(2)-Cl(4)	2.3785(8)	Cl(3)-Rh(1)-Cl(5)	82.66(3)	C(10)-C(11)-C(12)	111.0(4)
Rh(2)-Cl(5)	2.4729(8)	P(3)-Rh(1)-Cl(4)	172.84(3)	C(11)-C(12)-C(7)	110.6(3)
Rh(2)-Cl(3)	2.4977(7)	P(5)-Rh(1)-Cl(4)	96.02(3)	C(14)-C(13)-C(18)	111.6(3)
N(1)-C(2)	1.459(4)	Cl(1)-Rh(1)-Cl(4)	94.05(3)	C(14)-C(13)-P(3)	117.8(3)
N(1)-C(4)	1.461(4)	Cl(3)-Rh(1)-Cl(4)	80.42(3)	C(18)-C(13)-P(3)	112.2(2)
N(1)-C(6)	1.479(4)	Cl(5)-Rh(1)-Cl(4)	79.03(3)	C(13)-C(14)-C(15)	109.2(3)
C(2)-P(3)	1.838(3)	P(33)-Rh(2)-P(35)	90.67(3)	C(16)-C(15)-C(14)	113.0(3)
P(3)-C(7)	1.842(3)	P(33)-Rh(2)-Cl(2)	89.37(3)	C(17)-C(16)-C(15)	112.7(3)
P(3)-C(13)	1.849(3)	P(35)-Rh(2)-Cl(2)	89.47(3)	C(16)-C(17)-C(18)	110.0(3)
C(4)-P(5)	1.837(3)	P(33)-Rh(2)-Cl(4)	96.38(3)	C(17)-C(18)-C(13)	109.8(3)
P(5)-C(25)	1.849(3)	P(35)-Rh(2)-Cl(4)	95.98(3)	C(20)-C(19)-C(24)	110.7(3)
P(5)-C(19)	1.859(3)	Cl(2)-Rh(2)-Cl(4)	172.01(3)	C(20)-C(19)-P(5)	115.4(2)
C(7)-C(8)	1.536(4)	P(33)-Rh(2)-Cl(5)	94.90(3)	C(24)-C(19)-P(5)	113.5(2)
C(7)-C(12)	1.537(4)	P(35)-Rh(2)-Cl(5)	174.21(3)	C(21)-C(20)-C(19)	110.9(3)
C(8)-C(9)	1.522(5)	Cl(2)-Rh(2)-Cl(5)	92.14(3)	C(22)-C(21)-C(20)	111.5(3)
C(9)-C(10)	1.521(5)	Cl(4)-Rh(2)-Cl(5)	81.88(3)	C(21)-C(22)-C(23)	110.9(3)
C(10)-C(11)	1.514(6)	P(33)-Rh(2)-Cl(3)	174.74(3)	C(24)-C(23)-C(22)	111.1(3)
C(11)-C(12)	1.535(5)	P(35)-Rh(2)-Cl(3)	93.80(3)	C(23)-C(24)-C(19)	110.4(3)
C(13)-C(14)	1.533(5)	Cl(2)-Rh(2)-Cl(3)	93.43(3)	C(30)-C(25)-C(26)	109.6(3)
C(13)-C(18)	1.542(5)	Cl(4)-Rh(2)-Cl(3)	80.42(3)	C(30)-C(25)-P(5)	115.1(2)
C(14)-C(15)	1.542(5)	Cl(5)-Rh(2)-Cl(3)	80.56(2)	C(26)-C(25)-P(5)	112.2(2)
C(15)-C(16)	1.523(7)	Rh(1)-Cl(3)-Rh(2)	83.82(2)	C(27)-C(26)-C(25)	110.2(3)
C(16)-C(17)	1.509(6)	Rh(2)-Cl(4)-Rh(1)	83.53(3)	C(28)-C(27)-C(26)	110.7(3)
C(17)-C(18)	1.526(5)	Rh(2)-Cl(5)-Rh(1)	81.86(2)	C(27)-C(28)-C(29)	109.9(3)
C(19)-C(20)	1.535(4)	C(2)-N(1)-C(4)	113.9(3)	C(30)-C(29)-C(28)	112.3(3)
C(19)-C(24)	1.541(4)	C(2)-N(1)-C(6)	109.6(3)	C(29)-C(30)-C(25)	110.4(3)
C(20)-C(21)	1.525(5)	C(4)-N(1)-C(6)	109.5(3)	C(32)-N(31)-C(34)	114.4(3)
C(21)-C(22)	1.520(5)	N(1)-C(2)-P(3)	113.0(2)	C(32)-N(31)-C(36)	109.4(3)
C(22)-C(23)	1.526(5)	C(2)-P(3)-C(7)	104.92(15)	C(34)-N(31)-C(36)	108.7(3)
C(23)-C(24)	1.525(5)	C(2)-P(3)-C(13)	107.15(16)	N(31)-C(32)-P(33)	115.9(2)
C(25)-C(30)	1.532(4)	C(7)-P(3)-C(13)	106.19(15)	C(32)-P(33)-C(37)	102.60(15)
C(25)-C(26)	1.547(5)	C(2)-P(3)-Rh(1)	113.13(12)	C(32)-P(33)-C(43)	109.11(16)
C(26)-C(27)	1.523(5)	C(7)-P(3)-Rh(1)	114.13(10)	C(37)-P(33)-C(43)	106.01(17)
C(27)-C(28)	1.516(6)	C(13)-P(3)-Rh(1)	110.80(11)	C(32)-P(33)-Rh(2)	112.56(11)
C(28)-C(29)	1.528(6)	N(1)-C(4)-P(5)	113.0(2)	C(37)-P(33)-Rh(2)	116.14(11)
C(29)-C(30)	1.525(5)	C(4)-P(5)-C(25)	104.57(15)	C(43)-P(33)-Rh(2)	109.93(11)
N(31)-C(32)	1.462(4)	C(4)-P(5)-C(19)	106.15(15)	N(31)-C(34)-P(35)	111.3(2)
N(31)-C(34)	1.467(4)	C(25)-P(5)-C(19)	107.16(15)	C(34)-P(35)-C(55)	105.81(15)
N(31)-C(36)	1.482(4)	C(34)-P(35)-C(49)	105.15(15)	Cl(73)-C(70)-Cl(72)	110.8(4)
C(32)-P(33)	1.837(3)	C(55)-P(35)-C(49)	107.20(15)	Cl(71)-C(70)-Cl(72)	109.3(3)
P(33)-C(37)	1.855(3)	C(34)-P(35)-Rh(2)	111.71(11)	Cl(78)-C(70')-Cl(76)	106.7(12)
P(33)-C(43)	1.856(4)	C(55)-P(35)-Rh(2)	113.02(11)	Cl(78)-C(70')-Cl(77)	115.0(15)

C(34)-P(35)	1.824(3)	C(49)-P(35)-Rh(2)	113.35(11)	Cl(76)-C(70')-Cl(77)	107.0(13)
P(35)-C(55)	1.853(3)	C(38)-C(37)-C(42)	109.5(3)	Cl(82)-C(80)-Cl(81)	110.4(4)
P(35)-C(49)	1.853(3)	C(38)-C(37)-P(33)	116.8(2)	Cl(82)-C(80)-Cl(83)	112.3(4)
C(37)-C(38)	1.533(5)	C(42)-C(37)-P(33)	110.0(2)	Cl(81)-C(80)-Cl(83)	109.3(3)
C(37)-C(42)	1.554(5)	C(39)-C(38)-C(37)	110.2(3)	Cl(87)-C(80')-Cl(88)	112.3(13)
C(38)-C(39)	1.525(5)	C(38)-C(39)-C(40)	112.2(3)	Cl(87)-C(80')-Cl(86)	108.3(13)
C(39)-C(40)	1.532(6)	C(41)-C(40)-C(39)	110.4(4)	Cl(88)-C(80')-Cl(86)	109.6(13)
C(40)-C(41)	1.504(7)	C(40)-C(41)-C(42)	111.3(4)	Cl(93)-C(90)-Cl(91)	109.7(4)
C(41)-C(42)	1.531(5)	C(41)-C(42)-C(37)	111.0(3)	Cl(93)-C(90)-Cl(92)	109.9(4)
C(43)-C(44)	1.529(5)	C(44)-C(43)-C(48)	111.4(3)	Cl(91)-C(90)-Cl(92)	111.5(4)
C(43)-C(48)	1.536(5)	C(44)-C(43)-P(33)	117.4(3)	Cl(98)-C(90')-Cl(96)	106.6(13)
C(44)-C(45)	1.526(6)	C(48)-C(43)-P(33)	112.8(3)	Cl(98)-C(90')-Cl(97)	110.0(14)
C(45)-C(46)	1.522(7)	C(45)-C(44)-C(43)	109.8(3)	Cl(96)-C(90')-Cl(97)	105.4(13)
C(46)-C(47)	1.511(7)	C(46)-C(45)-C(44)	112.4(4)		
C(47)-C(48)	1.532(6)	C(47)-C(46)-C(45)	111.3(4)		
C(49)-C(54)	1.538(4)	C(46)-C(47)-C(48)	112.0(4)		
C(49)-C(50)	1.548(4)	C(47)-C(48)-C(43)	109.9(3)		
C(50)-C(51)	1.525(5)	C(54)-C(49)-C(50)	110.4(3)		
C(51)-C(52)	1.517(5)	C(54)-C(49)-P(35)	113.8(2)		
C(52)-C(53)	1.526(5)	C(50)-C(49)-P(35)	117.0(2)		
C(53)-C(54)	1.520(5)	C(51)-C(50)-C(49)	109.2(3)		
C(55)-C(60)	1.529(5)	C(52)-C(51)-C(50)	112.6(3)		
C(55)-C(56)	1.541(5)	C(51)-C(52)-C(53)	110.8(3)		
C(56)-C(57)	1.535(5)	C(54)-C(53)-C(52)	111.2(3)		
C(57)-C(58)	1.518(6)	C(53)-C(54)-C(49)	109.1(3)		
C(58)-C(59)	1.518(5)	C(60)-C(55)-C(56)	108.7(3)		
C(59)-C(60)	1.528(5)	C(60)-C(55)-P(35)	114.7(2)		
B(60)-F(62)	1.356(6)	C(56)-C(55)-P(35)	113.4(2)		
B(60)-F(64)	1.359(6)	C(57)-C(56)-C(55)	110.3(3)		
B(60)-F(63)	1.385(7)	C(58)-C(57)-C(56)	111.4(4)		
B(60)-F(61)	1.386(6)	C(57)-C(58)-C(59)	111.9(3)		
B(60')-F(62')	1.365(13)	C(58)-C(59)-C(60)	111.7(3)		
B(60')-F(61')	1.365(13)	C(59)-C(60)-C(55)	110.0(3)		
B(60')-F(63')	1.366(13)	F(62)-B(60)-F(64)	112.3(5)		
B(60')-F(64')	1.370(13)	F(62)-B(60)-F(63)	108.0(5)		
C(70)-Cl(73)	1.732(5)	F(64)-B(60)-F(63)	108.3(4)		
C(70)-Cl(71)	1.754(5)	F(62)-B(60)-F(61)	109.1(4)		
C(70)-Cl(72)	1.757(7)	F(64)-B(60)-F(61)	109.9(5)		
C(70')-Cl(78)	1.737(16)	F(63)-B(60)-F(61)	109.2(5)		
C(70')-Cl(76)	1.742(16)	F(62')-B(60')-F(61')	109.2(13)		
C(70')-Cl(77)	1.745(16)	F(62')-B(60')-F(63')	109.2(12)		
C(80)-Cl(82)	1.725(7)	F(61')-B(60')-F(63')	110.6(13)		
C(80)-Cl(81)	1.736(6)	F(62')-B(60')-F(64')	109.6(13)		
C(80)-Cl(83)	1.747(6)	F(61')-B(60')-F(64')	109.6(13)		
C(80')-Cl(87)	1.729(16)	F(63')-B(60')-F(64')	108.6(12)		
C(80')-Cl(88)	1.732(15)	Cl(73)-C(70)-Cl(71)	109.9(3)		
C(80')-Cl(86)	1.738(16)				
C(90)-Cl(93)	1.714(6)				
C(90)-Cl(91)	1.723(7)				
C(90)-Cl(92)	1.742(7)				
C(90')-Cl(98)	1.725(16)				
C(90')-Cl(96)	1.731(16)				
C(90')-Cl(97)	1.737(16)				

Table A27. Geometric parameters of [Co₂(N(CH₂PPh₂{CH₂P(O)Ph₂}₂))₂(μ²-OH)₂](BF₄)₂ (**32**).

Bond lengths (Å)		Bond angles (°)			
Co(1)-Cl(1')#1	1.99(3)	O(1)-Co(1)-O(1)#1	81.3(10)	P(5)-O(5)-Co(1)	115.83(15)
Co(1)-O(1)	2.02(2)	Cl(1')#1-Co(1)-O(3)	172.5(8)	N(1)-C(6)-P(7)	117.6(2)
Co(1)-O(1)#1	2.04(2)	O(1)-Co(1)-O(3)	91.9(7)	C(38)-P(7)-C(32)	105.96(18)
Co(1)-O(3)	2.051(3)	O(1)#1-Co(1)-O(3)	168.2(6)	C(38)-P(7)-C(6)	95.93(17)
Co(1)-Cl(1')	2.07(3)	Cl(1')#1-Co(1)-Cl(1')	81.4(14)	C(32)-P(7)-C(6)	104.43(17)
Co(1)-O(5)	2.108(3)	O(3)-Co(1)-Cl(1')	92.4(10)	C(38)-P(7)-Co(1)#1	115.98(13)
Co(1)-N(1)	2.296(3)	Cl(1')#1-Co(1)-O(5)	91.0(9)	C(32)-P(7)-Co(1)#1	121.07(13)
Co(1)-P(7)#1	2.4662(10)	O(1)-Co(1)-O(5)	170.9(6)	C(6)-P(7)-Co(1)#1	110.02(12)
O(1)-Co(1)#1	2.04(2)	O(1)#1-Co(1)-O(5)	91.5(6)	C(9)-C(8)-C(13)	120.1(4)
Cl(1')-Co(1)#1	1.99(3)	O(3)-Co(1)-O(5)	94.21(11)	C(9)-C(8)-P(3)	119.3(4)
N(1)-C(4)	1.478(5)	Cl(1')-Co(1)-O(5)	166.6(8)	C(13)-C(8)-P(3)	120.5(3)
N(1)-C(6)	1.483(5)	Cl(1')#1-Co(1)-N(1)	90.5(8)	C(10)-C(9)-C(8)	118.7(5)
N(1)-C(2)	1.495(4)	O(1)-Co(1)-N(1)	93.7(6)	C(11)-C(10)-C(9)	121.1(5)
C(2)-P(3)	1.818(4)	O(1)#1-Co(1)-N(1)	85.6(6)	C(10)-C(11)-C(12)	120.3(5)
P(3)-O(3)	1.505(3)	O(3)-Co(1)-N(1)	85.19(11)	C(11)-C(12)-C(13)	120.1(5)
P(3)-C(14)	1.789(4)	Cl(1')-Co(1)-N(1)	88.9(8)	C(12)-C(13)-C(8)	119.6(5)
P(3)-C(8)	1.789(4)	O(5)-Co(1)-N(1)	80.04(11)	C(15)-C(14)-C(19)	119.7(4)
C(4)-P(5)	1.829(4)	Cl(1')#1-Co(1)-P(7)#1	82.9(8)	C(15)-C(14)-P(3)	123.0(3)
P(5)-O(5)	1.505(3)	O(1)-Co(1)-P(7)#1	85.1(6)	C(19)-C(14)-P(3)	117.3(3)
P(5)-C(26)	1.786(4)	O(1)#1-Co(1)-P(7)#1	87.7(6)	C(14)-C(15)-C(16)	119.7(4)
P(5)-C(20)	1.805(4)	O(3)-Co(1)-P(7)#1	101.42(8)	C(17)-C(16)-C(15)	120.1(4)
C(6)-P(7)	1.861(4)	Cl(1')-Co(1)-P(7)#1	89.9(8)	C(16)-C(17)-C(18)	120.9(4)
P(7)-C(38)	1.821(4)	O(5)-Co(1)-P(7)#1	100.26(8)	C(17)-C(18)-C(19)	119.6(4)
P(7)-C(32)	1.823(4)	N(1)-Co(1)-P(7)#1	173.32(8)	P(5)-O(5)-Co(1)	115.83(15)
P(7)-Co(1)#1	2.4662(10)	Co(1)-O(1)-Co(1)#1	98.7(10)	N(1)-C(6)-P(7)	117.6(2)
C(8)-C(9)	1.388(6)	Co(1)#1-Cl(1')-Co(1)	98.6(14)	C(38)-P(7)-C(32)	105.96(18)
C(8)-C(13)	1.390(6)	C(4)-N(1)-C(6)	111.1(3)	C(38)-P(7)-C(6)	95.93(17)
C(9)-C(10)	1.380(7)	C(4)-N(1)-C(2)	111.1(3)	C(32)-P(7)-C(6)	104.43(17)
C(10)-C(11)	1.366(8)	C(6)-N(1)-C(2)	107.9(3)	C(38)-P(7)-Co(1)#1	115.98(13)
C(11)-C(12)	1.367(8)	C(4)-N(1)-Co(1)	105.1(2)	C(32)-P(7)-Co(1)#1	121.07(13)
C(12)-C(13)	1.380(7)	C(6)-N(1)-Co(1)	114.9(2)	C(6)-P(7)-Co(1)#1	110.02(12)
C(14)-C(15)	1.385(6)	C(2)-N(1)-Co(1)	106.7(2)	C(9)-C(8)-C(13)	120.1(4)
C(14)-C(19)	1.391(6)	N(1)-C(2)-P(3)	110.1(2)	C(9)-C(8)-P(3)	119.3(4)
C(15)-C(16)	1.391(6)	O(3)-P(3)-C(14)	113.10(18)	C(13)-C(8)-P(3)	120.5(3)
C(16)-C(17)	1.368(7)	O(3)-P(3)-C(8)	112.84(19)	C(10)-C(9)-C(8)	118.7(5)
C(17)-C(18)	1.377(7)	C(14)-P(3)-C(8)	108.55(19)	C(11)-C(10)-C(9)	121.1(5)
C(18)-C(19)	1.386(6)	O(3)-P(3)-C(2)	107.89(17)	C(10)-C(11)-C(12)	120.3(5)
C(20)-C(21)	1.376(6)	C(14)-P(3)-C(2)	105.45(18)	C(11)-C(12)-C(13)	120.1(5)
C(20)-C(25)	1.380(7)	C(8)-P(3)-C(2)	108.67(19)	C(12)-C(13)-C(8)	119.6(5)
C(21)-C(22)	1.382(7)	P(3)-O(3)-Co(1)	117.33(16)	C(15)-C(14)-C(19)	119.7(4)
C(22)-C(23)	1.359(9)	N(1)-C(4)-P(5)	108.4(2)	C(15)-C(14)-P(3)	123.0(3)
C(23)-C(24)	1.388(10)	O(5)-P(5)-C(26)	114.33(18)	C(19)-C(14)-P(3)	117.3(3)
C(24)-C(25)	1.374(8)	O(5)-P(5)-C(20)	111.61(18)	C(14)-C(15)-C(16)	119.7(4)
C(26)-C(31)	1.387(6)	C(26)-P(5)-C(20)	104.9(2)	C(17)-C(16)-C(15)	120.1(4)
C(26)-C(27)	1.391(6)	O(5)-P(5)-C(4)	108.53(17)	C(16)-C(17)-C(18)	120.9(4)
C(27)-C(28)	1.375(7)	C(26)-P(5)-C(4)	107.78(19)	C(17)-C(18)-C(19)	119.6(4)
C(28)-C(29)	1.379(7)	C(20)-P(5)-C(4)	109.55(19)	C(18)-C(19)-C(14)	120.0(4)
C(29)-C(30)	1.380(7)	C(21)-C(20)-C(25)	119.0(4)	F(3)-B(1)-F(1)	107.1(9)
C(30)-C(31)	1.386(6)	C(21)-C(20)-P(5)	120.5(3)	F(3)-B(1)-F(2)	116.7(10)
C(32)-C(33)	1.394(6)	C(25)-C(20)-P(5)	120.5(4)	F(1)-B(1)-F(2)	108.4(10)
C(32)-C(37)	1.399(6)	C(20)-C(21)-C(22)	120.7(5)	F(3)-B(1)-F(4)	108.0(9)

C(33)-C(34)	1.380(6)	C(23)-C(22)-C(21)	120.0(5)	F(1)-B(1)-F(4)	111.9(10)
C(34)-C(35)	1.373(7)	C(22)-C(23)-C(24)	119.9(5)	F(2)-B(1)-F(4)	104.8(9)
C(35)-C(36)	1.382(7)	C(25)-C(24)-C(23)	119.9(6)	F(3')-B(1')-F(4')	109.8(10)
C(36)-C(37)	1.377(6)	C(24)-C(25)-C(20)	120.3(6)	F(3')-B(1')-F(2')	111.8(10)
C(38)-C(43)	1.390(6)	C(31)-C(26)-C(27)	119.4(4)	F(4')-B(1')-F(2')	107.3(10)
C(38)-C(39)	1.393(6)	C(31)-C(26)-P(5)	123.2(3)	F(3')-B(1')-F(1')	111.0(10)
C(39)-C(40)	1.385(6)	C(27)-C(26)-P(5)	117.3(3)	F(4')-B(1')-F(1')	107.1(10)
C(40)-C(41)	1.388(7)	C(28)-C(27)-C(26)	120.7(4)	F(2')-B(1')-F(1')	109.7(10)
C(41)-C(42)	1.382(6)	C(27)-C(28)-C(29)	119.8(4)	F(3'')-B(1'')-F(1'')	107.1(10)
C(42)-C(43)	1.383(6)	C(28)-C(29)-C(30)	120.1(4)	F(3'')-B(1'')-F(4'')	111.0(11)
B(1)-F(3)	1.371(11)	C(29)-C(30)-C(31)	120.4(4)	F(1'')-B(1'')-F(4'')	110.5(11)
B(1)-F(1)	1.378(12)	C(30)-C(31)-C(26)	119.7(4)	F(3'')-B(1'')-F(2'')	114.0(11)
B(1)-F(2)	1.381(12)	C(33)-C(32)-C(37)	119.1(4)	F(1'')-B(1'')-F(2'')	106.8(11)
B(1)-F(4)	1.396(12)	C(33)-C(32)-P(7)	122.7(3)	F(4'')-B(1'')-F(2'')	107.4(10)
B(1')-F(3')	1.380(12)	C(37)-C(32)-P(7)	118.1(3)	Cl(3)-C(50)-Cl(2)	114.5(6)
B(1')-F(4')	1.382(12)	C(34)-C(33)-C(32)	120.4(4)	Cl(4)-C(60)-Cl(5)	104.4(12)
B(1')-F(2')	1.387(12)	C(35)-C(34)-C(33)	120.0(5)	Cl(4')-C(60')-Cl(5')	102.1(15)
B(1')-F(1')	1.392(12)	C(34)-C(35)-C(36)	120.3(4)		
B(1'')-F(3'')	1.375(12)	C(37)-C(36)-C(35)	120.5(5)		
B(1'')-F(1'')	1.387(13)	C(36)-C(37)-C(32)	119.8(4)		
B(1'')-F(4'')	1.387(12)	C(43)-C(38)-C(39)	119.1(4)		
B(1'')-F(2'')	1.388(12)	C(43)-C(38)-P(7)	117.5(3)		
C(50)-Cl(3)	1.718(10)	C(39)-C(38)-P(7)	123.3(3)		
C(50)-Cl(2)	1.733(10)	C(40)-C(39)-C(38)	120.2(4)		
C(60)-Cl(4)	1.718(16)	C(39)-C(40)-C(41)	120.2(4)		
C(60)-Cl(5)	1.722(15)	C(42)-C(41)-C(40)	119.8(4)		
C(60')-Cl(4')	1.732(19)	C(41)-C(42)-C(43)	120.1(4)		
C(60')-Cl(5')	1.763(19)	C(42)-C(43)-C(38)	120.5(4)		

Table A28. Geometric parameters of N(CH₂P(O)Ph₂)₃ (**34**).

Bond lengths (Å)		Bond angles (°)			
N(1)-C(6)	1.468(4)	C(6)-N(1)-C(2)	109.9(3)	C(24)-C(25)-C(20)	120.3(3)
N(1)-C(2)	1.471(3)	C(6)-N(1)-C(4)	110.3(2)	C(31)-C(26)-C(27)	119.3(3)
N(1)-C(4)	1.474(4)	C(2)-N(1)-C(4)	109.5(3)	C(31)-C(26)-P(5)	121.6(2)
C(2)-P(3)	1.805(3)	N(1)-C(2)-P(3)	116.8(2)	C(27)-C(26)-P(5)	119.0(2)
P(3)-O(3)	1.485(2)	O(3)-P(3)-C(8)	111.18(13)	C(28)-C(27)-C(26)	120.5(3)
P(3)-C(8)	1.793(3)	O(3)-P(3)-C(14)	111.60(14)	C(27)-C(28)-C(29)	119.6(3)
P(3)-C(14)	1.803(3)	C(8)-P(3)-C(14)	108.52(13)	C(30)-C(29)-C(28)	120.9(3)
C(4)-P(5)	1.816(3)	O(3)-P(3)-C(2)	114.24(14)	C(29)-C(30)-C(31)	119.6(3)
P(5)-O(5)	1.491(2)	C(8)-P(3)-C(2)	109.29(14)	C(26)-C(31)-C(30)	120.1(3)
P(5)-C(26)	1.795(3)	C(14)-P(3)-C(2)	101.51(14)	C(33)-C(32)-C(37)	118.9(3)
P(5)-C(20)	1.801(3)	N(1)-C(4)-P(5)	115.7(2)	C(33)-C(32)-P(7)	118.5(3)
C(6)-P(7)	1.810(3)	O(5)-P(5)-C(26)	112.12(14)	C(37)-C(32)-P(7)	122.6(3)
P(7)-O(7)	1.477(2)	O(5)-P(5)-C(20)	110.89(14)	C(32)-C(33)-C(34)	120.3(4)
P(7)-C(38)	1.795(3)	C(26)-P(5)-C(20)	108.39(13)	C(35)-C(34)-C(33)	119.5(4)
P(7)-C(32)	1.802(3)	O(5)-P(5)-C(4)	114.08(13)	C(34)-C(35)-C(36)	121.4(4)
C(8)-C(13)	1.391(4)	C(26)-P(5)-C(4)	102.24(13)	C(35)-C(36)-C(37)	119.3(5)
C(8)-C(9)	1.394(4)	C(20)-P(5)-C(4)	108.66(14)	C(36)-C(37)-C(32)	120.6(4)
C(9)-C(10)	1.378(4)	N(1)-C(6)-P(7)	115.0(2)	C(43)-C(38)-C(39)	120.0(3)
C(10)-C(11)	1.366(5)	O(7)-P(7)-C(38)	111.53(15)	C(43)-C(38)-P(7)	123.1(3)
C(11)-C(12)	1.383(5)	O(7)-P(7)-C(32)	111.61(16)	C(39)-C(38)-P(7)	117.0(3)
C(12)-C(13)	1.381(5)	C(38)-P(7)-C(32)	107.75(14)	C(40)-C(39)-C(38)	118.9(4)
C(14)-C(19)	1.390(4)	O(7)-P(7)-C(6)	114.80(14)	C(41)-C(40)-C(39)	119.9(4)
C(14)-C(15)	1.398(4)	C(38)-P(7)-C(6)	108.17(14)	C(40)-C(41)-C(42)	121.3(4)
C(15)-C(16)	1.380(5)	C(32)-P(7)-C(6)	102.40(15)	C(41)-C(42)-C(43)	119.7(4)
C(16)-C(17)	1.376(5)	C(13)-C(8)-C(9)	119.0(3)	C(42)-C(43)-C(38)	120.2(4)
C(17)-C(18)	1.380(5)	C(13)-C(8)-P(3)	123.4(2)	C(6')-N(1')-C(4')	114(3)
C(18)-C(19)	1.390(4)	C(9)-C(8)-P(3)	117.5(2)	C(6')-N(1')-C(2')	113(3)
C(20)-C(21)	1.389(4)	C(10)-C(9)-C(8)	120.7(3)	C(4')-N(1')-C(2')	110(3)
C(20)-C(25)	1.393(5)	C(11)-C(10)-C(9)	120.0(3)	N(1')-C(2')-P(3')	112(2)
C(21)-C(22)	1.386(5)	C(10)-C(11)-C(12)	120.1(3)	O(3')-P(3')-C(14')	113.3(14)
C(22)-C(23)	1.374(5)	C(13)-C(12)-C(11)	120.6(3)	O(3')-P(3')-C(8')	112.6(14)
C(23)-C(24)	1.382(5)	C(12)-C(13)-C(8)	119.6(3)	C(14')-P(3')-C(8')	109.5(14)
C(24)-C(25)	1.377(5)	C(19)-C(14)-C(15)	119.6(3)	O(3')-P(3')-C(2')	111.7(16)
C(26)-C(31)	1.386(4)	C(19)-C(14)-P(3)	122.0(2)	C(14')-P(3')-C(2')	102.2(13)
C(26)-C(27)	1.394(4)	C(15)-C(14)-P(3)	118.4(3)	C(8')-P(3')-C(2')	106.9(17)
C(27)-C(28)	1.378(5)	C(16)-C(15)-C(14)	119.9(3)	N(1')-C(4')-P(5')	116(2)
C(28)-C(29)	1.380(5)	C(17)-C(16)-C(15)	120.1(3)	O(5')-P(5')-C(26')	112.0(15)
C(29)-C(30)	1.376(5)	C(16)-C(17)-C(18)	120.6(3)	O(5')-P(5')-C(20')	111.1(15)
C(30)-C(31)	1.392(4)	C(17)-C(18)-C(19)	119.8(3)	C(26')-P(5')-C(20')	108.0(14)
C(32)-C(33)	1.374(5)	C(14)-C(19)-C(18)	119.9(3)	O(5')-P(5')-C(4')	117.1(17)
C(32)-C(37)	1.392(5)	C(21)-C(20)-C(25)	119.2(3)	C(26')-P(5')-C(4')	101.5(13)
C(33)-C(34)	1.401(6)	C(21)-C(20)-P(5)	123.6(3)	C(20')-P(5')-C(4')	106.4(16)
C(34)-C(35)	1.357(7)	C(25)-C(20)-P(5)	117.2(3)	N(1')-C(6')-P(7')	117(2)
C(35)-C(36)	1.368(7)	C(22)-C(21)-C(20)	120.1(3)	O(7')-P(7')-C(38')	109.2(15)
C(36)-C(37)	1.383(5)	C(23)-C(22)-C(21)	120.0(3)	O(7')-P(7')-C(6')	113.7(16)
C(38)-C(43)	1.389(4)	C(22)-C(23)-C(24)	120.3(3)	C(38')-P(7')-C(6')	111.9(16)
C(38)-C(39)	1.403(5)	C(25)-C(24)-C(23)	120.1(3)	O(7')-P(7')-C(32')	113.8(16)
C(39)-C(40)	1.395(6)	C(38')-P(7')-C(32')	108.1(15)		
C(40)-C(41)	1.373(6)	C(6')-P(7')-C(32')	99.9(14)		
C(41)-C(42)	1.374(6)	C(9')-C(8')-C(13')	120.0		
C(42)-C(43)	1.377(5)	C(9')-C(8')-P(3')	117.1(17)		

N(1')-C(6')	1.451(19)	C(13')-C(8')-P(3')	122.9(17)		
N(1')-C(4')	1.469(19)	C(8')-C(9')-C(10')	120.0		
N(1')-C(2')	1.473(19)	C(11')-C(10')-C(9')	120.0		
C(2')-P(3')	1.816(18)	C(10')-C(11')-C(12')	120.0		
P(3')-O(3')	1.477(16)	C(11')-C(12')-C(13')	120.0		
P(3')-C(14')	1.787(14)	C(12')-C(13')-C(8')	120.0		
P(3')-C(8')	1.792(15)	C(15')-C(14')-C(19')	120.0		
C(4')-P(5')	1.805(17)	C(15')-C(14')-P(3')	117.2(17)		
P(5')-O(5')	1.485(17)	C(19')-C(14')-P(3')	122.8(17)		
P(5')-C(26')	1.798(15)	C(14')-C(15')-C(16')	120.0		
P(5')-C(20')	1.802(15)	C(17')-C(16')-C(15')	120.0		
C(6')-P(7')	1.798(17)	C(16')-C(17')-C(18')	120.0		
P(7')-O(7')	1.485(17)	C(17')-C(18')-C(19')	120.0		
P(7')-C(38')	1.789(15)	C(18')-C(19')-C(14')	120.0		
P(7')-C(32')	1.808(15)	C(21')-C(20')-C(25')	120.0		
C(8')-C(9')	1.3900	C(21')-C(20')-P(5')	122.5(17)		
C(8')-C(13')	1.3900	C(25')-C(20')-P(5')	117.2(17)		
C(9')-C(10')	1.3900	C(22')-C(21')-C(20')	120.0		
C(10')-C(11')	1.3900	C(21')-C(22')-C(23')	120.0		
C(11')-C(12')	1.3900	C(22')-C(23')-C(24')	120.0		
C(12')-C(13')	1.3900	C(23')-C(24')-C(25')	120.0		
C(14')-C(15')	1.3900	C(24')-C(25')-C(20')	120.0		
C(14')-C(19')	1.3900	C(27')-C(26')-C(31')	120.0		
C(15')-C(16')	1.3900	C(27')-C(26')-P(5')	117.3(17)		
C(16')-C(17')	1.3900	C(31')-C(26')-P(5')	122.3(17)		
C(17')-C(18')	1.3900	C(28')-C(27')-C(26')	120.0		
C(18')-C(19')	1.3900	C(27')-C(28')-C(29')	120.0		
C(20')-C(21')	1.3900	C(30')-C(29')-C(28')	120.0		
C(20')-C(25')	1.3900	C(29')-C(30')-C(31')	120.0		
C(21')-C(22')	1.3900	C(30')-C(31')-C(26')	120.0		
C(22')-C(23')	1.3900	C(33')-C(32')-C(37')	120.0		
C(23')-C(24')	1.3900	C(33')-C(32')-P(7')	121.0(18)		
C(24')-C(25')	1.3900	C(37')-C(32')-P(7')	118.9(18)		
C(26')-C(27')	1.3900	C(34')-C(33')-C(32')	120.0		
C(26')-C(31')	1.3900	C(35')-C(34')-C(33')	120.0		
C(27')-C(28')	1.3900	C(34')-C(35')-C(36')	120.0		
C(28')-C(29')	1.3900	C(35')-C(36')-C(37')	120.0		
C(29')-C(30')	1.3900	C(36')-C(37')-C(32')	120.0		
C(30')-C(31')	1.3900	C(39')-C(38')-C(43')	120.0		
C(32')-C(33')	1.3900	C(39')-C(38')-P(7')	120.0(19)		
C(32')-C(37')	1.3900	C(43')-C(38')-P(7')	119.8(19)		
C(33')-C(34')	1.3900	C(40')-C(39')-C(38')	120.0		
C(34')-C(35')	1.3900	C(39')-C(40')-C(41')	120.0		
C(35')-C(36')	1.3900	C(40')-C(41')-C(42')	120.0		
C(36')-C(37')	1.3900	C(43')-C(42')-C(41')	120.0		
C(38')-C(39')	1.3900	C(42')-C(43')-C(38')	120.0		
C(38')-C(43')	1.3900				
C(39')-C(40')	1.3900				
C(40')-C(41')	1.3900				
C(41')-C(42')	1.3900				
C(42')-C(43')	1.3900				
O(50)-O(51)	1.419(4)				

Table A29. Geometric parameters of N(CH₂P(O)Cy₂)₃ (**35**).

Bond lengths (Å)		Bond angles (°)			
N(1)-C(4)	1.474(2)	C(4)-N(1)-C(6)	110.78(13)	C(24)-C(25)-C(20)	111.66(15)
N(1)-C(6)	1.475(2)	C(4)-N(1)-C(2)	110.08(13)	C(31)-C(26)-C(27)	112.01(15)
N(1)-C(2)	1.475(2)	C(6)-N(1)-C(2)	108.08(13)	C(31)-C(26)-P(5)	115.34(13)
C(2)-P(3)	1.8301(18)	N(1)-C(2)-P(3)	113.76(11)	C(27)-C(26)-P(5)	111.59(12)
O(3)-P(3)	1.4843(13)	O(3)-P(3)-C(14)	112.31(8)	C(28)-C(27)-C(26)	110.64(15)
P(3)-C(14)	1.8201(19)	O(3)-P(3)-C(8)	112.14(8)	C(29)-C(28)-C(27)	110.79(17)
P(3)-C(8)	1.8209(18)	C(14)-P(3)-C(8)	110.58(9)	C(30)-C(29)-C(28)	111.06(16)
C(4)-P(5)	1.8288(17)	O(3)-P(3)-C(2)	114.96(8)	C(29)-C(30)-C(31)	111.45(17)
O(5)-P(5)	1.4899(13)	C(14)-P(3)-C(2)	103.34(9)	C(30)-C(31)-C(26)	110.94(16)
P(5)-C(26)	1.8240(18)	C(8)-P(3)-C(2)	102.81(8)	C(33)-C(32)-C(37)	110.46(17)
P(5)-C(20)	1.8292(18)	N(1)-C(4)-P(5)	113.60(11)	C(33)-C(32)-P(7)	117.22(13)
C(6)-P(7)	1.8210(17)	O(5)-P(5)-C(26)	111.24(8)	C(37)-C(32)-P(7)	109.94(14)
O(7)-P(7)	1.4891(14)	O(5)-P(5)-C(4)	114.13(8)	C(32)-C(33)-C(34)	110.16(17)
P(7)-C(32)	1.8164(19)	C(26)-P(5)-C(4)	104.02(8)	C(35)-C(34)-C(33)	110.47(19)
P(7)-C(38A)	1.8307(18)	O(5)-P(5)-C(20)	112.28(8)	C(36)-C(35)-C(34)	110.7(2)
C(8)-C(13)	1.532(3)	C(26)-P(5)-C(20)	111.74(8)	C(35)-C(36)-C(37)	112.19(18)
C(8)-C(9)	1.535(3)	C(4)-P(5)-C(20)	102.90(8)	C(36)-C(37)-C(32)	110.98(17)
C(9)-C(10)	1.525(3)	N(1)-C(6)-P(7)	116.69(12)	C(39)-C(38A)-C(43)	109.19(15)
C(10)-C(11)	1.510(3)	O(7)-P(7)-C(32)	110.94(9)	C(39)-C(38A)-P(7)	111.00(13)
C(11)-C(12)	1.513(3)	O(7)-P(7)-C(6)	113.60(8)	C(43)-C(38A)-P(7)	115.38(12)
C(12)-C(13)	1.523(3)	C(32)-P(7)-C(6)	106.80(8)	C(40)-C(39)-C(38A)	110.56(16)
C(14)-C(19)	1.516(3)	O(7)-P(7)-C(38A)	112.38(8)	C(41)-C(40)-C(39)	111.76(16)
C(14)-C(15)	1.532(3)	C(32)-P(7)-C(38A)	108.92(8)	C(40)-C(41)-C(42)	111.06(17)
C(15)-C(16)	1.528(3)	C(6)-P(7)-C(38A)	103.79(8)	C(41)-C(42)-C(43)	110.73(17)
C(16)-C(17)	1.501(4)	C(13)-C(8)-C(9)	109.71(15)	C(42)-C(43)-C(38A)	110.58(16)
C(17)-C(18)	1.508(4)	C(13)-C(8)-P(3)	110.64(12)		
C(18)-C(19)	1.532(3)	C(9)-C(8)-P(3)	109.90(13)		
C(20)-C(25)	1.536(2)	C(10)-C(9)-C(8)	112.26(18)		
C(20)-C(21)	1.538(2)	C(11)-C(10)-C(9)	112.05(19)		
C(21)-C(22)	1.525(3)	C(10)-C(11)-C(12)	111.07(18)		
C(22)-C(23)	1.515(3)	C(11)-C(12)-C(13)	111.87(17)		
C(23)-C(24)	1.523(3)	C(12)-C(13)-C(8)	111.76(16)		
C(24)-C(25)	1.526(3)	C(19)-C(14)-C(15)	111.98(17)		
C(26)-C(31)	1.532(2)	C(19)-C(14)-P(3)	111.94(14)		
C(26)-C(27)	1.536(2)	C(15)-C(14)-P(3)	116.07(13)		
C(27)-C(28)	1.524(3)	C(16)-C(15)-C(14)	111.09(17)		
C(28)-C(29)	1.520(3)	C(17)-C(16)-C(15)	112.7(2)		
C(29)-C(30)	1.516(3)	C(16)-C(17)-C(18)	111.6(2)		
C(30)-C(31)	1.531(3)	C(17)-C(18)-C(19)	110.6(2)		
C(32)-C(33)	1.523(3)	C(14)-C(19)-C(18)	110.13(19)		
C(32)-C(37)	1.539(2)	C(25)-C(20)-C(21)	109.98(14)		
C(33)-C(34)	1.533(3)	C(25)-C(20)-P(5)	112.67(12)		
C(34)-C(35)	1.528(3)	C(21)-C(20)-P(5)	107.66(12)		
C(35)-C(36)	1.518(4)	C(22)-C(21)-C(20)	112.84(16)		
C(36)-C(37)	1.519(3)	C(23)-C(22)-C(21)	111.13(17)		
C(38A)-C(39)	1.532(3)	C(22)-C(23)-C(24)	109.26(15)		
C(38A)-C(43)	1.539(3)	C(23)-C(24)-C(25)	110.90(16)		
C(39)-C(40)	1.527(3)				
C(40)-C(41)	1.517(3)				
C(41)-C(42)	1.517(3)				
C(42)-C(43)	1.528(3)				

Table A30. Geometric parameters of [Fe{N(CH₂P(O)Ph₂)₃}₂](BPh₄)₂ (**37**).

Bond lengths (Å)		Bond angles (°)			
Fe(1)-O(7)	2.117(2)	O(7)-Fe(1)-O(7)#1	180.00(9)	C(12)-C(11)-C(10)	120.0(5)
Fe(1)-O(7)#1	2.117(2)	O(7)-Fe(1)-O(5)#1	90.81(10)	C(11)-C(12)-C(13)	120.8(5)
Fe(1)-O(5)#1	2.128(3)	O(7)#1-Fe(1)-O(5)#1	89.19(10)	C(12)-C(13)-C(8)	120.3(5)
Fe(1)-O(5)	2.128(3)	O(7)-Fe(1)-O(5)	89.19(10)	C(19)-C(14)-C(15)	119.8(5)
Fe(1)-O(3)#1	2.135(3)	O(7)#1-Fe(1)-O(5)	90.81(10)	C(19)-C(14)-P(3)	118.0(3)
Fe(1)-O(3)	2.135(3)	O(5)#1-Fe(1)-O(5)	180.0	C(15)-C(14)-P(3)	122.0(4)
N(1)-C(2)	1.435(5)	O(7)-Fe(1)-O(3)#1	90.70(10)	C(14)-C(15)-C(16)	119.1(6)
N(1)-C(4)	1.444(6)	O(7)#1-Fe(1)-O(3)#1	89.30(10)	C(17)-C(16)-C(15)	120.9(6)
N(1)-C(6)	1.456(5)	O(5)#1-Fe(1)-O(3)#1	89.37(11)	C(18)-C(17)-C(16)	120.1(5)
C(2)-P(3)	1.832(4)	O(5)-Fe(1)-O(3)#1	90.63(11)	C(17)-C(18)-C(19)	120.3(6)
P(3)-O(3)	1.491(3)	O(7)-Fe(1)-O(3)	89.30(10)	C(14)-C(19)-C(18)	119.8(5)
P(3)-C(8)	1.791(5)	O(7)#1-Fe(1)-O(3)	90.70(10)	C(21)-C(20)-C(25)	119.1(5)
P(3)-C(14)	1.796(5)	O(5)#1-Fe(1)-O(3)	90.63(11)	C(21)-C(20)-P(5)	117.6(4)
C(4)-P(5)	1.828(5)	O(5)-Fe(1)-O(3)	89.37(11)	C(25)-C(20)-P(5)	123.1(4)
P(5)-O(5)	1.492(3)	O(3)#1-Fe(1)-O(3)	180.0	C(22)-C(21)-C(20)	121.1(5)
P(5)-C(26)	1.782(5)	C(2)-N(1)-C(4)	118.9(3)	C(23)-C(22)-C(21)	119.0(5)
P(5)-C(20)	1.794(5)	C(2)-N(1)-C(6)	118.0(4)	C(22)-C(23)-C(24)	120.5(6)
C(6)-P(7)	1.828(4)	C(4)-N(1)-C(6)	118.4(4)	C(23)-C(24)-C(25)	121.1(6)
P(7)-O(7)	1.492(3)	N(1)-C(2)-P(3)	112.7(3)	C(24)-C(25)-C(20)	119.1(5)
P(7)-C(38)	1.784(5)	O(3)-P(3)-C(8)	110.26(19)	C(31)-C(26)-C(27)	118.2(4)
P(7)-C(32)	1.786(4)	O(3)-P(3)-C(14)	113.2(2)	C(31)-C(26)-P(5)	124.0(4)
C(8)-C(13)	1.389(6)	C(8)-P(3)-C(14)	106.5(2)	C(27)-C(26)-P(5)	117.6(3)
C(8)-C(9)	1.390(7)	O(3)-P(3)-C(2)	110.90(17)	C(28)-C(27)-C(26)	120.7(4)
C(9)-C(10)	1.373(7)	C(8)-P(3)-C(2)	105.9(2)	C(27)-C(28)-C(29)	120.0(5)
C(10)-C(11)	1.375(7)	C(14)-P(3)-C(2)	109.8(2)	C(30)-C(29)-C(28)	120.4(5)
C(11)-C(12)	1.359(8)	P(3)-O(3)-Fe(1)	144.59(19)	C(29)-C(30)-C(31)	119.9(5)
C(12)-C(13)	1.375(8)	N(1)-C(4)-P(5)	113.3(3)	C(30)-C(31)-C(26)	120.8(5)
C(14)-C(19)	1.380(6)	O(5)-P(5)-C(26)	113.20(18)	C(37)-C(32)-C(33)	117.8(4)
C(14)-C(15)	1.386(6)	O(5)-P(5)-C(20)	110.61(18)	C(37)-C(32)-P(7)	124.9(4)
C(15)-C(16)	1.391(8)	C(26)-P(5)-C(20)	107.0(2)	C(33)-C(32)-P(7)	117.3(3)
C(16)-C(17)	1.363(10)	O(5)-P(5)-C(4)	110.6(2)	C(32)-C(33)-C(34)	121.1(5)
C(17)-C(18)	1.362(9)	C(26)-P(5)-C(4)	110.0(2)	C(35)-C(34)-C(33)	119.4(6)
C(18)-C(19)	1.392(7)	C(20)-P(5)-C(4)	105.0(2)	C(36)-C(35)-C(34)	119.7(5)
C(20)-C(21)	1.383(6)	P(5)-O(5)-Fe(1)	143.29(17)	C(35)-C(36)-C(37)	121.4(6)
C(20)-C(25)	1.383(7)	N(1)-C(6)-P(7)	112.2(3)	C(32)-C(37)-C(36)	120.5(6)
C(21)-C(22)	1.381(7)	O(7)-P(7)-C(38)	113.19(18)	C(39)-C(38)-C(43)	118.6(4)
C(22)-C(23)	1.359(8)	O(7)-P(7)-C(32)	110.32(19)	C(39)-C(38)-P(7)	118.7(3)
C(23)-C(24)	1.368(8)	C(38)-P(7)-C(32)	106.3(2)	C(43)-C(38)-P(7)	122.6(3)
C(24)-C(25)	1.374(8)	O(7)-P(7)-C(6)	111.27(18)	C(40)-C(39)-C(38)	120.7(4)
C(26)-C(31)	1.396(6)	C(38)-P(7)-C(6)	109.7(2)	C(39)-C(40)-C(41)	120.1(5)
C(26)-C(27)	1.399(6)	C(32)-P(7)-C(6)	105.66(19)	C(42)-C(41)-C(40)	119.4(5)
C(27)-C(28)	1.378(6)	P(7)-O(7)-Fe(1)	143.89(17)	C(43)-C(42)-C(41)	120.7(5)
C(28)-C(29)	1.380(7)	C(13)-C(8)-C(9)	118.1(5)	C(42)-C(43)-C(38)	120.5(5)
C(29)-C(30)	1.376(7)	C(13)-C(8)-P(3)	124.6(4)	C(51)-B(50)-C(63)	105.6(4)
C(30)-C(31)	1.379(7)	C(9)-C(8)-P(3)	117.2(3)	C(51)-B(50)-C(69)	112.6(4)
C(32)-C(37)	1.349(7)	C(10)-C(9)-C(8)	120.9(4)	C(63)-B(50)-C(69)	111.9(4)
C(32)-C(33)	1.381(7)	C(9)-C(10)-C(11)	119.9(5)	C(51)-B(50)-C(57)	110.8(4)
C(33)-C(34)	1.390(6)	C(63)-B(50)-C(57)	110.5(4)		
C(34)-C(35)	1.354(9)	C(69)-B(50)-C(57)	105.5(4)		
C(35)-C(36)	1.335(10)	C(52)-C(51)-C(56)	114.3(6)		
C(36)-C(37)	1.387(8)	C(52)-C(51)-B(50)	120.4(5)		

C(38)-C(39)	1.397(6)	C(56)-C(51)-B(50)	125.2(5)		
C(38)-C(43)	1.400(6)	C(51)-C(52)-C(53)	123.4(6)		
C(39)-C(40)	1.375(6)	C(54)-C(53)-C(52)	119.3(7)		
C(40)-C(41)	1.391(7)	C(53)-C(54)-C(55)	119.6(7)		
C(41)-C(42)	1.387(7)	C(54)-C(55)-C(56)	120.1(6)		
C(42)-C(43)	1.367(7)	C(55)-C(56)-C(51)	123.3(6)		
B(50)-C(51)	1.622(8)	C(58)-C(57)-C(62)	115.2(5)		
B(50)-C(63)	1.646(7)	C(58)-C(57)-B(50)	120.3(4)		
B(50)-C(69)	1.650(8)	C(62)-C(57)-B(50)	124.5(4)		
B(50)-C(57)	1.657(7)	C(59)-C(58)-C(57)	123.3(5)		
C(51)-C(52)	1.379(8)	C(58)-C(59)-C(60)	120.3(6)		
C(51)-C(56)	1.393(7)	C(61)-C(60)-C(59)	118.3(6)		
C(52)-C(53)	1.396(9)	C(60)-C(61)-C(62)	120.7(6)		
C(53)-C(54)	1.358(9)	C(57)-C(62)-C(61)	122.1(5)		
C(54)-C(55)	1.362(9)	C(68)-C(63)-C(64)	114.5(4)		
C(55)-C(56)	1.372(8)	C(68)-C(63)-B(50)	125.4(4)		
C(57)-C(58)	1.377(7)	C(64)-C(63)-B(50)	120.0(4)		
C(57)-C(62)	1.389(7)	C(65)-C(64)-C(63)	123.3(5)		
C(58)-C(59)	1.373(7)	C(66)-C(65)-C(64)	119.9(5)		
C(59)-C(60)	1.376(8)	C(65)-C(66)-C(67)	118.7(5)		
C(60)-C(61)	1.362(8)	C(66)-C(67)-C(68)	121.2(5)		
C(61)-C(62)	1.391(7)	C(63)-C(68)-C(67)	122.3(5)		
C(63)-C(68)	1.378(6)	C(74)-C(69)-C(70)	114.4(5)		
C(63)-C(64)	1.391(7)	C(74)-C(69)-B(50)	124.9(5)		
C(64)-C(65)	1.389(7)	C(70)-C(69)-B(50)	120.7(4)		
C(65)-C(66)	1.356(8)	C(71)-C(70)-C(69)	124.1(6)		
C(66)-C(67)	1.356(8)	C(72)-C(71)-C(70)	119.4(7)		
C(67)-C(68)	1.389(7)	C(73)-C(72)-C(71)	119.4(6)		
C(69)-C(74)	1.384(7)	C(72)-C(73)-C(74)	120.8(6)		
C(69)-C(70)	1.403(7)	C(69)-C(74)-C(73)	122.0(6)		
C(70)-C(71)	1.377(7)	Cl(82)-C(80)-Cl(81)	111.0(13)		
C(71)-C(72)	1.373(8)	Cl(92)-C(90)-Cl(91)	110.3(10)		
C(72)-C(73)	1.353(9)				
C(73)-C(74)	1.410(9)				
C(80)-Cl(82)	1.715(18)				
C(80)-Cl(81)	1.720(16)				
C(90)-Cl(92)	1.740(10)				
C(90)-Cl(91)	1.749(10)				

Table A31. Geometric parameters of [Co{N(CH₂P(O)Ph₂)₃}₂](BPh₄)₂ (**38**) (A).

Bond lengths (Å)		Bond angles (°)			
Co(1)-O(5)	2.0677(13)	O(5)-Co(1)-O(5)#1	180.0	C(10)-C(9)-C(8)	120.1(2)
Co(1)-O(5)#1	2.0677(13)	O(5)-Co(1)-O(3)#1	89.74(5)	C(11)-C(10)-C(9)	120.1(2)
Co(1)-O(3)#1	2.1135(13)	O(5)#1-Co(1)-O(3)#1	90.26(5)	C(10)-C(11)-C(12)	120.2(2)
Co(1)-O(3)	2.1135(13)	O(5)-Co(1)-O(3)	90.26(5)	C(11)-C(12)-C(13)	120.1(2)
Co(1)-O(7)#1	2.1165(13)	O(5)#1-Co(1)-O(3)	89.74(5)	C(8)-C(13)-C(12)	119.9(2)
Co(1)-O(7)	2.1166(13)	O(3)#1-Co(1)-O(3)	180.0	C(15)-C(14)-C(19)	120.11(19)
N(1)-C(6)	1.441(2)	O(5)-Co(1)-O(7)#1	88.75(5)	C(15)-C(14)-P(3)	117.20(16)
N(1)-C(2)	1.445(2)	O(5)#1-Co(1)-O(7)#1	91.25(5)	C(19)-C(14)-P(3)	122.50(17)
N(1)-C(4)	1.448(2)	O(3)#1-Co(1)-O(7)#1	89.83(5)	C(16)-C(15)-C(14)	119.7(2)
C(2)-P(3)	1.834(2)	O(3)-Co(1)-O(7)#1	90.17(5)	C(17)-C(16)-C(15)	120.1(2)
P(3)-O(3)	1.4982(14)	O(5)-Co(1)-O(7)	91.25(5)	C(18)-C(17)-C(16)	120.4(2)
P(3)-C(14)	1.800(2)	O(5)#1-Co(1)-O(7)	88.75(5)	C(17)-C(18)-C(19)	120.4(2)
P(3)-C(8)	1.803(2)	O(3)#1-Co(1)-O(7)	90.17(5)	C(18)-C(19)-C(14)	119.3(2)
C(4)-P(5)	1.840(2)	O(3)-Co(1)-O(7)	89.83(5)	C(21)-C(20)-C(25)	119.41(19)
P(5)-O(5)	1.4969(14)	O(7)#1-Co(1)-O(7)	180.0	C(21)-C(20)-P(5)	117.70(15)
P(5)-C(26)	1.796(2)	C(6)-N(1)-C(2)	117.95(16)	C(25)-C(20)-P(5)	122.84(16)
P(5)-C(20)	1.799(2)	C(6)-N(1)-C(4)	118.28(16)	C(22)-C(21)-C(20)	120.6(2)
C(6)-P(7)	1.835(2)	O(5)-Co(1)-O(5)#1	180.0	C(23)-C(22)-C(21)	119.6(2)
P(7)-O(7)	1.4954(14)	C(2)-N(1)-C(4)	118.16(16)	C(24)-C(23)-C(22)	120.3(2)
P(7)-C(38)	1.803(2)	N(1)-C(2)-P(3)	111.55(13)	C(23)-C(24)-C(25)	120.5(2)
P(7)-C(32)	1.806(2)	O(3)-P(3)-C(14)	113.25(9)	C(24)-C(25)-C(20)	119.6(2)
C(8)-C(13)	1.387(3)	O(3)-P(3)-C(8)	111.69(9)	C(31)-C(26)-C(27)	119.84(19)
C(8)-C(9)	1.389(3)	C(14)-P(3)-C(8)	105.87(9)	C(31)-C(26)-P(5)	117.80(15)
C(9)-C(10)	1.389(3)	O(3)-P(3)-C(2)	111.14(8)	C(27)-C(26)-P(5)	122.20(16)
C(10)-C(11)	1.375(4)	C(14)-P(3)-C(2)	109.58(9)	C(28)-C(27)-C(26)	119.5(2)
C(11)-C(12)	1.382(4)	C(8)-P(3)-C(2)	104.85(9)	C(27)-C(28)-C(29)	120.6(2)
C(12)-C(13)	1.391(3)	P(3)-O(3)-Co(1)	143.91(8)	C(30)-C(29)-C(28)	119.7(2)
C(14)-C(15)	1.391(3)	N(1)-C(4)-P(5)	111.24(13)	C(31)-C(30)-C(29)	120.5(2)
C(14)-C(19)	1.396(3)	O(5)-P(5)-C(26)	113.65(9)	C(30)-C(31)-C(29)	119.82(19)
C(15)-C(16)	1.388(3)	O(5)-P(5)-C(20)	110.02(8)	C(33)-C(32)-C(37)	118.7(2)
C(16)-C(17)	1.382(4)	C(26)-P(5)-C(20)	106.43(9)	C(33)-C(32)-P(7)	118.01(16)
C(17)-C(18)	1.375(4)	O(5)-P(5)-C(4)	110.91(8)	C(37)-C(32)-P(7)	123.25(18)
C(18)-C(19)	1.389(3)	C(26)-P(5)-C(4)	109.39(9)	C(34)-C(33)-C(32)	121.2(2)
C(20)-C(21)	1.390(3)	C(20)-P(5)-C(4)	106.07(9)	C(35)-C(34)-C(33)	119.5(3)
C(20)-C(25)	1.394(3)	P(5)-O(5)-Co(1)	144.94(8)	C(34)-C(35)-C(36)	120.1(2)
C(21)-C(22)	1.388(3)	N(1)-C(6)-P(7)	113.06(13)	C(35)-C(36)-C(37)	120.7(3)
C(22)-C(23)	1.383(4)	O(7)-P(7)-C(38)	113.64(9)	C(36)-C(37)-C(32)	119.8(2)
C(23)-C(24)	1.377(4)	O(7)-P(7)-C(32)	111.57(9)	C(39)-C(38)-C(43)	119.83(19)
C(24)-C(25)	1.392(3)	C(38)-P(7)-C(32)	106.13(10)	C(39)-C(38)-P(7)	117.97(16)
C(26)-C(31)	1.392(3)	O(7)-P(7)-C(6)	111.38(8)	C(43)-C(38)-P(7)	122.05(16)
C(26)-C(27)	1.401(3)	C(38)-P(7)-C(6)	109.95(10)	C(40)-C(39)-C(38)	119.6(2)
C(27)-C(28)	1.384(3)	C(32)-P(7)-C(6)	103.58(9)	C(41)-C(40)-C(39)	120.4(2)
C(28)-C(29)	1.387(3)	P(7)-O(7)-Co(1)	143.27(9)	C(40)-C(41)-C(42)	120.4(2)
C(29)-C(30)	1.386(3)	C(13)-C(8)-C(9)	119.6(2)	C(41)-C(42)-C(43)	119.7(2)
C(30)-C(31)	1.385(3)	C(13)-C(8)-P(3)	122.41(16)	C(42)-C(43)-C(38)	120.0(2)
C(32)-C(33)	1.389(3)	C(9)-C(8)-P(3)	117.99(16)	C(69)-B(50)-C(51)	111.71(18)
C(32)-C(37)	1.391(3)	P(5)-O(5)-Co(1)	144.94(8)	C(69)-B(50)-C(63)	109.12(17)
C(33)-C(34)	1.383(3)	C(51)-B(50)-C(63)	109.87(17)		
C(34)-C(35)	1.373(4)	C(69)-B(50)-C(57)	109.00(17)		
C(35)-C(36)	1.378(5)	C(51)-B(50)-C(57)	107.25(18)		
C(36)-C(37)	1.384(4)	C(63)-B(50)-C(57)	109.86(17)		

C(38)-C(39)	1.389(3)	C(52)-C(51)-C(56)	115.0(2)		
C(38)-C(43)	1.398(3)	C(52)-C(51)-B(50)	124.4(2)		
C(39)-C(40)	1.388(3)	C(56)-C(51)-B(50)	120.60(19)		
C(40)-C(41)	1.380(4)	C(51)-C(52)-C(53)	122.4(2)		
C(41)-C(42)	1.386(4)	C(54)-C(53)-C(52)	120.8(2)		
C(42)-C(43)	1.388(3)	C(53)-C(54)-C(55)	118.8(2)		
B(50)-C(69)	1.644(3)	C(54)-C(55)-C(56)	119.8(2)		
B(50)-C(51)	1.647(3)	C(55)-C(56)-C(51)	123.3(2)		
B(50)-C(63)	1.649(3)	C(62)-C(57)-C(58)	114.9(2)		
B(50)-C(57)	1.654(3)	C(62)-C(57)-B(50)	125.0(2)		
C(51)-C(52)	1.394(3)	C(58)-C(57)-B(50)	120.0(2)		
C(51)-C(56)	1.405(3)	C(59)-C(58)-C(57)	123.2(2)		
C(52)-C(53)	1.399(3)	C(60)-C(59)-C(58)	119.9(3)		
C(53)-C(54)	1.376(4)	C(61)-C(60)-C(59)	119.1(2)		
C(54)-C(55)	1.385(4)	C(60)-C(61)-C(62)	120.4(2)		
C(55)-C(56)	1.390(3)	C(57)-C(62)-C(61)	122.5(2)		
C(57)-C(62)	1.390(3)	C(64)-C(63)-C(68)	115.0(2)		
C(57)-C(58)	1.403(3)	C(64)-C(63)-B(50)	123.8(2)		
C(58)-C(59)	1.383(4)	C(68)-C(63)-B(50)	121.2(2)		
C(59)-C(60)	1.380(4)	C(65)-C(64)-C(63)	122.7(3)		
C(60)-C(61)	1.371(4)	C(66)-C(65)-C(64)	120.3(3)		
C(61)-C(62)	1.398(3)	C(67)-C(66)-C(65)	119.0(2)		
C(63)-C(64)	1.398(3)	C(66)-C(67)-C(68)	120.1(3)		
C(63)-C(68)	1.404(3)	C(67)-C(68)-C(63)	122.8(2)		
C(64)-C(65)	1.392(4)	C(74)-C(69)-C(70)	114.7(2)		
C(65)-C(66)	1.382(4)	C(74)-C(69)-B(50)	125.08(19)		
C(66)-C(67)	1.376(4)	C(70)-C(69)-B(50)	120.04(19)		
C(67)-C(68)	1.391(3)	C(71)-C(70)-C(69)	122.6(2)		
C(69)-C(74)	1.394(3)	C(72)-C(71)-C(70)	120.7(2)		
C(69)-C(70)	1.409(3)	C(71)-C(72)-C(73)	118.5(2)		
C(70)-C(71)	1.387(3)	C(72)-C(73)-C(74)	120.6(2)		
C(71)-C(72)	1.375(4)	C(73)-C(74)-C(69)	122.9(2)		
C(72)-C(73)	1.379(4)	N(80)-C(81)-C(82)	176.6(6)		
C(73)-C(74)	1.390(3)	N(90)-C(91)-C(92)	179.4(4)		
N(80)-C(81)	1.118(4)				
C(81)-C(82)	1.444(6)				
N(90)-C(91)	1.135(5)				
C(91)-C(92)	1.451(5)				

Table A32. Geometric parameters of [Co{N(CH₂P(O)Ph₂)₃}₂](BPh₄)₂ (**38**) (B).

Bond lengths (Å)		Bond angles (°)			
Co(1)-O(5)#1	2.0655(10)	O(5)#1-Co(1)-O(5)	180.0	C(12)-C(11)-C(10)	120.49(17)
Co(1)-O(5)	2.0656(10)	O(5)#1-Co(1)-O(3)#1	90.28(4)	C(11)-C(12)-C(13)	120.20(19)
Co(1)-O(3)#1	2.1140(11)	O(5)-Co(1)-O(3)#1	89.72(4)	C(8)-C(13)-C(12)	119.84(18)
Co(1)-O(3)	2.1140(11)	O(5)#1-Co(1)-O(3)	89.72(4)	C(15)-C(14)-C(19)	119.99(15)
Co(1)-O(7)	2.1166(11)	O(5)-Co(1)-O(3)	90.28(4)	C(15)-C(14)-P(3)	117.27(13)
Co(1)-O(7)#1	2.1167(11)	O(3)#1-Co(1)-O(3)	180.0	C(19)-C(14)-P(3)	122.51(13)
N(1)-C(6)	1.442(2)	O(5)#1-Co(1)-O(7)	88.71(4)	C(16)-C(15)-C(14)	119.77(17)
N(1)-C(4)	1.444(2)	O(5)-Co(1)-O(7)	91.28(4)	C(17)-C(16)-C(15)	120.18(19)
N(1)-C(2)	1.4463(19)	O(3)#1-Co(1)-O(7)	90.19(4)	C(16)-C(17)-C(18)	120.42(18)
C(2)-P(3)	1.8307(16)	O(3)-Co(1)-O(7)	89.81(4)	C(17)-C(18)-C(19)	120.16(19)
P(3)-O(3)	1.4918(11)	O(5)#1-Co(1)-O(7)#1	91.29(4)	C(18)-C(19)-C(14)	119.47(18)
P(3)-C(14)	1.7993(16)	O(5)-Co(1)-O(7)#1	88.71(4)	C(25)-C(20)-C(21)	119.82(15)
P(3)-C(8)	1.8015(16)	O(3)#1-Co(1)-O(7)#1	89.81(4)	C(25)-C(20)-P(5)	122.79(13)
C(4)-P(5)	1.8410(16)	O(3)-Co(1)-O(7)#1	90.19(4)	C(21)-C(20)-P(5)	117.33(12)
P(5)-O(5)	1.4935(11)	O(7)-Co(1)-O(7)#1	180.0	C(22)-C(21)-C(20)	120.14(16)
P(5)-C(26)	1.7962(16)	C(6)-N(1)-C(4)	118.07(12)	C(23)-C(22)-C(21)	119.80(18)
P(5)-C(20)	1.8017(16)	C(6)-N(1)-C(2)	118.22(12)	C(12)-C(11)-C(10)	120.49(17)
C(6)-P(7)	1.8329(16)	C(4)-N(1)-C(2)	118.23(13)	C(11)-C(12)-C(13)	120.20(19)
P(7)-O(7)	1.4901(11)	N(1)-C(2)-P(3)	111.53(11)	C(8)-C(13)-C(12)	119.84(18)
P(7)-C(38)	1.8052(16)	O(3)-P(3)-C(14)	113.22(7)	C(15)-C(14)-C(19)	119.99(15)
P(7)-C(32)	1.8101(17)	O(3)-P(3)-C(8)	111.73(7)	C(15)-C(14)-P(3)	117.27(13)
C(8)-C(13)	1.391(2)	C(14)-P(3)-C(8)	105.85(8)	C(19)-C(14)-P(3)	122.51(13)
C(8)-C(9)	1.393(2)	O(3)-P(3)-C(2)	111.24(7)	C(16)-C(15)-C(14)	119.77(17)
C(9)-C(10)	1.389(3)	C(14)-P(3)-C(2)	109.48(8)	C(17)-C(16)-C(15)	120.18(19)
C(10)-C(11)	1.381(3)	C(8)-P(3)-C(2)	104.86(7)	C(16)-C(17)-C(18)	120.42(18)
C(11)-C(12)	1.376(3)	P(3)-O(3)-Co(1)	144.04(7)	C(17)-C(18)-C(19)	120.16(19)
C(12)-C(13)	1.391(3)	N(1)-C(4)-P(5)	111.36(11)	C(18)-C(19)-C(14)	119.47(18)
C(14)-C(15)	1.391(2)	O(5)-P(5)-C(26)	113.58(7)	C(25)-C(20)-C(21)	119.82(15)
C(14)-C(19)	1.400(2)	O(5)-P(5)-C(20)	109.99(7)	C(25)-C(20)-P(5)	122.79(13)
C(15)-C(16)	1.391(3)	C(26)-P(5)-C(20)	106.45(7)	C(21)-C(20)-P(5)	117.33(12)
C(16)-C(17)	1.381(3)	O(5)-P(5)-C(4)	110.86(7)	C(22)-C(21)-C(20)	120.14(16)
C(17)-C(18)	1.383(3)	C(26)-P(5)-C(4)	109.42(7)	C(23)-C(22)-C(21)	119.80(18)
C(18)-C(19)	1.392(3)	C(20)-P(5)-C(4)	106.20(7)	C(24)-C(23)-C(22)	120.34(17)
C(20)-C(25)	1.391(2)	P(5)-O(5)-Co(1)	145.04(7)	C(23)-C(24)-C(25)	120.33(17)
C(20)-C(21)	1.393(2)	N(1)-C(6)-P(7)	113.12(10)	C(24)-C(25)-C(20)	119.57(17)
C(21)-C(22)	1.388(3)	O(7)-P(7)-C(38)	113.81(7)	C(31)-C(26)-C(27)	119.70(15)
C(22)-C(23)	1.382(3)	O(7)-P(7)-C(32)	111.54(7)	C(31)-C(26)-P(5)	117.97(12)
C(23)-C(24)	1.381(3)	C(38)-P(7)-C(32)	106.11(8)	C(27)-C(26)-P(5)	122.14(12)
C(24)-C(25)	1.390(3)	O(7)-P(7)-C(6)	111.35(7)	C(28)-C(27)-C(26)	119.87(15)
C(26)-C(31)	1.392(2)	C(38)-P(7)-C(6)	109.88(7)	C(29)-C(28)-C(27)	120.37(16)
C(26)-C(27)	1.400(2)	C(32)-P(7)-C(6)	103.54(7)	C(28)-C(29)-C(30)	119.89(16)
C(27)-C(28)	1.386(2)	P(7)-O(7)-Co(1)	143.37(7)	C(31)-C(30)-C(29)	120.19(16)
C(28)-C(29)	1.385(3)	C(13)-C(8)-C(9)	119.45(15)	C(30)-C(31)-C(26)	119.97(15)
C(29)-C(30)	1.391(2)	C(13)-C(8)-P(3)	122.66(13)	C(37)-C(32)-C(33)	119.00(17)
C(30)-C(31)	1.389(2)	C(9)-C(8)-P(3)	117.89(13)	C(37)-C(32)-P(7)	122.99(14)
C(32)-C(37)	1.387(3)	C(10)-C(9)-C(8)	120.26(17)	C(33)-C(32)-P(7)	118.00(13)
C(32)-C(33)	1.389(3)	C(11)-C(10)-C(9)	119.75(19)	C(34)-C(33)-C(32)	121.01(18)
C(33)-C(34)	1.384(3)	C(35)-C(34)-C(33)	119.6(2)	C(74)-C(69)-C(70)	114.50(16)
C(34)-C(35)	1.374(3)	C(34)-C(35)-C(36)	120.1(2)	C(74)-C(69)-B(50)	125.21(15)
C(35)-C(36)	1.383(4)	C(35)-C(36)-C(37)	120.4(2)	C(70)-C(69)-B(50)	120.15(15)
C(36)-C(37)	1.388(3)	C(32)-C(37)-C(36)	119.9(2)	C(71)-C(70)-C(69)	122.96(17)

C(38)-C(39)	1.391(2)	C(39)-C(38)-C(43)	120.00(16)	C(72)-C(71)-C(70)	120.55(17)
C(38)-C(43)	1.393(2)	C(39)-C(38)-P(7)	117.60(13)	C(73)-C(72)-C(71)	118.41(17)
C(39)-C(40)	1.390(3)	C(43)-C(38)-P(7)	122.24(13)	C(72)-C(73)-C(74)	120.53(18)
C(40)-C(41)	1.377(3)	C(40)-C(39)-C(38)	119.40(17)	C(73)-C(74)-C(69)	123.02(17)
C(41)-C(42)	1.389(3)	C(41)-C(40)-C(39)	120.45(18)	N(80)-C(81)-C(82)	177.2(5)
C(42)-C(43)	1.389(3)	C(40)-C(41)-C(42)	120.58(17)	N(90)-C(91)-C(92)	178.9(3)
B(50)-C(69)	1.638(2)	C(43)-C(42)-C(41)	119.33(18)		
B(50)-C(51)	1.648(2)	C(42)-C(43)-C(38)	120.24(17)		
B(50)-C(63)	1.650(2)	C(69)-B(50)-C(51)	111.68(14)		
B(50)-C(57)	1.653(2)	C(69)-B(50)-C(63)	109.08(13)		
C(51)-C(52)	1.394(3)	C(51)-B(50)-C(63)	109.94(14)		
C(51)-C(56)	1.407(3)	C(69)-B(50)-C(57)	109.22(14)		
C(52)-C(53)	1.401(3)	C(51)-B(50)-C(57)	107.14(13)		
C(53)-C(54)	1.379(3)	C(63)-B(50)-C(57)	109.75(14)		
C(54)-C(55)	1.382(3)	C(52)-C(51)-C(56)	115.01(16)		
C(55)-C(56)	1.389(3)	C(52)-C(51)-B(50)	124.38(16)		
C(57)-C(62)	1.397(3)	C(56)-C(51)-B(50)	120.58(15)		
C(57)-C(58)	1.399(3)	C(51)-C(52)-C(53)	122.43(19)		
C(58)-C(59)	1.387(3)	C(54)-C(53)-C(52)	120.49(19)		
C(59)-C(60)	1.386(3)	C(53)-C(54)-C(55)	119.00(18)		
C(60)-C(61)	1.377(3)	C(54)-C(55)-C(56)	119.83(19)		
C(61)-C(62)	1.396(3)	C(55)-C(56)-C(51)	123.24(18)		
C(63)-C(64)	1.396(3)	C(62)-C(57)-C(58)	114.83(16)		
C(63)-C(68)	1.401(3)	C(62)-C(57)-B(50)	124.79(16)		
C(64)-C(65)	1.398(3)	C(58)-C(57)-B(50)	120.38(16)		
C(65)-C(66)	1.385(4)	C(59)-C(58)-C(57)	123.42(19)		
C(66)-C(67)	1.377(3)	C(60)-C(59)-C(58)	119.9(2)		
C(67)-C(68)	1.392(3)	C(61)-C(60)-C(59)	118.78(18)		
C(69)-C(74)	1.399(2)	C(60)-C(61)-C(62)	120.43(19)		
C(69)-C(70)	1.410(2)	C(61)-C(62)-C(57)	122.67(19)		
C(70)-C(71)	1.385(3)	C(64)-C(63)-C(68)	114.94(16)		
C(71)-C(72)	1.384(3)	C(64)-C(63)-B(50)	123.86(16)		
C(72)-C(73)	1.382(3)	C(68)-C(63)-B(50)	121.18(16)		
C(73)-C(74)	1.390(3)	C(63)-C(64)-C(65)	122.8(2)		
N(80)-C(81)	1.132(4)	C(66)-C(65)-C(64)	120.1(2)		
C(81)-C(82)	1.421(5)	C(67)-C(66)-C(65)	118.87(19)		
N(90)-C(91)	1.142(4)	C(66)-C(67)-C(68)	120.2(2)		
C(91)-C(92)	1.446(4)	C(67)-C(68)-C(63)	123.04(19)		

Table A33. Geometric parameters of [Ni{N(CH₂P(O)Ph₂)₃}₂](BPh₄)₂ (**39**).

Bond lengths (Å)		Bond angles (°)			
Ni(1)-O(5)	2.0451(11)	O(5)-Ni(1)-O(5)#1	180.0	C(10)-C(11)-C(12)	120.11(19)
Ni(1)-O(5)#1	2.0451(11)	O(5)-Ni(1)-O(3)#1	89.63(5)	C(11)-C(12)-C(13)	120.11(19)
Ni(1)-O(3)#1	2.0811(12)	O(5)#1-Ni(1)-O(3)#1	90.37(5)	C(12)-C(13)-C(8)	119.93(19)
Ni(1)-O(3)	2.0811(12)	O(5)-Ni(1)-O(3)	90.37(5)	C(15)-C(14)-C(19)	120.17(17)
Ni(1)-O(7)	2.0846(11)	O(5)#1-Ni(1)-O(3)	89.63(5)	C(15)-C(14)-P(3)	117.25(14)
Ni(1)-O(7)#1	2.0847(11)	O(3)#1-Ni(1)-O(3)	180.0	C(19)-C(14)-P(3)	122.36(14)
N(1)-C(6)	1.441(2)	O(5)-Ni(1)-O(7)	91.32(5)	C(14)-C(15)-C(16)	119.66(19)
N(1)-C(4)	1.444(2)	O(5)#1-Ni(1)-O(7)	88.68(5)	C(17)-C(16)-C(15)	120.1(2)
N(1)-C(2)	1.447(2)	O(3)#1-Ni(1)-O(7)	90.00(5)	C(16)-C(17)-C(18)	120.33(19)
C(2)-P(3)	1.8320(17)	O(3)-Ni(1)-O(7)	90.00(5)	C(17)-C(18)-C(19)	120.5(2)
P(3)-O(3)	1.4952(12)	O(5)-Ni(1)-O(7)#1	88.68(5)	C(18)-C(19)-C(14)	119.2(2)
P(3)-C(8)	1.8011(17)	O(5)#1-Ni(1)-O(7)#1	91.32(5)	C(25)-C(20)-C(21)	119.72(16)
P(3)-C(14)	1.8016(17)	O(3)#1-Ni(1)-O(7)#1	90.00(5)	C(25)-C(20)-P(5)	122.97(13)
C(4)-P(5)	1.8389(18)	O(3)-Ni(1)-O(7)#1	90.00(5)	C(21)-C(20)-P(5)	117.27(13)
P(5)-O(5)	1.4957(12)	O(7)-Ni(1)-O(7)#1	180.00(2)	C(22)-C(21)-C(20)	119.96(18)
P(5)-C(26)	1.7988(17)	C(6)-N(1)-C(4)	118.36(14)	C(23)-C(22)-C(21)	120.04(18)
P(5)-C(20)	1.8029(17)	C(6)-N(1)-C(2)	118.25(13)	C(22)-C(23)-C(24)	120.46(18)
C(6)-P(7)	1.8332(17)	C(4)-N(1)-C(2)	118.61(14)	C(23)-C(24)-C(25)	119.98(19)
P(7)-O(7)	1.4959(12)	N(1)-C(2)-P(3)	111.45(12)	C(20)-C(25)-C(24)	119.84(18)
P(7)-C(38)	1.8040(18)	O(3)-P(3)-C(8)	111.73(8)	C(31)-C(26)-C(27)	119.93(16)
P(7)-C(32)	1.8123(17)	O(3)-P(3)-C(14)	113.64(8)	C(31)-C(26)-P(5)	117.77(13)
C(8)-C(13)	1.392(3)	C(8)-P(3)-C(14)	105.66(8)	C(27)-C(26)-P(5)	122.10(14)
C(8)-C(9)	1.398(3)	O(3)-P(3)-C(2)	111.25(7)	C(28)-C(27)-C(26)	119.60(17)
C(9)-C(10)	1.384(3)	C(8)-P(3)-C(2)	104.52(8)	C(27)-C(28)-C(29)	120.49(17)
C(10)-C(11)	1.378(3)	C(14)-P(3)-C(2)	109.53(8)	C(28)-C(29)-C(30)	120.11(17)
C(11)-C(12)	1.388(3)	P(3)-O(3)-Ni(1)	144.24(7)	C(29)-C(30)-C(31)	119.90(18)
C(12)-C(13)	1.391(3)	N(1)-C(4)-P(5)	111.42(12)	C(26)-C(31)-C(30)	119.96(17)
C(14)-C(15)	1.389(3)	O(5)-P(5)-C(26)	113.78(7)	C(37)-C(32)-C(33)	119.24(17)
C(14)-C(19)	1.403(3)	O(5)-P(5)-C(20)	110.08(7)	C(37)-C(32)-P(7)	122.92(15)
C(15)-C(16)	1.394(3)	C(26)-P(5)-C(20)	106.14(8)	C(33)-C(32)-P(7)	117.84(14)
C(16)-C(17)	1.381(3)	O(5)-P(5)-C(4)	111.10(7)	C(32)-C(33)-C(34)	120.9(2)
C(17)-C(18)	1.383(4)	C(26)-P(5)-C(4)	109.25(8)	C(35)-C(34)-C(33)	119.3(2)
C(18)-C(19)	1.388(3)	C(20)-P(5)-C(4)	106.10(8)	C(34)-C(35)-C(36)	120.3(2)
C(20)-C(25)	1.390(3)	P(5)-O(5)-Ni(1)	145.05(7)	C(35)-C(36)-C(37)	120.3(2)
C(20)-C(21)	1.396(3)	N(1)-C(6)-P(7)	113.07(11)	C(32)-C(37)-C(36)	119.9(2)
C(21)-C(22)	1.389(3)	O(7)-P(7)-C(38)	114.15(8)	C(39)-C(38)-C(43)	119.93(17)
C(22)-C(23)	1.378(3)	O(7)-P(7)-C(32)	111.48(8)	C(39)-C(38)-P(7)	117.59(14)
C(23)-C(24)	1.384(3)	C(38)-P(7)-C(32)	105.87(8)	C(43)-C(38)-P(7)	122.29(15)
C(24)-C(25)	1.393(3)	O(7)-P(7)-C(6)	111.51(7)	C(40)-C(39)-C(38)	119.67(19)
C(26)-C(31)	1.392(3)	C(38)-P(7)-C(6)	109.79(8)	C(41)-C(40)-C(39)	120.1(2)
C(26)-C(27)	1.402(2)	C(32)-P(7)-C(6)	103.36(8)	C(42)-C(41)-C(40)	120.26(19)
C(27)-C(28)	1.386(3)	P(7)-O(7)-Ni(1)	143.30(7)	C(41)-C(42)-C(43)	120.0(2)
C(28)-C(29)	1.386(3)	C(13)-C(8)-C(9)	119.35(17)	C(42)-C(43)-C(38)	119.96(19)
C(29)-C(30)	1.391(3)	C(13)-C(8)-P(3)	122.61(14)	C(69)-B(50)-C(51)	111.83(15)
C(30)-C(31)	1.393(3)	C(9)-C(8)-P(3)	118.04(13)	C(69)-B(50)-C(63)	109.04(15)
C(32)-C(37)	1.387(3)	C(10)-C(9)-C(8)	120.26(18)	C(51)-B(50)-C(63)	109.95(14)
C(32)-C(33)	1.388(3)	C(11)-C(10)-C(9)	120.2(2)	C(69)-B(50)-C(57)	109.08(14)
C(33)-C(34)	1.389(3)	C(51)-B(50)-C(57)	107.06(15)		
C(34)-C(35)	1.380(4)	C(63)-B(50)-C(57)	109.85(15)		
C(35)-C(36)	1.381(4)	C(52)-C(51)-C(56)	114.86(18)		
C(36)-C(37)	1.390(3)	C(52)-C(51)-B(50)	124.41(17)		

C(38)-C(39)	1.393(3)	C(56)-C(51)-B(50)	120.70(16)		
C(38)-C(43)	1.396(3)	C(53)-C(52)-C(51)	122.6(2)		
C(39)-C(40)	1.390(3)	C(54)-C(53)-C(52)	120.5(2)		
C(40)-C(41)	1.388(3)	C(53)-C(54)-C(55)	118.9(2)		
C(41)-C(42)	1.384(3)	C(56)-C(55)-C(54)	119.9(2)		
C(42)-C(43)	1.387(3)	C(55)-C(56)-C(51)	123.25(19)		
B(50)-C(69)	1.641(3)	C(62)-C(57)-C(58)	114.81(18)		
B(50)-C(51)	1.647(3)	C(62)-C(57)-B(50)	124.94(17)		
B(50)-C(63)	1.649(3)	C(58)-C(57)-B(50)	120.26(17)		
B(50)-C(57)	1.655(3)	C(59)-C(58)-C(57)	123.4(2)		
C(51)-C(52)	1.396(3)	C(58)-C(59)-C(60)	119.7(2)		
C(51)-C(56)	1.411(3)	C(61)-C(60)-C(59)	118.9(2)		
C(52)-C(53)	1.396(3)	C(60)-C(61)-C(62)	120.5(2)		
C(53)-C(54)	1.382(4)	C(61)-C(62)-C(57)	122.8(2)		
C(54)-C(55)	1.386(3)	C(68)-C(63)-C(64)	115.14(18)		
C(55)-C(56)	1.384(3)	C(68)-C(63)-B(50)	121.11(17)		
C(57)-C(62)	1.394(3)	C(64)-C(63)-B(50)	123.72(18)		
C(57)-C(58)	1.400(3)	C(65)-C(64)-C(63)	122.6(2)		
C(58)-C(59)	1.387(3)	C(66)-C(65)-C(64)	120.1(2)		
C(59)-C(60)	1.388(3)	C(67)-C(66)-C(65)	119.1(2)		
C(60)-C(61)	1.375(4)	C(66)-C(67)-C(68)	120.3(2)		
C(61)-C(62)	1.394(3)	C(67)-C(68)-C(63)	122.8(2)		
C(63)-C(68)	1.399(3)	C(74)-C(69)-C(70)	114.82(17)		
C(63)-C(64)	1.403(3)	C(74)-C(69)-B(50)	125.01(17)		
C(64)-C(65)	1.396(3)	C(70)-C(69)-B(50)	120.00(16)		
C(65)-C(66)	1.386(4)	C(71)-C(70)-C(69)	122.69(18)		
C(66)-C(67)	1.374(4)	C(72)-C(71)-C(70)	120.60(18)		
C(67)-C(68)	1.395(3)	C(71)-C(72)-C(73)	118.38(18)		
C(69)-C(74)	1.399(3)	C(72)-C(73)-C(74)	120.73(19)		
C(69)-C(70)	1.409(3)	C(73)-C(74)-C(69)	122.76(18)		
C(70)-C(71)	1.389(3)	N(80)-C(81)-C(82)	176.9(5)		
C(71)-C(72)	1.381(3)	N(90)-C(91)-C(92)	179.5(4)		
C(72)-C(73)	1.383(3)				
C(73)-C(74)	1.389(3)				
N(80)-C(81)	1.115(4)				
C(81)-C(82)	1.439(5)				
N(90)-C(91)	1.140(4)				
C(91)-C(92)	1.451(5)				

Table A34. Geometric parameters of [Cu{N(CH₂P(O)Ph₂)₃}₂](BF₄)₂ (**40-A**).

Bond lengths (Å)		Bond angles (°)			
Cu(1)-O(3)	1.958(3)	O(3)-Cu(1)-O(3)#1	180.0	C(9)-C(8)-P(3)	117.7(3)
Cu(1)-O(3)#1	1.958(3)	O(3)-Cu(1)-O(7)	91.40(11)	C(10)-C(9)-C(8)	120.3(4)
Cu(1)-O(7)	2.043(3)	O(3)#1-Cu(1)-O(7)	88.60(11)	C(11)-C(10)-C(9)	120.1(5)
Cu(1)-O(7)#1	2.044(3)	O(3)-Cu(1)-O(7)#1	88.60(11)	C(12)-C(11)-C(10)	119.9(5)
Cu(1)-O(5)#1	2.318(3)	O(3)#1-Cu(1)-O(7)#1	91.40(11)	C(13)-C(12)-C(11)	120.9(5)
Cu(1)-O(5)	2.318(3)	O(7)-Cu(1)-O(7)#1	180.00(14)	C(12)-C(13)-C(8)	119.9(5)
N(1)-C(2)	1.437(5)	O(3)-Cu(1)-O(5)#1	91.21(11)	C(19)-C(14)-C(15)	119.9(4)
N(1)-C(6)	1.450(5)	O(3)#1-Cu(1)-O(5)#1	88.79(11)	C(19)-C(14)-P(3)	118.9(3)
N(1)-C(4)	1.452(6)	O(7)-Cu(1)-O(5)#1	89.74(11)	C(15)-C(14)-P(3)	121.0(3)
C(2)-P(3)	1.838(4)	O(7)#1-Cu(1)-O(5)#1	90.26(11)	C(16)-C(15)-C(14)	120.0(4)
O(3)-P(3)	1.504(3)	O(3)-Cu(1)-O(5)	88.79(11)	C(15)-C(16)-C(17)	120.3(5)
P(3)-C(8)	1.797(4)	O(3)#1-Cu(1)-O(5)	91.20(11)	C(16)-C(17)-C(18)	119.9(4)
P(3)-C(14)	1.802(4)	O(7)-Cu(1)-O(5)	90.26(11)	C(19)-C(18)-C(17)	119.7(4)
C(4)-P(5)	1.832(4)	O(7)#1-Cu(1)-O(5)	89.74(11)	C(14)-C(19)-C(18)	120.2(4)
O(5)-P(5)	1.494(4)	O(5)#1-Cu(1)-O(5)	180.0	C(21)-C(20)-C(25)	120.0
P(5)-C(26)	1.801(4)	C(2)-N(1)-C(6)	118.7(4)	C(21)-C(20)-P(5)	125.5(3)
P(5)-C(20)	1.801(4)	C(2)-N(1)-C(4)	119.0(3)	C(25)-C(20)-P(5)	114.5(3)
P(5)-C(20')	1.838(8)	C(6)-N(1)-C(4)	117.8(4)	C(20)-C(21)-C(22)	120.0
C(6)-P(7)	1.834(5)	N(1)-C(2)-P(3)	112.3(3)	C(23)-C(22)-C(21)	120.0
O(7)-P(7)	1.497(3)	P(3)-O(3)-Cu(1)	145.63(19)	C(22)-C(23)-C(24)	120.0
P(7)-C(38)	1.793(5)	O(3)-P(3)-C(8)	109.8(2)	C(25)-C(24)-C(23)	120.0
P(7)-C(32)	1.810(4)	O(3)-P(3)-C(14)	114.17(18)	C(24)-C(25)-C(20)	120.0
C(8)-C(13)	1.398(6)	C(8)-P(3)-C(14)	107.1(2)	C(21')-C(20')-C(25')	120.0
C(8)-C(9)	1.399(7)	O(3)-P(3)-C(2)	111.58(17)	C(21')-C(20')-P(5)	122.4(8)
C(9)-C(10)	1.378(7)	C(8)-P(3)-C(2)	105.3(2)	C(25')-C(20')-P(5)	117.5(8)
C(10)-C(11)	1.377(8)	C(14)-P(3)-C(2)	108.5(2)	C(20')-C(21')-C(22')	120.0
C(11)-C(12)	1.376(8)	N(1)-C(4)-P(5)	112.1(3)	C(21')-C(22')-C(23')	120.0
C(12)-C(13)	1.374(7)	P(5)-O(5)-Cu(1)	140.69(18)	C(24')-C(23')-C(22')	120.0
C(14)-C(19)	1.389(6)	O(5)-P(5)-C(26)	112.3(2)	C(23')-C(24')-C(25')	120.0
C(14)-C(15)	1.398(6)	O(5)-P(5)-C(20)	109.4(3)	C(24')-C(25')-C(20')	120.0
C(15)-C(16)	1.385(7)	C(26)-P(5)-C(20)	107.5(2)	C(27)-C(26)-C(31)	119.5(4)
C(16)-C(17)	1.391(8)	O(5)-P(5)-C(4)	111.58(19)	C(27)-C(26)-P(5)	117.9(3)
C(17)-C(18)	1.401(7)	C(26)-P(5)-C(4)	109.6(2)	C(31)-C(26)-P(5)	122.6(4)
C(18)-C(19)	1.393(6)	C(20)-P(5)-C(4)	106.2(3)	C(28)-C(27)-C(26)	120.6(5)
C(20)-C(21)	1.3900	O(5)-P(5)-C(20')	114.6(5)	C(27)-C(28)-C(29)	119.7(5)
C(20)-C(25)	1.3900	C(26)-P(5)-C(20')	107.7(5)	C(30)-C(29)-C(28)	120.3(4)
C(21)-C(22)	1.3900	C(4)-P(5)-C(20')	100.4(5)	C(29)-C(30)-C(31)	121.2(5)
C(22)-C(23)	1.3900	N(1)-C(6)-P(7)	112.7(3)	C(30)-C(31)-C(26)	118.7(5)
C(23)-C(24)	1.3900	P(7)-O(7)-Cu(1)	144.76(18)	C(37)-C(32)-C(33)	120.1(4)
C(24)-C(25)	1.3900	O(7)-P(7)-C(38)	112.8(2)	C(37)-C(32)-P(7)	121.9(4)
C(20')-C(21')	1.3900	O(7)-P(7)-C(32)	112.15(18)	C(33)-C(32)-P(7)	117.9(3)
C(20')-C(25')	1.3900	C(38)-P(7)-C(32)	106.1(2)	C(32)-C(33)-C(34)	120.5(4)
C(21')-C(22')	1.3900	O(7)-P(7)-C(6)	111.65(19)	C(35)-C(34)-C(33)	118.8(5)
C(22')-C(23')	1.3900	C(38)-P(7)-C(6)	109.4(2)	C(36)-C(35)-C(34)	121.0(4)
C(23')-C(24')	1.3900	C(32)-P(7)-C(6)	104.3(2)	C(35)-C(36)-C(37)	119.8(5)
C(24')-C(25')	1.3900	C(13)-C(8)-C(9)	118.8(4)	C(32)-C(37)-C(36)	119.6(5)
C(26)-C(27)	1.392(7)	C(13)-C(8)-P(3)	123.4(4)	C(39)-C(38)-C(43)	119.8(5)
C(26)-C(31)	1.409(7)	C(39)-C(38)-P(7)	118.3(4)		
C(27)-C(28)	1.386(6)	C(43)-C(38)-P(7)	121.7(4)		
C(28)-C(29)	1.394(8)	C(38)-C(39)-C(40)	120.0(5)		
C(29)-C(30)	1.365(8)	C(39)-C(40)-C(41)	119.7(6)		

C(30)-C(31)	1.403(6)	C(42)-C(41)-C(40)	119.6(5)		
C(32)-C(37)	1.386(7)	C(43)-C(42)-C(41)	121.5(5)		
C(32)-C(33)	1.392(7)	C(42)-C(43)-C(38)	119.4(6)		
C(33)-C(34)	1.401(6)	F(53)-B(50)-F(51)	115.2(8)		
C(34)-C(35)	1.399(8)	F(53)-B(50)-F(54)	107.9(7)		
C(35)-C(36)	1.375(8)	F(51)-B(50)-F(54)	106.6(6)		
C(36)-C(37)	1.415(6)	F(53)-B(50)-F(52)	114.6(7)		
C(38)-C(39)	1.384(7)	F(51)-B(50)-F(52)	105.7(6)		
C(38)-C(43)	1.413(7)	F(54)-B(50)-F(52)	106.1(6)		
C(39)-C(40)	1.399(7)	N(60)-C(61)-C(62)	178.4(11)		
C(40)-C(41)	1.405(9)	N(65)-C(66)-C(67)	177.0(12)		
C(41)-C(42)	1.375(10)				
C(42)-C(43)	1.374(8)				
B(50)-F(53)	1.296(9)				
B(50)-F(51)	1.327(8)				
B(50)-F(54)	1.369(8)				
B(50)-F(52)	1.375(9)				
N(60)-C(61)	1.108(12)				
C(61)-C(62)	1.454(13)				
N(65)-C(66)	1.136(12)				
C(66)-C(67)	1.425(14)				

Table A35. Geometric parameters of [Mn{N(CH₂P(O)Ph₂)₃}₂](BPh₄)₂ (**41**).

Bond lengths (Å)		Bond angles (°)			
Mn(1)-O(3)	2.164(2)	O(3)-Mn(1)-O(3)#1	180.00(12)	C(19)-C(14)-C(15)	120.3(3)
Mn(1)-O(3)#1	2.164(2)	O(3)-Mn(1)-O(5)	91.67(8)	C(19)-C(14)-P(3)	117.2(3)
Mn(1)-O(5)	2.168(2)	O(3)#1-Mn(1)-O(5)	88.33(8)	C(15)-C(14)-P(3)	122.3(3)
Mn(1)-O(5)#1	2.168(2)	O(3)-Mn(1)-O(5)#1	88.32(8)	C(16)-C(15)-C(14)	119.9(3)
Mn(1)-O(7)#1	2.184(2)	O(3)#1-Mn(1)-O(5)#1	91.67(8)	C(15)-C(16)-C(17)	119.8(4)
Mn(1)-O(7)	2.184(2)	O(5)-Mn(1)-O(5)#1	180.0	C(18)-C(17)-C(16)	120.3(4)
N(1)-C(2)	1.448(4)	O(3)-Mn(1)-O(7)#1	87.93(8)	C(17)-C(18)-C(19)	120.5(4)
N(1)-C(6)	1.461(4)	O(3)#1-Mn(1)-O(7)#1	92.07(8)	C(14)-C(19)-C(18)	119.1(4)
N(1)-C(4)	1.461(4)	O(5)-Mn(1)-O(7)#1	87.52(8)	C(25)-C(20)-C(21)	119.1(3)
C(2)-P(3)	1.833(3)	O(5)#1-Mn(1)-O(7)#1	92.48(8)	C(25)-C(20)-P(5)	123.4(3)
P(3)-O(3)	1.494(2)	O(3)-Mn(1)-O(7)	92.07(8)	C(21)-C(20)-P(5)	117.5(3)
P(3)-C(8)	1.802(3)	O(3)#1-Mn(1)-O(7)	87.93(8)	C(22)-C(21)-C(20)	120.4(4)
P(3)-C(14)	1.804(3)	O(5)-Mn(1)-O(7)	92.48(8)	C(23)-C(22)-C(21)	120.4(4)
C(4)-P(5)	1.827(3)	O(5)#1-Mn(1)-O(7)	87.52(8)	C(22)-C(23)-C(24)	119.5(4)
P(5)-O(5)	1.497(2)	O(7)#1-Mn(1)-O(7)	180.0	C(23)-C(24)-C(25)	120.6(4)
P(5)-C(26)	1.788(3)	C(2)-N(1)-C(6)	117.5(2)	C(20)-C(25)-C(24)	120.0(4)
P(5)-C(20)	1.801(3)	C(2)-N(1)-C(4)	117.4(2)	C(27)-C(26)-C(31)	119.1(3)
C(6)-P(7)	1.833(3)	C(6)-N(1)-C(4)	116.6(2)	C(27)-C(26)-P(5)	118.3(2)
P(7)-O(7)	1.493(2)	N(1)-C(2)-P(3)	111.2(2)	C(31)-C(26)-P(5)	122.5(3)
P(7)-C(38)	1.797(3)	O(3)-P(3)-C(8)	110.90(14)	C(28)-C(27)-C(26)	120.0(3)
P(7)-C(32)	1.808(3)	O(3)-P(3)-C(14)	112.90(14)	C(19)-C(14)-C(15)	120.3(3)
C(8)-C(13)	1.373(5)	C(8)-P(3)-C(14)	106.18(14)	C(19)-C(14)-P(3)	117.2(3)
C(8)-C(9)	1.382(5)	O(3)-P(3)-C(2)	110.70(13)	C(15)-C(14)-P(3)	122.3(3)
C(9)-C(10)	1.387(6)	C(8)-P(3)-C(2)	105.71(14)	C(16)-C(15)-C(14)	119.9(3)
C(10)-C(11)	1.370(7)	C(14)-P(3)-C(2)	110.12(15)	C(15)-C(16)-C(17)	119.8(4)
C(11)-C(12)	1.368(7)	P(3)-O(3)-Mn(1)	143.84(13)	C(18)-C(17)-C(16)	120.3(4)
C(12)-C(13)	1.389(5)	N(1)-C(4)-P(5)	112.5(2)	C(17)-C(18)-C(19)	120.5(4)
C(14)-C(19)	1.384(5)	O(5)-P(5)-C(26)	113.35(14)	C(14)-C(19)-C(18)	119.1(4)
C(14)-C(15)	1.393(5)	O(5)-P(5)-C(20)	111.18(13)	C(25)-C(20)-C(21)	119.1(3)
C(15)-C(16)	1.382(5)	C(26)-P(5)-C(20)	107.09(15)	C(25)-C(20)-P(5)	123.4(3)
C(16)-C(17)	1.385(6)	O(5)-P(5)-C(4)	110.85(13)	C(21)-C(20)-P(5)	117.5(3)
C(17)-C(18)	1.375(6)	C(26)-P(5)-C(4)	110.05(14)	C(22)-C(21)-C(20)	120.4(4)
C(18)-C(19)	1.392(5)	C(20)-P(5)-C(4)	103.85(14)	C(23)-C(22)-C(21)	120.4(4)
C(20)-C(25)	1.381(5)	P(5)-O(5)-Mn(1)	141.59(13)	C(22)-C(23)-C(24)	119.5(4)
C(20)-C(21)	1.384(5)	N(1)-C(6)-P(7)	111.1(2)	C(23)-C(24)-C(25)	120.6(4)
C(21)-C(22)	1.379(5)	O(7)-P(7)-C(38)	113.12(14)	C(20)-C(25)-C(24)	120.0(4)
C(22)-C(23)	1.371(6)	O(7)-P(7)-C(32)	111.21(14)	C(27)-C(26)-C(31)	119.1(3)
C(23)-C(24)	1.374(6)	C(38)-P(7)-C(32)	107.37(16)	C(27)-C(26)-P(5)	118.3(2)
C(24)-C(25)	1.384(6)	O(7)-P(7)-C(6)	110.78(14)	C(31)-C(26)-P(5)	122.5(3)
C(26)-C(27)	1.397(4)	C(38)-P(7)-C(6)	109.06(15)	C(28)-C(27)-C(26)	120.0(3)
C(26)-C(31)	1.403(4)	C(32)-P(7)-C(6)	104.92(14)	C(27)-C(28)-C(29)	120.2(3)
C(27)-C(28)	1.380(5)	P(7)-O(7)-Mn(1)	144.06(13)	C(30)-C(29)-C(28)	120.3(4)
C(28)-C(29)	1.388(5)	C(13)-C(8)-C(9)	118.7(3)	C(29)-C(30)-C(31)	120.4(3)
C(29)-C(30)	1.370(5)	C(13)-C(8)-P(3)	123.6(3)	C(30)-C(31)-C(26)	120.0(3)
C(30)-C(31)	1.383(5)	C(9)-C(8)-P(3)	117.5(3)	C(33)-C(32)-C(37)	119.8(3)
C(32)-C(33)	1.385(5)	C(8)-C(9)-C(10)	120.7(4)	C(33)-C(32)-P(7)	116.7(3)
C(32)-C(37)	1.388(5)	C(11)-C(10)-C(9)	119.7(4)	C(37)-C(32)-P(7)	123.5(3)
C(33)-C(34)	1.389(5)	C(12)-C(11)-C(10)	120.5(4)	C(32)-C(33)-C(34)	120.0(4)
C(34)-C(35)	1.368(6)	C(11)-C(12)-C(13)	119.6(4)	C(35)-C(34)-C(33)	120.1(4)
C(35)-C(36)	1.372(6)	C(8)-C(13)-C(12)	120.9(4)	C(34)-C(35)-C(36)	120.9(4)
C(36)-C(37)	1.405(5)	C(35)-C(36)-C(37)	119.7(4)	C(65)-C(64)-C(63)	122.3(4)

C(38)-C(43)	1.394(5)	C(32)-C(37)-C(36)	119.5(4)	C(66)-C(65)-C(64)	120.1(4)
C(38)-C(39)	1.401(5)	C(43)-C(38)-C(39)	119.2(3)	C(67)-C(66)-C(65)	119.1(3)
C(39)-C(40)	1.383(5)	C(43)-C(38)-P(7)	122.5(3)	C(66)-C(67)-C(68)	120.3(4)
C(40)-C(41)	1.385(6)	C(39)-C(38)-P(7)	118.3(2)	C(63)-C(68)-C(67)	122.7(3)
C(41)-C(42)	1.378(6)	C(40)-C(39)-C(38)	119.7(3)	C(74)-C(69)-C(70)	115.0(4)
C(42)-C(43)	1.384(5)	C(39)-C(40)-C(41)	120.8(4)	C(74)-C(69)-B(50)	123.2(3)
B(50)-C(51)	1.637(5)	C(42)-C(41)-C(40)	119.4(3)	C(70)-C(69)-B(50)	121.5(3)
B(50)-C(57)	1.642(5)	C(41)-C(42)-C(43)	120.7(4)	C(71)-C(70)-C(69)	123.4(4)
B(50)-C(69)	1.643(5)	C(42)-C(43)-C(38)	120.1(3)	C(72)-C(71)-C(70)	119.7(4)
B(50)-C(63)	1.650(5)	C(51)-B(50)-C(57)	112.4(3)	C(71)-C(72)-C(73)	119.3(4)
C(51)-C(56)	1.400(5)	C(51)-B(50)-C(69)	112.3(3)	C(72)-C(73)-C(74)	120.1(4)
C(51)-C(52)	1.400(5)	C(57)-B(50)-C(69)	103.8(3)	C(69)-C(74)-C(73)	122.5(4)
C(52)-C(53)	1.389(6)	C(51)-B(50)-C(63)	103.4(3)		
C(53)-C(54)	1.380(7)	C(57)-B(50)-C(63)	112.9(3)		
C(54)-C(55)	1.373(7)	C(69)-B(50)-C(63)	112.4(3)		
C(55)-C(56)	1.395(6)	C(56)-C(51)-C(52)	114.9(3)		
C(57)-C(62)	1.388(5)	C(56)-C(51)-B(50)	123.8(3)		
C(57)-C(58)	1.399(5)	C(52)-C(51)-B(50)	120.9(3)		
C(58)-C(59)	1.395(6)	C(53)-C(52)-C(51)	123.4(4)		
C(59)-C(60)	1.367(6)	C(54)-C(53)-C(52)	119.8(4)		
C(60)-C(61)	1.390(5)	C(55)-C(54)-C(53)	118.9(4)		
C(61)-C(62)	1.389(5)	C(54)-C(55)-C(56)	120.9(5)		
C(63)-C(68)	1.394(5)	C(55)-C(56)-C(51)	122.1(4)		
C(63)-C(64)	1.399(5)	C(62)-C(57)-C(58)	114.8(3)		
C(64)-C(65)	1.395(5)	C(62)-C(57)-B(50)	123.6(3)		
C(65)-C(66)	1.394(6)	C(58)-C(57)-B(50)	121.2(3)		
C(66)-C(67)	1.358(6)	C(59)-C(58)-C(57)	122.3(4)		
C(67)-C(68)	1.402(5)	C(60)-C(59)-C(58)	121.4(4)		
C(69)-C(74)	1.394(5)	C(59)-C(60)-C(61)	117.8(4)		
C(69)-C(70)	1.403(5)	C(62)-C(61)-C(60)	120.3(3)		
C(70)-C(71)	1.394(6)	C(57)-C(62)-C(61)	123.4(3)		
C(71)-C(72)	1.374(7)	C(68)-C(63)-C(64)	115.4(3)		
C(72)-C(73)	1.385(7)	C(68)-C(63)-B(50)	122.5(3)		
C(73)-C(74)	1.403(6)	C(64)-C(63)-B(50)	121.9(3)		

Appendix B

Supplementary Information: Catalytic Data

This appendix contains additional spectra relevant to the hydrogenation reactions.

Figure B1 – ^1H NMR spectrum of levulinic acid	B2
Figure B2 – ^1H NMR spectrum of gamma-Valerolactone	B2
Figure B3 – Representative ^1H NMR spectrum of a transfer hydrogenation experiment	B3
Figure B4 – $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a transfer hydrogenation experiment (1)	B3
Figure B5 – $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a transfer hydrogenation experiment (2)	B4
Figure B6 – Representative ^1H NMR spectrum of a high-pressure hydrogenation experiment	B4

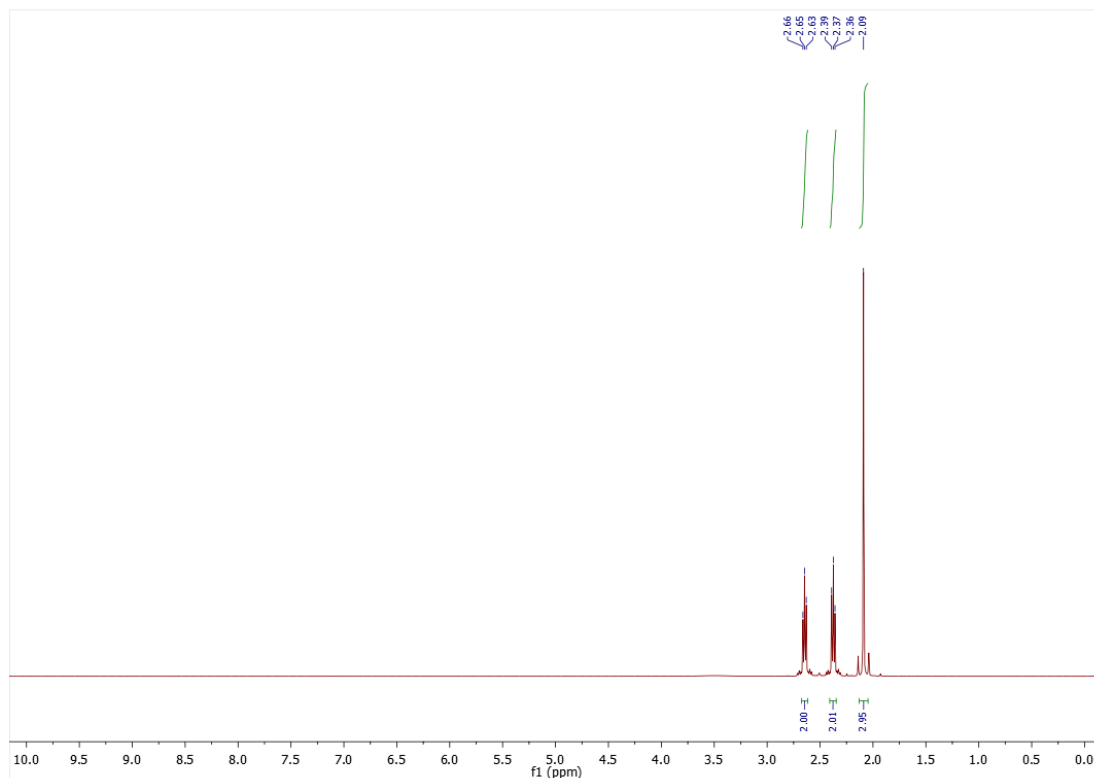


Figure B1. ^1H NMR spectrum (DMSO- d_6 , 400 MHz) of levulinic acid.

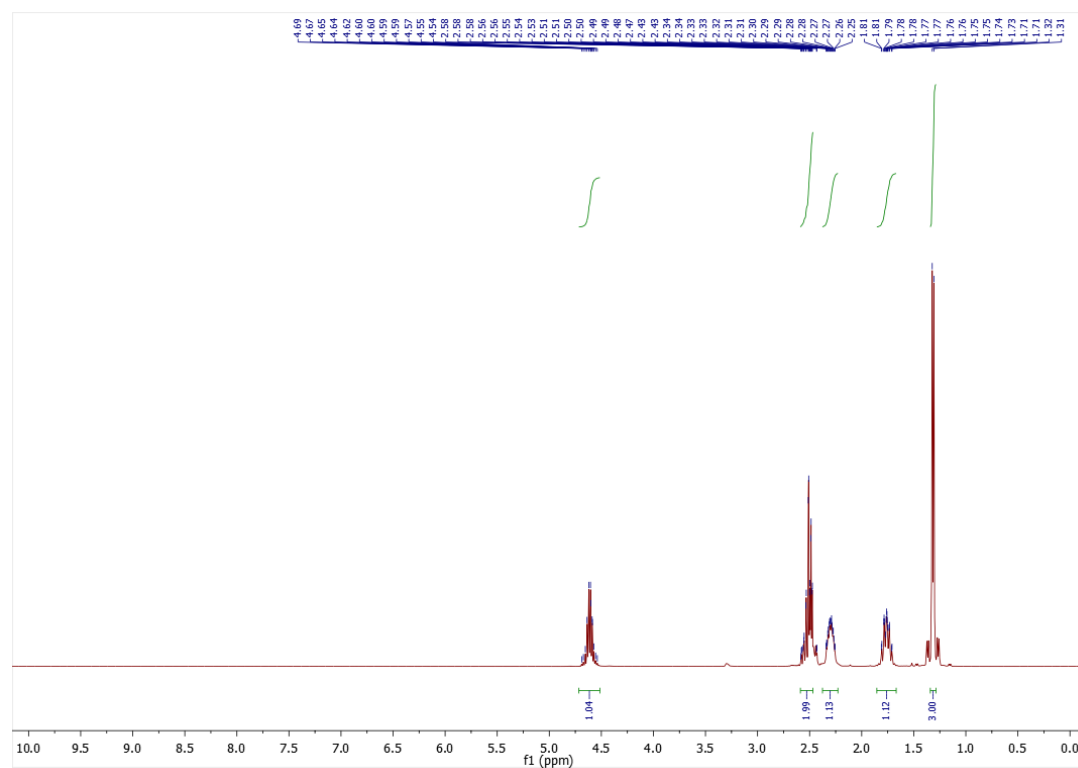


Figure B2. ^1H NMR spectrum (DMSO- d_6 , 400 MHz) of gamma-Valerolactone.

LA: **A**

GVL: **B**

NEt₃: **C**

* Signals used for determination of LA conversion

(Formic acid signals not observed due to full decomposition to gaseous products. Catalyst signals not observed due to low catalyst loading).

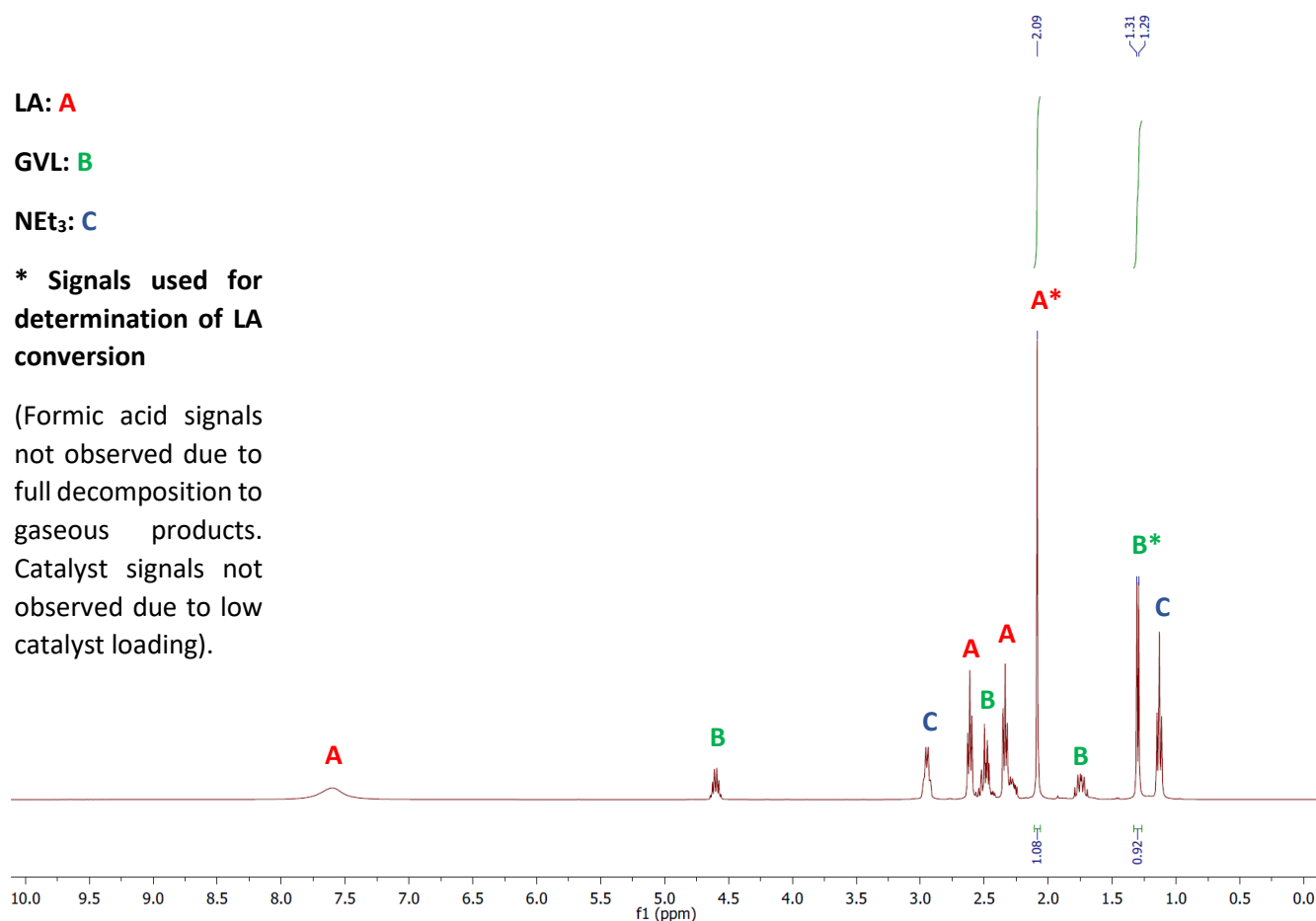


Figure B3. Representative ¹H NMR spectrum (DMSO-d₆, 400 MHz) of a transfer hydrogenation experiment, showing signals attributable to LA and GVL.

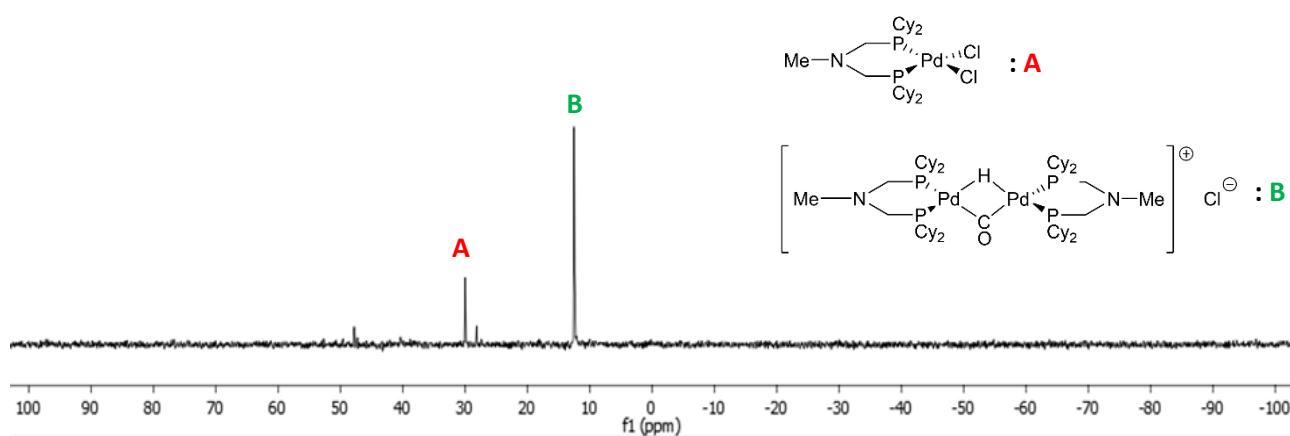


Figure B4. Representative ³¹P{¹H} NMR spectrum (DMSO-d₆, 162 MHz) of a transfer hydrogenation experiment, showing signals attributable to [Me-N(CH₂PCy₂)₂PdCl₂] (**1**) and [{Pd(Me-N(CH₂PCy₂)₂)₂(μ-H)(μ-CO)]Cl (**28**).

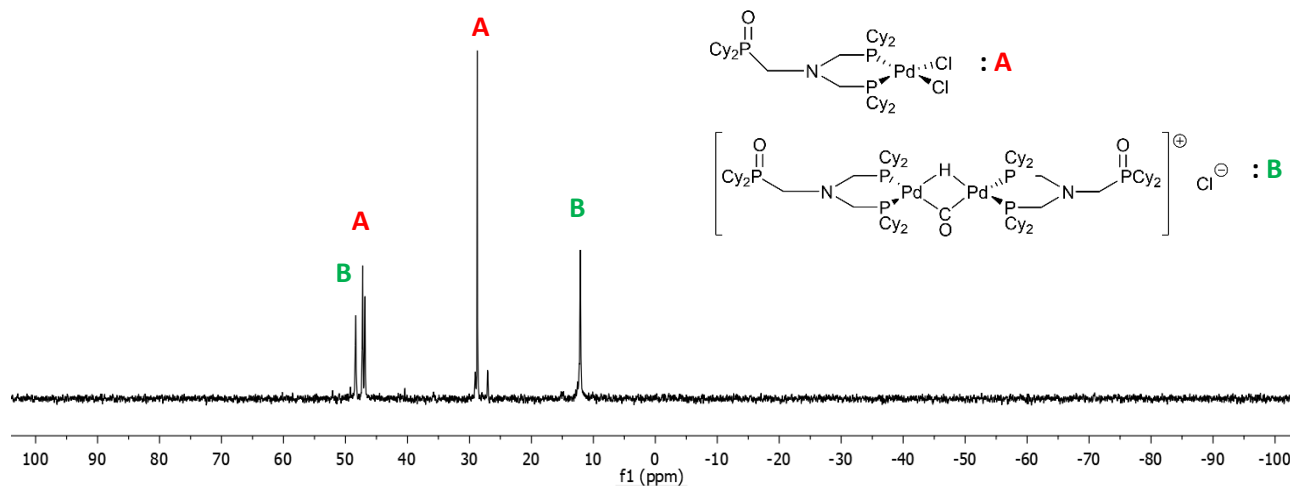


Figure B5. Representative $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (DMSO- d_6 , 162 MHz) of a transfer hydrogenation experiment, showing signals attributable to $[\text{P}(\text{O})\text{Cy}_2\text{CH}_2\text{-N}(\text{CH}_2\text{PCy}_2)_2\text{PdCl}_2]$ (**2**) and $[\text{Pd}(\text{P}(\text{O})\text{Cy}_2\text{CH}_2\text{-N}(\text{CH}_2\text{PCy}_2)_2)_2(\mu\text{-H})(\mu\text{-CO})]\text{Cl}$ (**29**).

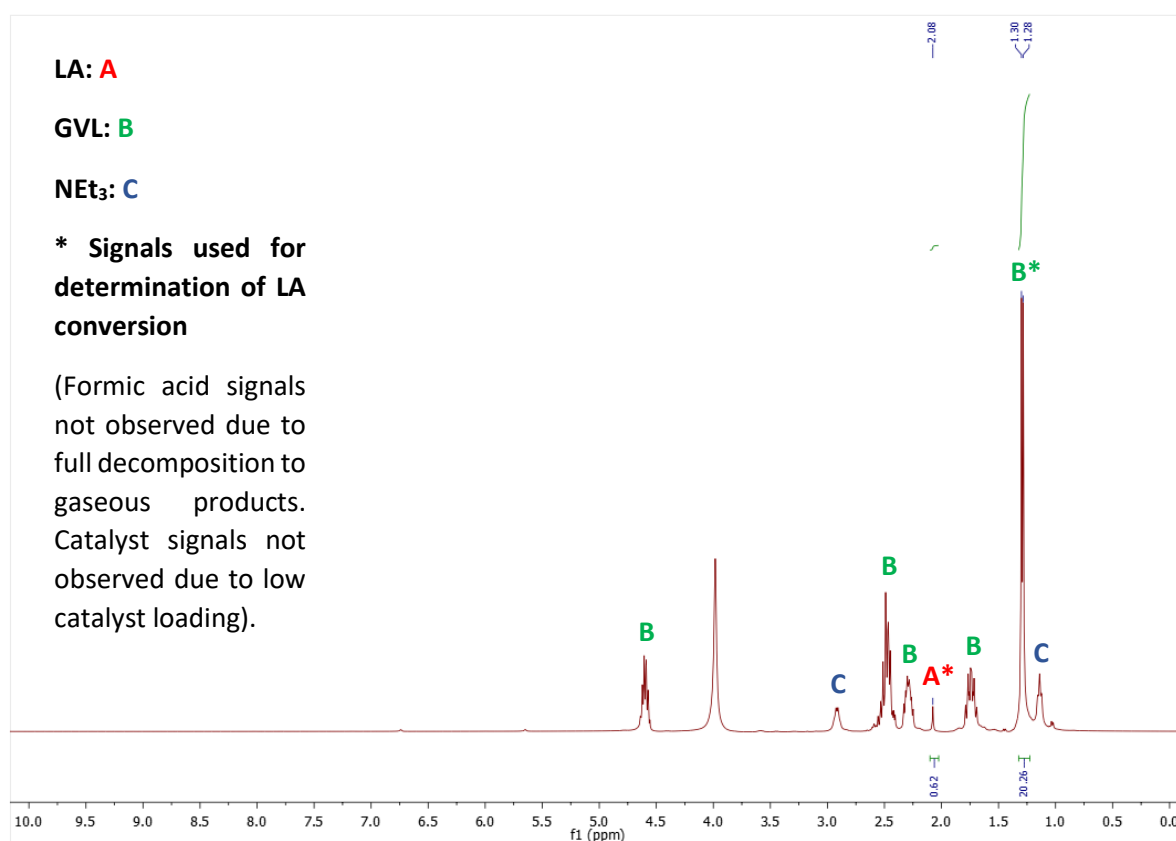


Figure B6. Representative ^1H NMR spectrum (DMSO- d_6 , 400 MHz) of a high-pressure hydrogenation experiment.