INVESTIGATING TRANSITION METAL FORMYL COMPLEXES FOR HOMOGENEOUS SYNGAS CONVERSION

by

Sarah Jane Gates

A dissertation submitted to the
Department of Chemistry of Imperial College London
for the degree of
Doctor of Philosophy

April 2016
Abstract
The conversion of synthesis gas, (syngas; a mixture of CO and H₂), to liquid fuels has been a process that has been studied for more than a century. Current heterogeneous operating procedures are poorly understood and as such are unselective, requiring costly refining to separate the desired products. It has long been hoped that an alternative homogenous process may allow for the mechanistic insight and understanding to rationally design the conversion of syngas to specific products. This thesis aims to explore the steric and electronic environment of the carbonyl ligand within iron transition metal complexes, as a model for homogenous syngas conversion. Particular attention has been paid to the first step of syngas conversion; hydride transfer to form a formyl complex.

Chapter 1 provides a general overview of the developments to date, in both heterogeneous and homogenous systems for syngas conversion. The use of frustrated Lewis pairs to hydrogenate a carbonyl directly from hydrogen is also discussed in addition to a discussion of the various mechanisms and intermediates present in a homogenous system.

Chapter 2 describes the reduction and subsequent reactivity of the carbonyl complex [Fe(CO)₂(Cp*)][BArF₂₄]. Hydrogenation, directly using hydrogen gas in conjunction with FLP systems is discussed.

Chapter 3 describes the use of bisphosphine ligands to impart electron density and stability to transition metal formyl complexes. This work is also discussed in relation to FLP hydrogenation.

Chapter 4 gives an overview of the reactivity of some neutral carbonyl complexes and their reactivity with FLP systems.

Chapter 5 provides an alternative approach for future homogenous transition metal carbonyl reduction chemistry. Some preliminary results are included to support the investigation of such a route for further study.

Chapter 6 details experimental procedures used in this work.
Declaration

The work described in this thesis was carried out within the Chemistry department of Imperial College London from October 2012 to March 2016, under the supervision of Dr Andrew Ashley and Dr Silvia Diez-Gonzalez. All the work is my own unless stated to the contrary, and has not been previously submitted for any degree at this or any other university.

Sarah Jane Gates

April 2016

Copyright

The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform or build upon it. For any reuse or redistribution, researchers must make clear to others the licence terms of this work.
Acknowledgements

I would firstly like to thank my supervisor Dr Andrew Ashley for the opportunity to work on this project and for offering constant enthusiasm, advice and invaluable direction throughout. I would also like to thank my co-supervisor Dr Silvia Diez-González for her support and advice and I wish you both the best of success for the future.

I would also like to thank the past and present members of the Ashley group. A huge thanks goes to Dr Laurence Doyle who possesses levels of patience not seen in many human beings and who constantly pleased with 70s disco playlists, and truly excellent advice in all things, especially air sensitive chemistry techniques. I would also especially like to thank Andrew Crawford, Peter Hill and Daniel Scott who were fantastic lab and pub companions. Andrew especially for understanding the incessant need for snacks and coffee breaks and providing entertainment with extremely impressive doodles. Pete I will never forget your lunch routine or your impeccable humour or your great T-shirts. Dan, thank you for all your help with proof reading, especially for this thesis, and for generally being a repository of chemistry knowledge – I hope one day you make it as the world’s best Brazilian house DJ. I would also like to thank other past and present members of the Harwood and Tilden labs Dr Anita Toscani, Dr Nick Phillips, Adam Piascik, and Florian Langmann.

Many thanks to my industrial supervisors Dr Russell Taylor and Dr Renan Cariou for the interesting discussions and valuable advice during the project and to the many people who provided invaluable support without which this work would not have been possible. In particular I would like to thank Pete Haycock and Dick Sheppard (NMR service), Dr Lisa Haigh (mass spectrometry) and Stephen Boyer (elemental analysis).

I am particularly thankful to my parents and fantastic friends for their advice and companionship over the past four years. Lastly, special thanks go to Tymon Kiepe for his constant patience, support, USB sticks and insanity preventing IT skills.
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ</td>
<td>chemical shift</td>
</tr>
<tr>
<td>σ&lt;sup&gt;±&lt;/sup&gt;m</td>
<td>Hammett parameter</td>
</tr>
<tr>
<td>ν</td>
<td>stretching frequency</td>
</tr>
<tr>
<td>{^1H}</td>
<td>proton decoupled</td>
</tr>
<tr>
<td>2,6-lut</td>
<td>2,6 lutidine (2,6-dimethylpyridine)</td>
</tr>
<tr>
<td>2,4,6-collidine</td>
<td>2,4,6-trimethylpyridine</td>
</tr>
<tr>
<td>Ar</td>
<td>aryl</td>
</tr>
<tr>
<td>BArF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>B[2,6-F&lt;sub&gt;2&lt;/sub&gt;-(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;]&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>BArF&lt;sub&gt;9&lt;/sub&gt;</td>
<td>B[2,4,6-F&lt;sub&gt;3&lt;/sub&gt;-(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;]&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>BArF&lt;sub&gt;15&lt;/sub&gt;</td>
<td>B(C&lt;sub&gt;6&lt;/sub&gt;F&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>BArF&lt;sub&gt;24&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>B[3,5-(CF&lt;sub&gt;3&lt;/sub&gt;)C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;]&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>bipyrr</td>
<td>2,2'-bipyridyl</td>
</tr>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>C&lt;sub&gt;5&lt;/sub&gt;</td>
<td>pentane</td>
</tr>
<tr>
<td>Cp</td>
<td>cyclopentadienyl</td>
</tr>
<tr>
<td>Cp*</td>
<td>pentamethylcyclopentadienyl</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>DABCO</td>
<td>diazabicyclo[2.2.2]octane</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>depe</td>
<td>1,2-bis(diethylphosphino)ethane</td>
</tr>
<tr>
<td>DFB</td>
<td>1,2-difluorobenzene</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>dmpe</td>
<td>1,2-bis(dimethylphosphino)ethane</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>dppe</td>
<td>1,2-bis(diphenylphosphino)ethane</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron Paramagnetic Resonance</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>ET</td>
<td>electron transfer</td>
</tr>
<tr>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>diethyl ether</td>
</tr>
<tr>
<td>FLP</td>
<td>frustrated Lewis pair</td>
</tr>
<tr>
<td>Fp</td>
<td>[Fe(CO)&lt;sub&gt;2&lt;/sub&gt;(Cp)]&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fp&lt;sup&gt;*&lt;/sup&gt;</td>
<td>[Fe(CO)&lt;sub&gt;2&lt;/sub&gt;(Cp*)]&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fp&lt;sup&gt;R&lt;/sup&gt;</td>
<td>[Fe(CO)&lt;sub&gt;2&lt;/sub&gt;(Cp*)]&lt;sup&gt;+&lt;/sup&gt; or [Fe(CO)&lt;sub&gt;2&lt;/sub&gt;(Cp)]&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>iPr</td>
<td>iso-Propyl</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>m</td>
<td>multiplet</td>
</tr>
<tr>
<td>Me</td>
<td>Methyl</td>
</tr>
</tbody>
</table>
MS Mass Spectrometry

"Bu n-Butyl

NMR Nuclear Magnetic Resonance

P₁ tert-butylimino-tri(pyrrolidino)phosphorane

P₂ bisphosphine

Ph Phenyl

ppm Parts Per Million

q quartet

RT Room Temperature

s singlet

t triplet

t₁/₂ half-life

TBME tert-butyl methyl ether

THF tetrahydrofuran

Tipp tris(2,4,6-triisopropylphenyl)

TM Transition Metal

TMP 2,2,6,6-tetramethylpiperidine

VT variable temperature

**Units**

°C degree Celsius

Å ångström

cal calorie

deg degrees

g gram

h hour
## Contents

Abstract .......................... 2  
Declaration .......................... 3  
Acknowledgements .................. 4  
Abbreviations ....................... 5  
Contents ............................ 7  

**Chapter 1: Introduction**  
1.1 Background ...................... 9  
1.2 Syngas conversion .............. 10  
1.3 Stoichiometric reduction of CO on a Transition Metal 16  
1.4 Intermediates in homogeneous syngas conversion 22  
1.5 Stabilising a formyl complex 30  
1.6 Heterolytic hydrogen activation 32  
1.7 Thesis Aims ..................... 40  
1.8 References ...................... 42  

**Chapter 2: Reduction studies of a cationic iron tricarbonyl complex**  
2.1 Introduction ..................... 45  
2.2 Synthesis of [Fp*CO][BArF\textsubscript{24}] 49  
2.3 Reduction studies of [Fp*CO][BArF\textsubscript{24}] 50  
2.4 FLP hydrogenation studies of [Fp*CO][BArF\textsubscript{24}] 62  
2.5 Conclusion ....................... 78  
2.6 References ....................... 81  

**Chapter 3: Reduction studies of bisphosphine substituted iron carbonyl complexes**  
3.1 Introduction ..................... 83  
3.2 Synthesis of $\kappa^2$-bisphosphine iron carbonyl complexes 88  
3.3 Reduction studies of $\kappa^2$-bisphosphine iron carbonyl complexes 95  
3.4 FLP hydrogenation studies of $\kappa^2$-bisphosphine iron carbonyl complexes 124  
3.5 Conclusion ....................... 129  
3.6 References ....................... 132
Chapter 1

Introduction

1.1 Background

As the global population continues to expand, the world’s energy demands are constantly increasing. These demands are currently heavily dependent on non-renewable resources such as oil and natural gas which are derived from finite fossil fuel stocks. Syngas, a mixture of carbon monoxide and hydrogen, provides a potential route to a new energy resource. Syngas is traditionally obtained from finite fossil fuels i.e. steam reforming of methane and coal gasification, but it can also be obtained from renewable resources such as the gasification of biomass. Using biomass as the raw material would provide a renewable energy source upon syngas conversion to fuels.

Historically, due to low efficiency and selectivity, processes for syngas conversion have not been competitive with oil. However, with fluctuating oil prices and the essential limited resources, syngas has gradually become an economically viable alternative. For this reason, research focused on the conversion of syngas in academia and industry, has flourished. Syngas provides an alternative route to producing energy and chemicals from the cleaner raw material natural gas or from completely renewable resources such as the aforementioned gasification of biomass.

Shell began developing gas to liquid (GTL) technology in the 1970s, a time in which oil prices were high spurring a surge in research into syngas conversion chemistry. The first commercial GTL plant was started in Germany in 1993. A clear indicator of the ongoing relevance of such a process is Shell’s development of the world’s largest GTL plant, Pearl GTL in Qatar in 2011 costing $19 billion and more recently Sasol Ltd. have developed plans to build a $14 billion plant in Lousiana, USA. In general, conversion of syngas to fuels and useful chemicals has attracted a vast amount of interest in the past 50 years and important discoveries are discussed in Section 1.2.
1.2 Syngas conversion

Although there are examples of both stoichiometric and catalytic homogeneous and heterogeneous syngas conversion processes, the heterogeneous systems investigated to date have been significantly more successful with regards to lower necessary temperatures and pressures reaping higher conversions. This has resulted in only heterogeneous systems reaching industrial application thus far. The heterogeneous systems are generally unselective and require significant costly refining. Homogeneous systems, if optimised, could provide improved selectivity over the heterogeneous methods and as such have been pursued by both academia and industry.

1.2.1 Heterogeneous syngas conversion

Heterogeneous syngas conversion began in 1902 with Sabbatier first reporting methane and water from carbon oxides and hydrogen over nickel at elevated temperatures. This was soon followed in 1926 by Fischer and Tropsch reporting the conversion of carbon monoxide and hydrogen to liquid hydrocarbons using an iron, cobalt or ruthenium catalyst at elevated temperatures (Equations 1.1 and 1.2).

$$\text{CO}_2 + 3\text{H}_2 \xrightarrow{\text{Ni}, \ T > 300 \degree \text{C}} \text{CH}_4 + \text{H}_2\text{O} \quad 1.1$$

$$n \text{CO} + (2n+1)\text{H}_2 \xrightarrow{\text{Ni}, \ T > 300 \degree \text{C}} C_n\text{H}_{2n+2} + n\text{H}_2\text{O} \quad 1.2$$

Although significant advances have been made in heterogeneous Fischer-Tropsch chemistry (FT), the problem of methane production always exists. The process follows an Anderson-Schulz Flory distribution (Figure 1.1) which means methane will always be the single largest product and it is not possible to select for any one desired range of products such as diesel. Since methane is not desired, in order to achieve useful products from FT chemistry, substantial
refining is necessary. The research into heterogeneous FT catalyst design is extensive, but will not be discussed here.⁶

**Figure 1.1**: Graph showing Anderson-Schulz Flory distribution of Cₙ products from heterogeneous syngas conversion – Reproduced from *Energy Environ. Sci.*, 2010, 3, 884-890 with permission from The Royal Society of Chemistry

### 1.2.2 Homogeneous syngas conversion

Developing an efficient system for homogeneous syngas conversion is an attractive alternative to unselective heterogeneous Fischer-Tropsch chemistry. Previously homogeneous chemistry has allowed for the design of selective reactions. For example, olefin polymerisation processes were revolutionised with the advent of homogeneous metallocene catalysts which allowed for the study of the polymerisation mechanism, something that could not be achieved prior with heterogeneous species.⁷ With knowledge of the mechanism of polymerisation it is possible to design the particular desired properties of the product polymer. In the case of FT chemistry, if successful, such detailed mechanistic insight and product selection would eliminate costly refining. In addition, although both homogeneous and heterogeneous processes can be studied spectroscopically, the possibility of using solution phase techniques makes it faster with a homogeneous process.

The first reported homogeneous syngas conversion to reduced products was reported by Gresham and Schweitzer from DuPont in 1950.⁸ They reported the production of poly-
functional oxygenates at syngas pressures of 1500-5000 atm using [CoF₂] as catalyst in water. By the 1970s Union Carbide had developed a more successful glycol synthesis with a rhodium catalyst [Rh₄(CO)₁₂] in the presence of AlBr₃. However each of these transformations required very high pressures (generally > 1000 atm).

The mildest homogeneous reactions are performed using [Ru₃(CO)₁₂] as precatalyst, with the primary product in this case being methanol. Given that an efficient heterogeneous route to methanol out-competes this homogenous reaction, it is not of significant interest for industrial application in its current form. The interest in these processes is the formation of higher products. The most successful homogeneous transformations that generate higher products rely on the addition of Brønsted or Lewis acids and in the case of [Ru₃(CO)₁₂], the substitution of a non-polar organic solvent with a carboxylic acid leads to ethylene glycol formation. The proposed mechanism in the presence of acid involves a Ru hydroxymethyl complex; transition metal hydroxymethyl compounds are considered key intermediates in homogeneous conversion. Similarly, ethane and higher alkanes can be obtained with [Ir₄(CO)₁₂] in a NaCl/AlCl₃ melt. Osmium and rhodium carbonyls have similarly been shown to produce alkanes with BBr₃ and AlBr₃. However all of these systems have remained economically unviable due to their high pressure demands. A detailed understanding of the role of the Lewis acid promoters is also necessary to deliver a satisfactory system. These are the main challenges facing homogeneous syngas conversion and therefore require detailed mechanistic study.

### 1.2.3 Mechanistic considerations for Fischer-Tropsch chemistry

Although the mechanism of heterogeneous Fischer-Tropsch chemistry has been studied for nearly a century, no satisfactory explanation which allows for the prediction of products has been found. Although there is much debate surrounding the mechanism of heterogeneous FT chemistry, it is usually still considered when attempting to design homogeneous conversion systems. The heterogeneous process is usually taken as a starting point however, this has questionable use given that it appears the mechanism of the two must vary significantly; heterogeneous routes produce mainly hydrocarbons whereas successful homogeneous routes have been shown to produce mainly oxygenates.

In heterogeneous FT chemistry, the relative amounts of products vary depending on the catalyst, temperature and pressure. Heterogeneous reactions start to produce products at
temperatures as low as 150°C and syngas pressures of 1 atm. All heterogeneous routes must start with physiosorption of H₂ and CO. Subsequent dissociation of CO produces a metal oxide and a metal carbide which is then available for reaction with a hydride (Scheme 1.1).\textsuperscript{16}

\[
\begin{align*}
\text{H}_2 + [M] & \rightleftharpoons [M]-\text{H}_2 \quad (1) \\
\text{H}_2 + [M] & \rightleftharpoons \text{H}[M]-\text{H} \quad (2) \\
\text{CO} + [M] & \rightleftharpoons [M]-\text{CO} \quad (3) \\
[M]-\text{CO} + [M] & \rightleftharpoons [M]-\text{C} + [M]-\text{O} \quad (4)
\end{align*}
\]

[M] = Metal surface

**Scheme 1.1:** Scheme shows heterogeneous FT steps - (1) and (2) show the initial physiosorption of hydrogen to the metal surface, subsequently both terminal and bridging hydrides can react with a metal carbide, (3) shows chemisorption of CO followed by dissociation of CO to form a metal carbide (4).

The most widely accepted mechanism for heterogeneous Fischer-Tropsch chemistry is actually that which was initially proposed by Fischer and Tropsch in 1926. The proposed mechanism of alkane formation involves the oligomerisation of surface metal methylidene CH\textsubscript{2} fragments. Initial labelling studies using \textsuperscript{13}C suggested that this mechanism was the most plausible and further studies by Brady et al. using \textsuperscript{13}CH\textsubscript{2}N\textsubscript{2} have further distinguished its accuracy (Scheme 1.2).\textsuperscript{17,18,19}

**Scheme 1.2:** Mechanism for oligomerisation of metal carbides in the heterogeneous FT process

Although bridging methylene units are favoured by many as being the most likely intermediate for chain growth, there is also evidence for the presence of mononuclear metal carbides. A polystyrene supported mononuclear cobalt complex, [Co(CO)\textsubscript{2}C\textsubscript{p}], was shown to be successful...
in producing saturated linear hydrocarbons whilst maintaining its mononuclear structure.\textsuperscript{20} Other proposed routes for heterogeneous Fischer-Tropsch processes suggest C-C bond formation \textit{via} subsequent condensation reactions and loss of H\textsubscript{2}O,\textsuperscript{21} or the insertion of CO into a metal alkyl bond.\textsuperscript{22}

The mechanism of homogeneous syngas conversion is undoubtedly different. Previously reported homogeneous systems have been shown to produce mainly C\textsubscript{1} and C\textsubscript{2} oxygenates, namely methanol and ethylene glycol and are usually carried out at much higher temperatures, T $\geq$ 230\textdegree{}C.\textsuperscript{23} It has been assumed that chain growth may be facilitated by a multi-metallic system, taking inspiration from the heterogeneous systems. As such much research has focused on metal carbonyl clusters. However, at the extreme temperatures needed for homogeneous conversion, it is questionable whether such clusters would stay intact.

A seemingly obvious first step for any homogeneous process would be migratory insertion of CO into a metal hydride bond to form a formyl species. However, unlike the metal alkyl insertions which are ubiquitous in organometallic chemistry, this reaction has been calculated to be too endergonic.\textsuperscript{24} A more plausible route proceeds \textit{via} hydride attack on an activated carbonyl ligand to form a formyl complex ‘[M-CHO]’. Therein lies the problem of homogeneous syngas conversion; finding a suitable catalytic process which facilitates this first step of hydride addition is a huge challenge. The presence of a formyl species is generally accepted to be the first step of any homogeneous CO hydrogenation route and it is the reactivity of such a species that would likely dictate the success of the subsequent catalytic cycle. A useful mechanism to refer to is the production of ethylene glycol (Scheme 1.3). This is one of the most common products of homogeneous syngas conversion and unusually has no known heterogeneous route for its production.
Scheme 1.3: Proposed mechanism for ethylene glycol production starting with hydride attack on a cationic metal carbonyl (taken from Ref. 23)

In the mechanism of homogeneous syngas to ethylene glycol production, first proposed by DuPont on cobalt in the 1950s and later developed using ruthenium by Union Carbide, the first step is formyl formation from a metal carbonyl.\textsuperscript{10} Calculations carried out on [Co(CO)]\textsubscript{4}H have indicated a formyl and an $\eta^2$-formaldehyde complex as intermediates. The $\eta^2$-formaldehyde complex forms either a hydroxymethyl or methoxy complex on subsequent reaction with dihydrogen; free formaldehyde was calculated to be unfavourable vs. further reaction.\textsuperscript{25,26} In the case of cobalt, the methoxy bond Co-OCH\textsubscript{3} is favoured whereas similar calculations for [Rh(CO)]\textsubscript{4}H show the hydroxymethyl species is favoured. This gives an indication of why methanol is the main product in cobalt reactions whereas rhodium mainly produces ethylene glycol.\textsuperscript{1,27,28} This could also be explained by looking at the properties of the metal centre, smaller 1\textsuperscript{st} row metals such as cobalt will prefer a harder donor such as oxygen favouring the methoxy functional group Co-OCH\textsubscript{3}. Second row metals such as rhodium are more likely to favour M-C bonds resulting in a hydroxymethyl functional group Rh-CH\textsubscript{2}OH.

The initial reduction of CO\textsubscript{2} as with any syngas reaction is undoubtedly the most difficult. In the case of ethylene glycol production it is suggested that intermolecular hydride transfer from [Ru\textsubscript{3}(CO)]\textsubscript{11}H\textsuperscript{-} could be responsible for formyl formation, supported by the observation of this species under catalytic conditions.\textsuperscript{10,29} The hydride [Ru\textsubscript{3}(CO)]\textsubscript{11}H\textsuperscript{-} forms in the presence of iodide promoters and the high temperature (230 °C) is attributable to the poor hydride donor capability of the Ru-H. The energy needed for such a hydride transfer means the elevated temperatures needed for a homogeneous route are unsurprising. Although the mechanism is plausible, the high pressure and temperatures needed for reaction preclude detailed analysis.
Any future successful homogeneous processes need detailed mechanistic understanding in order to overcome the high temperature problem and this is another major challenge facing the development of catalysis.

1.3 Stoichiometric reduction of CO on a transition metal

Much of the work surrounding homogeneous syngas conversion has been carried out on carbonyl ligands bound to a transition metal. We can use the Dewar-Chatt-Duncanson model for alkene bonding to a transition metal to demonstrate how a carbonyl ligand similarly interacts with a transition metal and how this affects reduction (Figure 1.2).

![Figure 1.2: Transition metal carbonyl bonding: electron density from filled metal ‘d’ orbitals is donated into the empty π* C-O orbital, electron density from a filled ‘p’ orbital on the CO ligand is donated to an empty metal ‘d’ orbital](image)

Increasing electron density on the metal increases the π back donation into the empty π* orbital on the carbonyl ligand. The metal-carbon bond strength is increased and the carbon-oxygen bond weakened. Varying the other ligands present on the metal, both sterically and electronically, greatly impacts any potential reactivity of the carbonyl ligand. By using a transition metal-ligand framework there is vast opportunity to modify the electronics of the carbonyl ligand hence the degree of activation and ease of reduction. This provides a model for investigating feasible conversion of syngas. A plethora of research has focused on the stoichiometric reduction of the carbonyl ligand. These reductions have been achieved with both main group and transition metal hydride reagents and the characterisation of a series of important intermediates has been reported.

1.3.1 Reduction of transition metal carbonyls with main group hydrides

In order to produce a reduced species, a C-O bond in the carbonyl must be broken with the concomitant formation of one or more C-H bonds. Main group hydrides, namely borohydrides and aluminium hydrides, have been used to study the breaking and formation of the aforementioned bonds. Traditional main group hydride reagents (NaBH₄, LiAlH₄, NaBH₃CN)
cannot be regenerated from hydrogen and are not compatible with acids. Any successful reduction of a carbonyl would necessitate an acid source to cleave the C-O bond produce water (Scheme 1.4). Hence a traditional main group hydride reagent could never be employed in a homogenous catalytic syngas conversion cycle. It is nonetheless extremely useful to use them to study each individual carbon reduction step.

Treichel and Schubkin first reported the full reduction of a M-CO bond to the M-CH₃ moiety in 1967 using NaBH₄. They postulated that this reduction took place via an unstable formyl complex of the type [M-CHO]. However this intermediary partially reduced species was not observed and characterised until 1973, when Collman and Winter isolated the first formyl complex, [Fe(CHO)(CO)₄][(Ph₃P)₂N] using Na₂Fe(CO)₄ and acetic formic anhydride. Attention soon turned to the use of main group hydrides to reduce carbonyl ligands, prompting further observation of a series of formyl complexes on varying transition metals including Re, Mn and Mo. Anionic formyls were reported using strong trisalkylborohydride reducing agents on neutral carbonyl ligands on Mn, Mo, Re and Fe (Scheme 1.5).
Neutral formyls have been characterised via the main group hydride reduction of cationic 18-electron carbonyl complexes. The most widely studied neutral formyls are on 18-electron Re complexes of the type \([\text{Re(CO)}\text{Cp(NO)(L)}][\text{BF}_4]\) (L = CO, PPh\(_3\))\(^{35,36,37,38}\). Depending on the specific conditions used, the starting carbonyl can be reduced to the hydroxymethyl via NaBH\(_4\). Astruc used NaBH\(_4\) at low temperatures to achieve full reduction of the cationic transition metal carbonyl \([\text{Fe(CO)}_3\text{Cp}^*][\text{PF}_6]\) to the neutral methyl complex \([\text{Fe(CH}_3\text{)(CO)}_2\text{Cp}^*]\); all intermediates were characterised by \(^1\text{H NMR}\) in THF-\(d_8\) (Scheme 1.6).\(^{39}\)

The importance of the BH\(_3\) Lewis acid is recognised as facilitating the reduction to the methyl substituent. For example, in the first hydride addition, it is likely that the BH\(_4^-\) forms an ion pair with the cationic carbonyl, facilitating hydride migration to the carbonyl carbon (Scheme 1.7). This formyl then coordinates the incipiently formed BH\(_3\) to prompt activation and a second and third hydride delivery with subsequent NaBH\(_4\) additions. This is supported by the result that if the reaction is carried out in a THF/H\(_2\)O mixture, the sole product of reduction is [Fp*H]. Since water hydrolyses BH\(_3\) there is no activation by the Lewis acid and as such no second hydride transfer resulting in only decarbonylation of the unstable formyl to the metal hydride, and only the first hydride would be delivered.
Scheme 1.7: Mechanism of reduction of NaBH₄ on [Fp*CO][PF₆] - it is proposed that the Lewis acid BH₃ activates the carbonyl for further reduction past the formyl complex as shown in a, b shows that without Lewis acid activation the formyl will not reduce further and instead is observed to decarbonylate to the metal-hydride

1.3.3 Reduction of transition metal carbonyls with transition metal hydrides

Transition metal hydride reagents are ubiquitous in organometallic chemistry and unlike traditional main group hydrides (e.g. NaBH₄, NaBH₃CN, LiAlH₄) may be regenerated from hydrogen. However, they are still incompatible with the acids required for proton mediated reduction of CO and loss of water. In addition, the early transition metals form highly acidic M-H bonds but their oxophilicity means the resultant strong M-O bonds formed would require large amounts of energy to be broken. Even so, transition metal hydrides have been observed as key intermediates in homogeneous syngas conversion and as such studying their reactivity is a worthwhile venture when postulating viable conversion cycles. Seminal work has been performed with zirconium and tantalum to achieve methoxy and C-C coupled products. [Zr(H₂)(Cp*₂)] was shown to react with CO and through intermolecular hydride transfer from [Zr(H₂)(Cp*₂)] it forms a variety of reduced species (Scheme 1.8). The 16-electron complex [Zr(H₂)(Cp*₂)] has a vacant orbital and upon association of CO, there is no back-bonding from the metal centre to the carbonyl ligand. This results in an extremely electropositive carbonyl facilitating hydride transfer from the polar Zr-H bonds in [Zr(H₂)(Cp*₂)]; however this system could never be catalytic due to the aforementioned strong M-O bonds of early transition metals.
DuBois et al. have synthesised a number of 16-electron cationic Pt, Pd and Ni complexes of the type [M(bisphosphine)_2]^{2+} which in the presence of base e.g. KO'Bu react directly with H_2 to form [M(bisphosphine)_2H]^+ (Scheme 1.9). These complexes are capable of reducing the rhenium carbonyl, [Re(CO)(NO)(Cp)(PPh_3)]^+ to the remarkably stable formyl [Re(CHO)(NO)(Cp)(PPh_3)] first reported by Gladysz.\(^{36,44}\)

The Du Bois group observed near quantitative hydride transfer to the rhenium carbonyl [Re(CO)(NO)(Cp)(PPh_3)]^+ when using [Pt(dmpe)_2H]^+ whereas negligible hydride transfer was observed when using the poorer hydride donor [Pt(depe)_2H]^+. With this observation they synthesised more electron-rich and as such more stable formyl [Re(CHO)(NO)(Cp)(PPh_3)] and
observed its equilibrium with the complex $[\text{Pt(dmpe)}_2\text{H}]^+$, finding the Pt complex to be a better hydride donor by 1.6 kcal/mol.

The concept of using two transition metal centres in tandem to activate both H$_2$ and CO has been at the focus of Bercaw’s most recent syngas work. In order to facilitate hydride transfer to a carbonyl, the carbonyl must be activated by one metal centre while a separate Lewis acid, which in this case is again a metal, activates hydrogen to deliver the hydride. The chosen carbonyl must be sufficiently electrophilic to accept a hydride and the metal hydride sufficiently nucleophilic to donate a hydride and neither should be so oxophilic as to form a strong M-O bond that precludes catalysis.$^1$

Bercaw’s group have proven this concept, using the platinum complex $[\text{Pt(dmpe)}_2\text{H}]^+$ to transfer hydride to a rhenium carbonyl possessing a pendant Lewis acid in the second coordination sphere. Initial reduction results in a formyl/boroxy carbine which accepts a second hydride and displays reductive coupling of a second CO ligand. This reaction demonstrates two equivalents of hydride can be transferred from a source directly derived from dihydrogen, the first example of its kind (Scheme 1.10).

Bercaw again demonstrated this concept using $[\text{Pt(dmpe)}_2\text{H}]^+$ with $[\text{Mn(CO)}_5\text{PPh}_3]^-$ generating a relatively unstable formyl which, when treated with acid in methanol produces methyl acetate.$^{45}$ Since this hydride complex is derived directly from hydrogen this is an important development en route to a feasible catalytic cycle. From this the group provided a stepwise stoichiometric reaction cycle for methyl acetate formation (Scheme 1.11).
Scheme 1.1: Stepwise cycle reported by Bercaw et al. for the reduction of a cationic Mn carbonyl in methanol to methyl acetate.

In this instance, a catalytic cycle is not possible since the platinum hydride is still not compatible with an acid necessary to catalyse C-O bond cleavage which remains a persistent challenge in this chemistry. Ultimately, a modified carbonyl complex that is capable of being reduced by weaker hydride reagents is necessary, and this is a priority when designing future syngas conversion chemistry.

1.4 Intermediates in homogeneous syngas conversion

The chemistry of homogeneous syngas conversion has been concerned with the observation and reactivity of a number of important functional groups achieved from reduction of a carbonyl – namely the formyl, hydroxymethyl and methylidene (Scheme 1.12). In this section the observation and typical reactivity of such species will be discussed.
1.4.1 The metal formyl complex: Reactivity and decomposition

The successful generation and stabilisation of a formyl is essential to creating a syngas reduction cycle. The formyl complex, although in most cases transient and extremely unstable, has been observed on numerous metals *via* hydride addition to a carbonyl. Formyls are electron-rich and are known to act as hydride donors. They have been shown to reduce ketones, alkyl halides and to disproportionate, reducing other metal carbonyls. This is demonstrated in work published by Casey *et al.* which documents the Cannizzaro-like disproportionation of the relatively stable rhenium formyl [Re(CHO)(CO)(Cp)(NO)] to give a dimeric metallo-ester (Scheme 1.13).

**Scheme 1.12:** Key intermediates from carbonyl reduction on an 18-electron cationic carbonyl complex

**Scheme 1.13:** Disproportionation of a formyl complex – the formyl attacks another molecule producing a dimeric metallo-ester species
This reaction displays the importance of the formyl intermediate as the first step in a successful homogeneous cycle. With a relatively stable formyl that persists for long enough in solution, a cascade of self-reductions can be initiated. With a compatible source of protons one can imagine how such a reaction could produce useful products (vide infra Scheme 1.4). However, unfortunately formyl complexes are rarely sufficiently stable in solution for very long and instead decompose via decarbonylation and radical pathways (Scheme 1.14). Decarbonylation results in the formation of the thermodynamically very stable metal hydride complex. Since carbonyl insertion into a metal hydride bond is energetically unfeasible this is a major hindrance to catalysis.24

![Scheme 1.14: Formyl decarbonylation to form a thermodynamically stable metal hydride](image)

Radical pathways also account for the decomposition of transition metal formyls and the formation of new metal-metal bonds again lead to new metal carbonyl dimers (Scheme 1.15).

![Scheme 1.15: Radical decomposition of the formyl complex to form a metal dimer](image)

1.4.2 The hydroxycarbene and hydroxymethyl complexes

The hydroxymethyl intermediate would be formed from addition of one equivalent of both hydride and proton to a formyl complex. On route to the hydroxymethyl complex it is likely that there could be a highly unstable transient hydroxycarbene. This elusive intermediate has attracted attention for this reason but has proved to be one of the hardest intermediates to observe (Scheme 1.16).
Chapter 1

Introduction

Scheme 1.16: Addition of a proton to a formyl complex produces a hydroxycarbene. Further reduction achieves the hydroxymethyl intermediate.

There are several known cases of substituted oxycarbenes at room temperature, independently synthesised via substitution reactions.\textsuperscript{48-49} A conceptually similar hydroxcarbenoid complex is also known. A Mn carbonyl complex was treated with LiBr, inducing carbonyl insertion into the Mn-CH\textsubscript{3} bond. Subsequent protonation using HCl affords the hydroxcarbenoid (Scheme 1.17).\textsuperscript{50} The product can be isolated as orange crystals; its unusual stability is a direct result of intramolecular hydrogen bonding to the halide substituent.

Scheme 1.17: Addition of LiBr to (CO)\textsubscript{5}MnCH\textsubscript{3} prompts insertion of CO into the Mn-CH\textsubscript{3} bond to form a methoxy species which, on protonation, produces a hydroxycarbene.

The same method utilising LiBr was attempted on Re and failed, probably due to the increased Re-alkyl bond strength. In this case, CO insertion is prompted instead by addition of methyllithium to a halopentacarbonyl complex (Scheme 1.18).

Scheme 1.18: CO insertion prompted by addition of MeLi and protonation produces hydroxycarbene species.

Hydroxymethyl species have also been shown to be unstable and difficult to characterise. They tend to undergo rapid β-hydride elimination to produce a stable metal hydride and
formaldehyde. In a rare example, Graham and co-workers document the synthesis of both a formyl and hydroxymethyl complex via reduction of a carbonyl on rhenium (Scheme 1.19).[^37]

![Scheme 1.19](image)

**Scheme 1.19:** Graham and co-workers report the synthesis and isolation of a rhenium hydroxymethyl via NaBH₄ reduction

From the scheme it is clear that products of NaBH₄ reduction are affected by the presence of H₂O. When using NaBH₄ in THF, three hydride equivalents are delivered to the carbonyl to produce the stable methyl ligand. However, in the presence of water, the reaction stops at the formyl and only one equivalent of hydride is delivered (*vide supra*). The hydroxymethyl complex [Re(CH₂OH)(CO)(NO)(Cp)]⁺ is successfully isolated by DCM extraction and is an air stable solid. Other cases of hydroxymethyl syntheses via reduction of a carbonyl have been reported by Astruc and Lapinte. They observe the hydroxymethyl complex [Fe(CO)₂(CH₂OH)(Cp*)] via reduction of the cationic carbonyl [Fe(CO)₃(Cp)]⁺ in DCM.[^51][^39][^52] They record its diagnostic CH₂ ¹H resonance as a doublet at δ 1.15 ppm. If the same reaction is carried out in water at 0 °C, they observed the stable complex [Fe(CO)₂(H)(Cp*]) as the only product. This supports Graham’s findings that the solvent used is essential in determining which product will be obtained. Although the hydride [Fe(CO)₂(H)(Cp*)] can be isolated at room temperature, the hydroxymethyl complex is unstable at room temperature and it is only possible to store it at 0 °C for several days.

1.4.3 **The methylidene complex**

On protonation of a hydroxymethyl complex, loss of water would produce a transient methylidene, the simplest of metal carbenes. Although there are no known cases of a methylidene reported from reduction of a CO ligand, it is widely accepted that this intermediate would be another key intermediate in a successful CO conversion cycle. Carbenes have been used in alkene ring closing metathesis (RCM), known for their C-C bond forming reactions...
and dimersations (Scheme 1.20).\textsuperscript{53,54,55} The stereochemistry of the ring closing is dictated by the substituents on the metal center.

![Scheme 1.20](image)

**Scheme 1.20:** Methylidene complexes are widely known for their RCM chemistry

This is relevant to syngas chemistry, since the ligands on the metal can be altered to stabilise a transient methylidene and effect C-C bond forming reactions upon carbonyl reduction. Carbenes can be distinguished from each other by their polarity which is dependent on the metal center. Early electropositive metals form double bonds with carbon rendering it electron-rich, prompting nucleophilic behaviour.\textsuperscript{38} Commonly, electron deficient metal centers with double bonds to ligands which only contain C or H are referred to as Schrock alkylidenes since Schrock isolated the first unsubstituted methylidene complex \([\text{Ta}(\text{CH}_3)(\text{=CH}_2)(\text{Cp})]\). At the opposite end of the ‘d’ block, the more electron-rich metals will form Fischer carbene complexes with a more electron deficient carbon resulting in electrophilic behaviour. Such carbenes are often stabilised using heteroatom substituents which can donate electron density to the electrophilic carbon; examples of non-heteroatom stabilised methylidenes are extremely unstable and therefore characterisation of these intermediates is limited.\textsuperscript{56,53,57}

The groups of Brookhart and Pettit have studied the reactivity of a number of electrophilic methylidene complexes of the later transition metals which do not require heteroatom stabilisation, namely on iron.\textsuperscript{58,56} One rare example that has been characterised is a bisphosphine stabilised electrophilic methylidene \([\text{Fe}(\text{=CH}_2)(\text{Cp})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]^+\) which is stable at room temperature \((t_{1/2} = 1 \text{ hour})\). As with most reports in the literature, it is achieved via acid protonation of an alkoxy species, using a strong acid such as HBF\(_4\) (pK\(_a\) -2) (Scheme 1.21). At \(-80 \degree C\) this unique methylidene has distinctive \(^1\text{H}\) resonances at \(\delta\) 13.89 (t) and 17.29 (br s) ppm; these resonances coalesce above \(-40 \degree C\) indicating dynamic behaviour.
Scheme 1.21: Protonation results in C-O bond cleavage and formation of the methyldiene complex [Fp=CH₂]

1.4.4 Methyldiene reactivity and C-C bond forming reactions

The “Fp^R” moiety, [Fe(CO)₂(η⁵-Cp^R)] (Cp^R = Cp or Cp*), is ubiquitous in organometallic carbonyl reduction chemistry. As discussed in Section 1.3.1 Treichel and Shubkin first used the Fp framework to demonstrate the reduction of a carbonyl ligand to a methyl group using NaBH₄.⁴⁰ Since then much work has focused on observing and characterising the highly unstable, transient intermediates of this reduction, namely the formyl and methyldiene. The electrophilic methyldiene complexes of the type [Fe(=CH₂)(Cp^R)(L)(L)]⁺ have been the focus of interest in relation to the final C-C bond forming steps in proposed catalytic cycles of syngas conversion. As discussed in Section 1.4.3 Brookhart has studied a series of methyldienes based on the “Fp^R” framework. Brookhart attempted to characterise the transient intermediates of the reaction, originally reported by Pettit et al., which produces norcarane from acid treatment of the alkoxy species [Fe(CO)₂CH₂OCH₃(Cp)] (FpCH₂OCH₃) in the presence of cyclohexene. They postulated that this reaction proceeds via a methyldiene intermediate upon C-O bond cleavage (vide infra Scheme 1.21).

Scheme 1.22: Protonation cleaves the alkoxy complex Fp^RCH₂OCH₃ to produce an electrophilic methyldiene, dimerisation leads to [Fp^R]⁺ and the ethylene complex [Fp^(CH₂=CH₂)]⁺.

Brookhart treated the Fe alkoxy compound at −100 °C with HBF₄ and then recorded the ¹H NMR spectrum at −80 °C. However, even at this low temperature the highly reactive electrophilic methyldiene had dimerised. They observed clean disproportionation to equimolar amounts of [Fp(η²-C₅H₄)]⁺ and [Fp]⁺. This disproportionation can be reasoned as proceeding
via a methyldiene dimer. In separate studies by Astruc and Lapinte, similar methyldiene reactivity is reported.51,59,60 They use the increased electron density of the permethylated cyclopentadienyl ligand (Cp*) to confer stabilisation in order to characterise the analogous complex [Fe(=CH2)(CO)2(Cp*)]+. This complex is unstable and in the absence of a trapping reagent, ethylene is produced at room temperature alongside the 16 e– fragment [Fe(CO)2(Cp)]+. This is again postulated to occur via a metallocycle mechanism (Scheme 1.23).

![Scheme 1.23: Protonation cleaves the alkoxy complex Fp8CH2OCH3 to produce an electrophilic methyldiene; dimerisation leads to [Fp8]+ and the ethylene complex [Fp8(CH2=CH2)]+](image)

In addition, Mo has demonstrated comparable chemistry using the [Cp8Mo(CO)4]+ fragment; one example reports the formation of ethylene at 0 °C from the bimetallic methyldiene [Mo(=CH2)(CO)3(η5, η5-fuvalene)]2+; as with previous examples the methyldiene is formed by protonation of an alkoxy precursor (Scheme 1.24).61 The group observe the dissociation of ethylene at room temperature over the course of 2 days.
Scheme 1.24: Protonation by HBF$_4$ leads to C-O cleavage and formation of a methylidene which is postulated to produce ethylene via the methylidene dimer shown.

If reduction of a carbonyl ligand on a transition metal can be facilitated with the correct choice of hydride donor, C-C coupling and therefore the production of C$_{1+}$ products appears to be a possibility via electrophilic methylidene reactivity. However, it is important to note that any scheme producing a methylidene should not include such a strong hydride donor, either formyl or otherwise, that prompts full reduction to the methyl ligand before any C-C bond forming reactions can occur.

1.5 Stabilising a formyl complex

This project aims to investigate reduction of a carbonyl on a transition metal as a model for homogeneous syngas conversion. The generation of a formyl is considered to be the most important step in homogeneous syngas conversion. Therefore, investigating the necessary electronic environment which affords a stable formyl with the potential for further reduction is a priority. The increased stability of a formyl complex is essential to prompt further reduction at a faster rate than the decomposition pathways discussed in Section 1.4.1. It has been shown briefly already in this introduction that there are two important factors for formyl stabilisation, that is, metal centre and ligand framework. When discussing the stability of a formyl complex it is useful to visualise its resonance form, the oxycarbene canonical form (Scheme 1.25).
Scheme 1.25: Schematic showing the resonance form for a formyl complex

1.5.1 The metal centre

Almost all reported formyl studies in the literature are on metals from the middle of the ‘d’ block, Groups 6-8. Formyl complexes are generally unstable at elevated temperatures but as discussed in Section 1.3.1, the most stable complexes have generally been achieved on rhenium and the complex \([\text{Re(CHO)}(\text{Cp})(\text{NO})(\text{PPh}_3)]\) is stable up to 90 °C.\(^{35}\) Early on, Gladysz reported a series of anionic formyls from mono-substituted pentacarbonyl complexes on Mn, Re and Mo. The stability of these complexes greatly depends on the metal centre. The anionic rhenium formyls were stable up to \(-10\) °C whereas the molybdenum and manganese complexes tend to decompose to the corresponding metal hydrides at much lower temperatures of \(-30\) to \(-50\) °C.\(^{33}\)

1.5.2 The ligand framework

In order to decrease the rate of decarbonylation of a formyl it is necessary to increase the electron density on the metal center which increases the metal carbon bond strength \(i.e.\) the oxycarbene canonical form dominates. Commonly used ligands in carbonyl reduction chemistry are bulky, chelating, and electron-rich in order to achieve this stabilisation. The two most common classes of ligands used are \(\text{mono-}\) and \(\text{bis}\)-phosphines and cyclopentadienyl and its derivatives. Gibson developed the use of phosphines and cyclopentadienyl ligands as a means to stabilise and isolate neutral formyl complexes at room temperature (Figure 1.3), employing \(\text{Et}_4\text{NBH}_4\) as the reductant and using methanol as solvent readily precipitates the formyl complexes as powders from solution.\(^{62}\) Only one formyl complex \(\text{cis-}\) and \(\text{trans-}\) \([\text{Mo(CHO)}(\text{CO})_2(\text{Cp}^*)(\text{P(OEt})_3)]\) was ever achieved as a crystalline solid. Gibson highlights the use of a mild reducing agent however it seems more likely that the borohydride reacted with the methanol, forming a much stronger hydrido-borate reducing agent and this in fact transfers the hydride to these electron-rich carbonyl complexes. Although isolable at room
temperature, each of the formyl complexes slowly decomposes to the metal hydride which is accelerated at elevated temperatures (> 45 °C).

![Figure 1.3](image)

**Figure 1.3:** Transition metal formyl complexes isolated using stabilising, electron-rich ligands including Cp* and PPh₃

An example of the stabilising effect of phosphines is the unusually high stability of a derivative of Casey’s rhenium formyl \([\text{Re}(\text{CHO})(\text{CO})(\text{Cp})(\text{NO})]\) which is only stable at room temperature for a short time. However, the aforementioned PPh₃ substituted analogue \([\text{Re}(\text{CHO})(\text{Cp})(\text{NO})(\text{PPh}_3)]\) decomposes at temperatures greater than 90 °C. One demonstration of the importance of steric bulk is by the use of \([\text{C}_5\text{Ph}_5]^–\) to isolate the complex \([\text{Fe}(\text{C}_5\text{Ph}_5)(\text{CHO})(\text{CO})(\text{PMe}_3)]\), a rare example of a stable and isolable iron formyl. This is in stark contrast to the analogue \([\text{Fe}(\text{C}_5\text{Me}_5)(\text{CHO})(\text{CO})_2]\) which is unstable at temperatures above –80 °C.

### 1.6 Heterolytic H₂ activation

A catalytic homogeneous syngas conversion cycle needs a compatible source of hydride and proton resulting from the activation of H₂. Traditionally examples of heterolytic H₂ activation are on transition metals. As discussed previously, transition metals present a number of problems namely the oxophilicity of the early transition metals, which are necessary for the formation of acidic metal hydrides. However, major discoveries relating to heterolytic H₂ activation have been made, not only with transition metal but more recently using main group compounds. These discoveries and their relevance to syngas conversion are discussed in Section 1.6.2.

#### 1.6.1 Introduction to frustrated Lewis pairs

In 2006 Stephan and co-workers reported the reversible heterolytic activation of dihydrogen using a frustrated Lewis pair. The term ‘frustrated Lewis pair’ (FLP) refers to a Lewis base
and Lewis acid that are prevented from forming a classical adduct due to steric hindrance. The vacant coordination sites in both lead to unique reactivity with small molecules. Since their discovery, a plethora of reactivity has been reported including activation of carbon dioxide and ethylene (Scheme 1.26). An extensive range of bases have been shown to facilitate small molecule activation with organoboranes including phosphines, amines and carbenes, both inter- and intramolecularly.\textsuperscript{64,65,66}

\textbf{Scheme 1.26:} Recent examples of small molecule activation by FLP $^t$Bu$_3$P/B(C$_6$F$_5$)$_3$

The properties of a frustrated Lewis pair and its ability to cleave dihydrogen are a direct result of the cumulative Lewis acid-base strength of the Lewis acid and Lewis base employed. Favourable thermodynamics, \textit{i.e.} negative $\Delta G$ values, are necessary for the cleavage of hydrogen but $\Delta G$ must not be so negative as to form an unreactive hydrogenated FLP. Conversely if $\Delta G$ for the reaction with hydrogen is too high then formation of the hydrogenated salt, and hence proton and hydride equivalents, will not occur. The activation of hydrogen by a FLP can be thought of in sequential processes involving (i) cleavage to form $H^+$ and $H^-$, (ii) separation of the Lewis acid and base, (iii) attachment of the $H^+$ and $H^-$ to the Lewis acid and base, and (iv) interaction of the new charged fragments. Papai \textit{et al.}\textsuperscript{67} used computational calculations to show that the final step (iv) has minimal thermodynamic impact on $H_2$ cleavage. It is therefore possible to think of FLP reactivity more simply as cumulative Lewis acid-base strength. It is possible to predict the success of $H_2$ cleavage using hydride affinities and $pK_a$ values. Quantitative $pK_a$ are available for a range of bases\textsuperscript{68} and much work has been done recently to determine calculated hydride affinities for various Lewis acids.\textsuperscript{44,69,70} Lewis acidity measurements can also be used as a qualitative measure for predicting hydride affinity. The commonly used strong Lewis acid B(C$_6$F$_5$)$_3$ is capable of reversibly cleaving dihydrogen with
a variety of relatively weak bases such as TMP \[\text{pK}_a (\text{ACN}) \ 10.15\] and \(\text{P}^\text{tBu}_3\) \[\text{pK}_a (\text{H}_2\text{O}) \ 11\] in which \(\Delta G = 0\) for the reaction. However, it is also possible to cleave dihydrogen with \(\text{B}(\text{C}_6\text{F}_5)_3\) and a variety of much weaker bases such as \(\text{Et}_2\text{O}\), dioxane, and THF \(\text{pK}_a < -2\); the Gibbs free energy for this reaction will be positive. Kinetic effects play a significant role in the reactivity of dihydrogen with a FLP when thermodynamically the process appears too unfavourable. Stephan et al. reported experimentally, the cleavage of dihydrogen with poorly Lewis acidic \(\text{BPh}_3\) and weakly basic \(\text{P}^\text{tBu}_3\) in toluene. The calculations of Papai and co-workers determine \(\Delta G\) for this reaction to be \(+18.2\) kcal/mol which is well above the expected thermodynamic limit for reaction. However, the precipitation of the salt \([\text{H} \text{P}^\text{tBu}_3][\text{HBPh}_3]\) from toluene drives the forward reaction.\(^{64}\)

### 1.6.2 Recent advances in Frustrated Lewis pair chemistry

Catalytic FLP hydrogenations have typically been facilitated via hydrogen activation using the strong Lewis acid \(\text{B}(\text{C}_6\text{F}_5)_3\) with a variety of Lewis bases including phosphines, amines and carbenes. This activation commonly results in the formation of a weak hydride source as a direct result of the significant Lewis acidity of the borane. Even modest reduction in the Lewis acidity of the borane used in FLP systems can prevent hydrogen activation. However, more recently advances have been made in altering both the Lewis acid and Lewis base thereby allowing activation of hydrogen using weaker Lewis acids which subsequently provide a stronger hydride source. This is of great importance to carbonyl reduction chemistry as carbonyls tend to require fairly strong hydride donors to facilitate reduction.

One such example is the elaborate zwitterionic carbanion \(\text{Na}[\text{C}(\text{SiMe}_2\text{OCH}_2\text{CH}_2\text{OMe})_3]\) synthesised by Krempner et al.\(^7\) This carbanion acts as a strong sterically encumbered base \[\text{pK}_a (\text{DMSO}) \ 22.5\] and as such can activate hydrogen with even very poorly Lewis acidic trisalkylboranes. This strongly Lewis basic species was shown to activate hydrogen with a series of poorly Lewis acidic trisarylboranes including \(\text{BPh}_3\). At the very limit of FLP hydrogen activation, the base was shown to activate hydrogen with the poor Lewis acid \(\text{BEt}_3\). On addition of the base to a hexane solution of \(\text{BEt}_3\), no Lewis acid-base adduct is formed, yet upon exposure of the solution to hydrogen, a precipitate of an adduct of the bridging borohydride \([\text{Et}_3\text{B}-\text{H}-\text{BEt}_3]\) with the protonated base is observed (Scheme 1.27). The precipitation of the solid adduct drives the cleavage of dihydrogen which otherwise would readily reverse if it remained in solution.
This discovery is important in relation to the reduction of carbonyls since a variety of transition metal formyl complexes have been synthesised via reduction of carbonyls using strong hydride donors of the type M[HBEt$_3$] (M = K, Na, Li) derived from the Lewis acid BEt$_3$ used in this example.

1.6.3 Direct homogeneous hydrogenation facilitated by frustrated Lewis pairs

A number of groups have harnessed the reactivity of dihydrogen with an FLP system to facilitate metal-free direct hydrogenation of CO$_2$ and CO. Although two very different molecules, the hydrogenation of both requires similar considerations with regards to the delivery of hydride and proton equivalents. Typically non-polar CO$_2$ has required activation by transition metal hydrides, however with the advent of FLPs we now observe metal-free activation and transformations.$^{65,72}$ The first metal-free homogeneous conversion of CO$_2$ to methanol was reported by Ashley and co-workers using the FLP system TMP/B(C$_6$F$_5$)$_3$ (Scheme 1.28).$^{73}$
The first step of CO\(_2\) insertion into the B-H bond is mediated by the product of hydrogen activation, the ammonium borohydride salt [TMPH][HB(C\(_6\)F\(_5\))\(_3\)]. This leads to quantitative formatoborate production at 100°C. Further activation by another molecule of B(C\(_6\)F\(_5\))\(_3\) and delivery of a second hydride equivalent from [TMPH][HB(C\(_6\)F\(_5\))\(_3\)] leads to the acetal [TMPH]\(_2\)[H\(_2\)C(OB(C\(_6\)F\(_5\))\(_2\))\(_3\)] which is reduced to [CH\(_3\)OB(C\(_6\)F\(_5\))\(_3\)]\(–\) with subsequent protonation by TMPH\(^+\). Although CH\(_3\)OH is obtained selectively in 17-25 % yield, catalysis is prevented by the proton mediated decomposition of the hydroxyl product (H\(_2\)O-B(C\(_6\)F\(_5\))\(_3\)) to the inert boroxin (OBC\(_6\)F\(_5\))\(_3\).

Although CO\(_2\) mediated reactivity with FLP systems is now well known, there are far fewer cases of CO activation or hydrogenation. Arguably the most significant development in homogeneous syngas conversion in recent years has been the reduction of a rhenium carbonyl (previously discussed in Section 1.3.2) directly from dihydrogen using a FLP system (Scheme 1.29). Bercaw’s group previously documented the reduction of this species using a Group 10 hydride. On trying to optimise this process with bulkier bases they discovered H\(_2\) activation by the phosphorane base 

\[
tert\text{-butylimino-}tris\text{(pyrrolidino)}\text{phosphorane}, (P\(_1\)) \quad \text{[pK}_a\text{ (ACN)} = 28.4]\]

and the tethered 9BBN-derived boron Lewis acid.
Scheme 1.29: H$_2$ activation using a pendant Lewis acid and phosphorane base (P$_1$).

The borohydride formed from the heterolytic cleavage of H$_2$ successfully delivers a hydride to the carbonyl once again producing a boroxycarbene as seen in Scheme 1.10 (*vide infra*). Unfortunately the conjugate acid [HP$_1$]$^+$ is evidently too weakly acidic to permit proton transfer and C-O bond cleavage.

A second example of FLP mediated CO hydrogenation was reported by Wass *et al.* The group used a traditional zirconocene Lewis acid in place of a boron Lewis acid affording the activation of dihydrogen (Scheme 1.30). On reaction with CO it forms an unusual zirconium carbonyl complex iii and on reaction with syngas it forms the bound formaldehyde complex iv. When left to stand at room temperature, mixtures of the dihydrogen complex ii and carbonyl iii combine to form complex iv. This indicates that the formaldehyde complex is formed from carbonyl coordination and insertion followed by hydride migration.
Scheme 1.30: Synthesis of an unusual Zr carbonyl complex reported by Wass et al.

An example of metal free activation of CO has been published by the Stephan group (Scheme 1.31). They use two equivalents of the strong Lewis acid B(C₆F₅)₃ with base P'Bu₃ to afford activation of syngas. A formyl intermediate is first observed by activation of dihydrogen followed by CO insertion into the B-H bond to form v. On addition of H₂, C-O bond cleavage is driven by the formation of the strong new B-O bond, prompting migration of C₆F₅, a common problem encountered with B(C₆F₅)₃ adducts. This migration is unsurprising given DFT calculations reveal that the HOMO and LUMO of formyl derivative v are almost completely concentrated on the C₆F₅ ring and the C=O fragment respectively.
Although this is a unique example of metal free syngas activation, a labelling experiment highlights the limitations of such a system. Free $^{13}$CO does not react with the salt $[\text{HP}^3\text{Bu}_3][\text{HB(C}_6\text{F}_5)_3]$. CO must be activated with a second equivalent of free Lewis acid $\text{B(C}_6\text{F}_5)_3$ in order to facilitate the delivery of a hydride equivalent. However, it is worth noting that the interaction of CO with the Lewis acid has not been observed spectroscopically. It once again provides evidence that a homogeneous syngas conversion cycle should proceed through a formyl intermediate but in this case the use of a strong Lewis acid precludes any catalysis due to the formation of strong B-O bonds.

Erker has shown CO activation via adduct formation using Piers’ borane $(\text{C}_6\text{F}_5)_2\text{BH}$. Subsequent treatment with a vicinal phosphane/borane FLP system prompts CO-hydroboration forming a “$\eta^2$-formylborane” (Scheme 1.32). Without a second equivalent of $\text{B(C}_6\text{F}_5)_3$, borane carbonyl adducts have previously been shown not to undergo CO-hydroboration to the formyl moiety.
Scheme 1.32: CO insertion into Piers’ borane prompted by a vicinal phosphane leads to a formyl borane after treatment with pyridine

The formyl is stabilised by electron donation from pyridine which via the boron center stabilises the CHO functional group. The formyl can be reduced to the hydroxymethyl oxidation state using another equivalent of HB(C₆F₅)₂. This reaction highlights a simple metal free route for synthesising an important formyl derived intermediate and the necessity of a strong Lewis acid when attempting to deliver a hydride to the carbonyl carbon.

1.7 Thesis Aims

Apart from the detailed work of Bercaw, very little is known about the hydrogenation, directly from dihydrogen, of a CO ligand in homogeneous chemistry. Although various reduction states have been achieved, the elusive step of protonation to release useful carbon containing products is yet to be demonstrated. With this in mind, the aims of this thesis are two-fold; firstly, to probe the electronic environment necessary to facilitate the synthesis of a stable formyl complex capable of further reactivity on a transition metal. Secondly, a thorough investigation of the capability of Frustrated Lewis pairs in facilitating direct hydrogenation of carbon monoxide from hydrogen is warranted. It was hoped that a FLP could be used to activate hydrogen in order to deliver the necessary proton and hydride equivalents needed for the complete reduction of carbon monoxide. Scheme 1.33 hypothesises a mechanism by which a
FLP system could be incorporated to achieve a formyl complex and subsequent important intermediates for reduction, migratory insertion, C-O bond cleavage and C-C bond formation. Gaining insight into the necessary electronic and kinetic requirements for these transformations would provide invaluable insight into a potential homogeneous syngas conversion cycle with compatible proton and hydride equivalents.

Scheme 1.33: Cycle showing the possible catalytic pathways for CO conversion. The first step involves hydride addition to a carbonyl to produce a metal formyl. This is followed by further hydride and proton equivalents to produce a hydroxymethyl and methylidene. A methylidene could dimerise to produce ethylene or reduce to the methyl.
1.8 References

Chapter 1
Introduction


Chapter 2

Reduction studies of a cationic iron tricarbonyl complex

2.1 Introduction

2.1.1 Reduction chemistry of [Fe(CO)\textsubscript{2}(Cp\textsuperscript{R})]\textsuperscript{+}

As discussed in Chapter 1, the cationic [Fe(CO)\textsubscript{2}(Cp\textsuperscript{R})]\textsuperscript{+} ([Fp\textsuperscript{R}]\textsuperscript{+}, Cp\textsuperscript{R} = Cp, Cp\textsuperscript{*}) moiety is ubiquitous in carbonyl reduction chemistry (Figure 2.1). In 1967, Treichel and Shubkin reported the full reduction of the tricarbonyl [Fe(CO)\textsubscript{3}(Cp)]\textsuperscript{+} to the methyl complex [Fe(CH\textsubscript{3})(Cp)]. Since then the [Fp\textsuperscript{R}]\textsuperscript{+} moiety central to homogeneous carbonyl reduction studies, providing a framework on which to study the electronic properties of postulated key intermediates.\textsuperscript{1,2,3} Crediting the work of Astruc, Lapinte and Brookhart on the permethylated analogue [Fp\textsuperscript{*}]\textsuperscript{+}, we have seen the characterisation of key intermediates for homogeneous syngas conversion including formyl [Fp\textsuperscript{*}CHO], hydroxymethyl and methylidene on the pentamethylated analogue [Fe(CO)\textsubscript{3}(Cp\textsuperscript{*})]\textsuperscript{+}, ([Fp\textsuperscript{*}CO]\textsuperscript{+}).\textsuperscript{4,5,6}

![Figure 2.1: Structures of the [CpFe(CO)\textsubscript{2}]\textsuperscript{+} and [Cp\textsuperscript{*}Fe(CO)\textsubscript{2}]\textsuperscript{+} fragments](image)

[Fp\textsuperscript{*}CO]\textsuperscript{+} has a markedly different stability and reduction chemistry when compared to the more sterically accessible [FpCO]\textsuperscript{+}. While the extra electron density and steric bulk\textsuperscript{7,8} has allowed for the characterisation of transient intermediates which are unobservable with [FpCO]\textsuperscript{+}, it has also shown markedly different reactivity towards hydride donors.\textsuperscript{9} While both complexes are known to undergo hydride attack on the carbonyl ligand, [FpCO]\textsuperscript{+} may also undergo endo and exo hydride attack on the sterically unencumbered Cp ring. The nature of the hydride donor can determine whether attack will occur at the carbonyl or on the ring, and it can also dictate whether the attack on the ring will be exo or endo.\textsuperscript{10} Whitesides used NaBD\textsubscript{3}CN to demonstrate exo hydride addition to the ring to give the $\eta^4$-cyclopentadiene...
complex [Fe(η⁴-C₅H₄D)(CO)₃] (Scheme 2.1). Interestingly, endo hydride migration or migration to the CO does not occur and only after heating at 80 °C will the complex decompose to the dimer [Fe₂(η⁵-C₅H₅)₂(CO)₄].

This example highlights the importance of the nature of the hydride donor. If the reduction of [FpCO]⁺ is carried out with NaBH₄ the hydride will add to the carbonyl to produce the corresponding formyl complex [FpCHO]. In contrast [Fp*CO]⁺ is not known to undergo exo or endo attack with any main group reducing agent, presumably due to the steric protection of the methyl groups. The hydride addition can then conveniently be guided to the carbonyl which, along with increased stability of reduced intermediates, presents the advantages of using [Fp*CO]⁺ to study carbonyl conversion chemistry (Scheme 2.2).

In 1988 Astruc used NaBH₄ to sequentially reduce [Fp*CO]⁺ in THF-d₈ allowing characterisation of a series of key functional groups namely formyl –CHO, hydroxymethyl –CH₂OH, and methyl –CH₃ (Scheme 2.3).
Chapter 2  Reduction studies on a cationic iron tricarbonyl complex [Fe(CO)₃(Cp*)][BArF₂₄]

Scheme 2.3: Reduction of [Fp*CO]⁺ to [Fp*CH₃] using three equivalents of NaBH₄ in THF-d₈

In a separate reaction, Astruc has shown that if the hydroxymethyl complex [Fe(CH₂OH)(CO)₂(Cp)] is protonated using [HPF₆] both free CH₂=CH₂ and the complex [Fe(η²-CH₂=CH₂)(CO)₂] are observed. The observation of these species are deemed the result of a transient electrophilic methylidene [Fp*=CH₂]'⁺, which dimerises via a metallocyclic species to produce ethylene (Scheme 2.4). In addition, the observation of free CH₂=CH₂, postulated to be produced via dimerisation of the methylidene [Fp*=CH₂]'⁺, has been reported by both Brookhart and Lapinte.

Scheme 2.4: Three equivalents of hydride and one proton equivalent produce the methyl complex [Fp*CH₃] - protonation of the intermediate hydroxymethyl produces a methylidene [Fp*=CH₂]'⁺ which has been observed to produce CH₂=CH₂
2.1.2 Objectives in reduction studies of [Fe(CO)₃(Cp*)][BArF₂₄]

This chapter will discuss the results of a range of stoichiometric reduction studies on the complex [Fp*CO][BArF₂₄] (1). The aim of these studies was two-fold:

1. Determine the hydride affinity of the cation [Fp*CO]⁺. It is known that NaBH₄ is a strong enough hydride donor to reduce this complex to the corresponding formyl [Fp*CHO]; however there are no other reports of hydride donors of a differing strength performing the same transformation.

2. Using the information of hydride affinity of the complex [Fp*CO]⁺, an attempt will be made to design a system for hydrogenation of this complex using a frustrated Lewis pair and H₂. By using a FLP and H₂ an attempt can be made to deliver hydride and proton equivalents directly from hydrogen, elucidating the feasibility of this carbonyl for use in a catalytic FLP syngas conversion cycle (Scheme 2.5).

**Scheme 2.5:** Postulated catalytic cycle for reduction of [Fp*CO]⁺ using a Lewis base (LB) and Lewis acid (LA) with H₂
2.2 Synthesis of [Fp*(CO)₃][BArF₂₄]

To date reduction studies on [Fp*CO]⁺ (1) have been carried out on the [PF₆]⁻ salt. This salt is not ideal for FLP hydrogenation studies given its poor solubility in a wide range of non-polar solvents. In addition, the potential for fluoride abstraction is a particular concern when employing the use of electrophilic boranes, which are required in our target FLP systems. In order to overcome these issues, the weakly-coordinating, lipophilic anion tetrakis[(3,5-trifluoromethyl)phenyl]borate [BArF₂₄]⁻ has been used as the anion for our reduction studies of the cation [Fp*CO]⁺. Using a modified literature procedure, the desired complex is obtained in two steps on a multi-gram scale from dimer [Fe(C₅Me₅)(CO)₂]₂, ([Fp*₂]). [Fp*CO][BF₄] is initially synthesised via oxidation of the dimer by [FeCp₂][BF₄] and is obtained as a purple solid. Salt metathesis with Na[BArF₂₄] is carried out at room temperature in THF and NaBF₄ is precipitated as a tan solid. [Fp*CO][BArF₂₄] (1) is obtained via crystallisation in Et₂O at −78 °C as a pale orange crystalline solid in an overall 78 % yield (Scheme 2.6). This results in a water tolerant complex which has poor solubility in aliphatic hydrocarbons, moderate solubility in aromatics and high solubility in donor and chlorinated solvents. Whilst the complex is manipulated and stored as an air sensitive compound, it appears to show significant thermal and hydrolytic stability. In our hands, 1 has been heated to 110 °C in toluene, benzene and 1,2-difluorobenzene while Asturic has reported details of reductions of 1 in THF/H₂O without decomposition occurring.

![Scheme 2.6: Synthetic route used to produce 1](image-url)
2.3 Reduction studies of [Fp*CO][BArF$_{24}$]

It is already known from the work of Astruc that the formyl complex 2 has limited stability above −80 °C, decomposing slowly at room temperature to the metal hydride [Fp*H] and dimer [Fp*$_2$] (Scheme 2.7). The instability of the formyl 2 does not necessarily impede this chemistry. If 2 is formed in high enough concentrations, proton-mediated reduction may occur in the presence of an acid [LBH]$^+$. However, when carrying out the stoichiometric reductions, conversions to these decomposed species have also been considered since their presence is an inevitable outcome if proton mediated reduction fails to occur either because of the insufficient acidity of the [LBH]$^+$ species or failure of [LAH]$^-$ to deliver a second hydride equivalent.

Scheme 2.7: Decomposition pathways of 2 resulting from inertness to [LBH]$^+$ or second equivalent of [LAH]$^-$

In order to probe the hydride affinity of 1, a series of stoichiometric reductions were carried out. Firstly, stoichiometric reductions were carried out with one equivalent of varying pre-formed trisarylborohydride salts to synthesise the formyl [Fp*CHO] (2) (Scheme 2.8). Secondly reactivity directly from hydrogen was investigated i.e. activating hydrogen with a
base producing the borohydride *in situ* to attempt reduction of 1 to 2 and any further reduced species (Scheme 2.9).

![Scheme 2.8](image)

**Scheme 2.8:** Reduction of 1 using preformed sodium borohydride salts

![Scheme 2.9](image)

**Scheme 2.9:** Reduction of 1 using a FLP and H₂

### 2.3.1 Designing a FLP system: Lewis acidity of the borane

As discussed in the introduction, a FLP describes a bulky Lewis acid and bulky Lewis base that, due to steric hindrance, are prevented from forming a classical adduct.\(^{19,20,21}\) This unquenched reactivity led to the discovery of reversible hydrogen activation which produces proton [LBH]⁺ and hydride [LAH]⁻ equivalents.\(^{19,22}\) It is this H₂ activation that we have attempted to harness in order to deliver hydride and proton equivalents to complex 1. When designing a FLP system for hydrogenation of any substrate three factors must be considered; (i) the extent of hydrogen activation, (ii) the hydride donor capability of the species [LAH]⁻ and (iii) the pKₐ of the acid [LBH]⁺.\(^{23}\) The Lewis acidity of the boron center used in the FLP will directly affect each of these factors. We therefore wanted to investigate the particular Lewis acidity of the borane which will favour hydride transfer from [LAH]⁻ to 1 (Equation 2.1).
Chapter 2  Reduction studies on a cationic iron tricarbonyl complex [Fe(CO)₃(Cp*)][BARF₂₄]

Equation 2.1: Hydride transfer from [LAH]⁻ to [Fp*CO]⁺ 1 produces Fp*CHO 2 and LA

Some work into quantifying the hydride donor capability of various boranes and other main group hydrides has aided in the design of the hydride donors used in this chapter. One example is work from the group of DuBois. They have developed a useful hydride affinity scale for some BX₃ compounds of varying Lewis acidity, allowing a relative comparison of hydride donor capability of the corresponding [HBX₃]⁻ compounds. These relative values are invaluable when designing hydride transfer reactions to substrates of unknown hydride affinity such as complex 1. To do this DuBois has experimentally determined the hydride donor capability of the complex [Rh(dmpe)₂H]. [Rh(dmpe)₂H] was found to have a hydride donor capability equal to that of Li[HBEt₃] (also known as Super-Hydride). Using this relationship, a series of electronic structure calculations on the isodesmic reaction of BX₃ and [HBEt₃]⁻ were carried out. Using those results the hydride affinity of various BX₃ compounds relative to BEt₃ is determined. Since BEt₃ and [Rh(dmpe)₂H] have the same hydride affinity, the values for hydride affinity of BX₃ compounds can be quantified according to the scale in Figure 2.2.

Figure 2.2: Hydride affinity scale of various BX₃ compounds developed by DuBois. The scale shown is taken directly from the article by Du Bois et al. (Reprinted Figure 1 with permission from J. Am. Chem. Soc., 2009, 131, 14454–14465. Copyright (2009) American Chemical Society.)

Another more comprehensive scale for the hydride donor capability of main group hydrides has been established by Heiden. In this case, computational methods were used to determine
the hydride donor capability of main group compounds by calculating $\Delta G^\circ$ for transferring a hydride.

The computational values determined in this study were verified using comparisons to experimentally determined hydride donor capability values e.g. for $[\text{HBEt}_3]^-$, $\Delta G_{\text{H}^-}$ is computed to be 24 kcal/mol agreeing well with the experimentally determined value of 26 kcal/mol. This study allows for useful comparisons between traditional main group hydrides (NaBH₄, LiAlH₄) and borohydrides resulting from sterically bulky boranes often employed in FLP reactions e.g. $[\text{HB(C₆F₅)}_3]^- ([\text{HBArF}_{15}]^-)$. Computational analysis of the hydride donor capability of $[\text{HBarF}_{15}]^-$ yields a hydride donor ability of 65 kcal/mol, which is a $\Delta G_{\text{H}^-}$ value 15 kcal/mol higher than $[\text{BH}_4]^-$ meaning it is a poorer hydride donor. The hydride donor ability of $[\text{BH}_3\text{CN}]^-$ is determined to be 68 kcal/mol. It has already been reported that $[\text{BH}_4]^-$ (50 kcal/mol) is capable of reducing complex 1.⁴ It is also known that $[\text{BH}_3\text{CN}]^- (68$ kcal/mol) is not capable of donating a hydride to complex 1. It was therefore envisaged from the outset that to prompt FLP mediated hydrogenation, activation and subsequent reduction of 1 use of a more electron rich borane would be necessary. The more electron rich borohydrde $[\text{HBPh}_3]^-$ has been calculated to have a $\Delta G_{\text{H}^-}$ of 36 kcal/mol which is less than the $\Delta G_{\text{H}^-}$ of the commonly used ‘strong’ reducing agent LiAlH₄ at 43 kcal/mol.⁹ The relatively poor hydride donor capability of $[\text{HB(C₆F₅)}_3]^- $ is not unsurprising and is attributed to the electron withdrawing nature of the pentafluorophenyl groups, increasing the Lewis acidity of the boron center and its hydride affinity.

**Figure 2.3:** Hydride donor scale developed from computational calculations. The figure is taken directly from the article published by Heiden et al.¹⁵ (Reprinted with permission from *Organometallics*, 2015, 34, 1818–1827. Copyright (2015) American Chemical Society.)

Recently much work has been done to develop less Lewis acidic boranes which are still capable of heterolytically splitting H₂ together with a base. This results in borohydrides with increased hydride donor capability. A series of electronically tuned boranes derived from BArF₁₅ have been synthesised.²⁷,²⁸ Sequential removal of electron withdrawing fluorine substituents provide
more electron rich boranes such as B(2,6-F2-C6H3)3 (BArF6), B(2,4,6-F3-C6H2)3 (BArF9) and B(p-(C6H4F))3 (Figure 2.4). Similarly, Stephan had already shown as early as 2007 that the known electron rich borane BPh3 can activate hydrogen with P"Bu3 [pK_a (H2O) 11.4] as base.29,30

![Figure 2.4: Series of boranes with varying electron density determined by number of fluorine substituents on the aryl ring](image)

### 2.3.2 Synthesis of trisarylboranes

In order to investigate the hydride affinity of 1, a series of trisarylboranes of varying Lewis acidity have been synthesised via modified literature procedures.27,28 As is common for many trisarylboranes and tetraarylborates, synthesis can be achieved via a methathesis reaction of a boron trihalide and an organolithium reagent.31 The archetypal FLP Lewis acid, B(C6F5)3 is synthesised from nucleophilic addition of MgBrC6F5 or LiC6F5 to either BF3·OEt2 or BCl3. Similarly, the commonly used non-coordinating anion [BArF24]– is synthesised via reaction of [3,5-bis(trifluoromethyl)phenyl]MgX (X = Cl or Br) with NaBF4 to form the complex NaBArF24.32 The same general methods can be employed to synthesise other modified BArF15 boranes such as BArF9 and BArF6.

Alcarazo reported the synthesis of B(2,6-F2-C6H3)3, BArF6 and B(2,4,6-F3-C6H2)3, BArF9. In both cases the published procedure was found not to be reliable in our hands.27 A modified
procedure was therefore developed after multiple attempts at synthesising both boranes. Unfortunately, BArF$_6$ was never obtained cleanly; although pristine by $^1$H and $^{11}$B NMR spectroscopy a 10 % impurity in the $^{19}$F NMR spectrum was always apparent. Scheme 2.10 details the successful procedure used to achieve pure BArF$_9$. After initial reaction with the Grignard $^3$PrMgCl, 2,4,6-trifluorobenzene and BF$_3$.OEt$_3$, a mixture of Mg salts and the borane-THF adduct is obtained. In order to remove the Mg salts a 12-hour reflux in heptane followed by hot filtration and solvent removal is necessary. The borane-THF adduct can be reacted with Me$_2$SiClH to produce the free borane. This final purification step was detailed by Paradies in a separate route published solely for BArF$_6$.\textsuperscript{28} The crude borane can be crystallised using a hexane/dichloromethane layer and isolated as a white, crystalline solid on a multi-gram scale in overall 55 % yield (2 steps).

\begin{center}
Scheme 2.10: Modified literature procedure for the synthesis of BArF$_9$
\end{center}

The most electron rich borane, BPh$_3$ required a comparatively straightforward synthesis published by Brown \textit{et al.} from Mg metal and BF$_3$.OEt$_2$ in diethyl ether, resulting in near quantitative yield of BPh$_3$.\textsuperscript{33} Likewise, BArF$_{15}$ was synthesised according to a published procedure.\textsuperscript{34} Further attempts at BArF$_6$ syntheses were deemed not worthwhile given the Hammett parameter of a \textit{para}-F substituent is 0.02.\textsuperscript{35} This low value was deemed unlikely to have significant effects on the Lewis acidity of the boron centre and as such there is little to suggest BArF$_6$ would have different H$_2$ activation and hydride donor capability when compared to BArF$_9$.

\textbf{2.3.3 Synthesis of trisarylborohydride salts}

Following synthesis of the parent boranes, the \textit{tris}arylborohydride salts were synthesised easily using hydride addition from the strong hydride donor NaBHEt$_3$. Given the increased Lewis acidity of the \textit{tris}arylborane, hydride transfer from NaBHEt$_3$ takes places readily at room temperature in toluene (Scheme 2.11). The salts precipitate from the toluene solution and can
be collected by filtration and washed with pentane to remove residual triethylborane. Each borohydride salt shows a doublet in the $^{11}$B NMR spectra for the B-H bond; $^{11}$B (CD$_2$Cl$_2$), $\delta$ (ppm) = Na[HBPh$_3$] −8.7, Na[HBArF$_9$] −24.7, Na[HBArF$_{15}$] −24.2 (Figure 2.5).

\[
\begin{align*}
\text{Ar} & \quad \text{Ar} + \text{NaBHEt}_3 \xrightleftharpoons[96-98 \%]{\text{RT, PhMe}} \text{BEt}_3 \\
\text{Ar} = \text{Ph}, \text{C}_6\text{F}_3\text{H}_2, \text{C}_6\text{F}_5
\end{align*}
\]

**Scheme 2.11:** Synthesis of borohydride salts using NaBHEt$_3$ in toluene

**Figure 2.5:** $^{11}$B NMR spectra in CD$_2$Cl$_2$ at room temperature of trisarylborohydride salts, from bottom: Na[HBArF$_{15}$], Na[HBArF$_9$] and Na[BHPPh$_3$]

2.3.4 Reactivity of sodium trisarylborohydride salts with [Fp*CO][BArF$_{24}$] (1)

As previously discussed information on the hydride affinity of 1 is necessary when designing a suitable FLP hydrogenation system. To determine this, it is possible to react 1 with each borohydride salt and look for evidence of hydride transfer (Scheme 2.12).
Chapter 2  Reduction studies on a cationic iron tricarbonyl complex [Fe(CO)_3(Cp*)][BArF_{24}]

Scheme 2.12: Addition of [HBAr_3]^- to 1 to form the formyl 2; X = BArF_{24}, Ar = Ph, C_6F_5H_2, C_6F_5

As discussed, this formyl has a limited lifetime at room temperature and as such hydride transfer is also evidenced by the formation of [Fp*H] and [Fp*2] (Scheme 2.13). Both [Fp*2] and [Fp*H] are known, characterised compounds and can be easily identified by ^1H NMR spectroscopy.\(^{3,7}\)

Scheme 2.13: Addition of one equivalent of [HBAr_3]Na to produce 2, [Fp*H] and [Fp*2] at room temperature

The solvent chosen for all the reductions studies discussed in Chapter Two is 1,2-difluorobenzene (DFB). This solvent was chosen for three main reasons; firstly, it provides solubility for all the salts used in these investigations. Secondly, it was envisaged that DFB would be an ideal solvent to carry out FLP hydrogenation reactions since DFB is polar and should allow for the stabilisation of charged species such as [LBH]^+ and [LAH]^-, which is advantageous in FLP reactions. DFB has a dielectric constant (\(\varepsilon\)) of 9.8 which is very similar to CH_2Cl_2 (8.95) which has been used in many FLP reactions. DCM however, will react with
[Fp*H] and other hydridic sources readily whereas DFB will not react with relatively non-polar hydrides such as [Fp*H]. So thirdly, it eliminates the possibility of reaction with reduced species and masking of conversions. As a control reaction, 1 was reduced with one equivalent of NaBH₄ in the chosen reaction solvent, 1,2-difluorobenzene (DFB) to give the formyl 2 in conversion of 10% after 0.5 hours at room temperature as evidenced by a singlet in the ¹H NMR at δ 13.6 ppm. Additionally 20% was converted to [Fp*H] and the rest remains as unreacted 1 (Scheme 2.14). Conversions to 2 or [Fp*H] do not increase after this time-point.

Scheme 2.14: Addition of one equivalent of NaBH₄ in DFB at room temperature produces 10% of 2; X = BArF₂₄

BArF₁₅ is the archetypal Lewis acid used for FLP hydrogenations of a variety of substrates including weakly basic substrates such as imines and ketones.¹⁹,³⁶,³⁷ The strongly Lewis acidic center activates H₂ with a variety of strong to weak bases and most recently has been shown to activate H₂ with the weakly basic solvent THF (pKₐ < −2.0).³⁸,³⁹,⁴⁰ The strongly Lewis acidic boron center renders the borohydride derived from this borane a weak hydride donor. Calculations carried out by Heiden et al. found ΔG_H⁻ for [HBArF₁₅]⁻ is 65 kcal/mol.²⁶ It has been previously reported experimentally that NaBH₃CN cannot deliver hydride to 1 ([BH₃CN]⁻ (ΔG_H⁻ 68 kcal/mol)).⁹ It was therefore predicted that Na[HBArF₁₅] would not deliver hydride to 1 and this was confirmed experimentally (Scheme 2.15). The reaction was heated to 90 °C for 12 hours and the lack of any new species in the ¹H NMR along with the remaining [B-H] resonance in the ¹¹B NMR, confirm Na[HBArF₁₅] is not a sufficiently strong hydride donor to donate to 1.
Scheme 2.15: Neither Na[BH$_3$CN] or Na[HBArF$_{15}$] deliver hydride to complex 1.

The strength of the hydride donor used to deliver hydride to 1 must have a $\Delta G_{\text{H}}$ less than 65 kcal/mol. The more electron rich borane BArF$_9$ is not listed in the calculations carried out by Heiden et al.$^{26}$ however we can roughly compare its electron density as being midway between BArF$_{15}$ and BPh$_3$. [HBPh$_3$]$^-$ has a calculated $\Delta G_{\text{H}}$ value of 36 kcal/mol, given that [BH$_4$]$^-$ reduces 1 it was predicted that Na[HBArF$_9$] should be a strong enough hydride donor to deliver hydride to 1. Again this was confirmed experimentally with the addition of one equivalent of Na[HBArF$_9$] to 1 in DFB at room temperature immediately (initial time point ca. 30 minutes) resulting in 10% conversion to 2 as evidenced by the characteristic singlet at $^1$H $\delta$ 13.6 ppm and 8% conversion to the decarbonylated product [Fp*H] ($^1$H $\delta$ –11.7 ppm, s) (Scheme 2.16). Subsequent monitoring of the reaction by $^1$H and $^{11}$B NMR indicate that conversions to 2 do not increase after 0.5 hours, but gradual decomposition from 2 to [Fp*H] occurs.

Scheme 2.16: Addition of [HBArF$_9$]$^-$ to 1 at room temperature results in 10% conversion to formyl 2 and 8% [Fp*H]; $X^-$ = BArF$_{24}$

These results indicate that the removal of two fluorine substituents from each aryl substituent on [HBArF$_{15}$]$^-$ imparts enough electron density onto the boron center to allow for favourable
hydride delivery to 1. Since [HBPh₃]⁻ is 7 kcal/mol ‘more reducing’ than LiAlH₄ (ΔGₜₐₐₜ = 43 kcal/mol) which has been used previously by the Davies group in stoichiometric reduction studies of more electron rich carbonyl complexes.⁴¹ This and our previous results indicated to us that [HBPh₃]⁻ should deliver a higher conversion to 2 and subsequently [Fp*H] when compared to the results seen with the reduction of 1 with [HBArF₉]⁻; this is what we observe to be the case experimentally. On addition of one equivalent of NaBHPh₃ to 1 at room temperature conversion is immediately observed (< 0.5 hours) (using ¹H NMR relative integration) to 2 (73 %) and [Fp*H] (< 5 %), with only 26 % remaining as unreduced 1 (Figure 2.6 & Scheme 2.17). If the reaction is left at room temperature, after 12 hours no further reduction of 1 is observed but 2 slowly converts to [Fp*H] which after this time now makes up 47 % of the reaction mixture while the formyl 2 is still present at 16 %. After 12 hours at room temperature, trace amounts (< 5 %) of [Fp*₂] are also observed (Figure 2.6).

Scheme 2.17: Results of the reduction of 1 with [HBPh₃]Na at 0.5 hours and 12 hours
Chapter 2  Reduction studies on a cationic iron tricarbonyl complex \([\text{Fe(}\text{CO})_3(\text{Cp*})][\text{BArF}_{24}]\)

**Figure 2.6:** $^1$H NMR spectrum at room temperature, of reaction of \(\text{I}\) with Na[HBP\(_\text{H}_3\)] in DFB at 0.5 hours (\([\text{Fp}^*\text{H}]\) is seen at trace conversions at $^1\text{H} \delta 1.76$ ppm)

**Figure 2.7:** $^1$H NMR in DFB expanded into Cp* region – reaction of \(\text{I}\) with Na[HBP\(_\text{H}_3\)] after 12 hours at room temperature
Chapter 2  Reduction studies on a cationic iron tricarbonyl complex [Fe(CO)₃(Cp*)][BArF₂₄]

It was envisaged from these results that if a Lewis base of appropriate strength was incorporated into an FLP hydrogenation of 1, observation of further reduced species such as a hydroxymethyl complex (3) and methyl complex (4) should be possible via protonation from the [LBH]⁺ species. Furthermore, confirmation of the stability of formyl 2 in these reactions indicated that DFB was in fact a good solvent choice for further hydrogenation studies. From the stoichiometric addition of the trisarylborohydride salts, it has been found that both [HBArF₉]⁻ and [HBPh₃]⁻ have sufficient hydride donor capabilities to reduce the transition metal carbonyl complex 1. ¹¹B NMR spectroscopy shows that in both cases, the boranes BPh₃ and BArF₉ do not coordinate to the formyl 2. In each case after hydride addition to 1, the ¹¹B NMR spectrum shows a doublet for the B-H bond (HBPh₃⁻ δ −8.7 ppm, HBArF₉⁻ −24.7 ppm), broad singlets for BPh₃ (δ 68.3 ppm) and BArF₉ (δ 60.4 ppm), and a sharp singlet for the counter-ion BArF₂₄⁻ (δ −6.0 ppm).

2.4 FLP hydrogenation studies of [Fp*CO][BArF₂₄]

The results of the stoichiometric addition of trisarylborohydride salts with 1, discussed in Section 2.3, indicated that both BArF₉ and BPh₃ may be capable of reducing 1 directly from hydrogen in tandem with bases of appropriate strength. Although BPh₃ is the strongest hydride donor it will require a stronger base for dihydrogen cleavage resulting in a weaker acid [LBH]⁺ source. A sufficiently strong acid is essential for further proton-mediated reduction past the formyl 2, so it is advantageous to attempt reduction with the strongest possible Lewis acid, allowing for the use of a weaker base and therefore conjugate acid of lower pKₐ. BArF₉ is a significantly stronger Lewis acid than BPh₃ and should therefore allow dihydrogen cleavage with bases with a wider range of pKₐ values. Previous reports of protonation of similar species [Fe(CH₂OR)(CO)(Cp*)] (R = H, alkyl) have occurred with acids of pKₐ 0 to −2. It is also worth noting that formyls themselves have a tendency to disproportionate resulting in self reduction. Therefore achieving the formyl itself via initial hydride transfer from the reductant is a key step in developing a catalytic cycle. To achieve the formyl 2 in a high concentration in solution both hydrogen activation and hydride transfer from [LAH]⁻ should be fast with regards to decomposition i.e. decarbonylation and radical decomposition (Scheme 2.1). Fast protonation from [LBH]⁺ will also be desired to facilitate reactivity before decomposition; the higher the concentration of 2 the faster reactivity with [LBH]⁺ can occur.
2.4.1 FLP hydrogenation of 1 using BArF₉, base and hydrogen

Alcarazo has reported the hydrogenation of alkylidene malonates by employing BArF₉ and DABCO (pKₐ 8.8). In their study they elude to the fact that these transformations occur via a cooperative approach in which the [HDABCO]+ hydrogen bonds with the weakly basic substrate and hydride transfer is the rate determining step. In previous reductions Alcarazo et al. used BArF₁₅ and they confirm a faster rate of hydride transfer on moving to the more electron rich borane. They had previously confirmed this mechanism by reacting their substrate sequentially with the borohydride K[HBArF₁₅] and then DABCO.HCl. The activation of H₂ is seen spectroscopically with a doublet at $^{11}$B δ -25.6 ppm for the complex which is in agreement with the shift seen for the complex Na[HBArF₉]. There is no information on whether the B-H doublet resonance can be observed at room temperature in solution. Paradies has reported the combination of DABCO, BArF₆ and H₂ to afford the hydrogenation of nitroolefins and acrylates. Hydrogen activation with the weaker bases 2,4,6-trimethylpyridine (2,4,6-collidine) [pKₐ (H₂O) 7.4] and 2,6-dimethylpyridine [2,6-lutidine, pKₐ (H₂O) 6.6] is also documented with BArF₆. The stronger bases tBu₃P and TMP prompt H₂ activation that can be observed spectroscopically in the solid state as the FLP salts [Hbase][HBArF₆] with doublets.
for the B-H at $^{11}$B δ −24.6 and −23.6 ppm respectively. Paradies reports that the weaker bases 2,4,6-collidine and 2,6-lutidine do not facilitate H₂ activation that can be observed spectroscopically nor in a manner in which the salts [Hbase][HBArF₆] are isolable, but they do hydrogenate the substrates.²⁸ This indicates that with these weaker bases hydrogen activation is occurring but highly reversible with $\Delta G = 0$ – therefore lower concentrations of B-H are present in solution.⁴²

With the knowledge that a range of nitrogen bases afforded successful hydrogenation of a variety of weakly basic substrates with BArF₉ and BArF₆, it was deemed logical to attempt hydrogenation of 1 using these systems. If weaker bases such as 2,4,6-collidine and 2,6-lutidine (2,6-lut) can activate H₂ with BArF₆ it was expected that H₂ activation should occur with BArF₉. Stronger bases such as tetramethylpiperidine (TMP) were also investigated, however, it was an aim to employ weak bases to provide the most strongly acidic [LBH]⁺ source. To test this hypothesis an initial hydrogenation was attempted with 1, BArF₉ and 2,6-lutidine under an atmosphere of H₂ (4 bar in DFB) (Scheme 2.19).

Scheme 2.19: Initial hydrogenation of 1 using 2,6-lutidine, BArF₉ and H₂ (4 bar) in DFB

Prior to this hydrogenation and to act as a control, a mixture of BArF₉, 2,6-lutidine and H₂ in DFB was monitored by $^1$H and $^{11}$B NMR at room temperature (< 0.5 – 12 hours) and 60 °C (< 0.5 – 12 hours). Immediately (≤ 0.5 hours) at room temperature H₂ activation is observed as evidenced by a doublet for the new B-H bond at $^{11}$B δ −24.5 ppm, accompanied by a broad singlet for the borane at δ 60.4 ppm and a second broad singlet at −4.0 ppm (Figure 2.8). This indicates reversible BArF₉-2,6-lut adduct formation and the broadening of both $^{11}$B resonances indicates the adduct is in exchange with the free borane.⁴³
Given the evidence for hydrogen activation, a reaction was carried out according to Scheme 2.20 (vide supra). Immediately (10 minutes) at room temperature evidence for H₂ activation is observed with a borohydride resonance in the ¹¹B NMR at δ −24.5 ppm and a singlet for the formyl 2 at ¹H δ 12.75 ppm, which curiously is lower than the resonance (¹H δ 13.6 ppm) observed for 2 resulting from addition of preformed Na[BHArF₉] to 1. This difference in shift indicates a possible interaction between the formyl and another species present in solution. It is possible that the Lewis acid BArF₉ is weakly interacting with the formyl however there is no supporting evidence for this by ¹¹B NMR spectroscopy. Conversion to the formyl species is low (< 5 %), however at this time-point no [Fp*H] is observed. The reaction was monitored for a further 12 hours at room temperature, during which time neither the concentration of 2 increases nor the intensity of the signals for [Fp*H] and no other products were observed in the ¹H or ¹¹B NMR spectra during this time. Given the low conversion to 2 and the discrepancy in the ¹H NMR shift, it was deemed necessary to provide unambiguous evidence that the peak at ¹H δ 12.75 ppm was in fact due to the hydrogenation of 1 producing the formyl 2. To do this a sample of 1 was labelled with ¹³CO using a Toepler line. The ligands were thermally exchanged.
in THF leading to ca. 20 % $^{13}$C enrichment (indicated by $^1$H relative integration), which is sufficient to observe coupling to $^{13}$C in the $^1$H NMR spectrum. Figure 2.9 shows the $^{13}$C-$^1$H coupling in the formyl complex 2, taken after 0.5 hours at room temperature in in the reaction of 1 with BArF$_9$/2,6-lut and H$_2$ (4 bar). The singlet δ 12.75 ppm for the uncoupled proton (1H-$^{12}$C) can be seen along with a doublet at δ 12.75 pm with coupling of $J = 145$ Hz, characteristic of formyl $^{13}$C-$^1$H coupling. This experimental value can be compared to the theoretical value for $^{13}$C-$^1$H coupling, derived from the percentage ‘s’ character of the carbon centre and the applied frequency; for an sp$^2$ hybridised carbon ($J = 0.33 \times 400$ Hz) the expected value is 132 Hz.

![Figure 2.9: $^1$H NMR spectrum after 0.5 h at room temperature, of the hydrogenation of 1 using BArF$_9$/2,6-lut and H$_2$ (4 bar) in DFB](image)

If the labelled sample is left at room temperature, [Fp*H] begins to form evidenced via a doublet at $^1$H δ –11.8 ppm. The results of the labelling of 1 indicated that the formyl 2 was responsible for the resonance at $^1$H δ 12.75 ppm. 2 was formed from transfer from [HBArF$_9$]$^-$ produced by heterolytic H$_2$ activation with 2,6-lutidine. In this reduction beyond the formyl 2 is not observed. When the reaction is heated at 60 °C for 1 hour, the resonance for 2 disappears completely, converting to [Fp*H]. This indicates that 2 was inert to reaction with [H-2,6-lut]$^+$ and that elevated temperatures accelerate decarbonylation. The fact that higher temperatures
facilitate the decomposition of 2 (if left unreacted) is expected given its limited stability at room temperature (as shown in the results presented here and by Astruc) (Scheme 2.20).^{4}

**Scheme 2.20:** Results from the hydrogenation of 1 using BArF$_9$/2,6-lut and H$_2$

To further investigate the hydrogenation of 1 and to determine if these results applied to other bases; a series of hydrogenation reactions were carried out using a variety of bases according to Scheme 2.21. The conversions are measured by integration of the $^1$H NMR Cp* peaks for each species: 1 δ 1.94 ppm, 2 δ 1.63 ppm, [Fp*H] δ 1.79 ppm and [Fp*$_2$] δ 1.60 ppm. The NMR integral conversions are summarised in Table 2. Time points of 12 hours at room temperature are used as each of the systems appears to reach maximum conversion to 2 at this point. Each of the reactions is heated and conversions to species 2, [Fp*H] and [Fp*$_2$] are given after 12 hours of heating. Time points were taken at shorter intervals however no appreciable difference is seen in these times.
Chapter 2  Reduction studies on a cationic iron tricarbonyl complex \([\text{Fe(CO)}_3(\text{Cp}^*)][\text{BArF}_{24}]\)

Scheme 2.21: General scheme for hydrogenation reactions of 1 with various bases

![Scheme 2.21](image)

The results from Table 2 show 1 can be reduced directly from hydrogen using BArF₉ and a variety of relatively weak bases however the results show that proton-mediated reduction beyond 2 has not been achieved. By 12 hours at room temperature all reactions had reached a steady state concentration of 2 and after this, 2 decomposes via decarbonylation to \([\text{Fp}^*\text{H}]\) or via radical decomposition to \([\text{Fp}^*\text{2}]\), which can be accelerated upon heating. This indicates two things (i) hydride addition from \([\text{HBArF}_9^-]\) to 1 is intially fast then slows rapidly, (ii) formyl 2

<table>
<thead>
<tr>
<th>Bases in order of increasing pKₐ</th>
<th>(1/\text{BArF}_9/\text{base/H}_2 \text{ (4 bar)}): NMR integral conversions</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT, 12 hours</td>
<td>60 °C, 12 hours</td>
</tr>
<tr>
<td></td>
<td>2 ( (%) )</td>
</tr>
<tr>
<td>2,6-lutidine</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>2,4,6-collidine</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>DABCO</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>TMP</td>
<td>&lt; 5</td>
</tr>
</tbody>
</table>

Table 2: Conversions (\%) to reduced species from hydrogenation using BArF₉ and various bases with H₂ (4 bar).
is inert to the $[\text{LBH}]^+$ species formed from all of the bases listed in Table 2, i.e. the pK$_a$ of each is too high. In addition, hydride transfer from $[\text{HBArF}_9]^{-}$ to 1 is slow and results in a low steady state concentration of 2, and subsequently the products of decomposition $[\text{Fp*H}]$ and $[\text{Fp*}_2]$. Importantly, the borohydride resonance is observed indefinitely at room temperature indicating an equilibrium between $[\text{HBArF}_9]^{-}$ and 2 which lies far towards the borohydride (Scheme 2.22).

**Scheme 2.22:** Reaction pathways at room temperature in the hydrogenation of 1 using BArF$_9$ as Lewis acid

If the reaction is heated, hydride transfer is favoured and the species 2 is formed transiently in higher conversions resulting in higher concentrations which subsequently rapidly decomposes to $[\text{Fp*H}]$ and $[\text{Fp*}_2]$ (Table 2, *vide supra*). The identity of the base does not appear to have a significant impact on the products formed in the 1/BArF$_9$ hydrogenation reactions. This is indicated by similar $^{11}$B NMR spectra before and after H$_2$ addition, in each case. Before H$_2$ addition and in the presence of base (TMP, 2,6-lut, 2,4,6-collidine or DABCO) the free borane BArF$_9$ is observed as a broad singlet at 60.4 ppm. On addition of hydrogen, a broad singlet appeared at $\delta$ –3.9 ppm with the doublet for the borohydride also observed at $\delta$ –25.4 ppm. The
species at $\delta -3.9$ ppm shares the same shift as the 2,6-lut-BArF$_9$ adduct (vide infra) ($\delta -4.0$ ppm) which indicates each of the bases is reversibly forming an adduct with the borane.

2.4.2 FLP hydrogenation of 1 using BPh$_3$, base and hydrogen

To overcome the equilibrium that appears to form between 2 and [HBArF$_9$]$^-$, hydrogenation reactions were attempted with the more electron rich borane BPh$_3$. It was envisaged that BPh$_3$ would show faster hydride transfer to 1 if hydrogen activation could be achieved and being more electron rich it should also not reach an equilibrium with 2. However, in the case of such an electron rich borane, hydrogen activation was expected to be a significant challenge. Stephan et al. reported the heterolytic cleavage of hydrogen using $\text{P}^\text{tBu}_3$ ($pK_a$ 11.4) and BPh$_3$ in toluene, precipitating the salt [HP'$\text{tBu}_3$][HBPh$_3$]. The report also gave evidence for the borohydride species in solution, evidenced by a doublet for the B-H bond at $^{11}$B $\delta -6.9$. Using this evidence it was therefore predicted that an FLP system using BPh$_3$/P'$\text{tBu}_3$ would be able to directly hydrogenate 1 with H$_2$. When the dihydrogen activation using BPh$_3$ and P'$\text{tBu}_3$ was attempted by us in toluene, according to the procedure used by Stephan et al., a white solid (presumed to be [HP'$\text{tBu}_3$][HBPh$_3$]) was obtained. However, dihydrogen activation was never observed by us in solution. Upon redissolution of the white precipitate in DCM, the starting materials BPh$_3$ and P'$\text{tBu}_3$ were observed cleanly by $^{11}$B, $^{31}$P and $^1$H NMR spectroscopy along with H$_2$ in the $^1$H NMR spectrum. These results indicate that BPh$_3$ and P'$\text{tBu}_3$ are capable of activating hydrogen in a non-polar solvent due to the favourable kinetic effect of salt precipitation. This is supported by Papai’s calculations which give $\Delta G = 18.2$ kcal/mol for the cleavage of dihydrogen using BPh$_3$ and P'$\text{tBu}_3$ indicating an equilibrium that lies far towards the FLP (Equation 2.3).

\[
\text{BPh}_3 + \text{P'}\text{Bu}_3 \xrightleftharpoons[1 \text{ atm, } 25 \text{ °C}]{} \text{H}_2 [\text{HPPh}_3][\text{HP'Bu}_3]
\]

**Equation 2.3**: Hydrogen activation using BPh$_3$ and P'$\text{tBu}_3$

Since H$_2$ activation using BPh$_3$/P'$\text{tBu}_3$ was reported in toluene, it was our initial aim to confirm if activation was possible in our chosen solvent DFB; it was predicted that H$_2$ activation should be favoured in DFB over toluene, given its increased polarity. If H$_2$ (4 bar) is added to a mixture of BPh$_3$ and P'$\text{tBu}_3$ in DFB, no indication of hydrogen activation is observed at room temperature as observed by $^1$H, $^{11}$B and $^{31}$P NMR spectroscopy. Curiously there was also no evidence of hydrogen activation in THF at room temperature and, when the reaction is heated...
in this solvent, decomposition of the borane appears to occur via aryl migration to form \([\text{BPh}_4]^–\) and \(\text{H-BPh}_2\), which are observed \(\delta = -6.4\) ppm and \(\delta = 53.3\) ppm respectively, in the \(^{11}\text{B}\) NMR spectrum. However, in DFB, NMR spectroscopy analysis after heating for 12 hours at 60 °C, allows for the observation of the phosphonium \([\text{HPtBu}_3]^+\) at \(^{31}\text{P}\) \(\delta = 60.2\) ppm indicating dihydrogen activation had occurred at very low concentrations; the phosphonium was present at 6 % conversion after this time. In order to determine whether transient hydrogenation of \(\mathbf{1}\) could occur, a hydrogenation experiment was set up with \(\text{BPh}_3\) and \(\text{PtBu}_3\) under \(\text{H}_2\) (4 bar). The reaction was monitored intermittently between 2 and 12 hours at room temperature; no evidence for hydrogen activation is observed along with no reduced products of \(\mathbf{1}\). On heating the reaction for 12 hours at 60 °C, \(^1\text{H}\) NMR spectrum shows evidence for the phosphonium \([\text{HPtBu}_3]^+\), 5 % conversion to \([\text{Fp*H}]\) and trace conversion to \([\text{Fp*}_2]\), formyl \(\mathbf{2}\) is never observed (Figure 2.10). After leaving the reaction at room temperature for a further 2 weeks, the conversions do not change. Curiously even heating the reaction at 80 °C for up to 12 hours does not affect the reduction yields.

![Figure 2.10](image)

**Figure 2.10:** \(^1\text{H}\) NMR (of the Cp* region \(\delta = 1–2\) ppm) spectrum of the hydrogenation of \(\mathbf{1}\) using \(\text{BPh}_3\), \(\text{PtBu}_3\) and \(\text{H}_2\) (4 bar) in DFB at room temperature, after heating at 60 °C for 12 hours

It appears that \(\text{H}_2\) activation may occur with the FLP \(\text{BPh}_3\) and \(\text{PtBu}_3\), however, the equilibrium lies far towards the FLP which makes the rate of hydride transfer to \(\mathbf{1}\) very slow resulting in only low concentrations of hydride being observed with heating. Given that the salts formed as a result of hydrogen activation will be soluble in our highly polar reaction medium, there is no
additional lattice enthalpy factor to favourably influence the equilibrium of hydrogen activation. If the equilibrium lies too far towards the left, reduction of 1 will not occur at a fast enough rate. It was envisaged that a stronger nitrogen base such as Et$_3$N [pK$_a$ (MeCN) 18.82]$^{44}$ could push the equilibrium towards H$_2$ activation. A HD scrambling experiment was carried out to determine if this FLP was capable of activating HD and as such H$_2$; gratifyingly under HD BPh$_3$ and Et$_3$N was found to form a 1:1:1 mixture of H$_2$:HD:D$_2$, indicating its ability to activate H$_2$. No borohydride resonance is observed in the $^{11}$B NMR spectrum during activation. Other work within the Ashley group also determined that the FLP BPh$_3$/Et$_3$N could transiently hydrogenate a number of organic carbonyl substrates. The hydrogenation of 1 under 4 bar of H$_2$ was pursued with this FLP system, again no evidence for H$_2$ activation at room temperature was observed by $^{31}$P, $^{11}$B or $^1$H NMR spectroscopy analysis. The reaction was heated once again at 60 $^\circ$C for 12 hours and the reduction results were analogous to those previously reported for the P$^\text{3}$$^\text{Bu}$/BPh$_3$ system i.e. minimal conversion (< 5 %) to [Fp**H]. The results seemed curiously unsuccessful, given the evidence of hydrogen activation in solution by the observation of the phosphonium [H$^\text{p}$Bu$_3$]$^+$, in conjunction with the fast hydride transfer observed from Na[BHPh$_3$] to 1 (demonstrated $\text{vide infra}$); we hypothesised that some other factor might be favouring faster hydride addition to 1 in the Na[HBPh$_3$] reactions.

2.4.3 Role of the secondary Lewis acid, Na$^+$

The stoichiometric reactions of Na[HBAr$_3$] and 1 which were discussed in Section 2.3.4 differ from the FLP hydrogenations by lack of base and Na$^+$. The cooperative action of [LBH]$^+$, through hydrogen bonding to the oxygen in the substrate, was reported by Alcarazo to be essential for the reductions of alkylidene malonates, however this is less likely to occur for a cationic transition metal carbonyl for reasons of basicity and charge.$^{27}$ Rather than the base hindering reduction of 1 it was deemed more likely that Na$^+$ was providing cooperative action to facilitate the reduction of 1. It also seemed possible that an interaction between Na$^+$ and 2 or a disturbance of the interaction of 2 with a borane could be responsible for the discrepancy in NMR shifts for the formyl proton of 2. As previously mentioned, when is 2 formed from the reduction of 1 using sodium trisarylborohydride salts the formyl proton is observed at $^1$H (DFB) $\delta$ 13.6 ppm. When the same species is formed from reduction by [HBArF$_9$]$^-$ in the FLP hydrogenations the formyl proton is observed at $^1$H (DFB) $\delta$ 12.75 ppm. However, it should be considered that this difference could also be down to the equilibrium or exchange with BArF$_9$ in the FLP hydrogenations and the small difference in chemical shift is not enough to draw a conclusion alone. In order to probe this further, a cation exchange was carried out in
order to synthesise [Bu₄N][HBarF₉]. Addition of one equivalent of [Bu₄N][HBarF₉] results in trace conversion to the formyl 2 as evidenced by a singlet at δ 12.75 ppm in the ¹H NMR spectrum. It was deemed necessary to investigate the hypothesis of Na⁺ being active in the reduction. To investigate this, Na⁺ was added in the form of NaBArF₂₄ to a hydrogenation of 1 using BPh₃ and Et₃N under H₂ (4 bar) (Scheme 2.23). NaBArF₂₄ was chosen since the [BArF₂₄]⁻ anion is non-coordinating and allows for study of the effect of free Na⁺ in the reaction mixture.

![Scheme 2.23: Hydrogenation of 1 in the presence of Na⁺](image)

The results of the hydrogenation of 1 in the presence of NaBArF₂₄ are significantly different. Immediately 6 % conversion to 2 is observed, with trace conversions to [Fp*H] and [Fp*₂]. Formyl 2 is observed at ¹H (DFB) δ 13.62. Again, no evidence was provided for reaction with [LBH]⁺ and the ¹¹B spectrum of the reaction mixture shows no evidence for hydrogen activation. The reaction was left at room temperature and the conversions recorded after 12 hours. Conversion to 2 reached 15 %, while [Fp*H] was at 50% with [Fp*₂] at 11 % conversion. The total consumption of 1 is seen after 48 hours at room temperature. This result could be considered the most remarkable since consumption of 1 has not been reported in any other reaction discussed in this chapter, even at elevated temperatures (Figure 2.11). The consumption of [Fp*CO]⁺ implies that Na⁺ is accelerating the rate of hydride transfer to 1.
One plausible hypothesis for the effect of Na$^+$ is that Na$^+$ interacts with the carbonyl oxygen, polarising the C=O bond, making it more susceptible to hydride attack by creating a more electrophilic carbonyl. This particular action could be likened to the hydrogen bonding effect of [LBH]$^+$ on the carbonyl oxygen, reported by Alcarazo (Scheme 2.24).  

Another possibility is that the Na$^+$ is stabilising the formyl produced and this could explain why there is a slight discrepancy in the shifts reported for the formyl proton when observed in FLP hydrogenations vs. sodium trisarylborohydride salt reductions (Scheme 2.25). However,
the formation of [Fp*H] and [Fp*₂] are still observed so if Na⁺ is stabilising 2, the effect is not significant enough to alter the course of the reaction.

A number of reactions were carried out to investigate its role further. It was reasoned that if Na⁺ was stabilising 2 then other alkali metals may have a similar effect and this could perhaps be evidenced via a different chemical shift. The addition of KBArF₂₄ to a FLP hydrogenation of 1 again using BPh₃ and Et₃N under H₂ resulted in analogous conversion to 2 with the formyl proton being observed at ¹H (DFB) δ 13.62 with conversion of around 5 % and trace amounts of [Fp*H] and [Fp*₂] after 0.5 hours at room temperature. Similarly, 1 equivalent of LiBArF₂₄ was added to the hydrogenation of 1 producing similar conversions as seen for NaBArF₂₄ and KBArF₂₄. These results do not indicate a particularly strong interaction between the specific alkali metal and 2 in solution. It is possible that rather than a direct interaction between Na⁺ and 2 a transient complex [2-BPh₃][M] (M = Li, Na, K) is formed, this would explain the lack of change in ¹H chemical shift. However overall the predominant effect of the alkali appears to be the acceleration in the rate of hydride transfer. Further to this, it was reasoned that if Na⁺ is stabilising 2 an effect would also be seen on the hydrogenations of 1 using BArF₉, a base and H₂. If an alkali metal stabilises the formyl complex, it should increase the observed yield of formyl at room temperature since decarbonylation would be slowed. To probe this, NaBArF₂₄ was added to a FLP hydrogenation of 1 using BArF₉, TMP and H₂. The addition of Na⁺ does not have an effect on the conversions result which were recorded for the 1, TMP, BArF₉ and H₂ system in the absence of Na⁺. A reaction was also carried out with 1, Et₃N, BArF₉ and H₂; before the addition of H₂ an adduct is observed in the ¹¹B NMR spectrum at δ – 2.7 ppm. On addition of H₂, the ¹¹B NMR spectrum remains unchanged, in this case no borohydride is observed spectroscopically nor is any formyl species observed in the ¹H NMR. When the reaction is heated the borane appears to decompose giving rise to a new uncharacterised resonance at ¹¹B δ 17.8, but again no reduced nor proton-mediated reduced species are observed in the ¹H NMR spectrum except for trace conversions to [Fp*H]. A control
reaction of BArF$_9$ and Et$_3$N alone shows the new species is independent of the carbonyl 1. This result demonstrates that the effect of Na$^+$ is specific to the reductions employing BPh$_3$ as borane which points to a cooperative action between [HBPh$_3$]$^-$ and Na$^+$ in hydride addition to 1. In fact, when using BArF$_9$ as the Lewis acid, the borane itself may interact with the formyl proton upon hydride addition to 1. If there is an interaction of BArF$_9$ with the formyl, this may stabilise the species and produce a lower chemical shift of 12.75 ppm for the formyl proton in the $^1$H NMR; it is possible that the aforementioned $^{11}$B NMR resonance at $\delta$ -3.9 ppm could be responsible for a species such as the formyl borane [Fp*CHO-BArF$_9$]Na. It appears that although hydride transfer is faster in the case of Na$^+/$/BPh$_3$ there is no particular Lewis acid stabilisation which is not unsurprising given the electrophilicity of BPh$_3$. The very small change in $^1$H chemical shift when using BArF$_9$ vs. BPh$_3$ points to the fact that any stabilisation by BArF$_9$ is minimal and does not affect the overall reactivity of the formyl 2. Unfortunately, in neither case does [LBH]$^+$ appear to interact with the carbonyl oxygen indicating a stronger conjugate acid is necessary for proton mediated reduction of both 1 and 2.

2.4.4 Effect of pressure and syngas

The most promising results achieved in the hydrogenation studies of 1 were 15 % conversion to 2 at room temperature achieved with the FLP BPh$_3$/Et$_3$N in the presence of NaBArF$_{24}$ under 4 bar of H$_2$. The formyl 2 appears to be inert to [Et$_3$NH]$^+$ at ambient temperatures and pressure. We have reported that heating the hydrogenations quickly favours the production of decomposed species [Fp*H] and [Fp*$_2$]. Another challenge of this chemistry is the equilibrium of the hydrogen activation that occurs with an electron rich borane like BPh$_3$; the equilibrium lies towards the FLP hence low concentrations of borohydride are present in solution.

The key to the successful conversion of 1 to useful species is determining the correct conditions for the reactivity of [LBH]$^+$ with 2 to facilitate further reduction before decarbonylation. There are two possibilities for the inertness to [LBH]$^+$, which are not mutually exclusive; (i) the pK$_a$ of [LBH]$^+$ is too high or (ii) the concentrations of the reactive species (2, [LAH]$^-$ and [LBH]$^+$) in solution are too low, resulting in unfavourable reaction kinetics at room temperature. One way to favour the kinetics for hydrogen activation and possibly reactivity is to increase the overall H$_2$ pressure of the system. To probe the effect of increased pressure, the hydrogenation of 1 was carried out with the FLP BPh$_3$/Et$_3$N with NaBArF$_{24}$ under 10 bar of H$_2$. The conversions recorded indicate that the reduction rate is indeed faster with 33 % conversion to 2 after 0.5 hours at room temperature (cf. 6 %, H$_2$ 4 bar), 13 % conversion to [Fp*H] (cf. < 5
Chapter 2  Reduction studies on a cationic iron tricarbonyl complex [Fe(CO)_3(Cp*)][BArF_{24}]

% H_2 4 bar) and trace amounts of [Fp*$_2$]. Total consumption of 1 is observed after 12 hours at room temperature (cf. 48 hours, H$_2$ 4 bar), however the only products observed after 12 hours at room temperature are [Fp*H] and [Fp*$_2$]. The increasing hydrogen pressure has not facilitated a second hydride transfer to 2.

The results from the stoichiometric and FLP hydrogenations discussed in this chapter, clearly show that fast decarbonylation to form the stable hydride [Fp*H], coupled with radical decomposition to the metal-metal dimer [Fp*$_2$], hinder the accumulation of any significant concentration of the formyl 2 in the reaction mixture. This low concentration of species 2 could be responsible for the lack of ensuing reactivity. It could therefore be reasoned that a large excess of CO in the reaction mixture could hinder decarbonylation of 2. In order to investigate the effects of this, FLP hydrogenations were carried under an atmosphere of syngas (CO:H$_2$, 1:3) at 4 bar and 10 bar using the reducing system BPh$_3$, Et$_3$N and NaBarF$_{24}$. Comparative conversions to 2 and [Fp*H] are observed when CO:H$_2$ (4 bar) is used vs. H$_2$ (4 bar) alone after 12 hours (6 % and < 5 % respectively), although the presence of CO appears to prevent the formation of [Fp*$_2$]. There is a noticeable difference in reactivity with longer reaction times; the consumption of [Fp*CO] is noticeably slowed and the stability of 2 increases. After 1 month at room temperature 1 is still observed along with 2 although the majority of the product is still [Fp*H] at 85 % of the final reaction mixture. The presence of a large excess of free CO clearly slows dimer formation and decarbonylation of 2 but it ultimately does not have an effect on the conversion of 2 to other products (Figure 2.12). The presence of CO does not alter the reactivity of 2 with the acid source present, preventing further reactivity.
Chapter 2  Reduction studies on a cationic iron tricarbonyl complex [Fe(CO)$_3$(Cp*)][BArF$_{24}$]

Figure 2.12: $^1$H NMR (Cp* region 1–2 ppm) at 0.5 hours and 12 hours at room temperature, of the hydrogenation of 1 using BPh$_3$, Et$_3$N, NaBArF$_{24}$ under 4 bar CO:H$_2$(1:3)

2.5 Conclusion

1 was chosen as an initial candidate for the study of the hydride donor capability of various borohydrides to facilitate the initial step of CO reduction, formation of a metal formyl. By starting with this carbonyl, it was possible to garner useful information on the behaviour of more electron rich boranes regarding H$_2$ activation and rate of hydride delivery. The feasibility of 1 as a transition metal framework for a syngas conversion cycle was also investigated.

In this chapter, the hydrogenation of 1 directly from hydrogen has been demonstrated with two boranes BArF$_9$ and BPh$_3$. It has been confirmed that the borohydride [HBArF$_{15}$]$^-$, derived from the archetypal FLP borane BArF$_{15}$, is not capable of reducing 1. The effect of a secondary Lewis acid Na$^+$ has been investigated and the evidence presented indicates that the presence of this Lewis acid is likely to accelerate the first step of hydride transfer to form the formyl 2 in FLP hydrogenations using BPh$_3$. By increasing the pressure of H$_2$ faster reaction rates have been achieved but the formyl 2 remains inert to the conjugate acid of the FLP system [LBH]$^+$,
producing ultimately the same final products 2, [Fp*H] and [Fp*2]. A syngas (3:1 H₂/CO) atmosphere has been shown to inhibit decarbonylation and radical decomposition whilst also stabilising the formyl 2, however no change in reactivity is observed.

In all reduction studies of 1, the instability of 2 at room temperature and above coupled with its reluctance to further reduction by reaction with [LAH]⁻ and [LBH]⁺ has prevented observation of any further reduced species. In all experiments discussed in this chapter, hydride delivery to 1 results in formation of only 2, [Fp*H] and [Fp*2]. No hydroxymethyl, methylidene or methyl complexes are observed at room temperature and heating only serves to increase the rate of decomposition of 2 to undesired products. A significant increase in the concentration of borohydride in solution in conjunction with proton transfer from a stronger protonated Lewis base (pKₐ << 9) would be required to see such intermediates. In this case neither of these factors has been achievable. A summary of the reactions involved in the reduction of 1 are summarised in Scheme 2.26.

![Scheme 2.26: Summary of the various reaction pathways present in the hydrogenation reactions of 1](image-url)
For successful reduction, reaction rates \( k_1 \) and \( k_2 \) should be fast to prompt a high concentration of both \( \textbf{2} \) and \([\text{LBH}]^+\) in solution thereby allowing further proton mediated reduction. However, with a weak Lewis acid, which is essential for hydride delivery to \( \textbf{1} \), the equilibrium of \( k_1 \) lies in the left hand side (LHS). This means the rates of decomposition \( \text{via} \) decarbonylation \( k_3 \) and radical reactivity \( k_4 \) are always greater than \( k_1 \) and \( k_2 \) \( (k_1 \approx k_2 < k_4 << k_3) \). When free \( \text{Na}^+ \) is present \( k_2 \) is favoured, but the rate of decarbonylation is still much faster and as such, total consumption of \([\text{Fp}*\text{CO}]^+\) is observed. When a higher pressure of \( \text{H}_2 \) is introduced, \( k_1 \) and in turn \( k_2 \) are clearly increased but the effect is not significant enough to see proton mediated or Lewis acid activated reduction. Without the presence of a sufficiently activating Lewis acid or sufficiently strong proton source, the formyl \( \textbf{2} \) is unreactive towards further reduction. This is analogous to the findings of Astruc in which \( \text{BH}_3 \) was identified as facilitating further addition of hydride equivalents.\(^4\)

The presence of \( \text{CO} \) in a syngas atmosphere appears to hinder radical reactivity, presumably by preventing loss of \( \text{CO} \) from the \( \text{Fp}*\text{CO}^- \) radical. Heat has been found to favour formation of the dimer. Ultimately the results presented in this chapter indicate that the strength of Lewis base needed for \( \text{H}_2 \) activation with an electron rich borane is likely too strong to provide a conjugate acid potent enough for proton transfer from \([\text{LBH}]^+\). It has been shown that \( \textbf{1} \) is not a suitable candidate for hydrogenation studies using our methodology since \( \textbf{2} \) is unstable at elevated reaction temperatures; decomposition is favoured over protonation thereby rendering it unsuitable for homogenous syngas conversion. In the following chapter the use of increasingly electron rich ligands to confer greater stability to the formyl complex, allowing for higher reaction temperatures, will be examined.


2.6 References

Chapter 2  Reduction studies on a cationic iron tricarbonyl complex [Fe(CO)₃(Cp*)][BArF₂₄]

Chapter 3

Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

3.1 Introduction

Phosphine ligands are ubiquitous in organometallic chemistry, being arguably the most important class of spectator ligands.\(^1\) They offer predictable and systematic electronic and steric alterations, allowing for facile complex design along with a highly convenient \(^{31}\)P NMR handle. Like NR\(_3\) compounds, PR\(_3\) compounds possess a lone pair, however this lone pair is less localised due to the increased atomic radius of phosphorous. Their bonding to metal centres involves donation of a lone pair, acting as a \(\sigma\) donor however unlike NR\(_3\) they can also accept electron density as \(\pi\) acids. Their \(\pi\) acidity is dependent on the R substituents. Alkyl phosphines are poor acceptors while aryl and alkoxy substituents offer greater electron withdrawing effects. For PF\(_3\) the \(\pi\) acceptor qualities are equal to that of CO, although while CO uses a pair of \(\pi^*\) orbitals to act as electron acceptors, PR\(_3\) uses P-R \(\sigma^*\) orbitals (Figure 3.1).\(^2\)

![Figure 3.1: Schematic showing orbitals used in \(\pi\) back-bonding to a PR\(_3\) from a metal](image)

Bisphosphine ligands have two lone pairs to donate to a metal centre thereby creating a chelate. Chelating bisphosphine ligands are commonly used when attempting to impart stability to a metal coordination complex. A vast range of bisphosphine ligands have been synthesised including aryl, phosphite and alkyl derivatives.\(^3,4\) Alkyl bisphosphines, although more rarely used, can be easily modified for steric, bite angle and electronics (Figure 3.2) and they are much better \(\sigma\) electron donators than their aryl and alkoxy analogues.\(^5,6,7\)
3.1.1 Use of mono- and bisphosphines for stabilising homogeneous syngas intermediates

Much like the cyclopentadienyl ligand series, significant interest has been placed on the ability of phosphine ligands to stabilise homogeneous syngas conversion intermediates, namely the formyl and methylidene.\textsuperscript{8,9,10} In contrast to the Cp\textsuperscript{R} ligands, the readily tuneable sterics and electronics of phosphines has allowed for more variation and as such more insight into the most suitable environment for the reduction of carbonyl ligands, acting as a model for homogeneous syngas conversion. The electron donating properties of the phosphine ligands, and alkyl phosphines in particular, are credited with an increased metal-carbon bond strength, therefore supressing decarbonylation which directly involves the breaking of this bond in an unstable formyl complex (Figure 3.3).

![Figure 3.3: Schematic showing electron density from filled ‘d’ orbitals being donated to the C-O ligand, increased electron density of ligands on the metal will in turn increase the strength of this interaction](image)

From the early postulation of metal formyl complexes,\textsuperscript{11,12,13,14} their instability has constantly challenged attempts to characterise them. Davies and co-workers have used 1,2-bis(dimethylphosphino)ethane (dmpe) to stabilise a cyclopentadienyl iron carbonyl complex and achieve full reduction to the methyl complex using LiAlH\textsubscript{4} (Scheme 3.1). The authors attributed this reactivity to the increased stability of the formyl [Fe(CHO)(Cp)(κ\textsuperscript{2}-dmpe)]
towards CO loss, when compared to a less electron-rich complex, such as [FpCHO], thereby allowing further reduction to the methyl complex.\textsuperscript{15}

![Scheme 3.1](image1)

**Scheme 3.1:** Reduction of cationic carbonyl complex [Fe(CO)(Cp)(κ²-dmpe)][PF₆] using LiAlH₄ in THF - instead of decarbonylating the formyl remains in solution long enough to be reduced to the methyl complex.

In the same publication Davies highlighted the varying behaviour when the less electron donating, sterically more demanding bisphosphine ligand, 1,2-\textit{bis}(diphenylphosphino)ethane (dppe) is used. On addition of a THF solution of LiAlH₄, the hydride attacks the carbonyl forming the formyl complex, as evidenced by a \textsuperscript{1}H resonance at \(\delta 11.5\) ppm, followed by partial phosphine dissociation and hydride migration to the metal to form the carbonyl hydride [Fe(CO)(κ¹-dppe)(H)] (Scheme 3.2).

![Scheme 3.2](image2)

**Scheme 3.2:** Reduction of cationic carbonyl complex [Fe(CO)(Cp)(κ²-dppe)][PF₆] using LiAlH₄ in THF, the bisphosphine is larger and less electron-rich and therefore readily reverts to a carbonyl hydride species.

This reaction has been studied on numerous occasions and the reduction always results in the dissociation of one arm of the chelating phosphine.\textsuperscript{16,17,18} Importantly, the observation of a characteristic formyl resonance in the \textsuperscript{1}H NMR spectrum confirms that the hydride does not attack the metal directly in the first instance. The group also postulated the likelihood of an equilibrium between the formyl and carbonyl-hydride. If the carbonyl hydride is isolated and left to stand at room temperature in THF, it will disproportionate to the methyl complex and an uncharacterised species, presumed to be a metal-metal carbonyl dimer (Scheme 3.3). It is reasoned that if AlH₃ is present and coordinates to the unbound phosphine, the equilibrium...
between formyl and carbonyl hydride is prevented and as such further reduction to the methyl is possible.

Scheme 3.3: Disproportionation of the carbonyl hydride to the methyl complex and metal-metal carbonyl dimer

Another impressive example of the extent of the stabilising effect of bisphosphines is Brookhart’s characterisation of a methylidene complex $[\text{Fe}(=\text{CH}_2)(\text{Cp})(\kappa^2\text{-dppe})]^+$ at $-80^\circ\text{C}$. Prior to this, iron methylidene complexes had been postulated to exist, but their intrinsic instability precluded their observation. With the use of the dppe ligand, the endo and exo proton resonances for the methylidene are observed using low temperature $^1\text{H}$ NMR (CD$_2$Cl$_2$) $\delta$ 13.89 and 17.29 ppm. This bisphosphine substituted methylidene complex displays a markedly increased stability relative to the dicarbonyl analogue, which disproportionates immediately at temperatures as low as $-90^\circ\text{C}$ (Scheme 3.4).

Scheme 3.4: The dppe ligand imparts sufficient stability to $[\text{Fe}(=\text{CH}_2)(\text{Cp})(\kappa^2\text{-dppe})]^+$ to allow for characterisation

In another example, Astruc uses the monophosphine PMe$_3$ in conjunction with the C$_5$Me$_5$ (Cp*) ligand. The reduction of $[\text{Fe(CO)}_2(\text{Cp}^*)(\text{PMe}_3)]^+$ with NaBH$_4$ at $-80^\circ\text{C}$ in THF with
Chapter 3  Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

subsequent warming to room temperature, gives the methyl complex [Fe(CH$_3$)(Cp*)(PMe$_3$)] in 100 % yield. However when the reaction is conducted at room temperature, PMe$_3$ is lost and 100 % yield of ([Fp*H]) is obtained. This indicates that monophosphines may be significantly inferior when attempting to stabilise a carbonyl complex of the type [Fe(CO)(Cp*)(L)(L)][X]. A bisphosphine has increased kinetic and thermodynamic stability due to the chelate effect. In this example, the increased difficulty in delivering a hydride to an especially electron-rich complex is also highlighted. Although a formyl is observed immediately at −80 °C when reducing [Fp*CO]$^+$ with NaBH$_4$ in THF, warming to −30 °C is required before the appearance of the $^1$H formyl resonance of [Fe(CHO)(Cp*)(PMe$_3$)] ($^1$H δ 14.38 ppm). Similarly, the relatively electron-rich formyl [Fe(CHO)(Cp*)(P$^*$Bu$_3$)] is only observed at −30 °C ($^1$H δ 14.39 ppm) while the less electron-rich formyl [Fe(CHO)(Cp*)(PPh$_3$)] is more readily formed at −40 °C ($^1$H δ 14.26 ppm). Since BH$_3$ will be present after hydride delivery from NaBH$_4$, each of these ‘free’ formyl complexes is observed in the presence of their borane adducts of general formula [Fe(CHO)(Cp*)(PR$_3$)(·BH$_3$)]. While each of the free formyls are observed as doublets at ca. δ 14.0 ppm, the borane adducts produce broad signals at lower chemical shifts of $^1$H (THF-d$_8$) δ 12.4-12.8 ppm.

3.2  Synthesis of $\kappa^2$-bisphosphine iron carbonyl complexes

It has been shown that mono- and bisphosphine ligands can confer stability to cyclopentadienyl iron complexes. This heightened stability has facilitated the observation of typically highly unstable intermediates e.g. electrophilic methyldiene complexes. It seemed logical to synthesise a series of bisphosphine substituted complexes for further carbonyl reduction studies. The major drawback in the [Fp*CO][BArF$_{24}$] reduction studies discussed in Chapter Two was the lack of stabilisation of the generated formyl at room temperature and its inertness to other species including hydride and protonated base. It was envisaged that incorporation of a bisphosphine in a [Fe(CO)(Cp*)(L)(L)]$^+$ framework could impart electron density, combatting both problems and thus aid characterisation of a further reduced species.

3.2.1  Synthesis of complexes of the type [Fe(CO)(Cp*)($\kappa^2$-bisphosphine)][BArF$_{24}$]

A family of sterically and electronically tuned bisphosphine iron carbonyl complexes of the type [Fe(CO)(Cp*)P$_2$][BArF$_{24}$] (P$_2$ = bisalkylphosphine) were synthesised. The bisphosphine ligands were specifically chosen to offer predictable, systematic subtle steric and electronic differences. This ranges from the smallest, least electron-rich ligand 1,2-
Chapter 3  
Reduction studies of bisphosphine substituted cationic iron carbonyl complexes  

*bis*(dimethylphosphino)ethane (dmpe), via 1,2-*bis*(diethylphosphino)ethane (depe), to the most sterically demanding and electron-rich 1,2-*bis*(diisopropylphosphino)ethane (dippe) (Figure 3.4).

**Figure 3.4:** Ligands used to synthesise a family of bisphosphine substituted carbonyl complexes

Although some studies have previously been carried out by Davies on the cation [Fe(CO)(Cp)(κ²-dmpe)]⁺,¹⁶,¹⁷ bidentate alkyl phosphines are relatively under explored for carbonyl reduction chemistry. Most studies have focused on the less electron-rich dppe ligand which has been shown to dissociate easily upon hydride delivery. The monodentate ligands PMe₃ and PPh₃ have also been shown to dissociate, favouring formation of the stable complex [[(Fp*H)]] upon reduction.¹¹

Previously published procedures for complexes of the type [Fe(CO)₂(Cp*)(κ¹-P)][X]²² and [Fe(CO)(Cp*)(κ²-P₂)][X]²³ involve multi step, low yielding syntheses including undesirable photolysis and salt metathesis of the chlorides [Fe(Cl)(Cp*)(κ²-P₂)] under a CO atmosphere. Although a published procedure for the synthesis of [Fe(CO)(Cp*)(κ²-dippe)][BF₄] exists, surprisingly syntheses of the analogues [Fe(CO)(Cp*)(κ²-depe)][X] and [Fe(CO)(Cp*)(κ²-dmpe)][X] have not previously been published. For the same reasons discussed in Chapter Two, the non-coordinating anion BArF₂₄⁻ was chosen as the counteranion for each carbonyl complex. Initially synthesis of [Fe(CO)(Cp*)(κ²-dippe)][BArF₂₄] was attempted following the route reported by Tenorio et al.²³ This procedure relies on the initial synthesis of the paramagnetic complex [Fe(Cl)₂(dippe)] from FeCl₂ published by Girolami and Hermes²⁴ followed by substitution with Cp*Li and finally salt metathesis with NaBF₄ in the presence of CO (in our case NaBArF₂₄ was used in place of NaBF₄) (Scheme 3.5).

**Scheme 3.5:** Procedure for the synthesis of [Fe(CO)(Cp*)(κ²-dippe)][BArF₂₄]
It quickly became clear that this route was unnecessarily long and involved several unreliable and low yielding steps in particular the *in situ* synthesis of LiCp* from Li^nBu and Cp*H at −78 °C in THF, and subsequent reaction with [Fe(Cl)]_2(dippe)]. This step involves significant production of [Fe(Cp*)_2], lowering the yield and rendering it unattractive for the centre transformation in a multi-step synthesis. Given the aim to synthesise a family of these complexes, it seemed worthwhile to invest some effort into the design of a significantly more practical route. Van Rijn *et al.* reported the synthesis of complexes of the type [Fe(CO)(Cp)(κ^2-PP)]X (X = Cl, Br, I) with some bisarylphosphines in toluene from the halides [Fe(CO)_2(Cp)(X)]. Fortunately this route worked well with our chosen alkylphosphines from the pentamethylated analogue [Fe(Cl)(CO)_2(Cp*)] (Fp*Cl), with NaBArF_24 then used to precipitate NaCl in toluene and generate the target [Fe(CO)(Cp*)(κ^2-P)]][BArF_24]. This was accompanied by the discovery of a facile synthesis of [Fe(Cl)(CO)_2(Cp*)] from the oxidation of the dimer [Fe(CO)_2(Cp*)]_2 using CuCl_2.6H_2O in acetone. This oxidation can be carried out in air, at room temperature and takes around 5 minutes followed by a simple extraction and separation on alumina in CHCl_3. Combining these two straightforward steps forms a facile and reliable general way to synthesise a variety of bisphosphine complexes of the type [Fe(CO)(Cp*)(κ^2-P)][BArF_24] (Scheme 3.6).

**Scheme 3.6:** One pot procedure used for the synthesis of complexes [Fe(CO)(Cp*)(κ^2-dippe)][BArF_24] and [Fe(CO)(Cp*)(κ^2-depe)][BArF_24]

For the synthesis of all complexes the toluene reflux is complete in 2–3 hours and the reaction is worked up with a CHCl_3 extraction. In the case of [Fe(CO)(Cp*)(κ^2-dippe)][BArF_24] and [Fe(CO)(Cp*)(κ^2-depe)][BArF_24] a one pot procedure and extraction can be employed to obtain clean samples. In each case during the reaction, a small amount of [(κ^1-P_2)Cp*Fe(CO)_2][BArF_24] is also formed by incomplete phosphine association; easily observed by two up field doublet resonances in the 31P NMR (Figure 3.5). In the case of the synthesis of the [Fe(CO)(Cp*)(κ^2-dmpe)][BArF_24] complex, this intermediary complex is more favourable due to the decreased electron density of the bisphosphine, the solubility of the various species.
are also very similar. Attempts at using a one pot procedure result in mixtures of $[\text{Fe(CO)(Cp*)(κ}^2\text{-dmpe})][\text{BARF}_{24}]$, $[\text{Fe(CO)}_2(\text{Cp*})(μ\text{-dmpe})]^{2+}$ and $[\text{Fe(CO)}_2(\text{Cp*})(κ^1\text{-P}_2)\text{Cp*Fe(CO)}_2][X]$ ($X = \text{Cl}^-, \text{BARF}_{24}$).

Figure 3.5: $^{31}\text{P}^{1}H$ NMR spectrum at room temperature of an aliquot in toluene after a 12-hour reflux of dmpe, Fp*Cl and NaBARF$_{24}$ - NMR shows a mixture of $^{31}\text{P}$ δ (ppm) δ 70.1 $[\text{Fe(CO)}(\text{Cp*})(κ^2\text{-dmpe})][\text{BARF}_{24}]$, 56.8 $[\text{Fe(CO)}_2(\text{Cp*})(μ\text{-dmpe})]^{2+}$, 37.8 and -43.6 ($J = 29.4$ Hz) $[\text{Fe(CO)}_2(\text{Cp*})(κ^1\text{-P}_2)][X]$ ($X = \text{BARF}_{24}$ or Cl$^-$).

To circumvent this issue, the procedure should be done in two steps. Substitution in toluene forms the chloride salt $[\text{Fe(CO)}(\text{Cp*})(κ^2\text{-dmpe})]\text{Cl}$ which precipitates on formation preventing any back reaction to $[\text{Fe(CO)}_2(\text{Cp*})(κ^1\text{-P}_2)][X]$ or $[\text{Fe(CO)}_2(\text{Cp*})(μ\text{-dmpe})]^{2+}$; this is isolated by filtration (Scheme 3.7 (1)). This is followed by salt metathesis with NaBARF$_{24}$ in THF (Scheme 3.7 (2)) which occurs quickly at room temperature to give clean $[\text{Fe(CO)}(\text{Cp*})(κ^2\text{-dmpe})][\text{BARF}_{24}]$. 

90
Chapter 3  Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

Scheme 3.7: Stepwise synthesis of [Fe(CO)(Cp*)(κ^2-dmpe)][BArF$_{24}$]

Yellow-orange crystals of each of the complexes [Fe(CO)(Cp*)(κ^2-dmpe)][BArF$_{24}$] (3), [Fe(CO)(Cp*)(κ^2-depe)][BArF$_{24}$] (4) and [Fe(CO)(Cp*)(κ^2-dippe)][BArF$_{24}$] (5) can be obtained from slow diffusion of an Et$_2$O and C$_5$ layered solution at room temperature in yields of 55 %, 80 % and 85 % respectively. The crystal structures for the complexes containing novel cations [Fe(CO)(Cp*)(κ^2-dmpe)][BArF$_{24}$] and [Fe(CO)(Cp*)(κ^2-depe)][BArF$_{24}$] are shown in Figures 3.6 and 3.7.

Figure 3.6: Thermal ellipsoid plots of the atoms in the unit cell of [Fe(CO)(Cp*)(κ^2-dmpe)][BArF$_{24}$] (3). Hydrogen atoms have been omitted for clarity. Anisotropic displacement ellipsoids are pictured at 50 % probability. Fe atom is blue, O is red, C are grey, B is purple and F are green. Selected bond lengths are listed in Table 3.1.
Chapter 3  
Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-O</td>
<td>1.053 (5)</td>
</tr>
<tr>
<td>Fe-C1</td>
<td>1.792 (6)</td>
</tr>
<tr>
<td>Fe-P1</td>
<td>2.2030 (12)</td>
</tr>
<tr>
<td>Fe-P2</td>
<td>2.2030 (12)</td>
</tr>
</tbody>
</table>

**Table 3.1:** Selected bond lengths from the solid state structure of 3

![Thermal ellipsoid plots](image)

**Figure 3.7:** Thermal ellipsoid plots of the atoms in the unit cell of [Fe(CO)(Cp*)(κ²-depe)][BArF₂₄] (4). Hydrogen atoms have been omitted for clarity. Anisotropic displacement ellipsoids are pictured at 50 % probability. Fe atom is blue, O is red, C are grey, B is purple and F are green. Selected bond lengths are listed in Table 3.2.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-O</td>
<td>1.150 (8)</td>
</tr>
<tr>
<td>Fe-C1</td>
<td>1.738 (7)</td>
</tr>
<tr>
<td>Fe-P1</td>
<td>2.2195 (17)</td>
</tr>
<tr>
<td>Fe-P2</td>
<td>2.2260 (17)</td>
</tr>
</tbody>
</table>

**Table 3.2:** Selected bond lengths from the solid state structure of 4

The solid state structures of 3 and 4 demonstrate that the degree of electron density from the bisphosphine ligands directly influences the strength of the M-C bond and C-O bond. The less electron-rich complex 3 has a Fe-C bond length of 1.79 Å while complex 4 has a slightly shorter Fe-C bond length of 1.74 Å. This supports the concept that imparting electron density will strengthen the Fe-C bond, potentially disfavouring decarbonylation. Complex 4 which has more electron density from the depe ligand possesses a longer C-O bond as expected.

3.2.2  C-O bond strength in [Fe(CO)(Cp*)(κ²-bisphosphine)][BArF₂₄] complexes

The CO bond strength in carbonyl complexes can be probed by recording the IR stretching
frequencies \((\nu/\text{cm}^{-1})\) of the compounds. Although the C-O bond strength is not necessarily a direct indication of the ease of reduction, it does indicate the extent of back bonding which should correlate with hydride affinity. We know \((\text{vide supra})\) that increased electron density from the metal will strengthen the M-C bond and weaken the C-O bond so the stretching frequencies could also give a relative indication of formyl stability upon hydride addition to the starting carbonyl; \textit{i.e.} assuming a stronger M-C bond could disfavour decarbonylation.\(^\text{6,28}\)

These are especially useful when comparing the family of electronically modified carbonyl complexes discussed in this chapter. As such, solution IR spectra of the relevant compounds were recorded in CH\(_2\)Cl\(_2\) under N\(_2\). The frequencies obtained are shown in Table 3.3 and \(\nu/\text{cm}^{-1}\) for [Fp\(^*\)CO]\(^+\) is included for comparison.

<table>
<thead>
<tr>
<th>Carbonyl Compound</th>
<th>CO (\nu/\text{cm}^{-1}) (CH(_2)Cl(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(CO)(_3)(Cp(^*))](^+)</td>
<td>2072, 2135</td>
</tr>
<tr>
<td>[Fe(CO)(Cp(^*))((\kappa^2)-P(^n)Bu(_3))](^+)</td>
<td>2040, 1965</td>
</tr>
<tr>
<td>[Fe(CO)(Cp(^*))((\kappa^2)-dmpe)](^+) (3)</td>
<td>1947</td>
</tr>
<tr>
<td>[Fe(CO)(Cp(^*))((\kappa^2)-depe)](^+) (4)</td>
<td>1944</td>
</tr>
<tr>
<td>[Fe(CO)(Cp(^*))((\kappa^2)-dippe)](^+) (5)</td>
<td>1940</td>
</tr>
</tbody>
</table>

\textbf{Table 3.3:} CO Stretching frequencies for [Fe(CO)(Cp\(^*\))(\(\kappa^2\)-bisphosphine)]\(^+\) cations. Stretching frequencies vary slightly depending on electron density of ligand. Complexes containing chelating phosphine ligands have distinctly weaker CO bond strengths, (Tenorio \textit{et al.} report CO \(\nu = 1928 \text{ cm}^{-1}\) for [Fe(CO)(Cp\(^*\))(\(\kappa^2\)-dippe)]\(^+\)).\(^\text{13}\)

The stretching frequencies shown in Table 3.3 confirm that as the electron density on the ligands increases, the back bonding from the iron centre increases and the C-O bond strength decreases. Although amongst themselves, the \(\kappa^2\)-bisphosphine carbonyl complexes (3-5) show subtle differences in M-C bond strength; the increased electron density from using a \textit{bis}phosphine compared to a \textit{monophosphine} is clearly demonstrated. The complex [Fe(CO)(Cp\(^*\))(\(\kappa^2\)-P\(^n\)Bu\(_3\))]\(^+\) has a distinctly higher C-O stretching frequencies of 2040 cm\(^{-1}\) and 1965 cm\(^{-1}\) indicating a stronger CO bond. Astruc reported more difficulty in reducing the phosphine substituted carbonyl complex, only observing reduction with NaBH\(_4\) at \(-30 ^\circ\text{C}\), \textit{vs.} \(-80 ^\circ\text{C}\) for [Fp\(^*\)CO]\(^+\).\(^\text{29}\) It was therefore envisaged that reaction of the more electron-rich complexes 3-5 would be even more challenging.
3.3 Reduction studies of $\kappa^2$-bisphosphine iron carbonyl complexes

3.3.1 Stoichiometric reduction using trisarylborohydrides

In order to investigate the reactivity of complexes 3-5, stoichiometric reduction studies were carried out using trisaryl- and trisalkylborohydrides. Initially reactions were set up with the same trisarylborohydrides used in the reduction studies of [Fp*CO]$^+$ discussed in Chapter Two (Figure 3.8).

It was important to first establish whether these FLP chemistry compatible boranes would be capable of reducing the more electron-rich bisphosphine carbonyl complexes on formation of their corresponding borohydrides. It was expected that these carbonyl complexes would be significantly more challenging to reduce given the increased electron density on the CO moiety. Unfortunately, this was confirmed experimentally with no reduction of any of the bisphosphine complexes being observed either in THF or DFB, even with the most electron-rich trisarylborohydride salt, Na[BHPh$_3$] (Scheme 3.8).
Scheme 3.8: No stoichiometric hydride delivery to bisphosphine complexes is observed with the preformed sodium trisarylborohydrides

Each addition of trisarylborohydride salt to complexes 3-5 was attempted stoichiometrically and with hydride in excess with no difference in reactivity observed. The complexes were also heated for prolonged times (2-12 hours) at 60-90 °C without any change being observed. However, complexes 3-5 did not show any signs of decomposition after heating, confirming that the starting carbonyl complexes are stable and robust complexes for a potential catalytic cycle.

The results of the trisarylborohydride additions are distinctly different to those discussed in Chapter Two for [Fp*CO]+ which accepted hydride from all but the most Lewis acidic trisarylborohydride [HBArF₁₅]⁻. Given that even [HBPh₃]⁻ with ΔGₗ⁻₃₆ kcal/mol (c.f. LiAlH₄ 43 kcal/mol) could not deliver hydride to any of the complexes, it was envisaged that reduction of 3-5 using a FLP and hydrogen would be complex. Instead of the challenge of formyl stability and reactivity, these complexes faced the initial challenge of even accepting hydride to form the corresponding formyl complexes.

3.3.2 Stoichiometric reduction using trisalkylborohydrides

Given the unsuccessful results from the attempted reductions with trisarylborohydrides, it was clear that in order to study the behaviour of the bisphosphine carbonyl complexes, more powerful, electron-rich borohydrides would be necessary. A series of experiments were carried out with addition of one equivalent of the strong hydride donor sodium ‘Superhydride’ Na[BHEt₃] (24 kcal/mol) to 3-5 in THF solution. The results of these reductions were more promising, with reduction to the formyl being observed for each of the bisphosphine complexes 3-5 (Scheme 3.9).
Each of the complexes 3-5 produced a distinct formyl resonance when reduced with sodium superhydride. The more electron-rich, sterically demanding complex 5 shows different reactivity to 3 and 4. At room temperature no formyl resonance is observed, however a Fe-H doublet resonance can be seen at $^1$H (THF) $\delta$ $-14.39$ ppm, $^2$J $= 77$ Hz which is consistent with a carbonyl-hydride species [Fe(CO)(Cp*)(κ$^1$-dippe)(H)] (Figure 3.9). These results are analogous to those reported by Davies for the reaction of [Fe(CO)(Cp)(κ$^2$-dppe)]$^+$ and LiAlH$_4$.$^{16,15}$ He proposes the formation of a carbonyl hydride via initial attack on the carbonyl to form a formyl complex.
Chapter 3  Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

Figure 3.9: $^1$H doublet resonance observed at $\delta -14.39$ ppm, indicating dissociation of one arm of bisphosphine to form a carbonyl hydride species.

Figure 3.10: $^1$H NMR spectrum at room temperature, showing the broad formyl resonance produced when 5 was heated at 60 °C for 2 hours with 1 equivalent of Na[BHEt$_3$] in THF.

After heating the reaction for 2 h at 60 °C a formyl resonance can be observed as a broad unresolved signal at the relatively low chemical shift of $\delta$ 10.20 ppm (Figure 3.10). A similar characteristic broad resonance was reported previously by Astruc for the formyl-borane adduct [Fe(CHO-BH$_3$)(Cp*)(P$^\prime$Bu$_3$)]($^1$H $\delta$ 12.8 ppm, (br m)). The broad resonance observed at 10.2 ppm indicated that as a consequence of the extremely electron-rich complex formed from addition of hydride to 5, even a very weak Lewis acid such as BEt$_3$ could interact to form 5•BEt$_3$. It is highly unusual to observe a formyl at higher temperatures. This observation must
be as a direct result of the steric and electronic stabilisation provided by the dippe ligand. Given the observation of this formyl resonance it seems likely that, analogously to the work of Davies, the carbonyl-hydride is formed via initial attack on the carbonyl forming a formyl complex followed by hydride migration, as opposed to direct attack on the metal resulting in immediate dissociation of one arm of the bisphosphine (Scheme 3.10).

![Scheme 3.10: Formation of bound formyl followed by dissociation of one arm of dippe ligand and formation of M-H bond to form carbonyl hydride species](image)

If the complex is heated for a further 10 hours at 60 °C, the yield of the carbonyl hydride increases and a third new very broad resonance can be observed at \( ^1H \delta (\text{THF}) -2.0 \) ppm. The methyl complex \([\text{Fe(CH}_3](\text{Cp}^*)(\kappa^2\text{-dppe})]\), reported by Davies and co-workers, has a distinct resonance at a very similar chemical shift \( ^1H (\text{THF}) \delta -1.3 \) ppm, \( t, 3J = 7 \) Hz, raising the possibility that this signal corresponds to the fully reduced complex \([\text{Fe(CH}_3](\text{Cp}^*)(\kappa^2\text{-dippe})]\). However, this assignment cannot be established definitively due to its broad nature and the failure to observe any coupling. This is possibly due to exchange with other species e.g. the free formyl complex. Furthermore on heating for prolonged periods, it would be expected to see further conversion to the methyl complex given that conversion back to a formyl or carbonyl hydride is unlikely. However, instead a steady concentration of carbonyl hydride is observed while the formyl resonance disappears. The reaction can be monitored by \( ^{31}P \) NMR spectroscopy, which shows that with prolonged time, free ligand begins to form \( ^{31}P \{^1H\} (\text{THF}) \delta 8.9 \) ppm, s) which can only realistically be as a result of \([\text{Fp}^\#H]\) formation which is evidenced by a singlet at \( ^1H \delta -11.8 \) ppm. With prolonged heating small amounts of \([\text{Fe}(\text{Cp}^*)(\kappa^2\text{-dippe})(\text{H})]\) \( ^1H (\text{THF}) \delta -15.6, t \) are also observed indicating free CO present in the mixture (Figure 3.11 and Scheme 3.11). The metal hydride \([\text{Fe}(\text{Cp}^*)(\kappa^2\text{-dippe})(\text{H})]\) is observed as an unresolved broad signal at \( ^{31}P \{^1H\} (\text{THF}) \delta 98.0 \) ppm.
Chapter 3  Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

![Diagram of molecular structures](image)

**Figure 3.11:** $^{31}$P{¹H} NMR spectrum at room temperature, of the reduction of [Fe(CO)(Cp*)($\kappa^2$-dippe)]$^+$ (5) with one equivalent of Na[BHET]$_3$ in THF after heating at 60 °C for 2 – 12 hours – a = dippe, b = [Fe(CO)(Cp*)($\kappa^1$-dippe)(H)], c = [Fe(Cp*)($\kappa^2$-dippe)(H)]

**Scheme 3.11:** Reactivity observed when 1 equivalent of Na[BHET]$_3$ is added to [Fe(CO)(Cp*)($\kappa^2$-dippe)]$^+$ in THF and heated at 60 °C for 2 – 12 hours

The least electron-rich species 3 and 4 produce significantly different reduction results with one equivalent of Na[BHET]$_3$. The corresponding formyl complexes [Fe(CHO)(Cp*)($\kappa^2$-dmpe)](3a) and [Fe(CHO)(Cp*)($\kappa^2$-depe)](4a) are observed immediately at room temperature as distinct triplets at $^1$H (THF) δ 13.06 and 13.28 ppm respectively, indicative of ‘free’ uncoordinated formyl complexes (Figure 3.12). The coupling constants of 7 Hz are consistent with a $^3$J coupling. These observations are similar to that reported by Astruc for the formyl complexes [Fe(CHO)(CO)(Cp*)($\kappa^1$-PR$_3$)] (R = Me, Ph, $^4$Bu), which each have coupling constants of around $^3$J = 5 Hz.$^{11,16}$
Analysis of the $^{31}$P {$^1$H} spectra for species 3a and 4a clearly indicates incomplete conversion to the product formyl species. On addition of one equivalent of Na[BHEt$_3$] to either complex in THF, the $^{31}$P {$^1$H} spectrum immediately produces 3 singlet resonances (Figure 3.13). The two most upfield resonances correspond to the starting material and formyl. A heteronuclear multiple bond correlation NMR experiment (HMBC) was used to confirm the identity of the formyl complexes in the $^{31}$P spectrum for 3a and 4a at $\delta$ 85.4 and 100.0 ppm respectively. These resonances are ca. 15 ppm downfield of the respective starting carbonyl complex in each case. The third unknown resonances ($\delta$ 58.6 and 76.8 ppm, 3b and 4b respectively) could be expected to be a product of further reduction, however the $^1$H data for both reaction mixtures shows limited evidence for this and there are no distinctive methyl peaks in the $\delta$ 0 to $\sim$1 ppm region or hydride species in the $\delta$ $\sim$1 to $\sim$20 ppm region (Figure 3.13). Importantly, it appears both 3 and 4 behave in the same manner and this is probably down to the very small difference in electron density, as highlighted by their similar CO stretching frequencies.
Chapter 3  Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

Figure 3.13: $^{31}$P{¹H} NMR spectrum at room temperature, for Na[BHEt₃] reductions of [Fe(CO)(Cp*)(x²-dmpe)]⁺ (3) and [Fe(CO)(Cp*)(x²-depe)]⁺(4) at room temperature: a HMBC NMR experiment confirmed that the formyl complexes 3a and 4a produce singlet resonances at δ 85.4 and 100.0 ppm respectively.

If the carbonyl(3, 4)/Na[BHEt₃] reaction mixtures are heated an equilibrium exists between the starting material, formyl and third unknown species; heating causes an increase in the concentration of the unknown species 3b and 4b. Further reductions of both 3 and 5 were carried out with one equivalent of each of M[BHEt₃] M = Li, Na, K in order to investigate whether the alkali metal present would have any effect on the equilibrium. The results of these reactions showed that the equilibrium is not dependent on the alkali metal present and a similar product distribution is seen for all reactions. In order to confirm the identity of this unknown species present in the equilibrium, a series of experiments were carried out on complex 3. Since both 3 and 4 share the same reactivity only one complex was used for further investigation.

With the formyl complexes and starting material resonances left unambiguous in the reaction NMR spectra, it was possible to attempt further characterisation of the other unknown species 3b. To confirm the hypothesis that the various species 3, 3a and 3b exist in equilibrium, a $^{31}$P{¹H} NMR variable temperature (VT) experiment was carried out on the reaction mixture 3/Na[BHEt₃] showing that 3b is favoured at higher temperatures. The concentration of the starting material 3 stays generally constant while the concentrations of the reduced species 3a and 3b change subtly with heating and cooling (Figure 3.14).
Chapter 3  Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

![Figure 3.14: Stack plot showing results of VT (298–333 K) $^{31}$P{H} NMR of reduction of [Fe(CO)(Cp*)(κ²-dmpe)]⁺ with 1 equivalent of Na[BHEt₃]. 3b is preferred at higher temperatures. The spectrum also shows the presence of a small amount of hydride (*) δ 80.5 which is always observed whether the reaction is left at room temperature or heated for a prolonged period; conversions to the hydride are low and it does not appear to feature in the equilibrium.](image)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>3a (%)</th>
<th>3 (%)</th>
<th>3b (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>333</td>
<td>13</td>
<td>76</td>
<td>11</td>
</tr>
<tr>
<td>323</td>
<td>15</td>
<td>76</td>
<td>9</td>
</tr>
<tr>
<td>313</td>
<td>17</td>
<td>76</td>
<td>7</td>
</tr>
<tr>
<td>303</td>
<td>18</td>
<td>77</td>
<td>5</td>
</tr>
<tr>
<td>298</td>
<td>19</td>
<td>77</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 3.4: The ratio (%) of each species (3, 3a, 3b) present in the equilibrium at various temperatures

This observation led us to the possibility that 3b may be some further reduced species and this indicated that the hydride is potentially formed from a different mechanism, outside of the observed equilibrium. It is clear that this equilibrium involves BEt₃ since full hydride delivery is never observed (Scheme 3.12), this indicates that the BEt₃, 3a and 3b all have a similar hydride donor capability.
In order to obtain more spectroscopic information, conversion to and isolation of unknown \(3b\) was attempted. It is possible to convert all of the starting carbonyl to \(3b\) by using a large excess of hydride (Figure 3.15). This can be achieved by adding 3 equivalents of \(\text{BEt}_3\) and 10 equivalents of \(\text{NaH}\) (which readily generates \(\text{Na}[\text{BHEt}_3]\) \textit{in situ} at room temperature).\(^{32}\) The large excess of hydride means all \(\text{BEt}_3\) in solution exists as the reduced borohydride \([\text{HBEt}_3]^-\), evidenced by a doublet for the B-H bond in the \(^{11}\text{B}\) NMR spectrum (\(\delta \sim 8.9\) ppm), which pushes the equilibrium towards \(3b\) (\(^{31}\text{P}^{\{^1\text{H}\}}\) (THF) \(\delta 60.0\) ppm). Under these conditions, in addition to the doublet for the borohydride \([\text{HBEt}_3]^-\) and singlet for the \(\text{BArF}_{24}^-\) counter-ion; the \(^{11}\text{B}\) NMR spectrum also displays a broad singlet at \(\delta \sim 1.9\) ppm. This singlet was initially presumed to have arisen from the product \(3b\), however various experiments varying the concentration of \(\text{BEt}_3\) didn’t have a significant impact. The reaction is faster with multiple equivalents of \(\text{BEt}_3\) but in addition requires a vast excess of \(\text{NaH}\) (\(\sim 10\) equivalents) since \(\text{Na}[\text{BHEt}_3]\) has a tendency to form a bridging hydride species \(\text{Na}[\text{Et}_3\text{B-H-BEt}_3]^-\) (\(\delta \sim 12.2\) ppm) which can hamper full conversion to \(3b\). With a large excess of \(\text{NaH}\), the borohydride will only exist as the monomer. The lack of strong dependence on \(\text{BEt}_3\) led to the hypothesis that the broad singlet was a product of \(\text{NaH}\) and \(\text{BEt}_3\) which can upon completing a control of the two reactants in THF turned out to be correct. It is presumed to be a product of small amounts of moisture in the \(\text{NaH}\) even after activation (using \(\text{LiAlH}_4\)) which would form borate species such as \(\text{Na}[\text{BEt}_3\text{OH}]\).

**Scheme 3.12:** Equilibrium that exists between \([\text{HBEt}_3]^{-}\), \(3a\) and \(3b\)
Figure 3.15: $^{31}$P{$^1$H} NMR spectrum at room temperature, of the reaction of 3, excess NaH and 3 equivalents of BE$_3$ in THF.

In order to probe the identity of this species further, a sample of 3 was labelled with $^{13}$CO gas, administered via use of a Toepler line. The sample was irradiated at 254 nm for 5 hours in THF in order to prompt carbonyl ligand exchange which can be followed by $^{13}$C{$^1$H} NMR spectroscopy. The labelled compound gives rise to triplet resonance in the $^{13}$C{$^1$H} NMR spectrum at δ 215 ppm (Figure 3.16).
Reduction of the labelled sample of 3 was carried out using 1 equivalent of Na[BHEt]₃ resulting in observable ¹³C shifts for a mixture of 3, 3a and 3b (Figure 3.17). Initially it seemed reasonable to assume that 3b could possess a –CH₂O⁻ functional group. However, such carbon environments typically produce a resonance at ca. 90 ppm. However, when the ¹³C {¹H} NMR analysis was carried out, only two new downfield triplet resonances were observed at δ 223 and 296 ppm. Further HMBC (¹³C-¹H and ³¹P-¹H) experiments were used to determine correlation between the triplet at δ 296 ppm and the formyl singlet (3a) at ³¹P {¹H} δ 80.0 ppm.
Figure 3.17: $^{13}$C{¹H} NMR spectrum at room temperature, of the reduction of $^{13}$CO labelled 3 with 1 equivalent of Na[BHEt]$_3$ in THF at room temperature – new species 3a and 3b give rise to triplets at $\delta$ 223 ppm and $\delta$ 296 ppm

Given the characteristically high carbon shift of 3b, $\delta$ 223 ppm, it appears that the CO ligand remains unchanged. Instead it seemed likely that the hydride was present somewhere else in the complex 3b. 3b gives rise to one singlet indicating a symmetric phosphorous environment. It also appears to be in equilibrium with 3 and 3a, indicating the presence of one additional ‘hydride environment’ in the molecule. The possibilities for hydride attack on 3, and as such the possible identities of 3b, are shown in Scheme 3.13.
Scheme 3.13: Various possibilities for hydride addition to the starting carbonyl complex 3. Pathway 1 shows attack on the carbonyl ligand producing a formyl - migration to the ring forms a $\eta^4$-Cp* adduct. Pathway 2 shows direct attack on the Cp* ring to form the adduct followed by migration to the carbonyl ligand. Pathway 3 would result from attack on the metal forming a metal hydride, this species is likely to decarbonylate to form $\left[\text{Fe(Cp*}(\kappa^2\text{-dmpe})(\text{H})]\right]$.

Pathway 1 shows hydride attack at CO followed by hydride migration to form a $\eta^4$-CpH adduct. Some theoretical calculations carried out on the related cation $[\text{Fe(CO)}_2(\eta^5\text{-C}_5\text{H}_5)(\text{PH}_3)]^+$ by Brown et al. indicate that pathway 1 is the most energetically feasible. They have used Density Functional Theory (DFT) calculations to show that, in the case of hydride attack on $[\text{Fe(CO)}_2(\eta^5\text{-C}_5\text{H}_5)(\text{PH}_3)]^+$, the $\eta^4$-CpH adduct is more energetically favourable than the formyl complex. However, the energy barrier leading to attack at the Cp ring is relatively large given the repulsion between the $\pi$ electrons of the formally anionic Cp ligand and the incoming nucleophile, indicating that pathway 2 is unlikely. Although the $\eta^4$-CpH adduct is thermodynamically more stable, the energy barrier to formyl formation is smaller explaining both species are observed at room temperature. This data helps to explain the observed equilibrium in the reduction of 3; the formyl complex 3a is formed quickly at lower temperatures i.e. the kinetic product. However, a thermodynamic mixture of the complexes 3, 3a and 3b is allowed to form when 1 equivalent of hydride is present. A large excess of hydride favours the $\eta^4$-CpH adduct which indicates that BEt3 may be interacting with the formyl oxygen.
Chapter 3  Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

albeit there is no unambiguous NMR spectroscopy evidence for this (Scheme 3.14). The reason for this is due to the aforementioned broad singlet in the $^{11}$B NMR spectrum $\delta$ –1.9 ppm which is potentially masking a borane-$3b$ interaction. However, it should be noted that other than Na[BEt$_3$OH] ($\delta$ –1.9 ppm), BArF$_2$ (δ –6.0 ppm) and Na[BHEt$_3$] (δ –8.9 ppm), no other $^{11}$B resonances are observed during the reaction. When the reaction is carried out with excess NaH there is no free BEt$_3$ present and the adduct is the sole product of the reduction.

![Scheme 3.14: Possible interaction of BEt$_3$ with formyl in the Na[BHEt$_3$] reduction of 3](image)

These computational results are based on a less electron-rich system with (Cp)$^-$ and a monophosphine present vs. (Cp*)$^-$ and a bisphosphine. In the case of the pentamethylated analogue, the repulsion between incoming nucleophile and the π-electrons of the Cp* would make hydride attack on the ring kinetically less favourable. The differences in barriers to formation between the formyl and the $\eta^4$-adduct could therefore be much larger in the case of hydride attack on 3. Pathway 3 would produce a 7-coordinate Fe(II) species [Fe(CO)(η$^3$-C$_5$Me$_5$H)(κ$^2$-dmpe)(H)] after hydride attack on the metal. The most compelling evidence against the presence of such a species during the reaction is the lack of any characteristic up-field Fe-H resonance and furthermore such a small $^{13}$C resonance shift of 8 ppm from the starting material 3 would not be expected for such a species. The authors go on to highlight that formation of a 7-coordinate Fe(II) hydride species is unlikely given the unfavourable energetics.

The NMR data presented for the reduction of 3 coupled with the calculations of the energetics of the various modes of hydride attack from Brown et al. indicate that the unknown species $3b$ is the product of hydride migration from the formyl to the Cp* ring, the $\eta^4$-adduct [Fe($\eta^4$-C$_5$Me$_5$H)(CO)(κ$^2$-dmpe)].$^{34}$ There are extensive examples in the literature of hydride attack or migration to the cyclopentadienyl ring in relation to carbonyl reduction chemistry but it should
be noted that there are no known examples of attack or migration to the pentamethylated analogue.\textsuperscript{35,18} Davies reports that the reduction of $[\text{Fe(CO)(Cp)}(\kappa^2\text{-dppe})]^+$ with LiAlD\textsubscript{4} in THF at low temperatures ($-78 \, ^\circ\text{C}$) allows for formyl formation, whereas immediate refluxing produces 100% conversion to the ring attack product $[\text{Fe}(\eta^4\text{-C}_5\text{H}_5\text{D})(\text{CO})(\kappa^2\text{-dppe})]$, with the deuteride added \textit{exo} to the ring. If the formyl is warmed slowly to room temperature, the carbonyl-deuteride will form. Heating this species at 90 °C in toluene produces 100% conversion to $[\text{Fe}(\eta^4\text{-C}_5\text{H}_5\text{D})(\text{CO})(\kappa^2\text{-dppe})]$ adduct in which the deuteride is on the \textit{endo} face of the ring (Figure 3.18). Decarbonylation to form an $[\text{Fe(Cp)}(\text{D})(\kappa^2\text{-dppe})]$ species is never reported and this is likely due to the facile dissociation of one arm of the large \textit{bis}phosphine ligand, meaning the carbonyl hydride is kinetically stable towards CO loss.

![Chemical Structures](image)

**Figure 3.18**: Reactivity reported by Davies - the \textit{exo} adduct is formed from initial hydride attack at higher temperatures

The lack of literature precedent for Cp* attack may simply be attributable to the fact that studies on Cp*-substituted 18-electron carbonyl complexes are underdeveloped. Much more work has focused on the Cp analogue given the relative expense and the more demanding synthesis of the Cp* ligand. In addition, examples that report using Cp* have not included small, electron-rich \textit{bis}phosphines. Work investigating hydride addition to the Cp ring has focused somewhat on spectroscopic techniques to determine whether the attack will be \textit{exo} or \textit{endo} to the ring (Scheme 3.15).\textsuperscript{18} Given the lack of prior examples for the Cp* analogue it was harder to
Chapter 3  Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

determine the stereochemistry of the hydride on the Cp* ring in the complex \([\text{Fe(CO)}(\kappa^2-\text{dmpe})(\eta^2-\text{Cp}^*\text{H})]\). Green, Mingo, and Davies published rules on predicting the particular geometry of attack on a \(\pi\) ring coordinated to a metal center, but these do not apply to substituted cyclopentadienyl ligands.\(^{36}\)

![ Scheme 3.15: Plausible different modes of hydride attack on the substituted cyclopentadienyl ring of \([\text{Fe(CO)}(\text{Cp}^*)(\kappa^2-\text{dmpe})]^+ (3)\) ](image)
Chapter 3  Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

In the case of Astruc’s work on Cp*-substituted complexes monophosphines are used which, when left for prolonged periods, will produce \([\text{[Fp*H]}]\) via phosphine dissociation. Undemanding sterics and chelation in 3 result in a strongly bound dmpe ligand preventing decomposition to an [Fe]-H species. The \(\eta^4\)-adduct 3b, formed from hydride attack on the Cp*, would therefore be an electron-rich Fe(0) complex which can oxidise readily to reform the starting Fe(II) complex. The presence of the hydride on the already electron-rich Cp* substituent would produce a very powerful hydride donor which must have a similar hydride donor capability to Na[BHEt$_3$] (26 kcal/mol), presumably explaining why all attempts to crystallise the adduct were unsuccessful.\(^3\) Each of the species in the equilibrium can now be assigned to \(^{13}\text{C}\) resonances resulting from reduction of the \(^{13}\text{CO}\) labelled sample of 3 (Figure 3.18).

![Diagram of complexes](image)

**Figure 3.18:** \(^{13}\text{C}\) NMR at room temperature, taken after reduction of \([\text{Fe}(^{13}\text{CO})(\text{Cp}^*)(\kappa^2\text{-dmpe})]^+ (3)\) with Na[BHEt$_3$] in THF - two new downfield triplet resonances can be assigned to the formyl observed at δ 296.6 and the proposed \(\eta^4\)-adduct at 223.6 ppm.

3b can be characterised further using HMBC experiments. The starting carbonyl 3 displays complex second order coupling in the \(^1\text{H}\) NMR spectrum and the phosphine ligand \(^1\text{H}\) resonances overlap with the cyclopentadienyl region so the \(\eta^4\)-adduct is difficult to characterise.
Chapter 3  Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

via 1D $^1$H NMR analysis alone. By using comparison to the $^1$H NMR spectrum for the uncomplexed Cp*H ligand it was possible to deduce each of the resonances for the methyl groups and hydride present on the Cp*-H ring of the new species $3b$. The $^1$H resonance for the hydride on the $\eta^4$-ring appears as a multiplet at $\delta$ 2.78 ppm and this is shown to correspond to the peak at $\delta$ 223 ppm in the $^{13}$C NMR and $\delta$ 60.0 ppm in the $^{31}$P NMR. This shift is similar to hydride shifts of analogous Cp adducts reported by Davies in which the endo or exo hydride is observed as a multiplet at $^1$H (THF) $\delta$ 2-3 ppm. There is another unresolved doublet resonance at $\delta$ 2.05 which can be assigned to the 12 allylic methyl protons on the Cp* ligand (Figure 3.19). The resonance for the methyl group adjacent to the hydride substituent is masked by the $^1$H hexane resonances which are present in commercial solutions of BEt$_3$. However this would be expected to appear around $\delta$ 1.2-1.3 ppm. The HMBC $^{31}$P-$^1$H spectra confirm multiple peaks in this region that correlate with the $^{31}$P resonances for the $\eta^4$-adduct.

![Figure 3.19: $^1$H NMR spectrum in THF-d$_8$ at room temperature: resonances have been determined for $[\text{Fe}(\text{CO})(\kappa^2$-dmpe)($\eta^4$-Cp*H)] using comparison to the original uncoordinated Cp*H ligand - the $^1$H NMR spectrum of the Cp*H ligand is red, $^1$H NMR spectrum for $[\text{Fe}(\text{CO})(\kappa^2$-dmpe)($\eta^4$-Cp*H)] is green and the $^1$H NMR spectrum for the starting material $[\text{Fe}(\text{CO})(\text{Cp}^*)(\kappa^2$-dmpe)]$^+$ is shown in blue. $^1$H NMR](image-url)
To investigate whether the hydride adds \textit{exo} or \textit{endo} to the Cp* ring, a $^1$H NOESY NMR experiment was carried out to determine if this hydride was in close proximity to the methyl groups of the \textit{bis}phosphine ligand. These P–Me$_2$ groups produce unresolved multiplets at $^1$H $\delta$ 1.53-1.62. The NOESY spectra do not indicate any through space correlation between these groups and the hydride. This could indicate that the hydride resides on the \textit{exo} face of the ring however the lack of correlation between these groups is not conclusive. This is especially true since the methyl groups of the \textit{bis}phosphine (-PMe$_2$) produce multiplets in a region of many different resonances not allowing for conclusive analysis. Since there is significant steric bulk on the \textit{endo} face of the ring, the \textit{exo} face is sterically most accessible (Scheme 3.16). However the evidence presented thus far indicates an equilibrium between 3a and 3b indicating \textit{intramolecular} hydride transfer. It is very difficult to see how this incoming hydride could reside on the \textit{exo} face of the ring unless \textit{endo} attack is followed by rearrangement. It is possible that the ring de-coordinates to facilitate rearrangement to the \textit{exo} species however it seems unlikely that 100 % of the \textit{endo} species would isomerise. Another possibility is intermolecular \textit{exo} attack from [HBEt$_3$]$^-$ which would mean the species 3a and 3b are not in equilibrium but forming simultaneously.

\begin{center}
\textbf{Scheme 3.16:} Intermolecular \textit{exo} attack on 3
\end{center}

3.3.3 Further stoichiometric studies on previously investigated 18-electron \textit{bis}phosphine complexes

To further investigate the reduction behaviour of similar 18-electron carbonyl complexes, the complexes [Fe(CO)(Cp)(κ$^2$-dmpe)][BArF$_{24}$] (6) and [Fe(CO)(Cp*)(κ$^2$-dppe)][BArF$_{24}$] (7) were synthesised. Unlike the complexes discussed in the previous Section 3.3.2, the groups of Davies and Astruc have previously investigated the reduction behaviour of the PF$_6^-$ salt of both 6 and 7. In addition Davies reported a procedure for generating the complex [Fe(CO)(Cp)(κ$^2$-
Chapter 3  Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

dmpe][PF₆], and detailed its behaviour in a THF solution of LiAlH₄. A complex, multi-step procedure for the synthesis of the PF₆⁻ salt of [Fe(CO)(Cp*)(κ²-dppe)]⁺ is also known,³⁸,¹⁸ however due to the differences in solubility of the anions neither previously published procedure is suitable for use with the BArF₂₄⁻ anion and they are also unnecessarily complex. The simple two step route described in Section 3.2.1 has been used again for the synthesis of 6 via complexation and salt metathesis using the bisphosphine and [Fe(Cl)(CO)₂(Cp)] (FpCl) in toluene. FpCl can be obtained in a similar way to Fp*Cl via oxidation of [Fe(CO)₂(Cp)]₂ (Fp₂) using CuCl₂.2H₂O in acetone (Scheme 3.17).

![Scheme 3.17: Synthetic procedure used for the synthesis of [Fe(CO)(Cp)(κ²-dmpe)][BArF₂₄]](image1)

The more sterically demanding complex [Fe(CO)(Cp*)(κ²-dppe)][BArF₂₄] is made in the same manner as [Fe(CO)(Cp*)(κ²-dippe)]⁺ via a one-pot reflux with the bisphosphine, Fp*Cl and NaBArF₂₄ in toluene (Scheme 3.18).

![Scheme 3.18: Synthetic procedure used for the synthesis of [Fe(CO)(Cp*)(κ²-dppe)][BArF₂₄]](image2)
When \([\text{Fe(CO)(Cp)(\kappa^2{-}\text{dmpe})}]^+\) is reduced with \(\text{Na[BH}_{3}\text{Et}_3}\) in THF, the carbonyl is cleanly converted to the \(\eta^4\)-adduct \([\text{Fe(CO)(\eta^4{-}\text{C}_5\text{H}_6})(\kappa^2{-}\text{dmpe})]}\) (6a) as evidenced by complete conversion to a singlet at \(31\text{P }\delta\) (THF) 65.5 ppm. The identity of the adduct is determined by using comparison of \(^1\text{H}\) and \(^31\text{P}\{^1\text{H}\}\) NMR chemical shifts and splitting to the adducts formed from the reduction of complexes 3 and 4. This is very different to the reactivity reported by Davies. As discussed in Section 3.1.1 Davies used \(\text{LiAlH}_4\) in THF to reduce 6 directly to the methyl complex at room temperature (Scheme 3.19).\(^{17}\)

\[\text{Scheme 3.19: } \text{LiAlH}_4 \text{ reduction produces a strong Lewis acid upon hydride delivery. AlH}_3 \text{ is available for carbonyl activation preventing hydride migration and facilitating reduction to the methyl complex } [\text{Fe(CH}_3\text{)(Cp)}(\kappa^2{-}\text{dmpe})] \]

The difference in reactivity between the two reductants may be attributable to the strength of the Lewis acid generated upon hydride transfer. \(\text{Na[BH}_{3}\text{Et}_3}\) is a strong hydride donor but the resulting borane BEt\(_3\) is a very poor Lewis acid, and as such shows no signs of strong interaction with the formyl in the \(^{11}\text{B}\) NMR spectra in the reductions of 3, 4 and 6. Without Lewis acid activation to withdraw electron density from the neutral, electron-rich formyl complex, further reduction via hydride transfer is strongly disfavoured (Scheme 3.20). By contrast, AlH\(_3\) (generated from \(\text{LiAlH}_4\)) is a much stronger, harder and more oxophilic Lewis acid and therefore strongly activates the formyl, relieving electron density from the carbonyl carbon and prompting a second nucleophilic hydride attack.
Chapter 3  Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

Scheme 3.20: When using Na[BHEt]₃, the corresponding borane produced from hydride delivery is not sufficiently Lewis acidic to interact strongly with the formyl oxygen thereby hindering further hydride attack.

The reduction of 7 can be carried out with 1 equivalent of Na[BHEt]₃ to give identical results. On addition of hydride, the formyl complex 7a is immediately observed in trace (< 5 %) conversions signalled by a triplet at ¹H δ (THF) 14.62 ppm. No methyl or hydride complex is observed initially at room temperature.

Scheme 3.21: Low conversions to the formyl 7a are seen at room temperature when 7 is reduced with 1 equivalent of Na[BHEt]₃.

If the solution in THF is left to stand for 12 hours at room temperature, formation of the carbonyl hydride is observed (ca. 10 %) and the formyl is no longer seen in the ¹H NMR spectrum. This implies that the formation of the carbonyl hydride is occurring via hydride migration to the metal from the formyl carbon. This is initially similar to the results reported by Davies in the reduction of the Cp and Cp* analogues, [Fe(CO)(Cp)(κ²-dppe)]⁺ and [Fe(CO)(Cp*)(κ²-dppe)]⁺ with LiAlH₄. However unlike the Cp complex, if the carbonyl
hydride of the Cp* complex is left at room temperature we do not see any disproportionation to the methyl. Instead a mixture of [[[[Fp*H]]], [Fe(CO)(κ^1-dppe)(H)] (7c), [[[[Fp*H]]] and [Fe(Cp*)(κ^2-dppe)(H)] is formed (Scheme 3.22 & Figure 3.21).

**Scheme 3.22**: Observed reactivity when 7 is reduced with 1 equivalent of Na[BHEt]_3. A mixture of hydride species is formed with no evidence of methyl complex.

**Figure 3.20**: ¹H NMR spectrum at room temperature (of upfield hydride region δ -7.5—20.5 ppm) of a mixture of hydride species resulting when [Fe(CO)(Cp*)(κ^2-dppe)]⁺ is reduced with Na[BHEt]_3 and left at room temperature for several days.
Similar to the reduction results of \([\text{Fe(CO)(Cp*)}(\kappa^2-\text{dippe})]^+ \) (5) previously discussed in this section, the formyl proton of 7a appears as an unresolved signal, suggesting that BEt₃ is interacting with the formyl complex also indicated by a broad singlet in the ¹¹B NMR spectrum at δ -0.25 ppm and free BEt₃ at δ 75.5 ppm which is lower than expected perhaps due to exchange with the formyl complex. The results are consistent with the pattern of reactivity observed with Na[BHET]₃ and the various carbonyl compounds 3-7. Similarly in the reduction of 3 and 4 the lack of a strongly interacting Lewis acid for activation prevents the addition of a second or third hydride equivalent.

Alternatively it may be possible to consider the reduction of 7 and other less electron-rich complexes in a different manner. Astruc has previously reported the formation of the carbonyl hydride from the reduction of 7 and investigated a possible electron transfer (ET) mechanism, given the unexpected difference in reactivity between the Cp and Cp* analogues (Scheme 3.23).[^39] They carry out the reaction between 7 and LiAlH₄ in THF at −80 °C. No formyl complex is reported at this temperature; however, the EPR spectrum of the reaction at −80 °C displays three signals with \textit{ca. } g = 2 which are indicative of a Fe(I) monomer and is proposed to be the 19-electron carbonyl complex. Mössbauer spectroscopy indicates this Fe(I) intermediate is only present as a small proportion of the reaction medium, hinting that a steady state concentration leading to the carbonyl hydride 7c is likely. It is reasoned that a 19-electron intermediate leads to dissociation of the bisphosphine and in the presence of a H atom donor (\textit{e.g.} LiAlH₄) produces the carbonyl hydride (Scheme 3.23).
Scheme 3.23: An electron transfer pathway has been suggested by Astruc for the reduction of 7 using LiAlH₄ in THF – the pathway shown in blue shows hydride attack on the carbonyl forming the formyl. Mossbauer spectroscopy discredits the hydride attack pathway.

No formyl complex is observed and Astruc postulated that even though the permethylation of the Cp* should stabilise any formyl generated, it appears that H⁻ attack on the carbonyl carbon is disfavoured by decreasing the positive charge on the carbonyl carbon. The Mossbauer evidence presented by Astruc appears to suggest an ET pathway is producing the carbonyl-hydride 7c rather than a simple hydride attack on the carbonyl carbon (blue pathway Scheme 3.23). This is a possibility for the reduction of 7 using Na[BHEt]₃ which is reported here (vide supra); we observed trace amounts of formyl conversion followed by a steady state concentration of a mixture of hydride complexes. It is possible that these observations are the result of both hydride attack and/or the ET pathway reported by Astruc. This indicates that simply imparting electron density onto a system may not be a straightforward way of stabilising a formyl if it actually disfavours formyl generation in the first instance. Imparting electron
density appears to work in the case of small, electron-rich phosphines such as 3 and 4. It fails when using a larger bisphosphine with superior π acid properties such as 7; which instead is capable of stabilising a 19-electron intermediate such as $[\text{Fe}^{0}(\text{CO})(\text{Cp}^*)(\kappa^2\text{-dppe})]$ by delocalising the extra electron.

### 3.3.4 Attempted stabilisation of $[\text{Fe}(\text{CHO}(\text{Cp})(\kappa^2\text{-dmpe})]]$ (3a) using electrophiles

We have shown in Section 3.3.2 that the addition of 1 equivalent of a strong hydride donor of the type $\text{M}[\text{BHEt}_3]$ to 3 prompts an equilibrium between 3, $[\text{HBEt}_3]^{-}$, 3a and 3b. It has been shown that the presence of a strong Lewis acid or electrophile can activate electron-rich formyl complexes towards further reduction.\textsuperscript{16,11,35} In all examples of methyl ligand formation from a carbonyl, a strongly coordinating Lewis acidic species ($\text{AlH}_3$, $\text{BH}_3$) has been present.\textsuperscript{11,16} Given the sharp \textsuperscript{1}H triplet for the complex 3a it appears that $\text{BET}_3$ is not binding or otherwise interacting strongly with the formyl oxygen. Clearly $\text{BET}_3$ is not sufficiently Lewis acidic to provide the necessary stabilisation. It therefore seemed reasonable to suppose that the formyl could be trapped by the addition of another electrophile. To probe this, a number of boranes and acids were used to attempt trapping of this electronically rather unstable species. It was hoped that a new thermodynamically stable adduct could be achieved, thereby blocking the hydride migration to give the undesired $\eta^4$-adduct 3b. This ‘trapped’ species containing the ‘CHO’ moiety could then be available for further hydride attack and reduction.

Initially some attempts were made with species such as $\text{Me}_3\text{SiCl}$ (TMSCl); upon addition of one equivalent of TMSCl, the silane $\text{Me}_3\text{SiH}$ was immediately observed in the \textsuperscript{1}H NMR spectrum and the starting carbonyl complex was the only species observable by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Scheme 3.24).
Introduction of bisphosphine substituted cationic iron carbonyl complexes

Scheme 3.24: Observed reactivity when carbonyl 3 is reduced with 1 equivalent of Na[BHEt]₃ followed by Me₃SiCl to attempt ‘trapping’ of the formyl 3a.

Various Brønsted acidification experiments were attempted including addition of 1-2 equivalents of the strong acid [H(OEt)₂][HBArF₂₄] [pKₐ(H₂O) – 3] and the weaker acid tBuOH [pKₐ(H₂O) 17]. Neither resulted in protonation of the intermediate formyl. The presence of protons produces hydrogen and converts 3a to the starting carbonyl 3 indicating 3a and 3b are highly electron-rich, potent hydride donors (Scheme 3.25).

Scheme 3.25: Reactivity observed in reaction of a H⁺ source and a mixture of 3, 3a and 3b.
Chapter 3  
Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

It has already been demonstrated that the formyl complex 3a has a similar hydride donor capability to [HBEt3]− (26 kcal/mol) which is also present in the equilibrium mixture along with the other strong hydride donor 3b. Due to the formation of this equilibrium, it has proved impossible to selectively synthesise the formyl 3a without also immediately producing 3b. As such any species, such as TMSCl, that can accept a hydride is going to undergo rapid reduction. It was envisaged that a species that was not capable of accepting hydride could provide the desired reactivity e.g. Sc(OTf)3. However, on addition of one equivalent of Sc(OTf)3, not only is the formyl not stabilised but slow conversion back to the carbonyl is observed over 12 hours at room temperature leading to complex 3 being the only observable species in the 31P{1H} NMR spectrum.

It was envisaged that the boranes BH3 and (9BBN)2 could provide electrophilic hydride sources, analogous to the reduction of Fp*CHO with NaBH4 reported by Astruc, thereby trapping the formyl and delivering a hydride equivalent (Scheme 3.26).

![Scheme 3.26: Possible role of a second Lewis acid present in the reduction of 3](image)

The reactions were carried out by adding 1 equivalent of Na[BHEt]3 followed by 1 equivalent of each borane. In both cases the η4-adduct 3b immediately ceased to be observed indicating an initial stabilisation of the formyl 3a. After 2-3 hours at room temperature the conversion of the formyl depletes significantly and by 6 hours at room temperature the starting carbonyl 3 is the only species observable by 31P{1H} NMR analysis. In the case of BH3, presumably there is a weak interaction between the formyl oxygen of 3a briefly leading to the observation of 3a and 3. However it is likely that the formyl and/or Na[BHEt]3 quench the borane BH3 by delivering hydride to form [BH4]− which cannot deliver hydride back to 3 thereby shutting down hydride transfer. This is confirmed with the observation of resonances for BEt3 and...
Chapter 3  Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

$[\text{BH}_4^-]$ in the $^{11}$B NMR spectrum, at $\delta$ 80.7 ppm and $\delta$ –42.8 ppm respectively. A third resonance at $\delta$ 18.1 ppm is likely due to the intermediate $[\text{Fe(=CHO-BH}_3)(\text{Cp}^*)(\kappa^2-\text{dmpe})]$ (Scheme 3.27).

![Scheme 3.27](image)

**Scheme 3.27:** Observed reactivity when mixture of $\text{Na[BHEt}_3]/3a$ and $3b$ is treated with 1 equivalent of BH$_3$-THF.

In the case of $(9\text{BBN})_2$ the same pattern of reactivity is observed via $^{31}$P{$^1$H} analysis, indicating a similar effect to that of BH$_3$. Immediately the $^{11}$B NMR spectrum shows resonances for $9\text{BBN}$-$\text{H}$(δ 27.8 ppm, s) along with a sharp triplet for the monomeric anion $9,9$-$\text{H}_2\text{BBN}^-$ at $\delta$ –16.0 ppm, indicating that any hydride present in the system is now sequestered, residing on the secondary, more Lewis acidic borane, disfavouring reduction of 3. If the solution is left for one week at room temperature, the only signals that remain observable in the $^{11}$B NMR spectrum are of BEt$_3$ and $9,9$-$\text{H}_2\text{BBN}^-$. This is unexpected given that $9\text{BBN}$-$\text{H}$ has recently been calculated by Krempner et al. to be a better hydride donor than BEt$_3$.

However clearly $9\text{BBN}$-$\text{H}$ is not capable of interacting with $3a$ and instead the reduction of $9\text{BBN}$-$\text{H}$ is favoured over its stabilisation through adduct formation ($3a$-$9\text{BBNH}$) and reduction of the formyl group.

### 3.4 FLP hydrogenation studies of $\kappa^2$-bisphosphine iron carbonyl complexes

Ultimately the aim of this work is to deliver hydride and proton equivalents directly from molecular hydrogen, $\text{H}_2$. In Section 3.3.2, the stoichiometric reduction of several bisphosphine stabilised Fe carbonyl complexes was demonstrated. The unusual stability of the reduced formyl complexes at room temperature and elevated temperatures ($T \geq 60 \, ^\circ\text{C}$) make them promising candidates for incorporation into a catalytic system; minimal conversion to hydride $[\text{Fe(Cp}^*)(\kappa^2$-$\text{P}_2)$(H)] and no conversion to carbonyl hydride $[\text{Fe(CO)}($Cp$^*$(H)] species
was observed in the reductions of 3 [Fe(CO)(Cp*)(κ²-dmpe)]⁺ and 4 [Fe(CO)(Cp*)(κ²-depe)]⁺ suggesting that the smaller bisalkylphosphine complexes were the most suitable for further study. These ligands do not dissociate from the metal readily and an equilibrium exists in which hydride can shuttle between the formyl and borohydride donor. Ideally we would like to generate an electron-rich formyl that can reduce other species (and itself) in preference to decomposing; however, the challenge of electrophilic activation remains. Reduction of these complexes has only been achieved with very strong hydride donors such as (vide supra) M[BH3], so the strategy redirects as to how to generate suitably powerful reductants directly from hydrogen. If strongly reducing hydrides are to be generated via FLP activation of H2, this will require a concomitantly powerful base unfortunately this leads to weak Brønsted and Lewis acids in the reaction medium, which limits the extent of electrophilic activation of a formyl to prompt further reduction.

As discussed in Chapter 1, BEt₃ has been shown to activate hydrogen with the unusual carbanion [C(SiMe₂OCH₂CH₂OMe)₃]Na synthesised by Krempner et al. (Scheme 3.28). Theoretically it should be possible to reduce the complexes 3 and 4 using a similar FLP (i.e. a strong base and BEt₃) and hydrogen. The structural and synthetic complexity of the aforementioned carbanion mean it was not ideal for use in a CO conversion cycle. Instead it was thought that a simpler system would ideally make use of a commercially available base. Since the pKₐ for Krempner’s carbanion is known [pKₐ (DMSO) 22.8] it was envisioned that BEt₃ would also activate hydrogen with the stronger, bulky phosphazene base tert-butylimino-tris(pyrrilidino)phosphorane, (P₃) [pKₐ (acetonitrile) 28.4].

Scheme 3.28: Hydrogen activation by the carbanion [C(SiMe₂OCH₂CH₂OMe)₃]Na and BEt₃
When the acid base pair (BEt₃/P₁) was mixed in THF the ¹¹B NMR spectrum produces a broad singlet at δ 73.9 ppm, ca. 6 ppm upfield from its usual shift of ¹¹B (THF) δ 80.3, indicating only a weak interaction between the acid-base pair in solution. On addition of H₂ (4 bar) there is an obvious broadening of the BEt₃ resonance indicating an interaction (Figure 3.21). Importantly, no ¹¹B B-H, or bridging B-H-B bond resonances are observed in the ¹¹B NMR spectrum, providing no evidence for hydrogen activation.

![Figure 3.21](image)

**Figure 3.21**: ¹¹B NMR spectrum at room temperature of the FLP P₁/BEt₃ interaction with H₂ in THF; the blue spectrum is before the addition of H₂ and the black spectrum is after.

When BEt₃, P₁ and H₂ (4 bar) are added to a THF solution of 3 no reaction is observed at room temperature or elevated temperatures. Given the lack of evidence for hydrogen activation this result could be attributable to a complete lack of borohydride in solution, or a very low concentration. In any case a high concentration of borohydride in solution is necessary to facilitate hydride transfer to 3; as discovered in Section 3.3.2 the addition of 1 equivalent of Li[BHEt₃] to 3 in THF, produced the reduced species 3a and 3b in a maximum combined yield of ca. 23 %, which indicates the equilibrium lies towards the borohydride (Figure 3.23). In the FLP system, there is no alkali metal present which could also disfavour the reduction.
Chapter 3  Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

Figure 3.22: $^{31}$P NMR spectrum in THF at room temperature, of the reduction of carbonyl 3 with 1 equivalent of Na[BHEt$_3$]

The BEt$_3$/P$_1$ system was also used to attempt hydrogenation of [Fe(CO)(Cp)(κ$_2$-dmpe)]$^+$ (6). Given the decreased electron density of this carbonyl complex, it was envisaged that formyl formation should be significantly more favourable, and as such should allow more facile hydride migration from [HBEt$_3$]$^+$ prompting the aforementioned equilibrium. Again, however, no reduction was observed and all NMR spectra ($^1$H, $^{31}$P and $^{11}$B) remain unchanged at room temperature and with heating at 60 °C for 12 hours; this implies that a lack of hydrogen activation prevents reduction chemistry. Importantly Krempner has reported recently, after this work was already carried out, BEt$_3$ and P$_1$ do not activate hydrogen which is attributed to the weak Brønsted basicity of P$_1$. A number of experiments with BEt$_3$ and P$_1$ carried out by us seem to support this finding.$^{40}$

Bercaw has reported the reduction of a rhenium complex [(B)$_2$Re(CO)$_4$][BARF$_{24}$] containing a tethered borane, B = $^t$BuCH$_2$CH$_2$B(C$_8$H$_{14}$), in its second coordination sphere.$^{33}$ The borane was initially included in the complex to promote Lewis acid assisted reduction of the rhenium
complex using \((P_1)\) as base. The authors report reduction of the untethered complex, 
\([\text{PPh}_3]_2\text{Re(CO)}_4[B\text{ArF}_{24}]\), using the free borane \(^7\text{BuCH}_2\text{CH}_2\text{B(C}_8\text{H}_{14})\) and \(P_1\), to afford hydrogen activation with subsequent reduction to the unstable formyl \((\text{PPh}_3)_2\text{Re(CO)}_3\text{CHO}\); the latter decarbonylates to \((\text{PPh}_3)_2\text{Re(CO)}_3\text{H}\) and \((\text{PPh}_3)\text{Re(CO)}_4\text{H}\). This prompted the use of this system to attempt hydrogenation of the carbonyls 3 and 6. The borane, \(^7\text{BuCH}_2\text{CH}_2\text{B(C}_8\text{H}_{14})\) should be a poorer Lewis acid than \(\text{BEt}_3\), which should make hydride transfer even more facile. \(^7\text{BuCH}_2\text{CH}_2\text{B(C}_8\text{H}_{14})\) was synthesised according to a literature procedure\(^{33}\) and FLP experiments with \(H_2\) (4 bar) were performed with \(P_1\) as base. Once again, no reduction of 3 or 6 was observed at either room temperature or at elevated temperatures (\(T = 60^\circ\text{C}\)) over 12 hours.

With these results it is clear that although the use of the dmpe ligand appears to stabilise the complexes to ligand decomplexation and decarbonylation, yet these species are too electron-rich to permit further reactivity. Although it has been shown that reduction is possible stoichiometrically and using an excess of hydride, catalytically it remains unfeasible. In order to remove electron density while preserving the same steric demands, less electron-rich \textit{bis} phosphine ligands of a similar size and bite angle could be used. The use of a \(\pi\)-acceptor bipyridyl ligand was also considered as a small, less electron-rich alternative. The complex \([\text{Fe(\kappa^2-bipy)(CO)(Cp*})]^+\) was synthesised, by analogous methods to the \textit{bis} phosphine complexes (Scheme 3.29).

![Scheme 3.29: Synthetic procedure for the synthesis of ([Fe(bipy)(CO)(Cp*)][BArF]24) (8), bipy = 2,2'-bipyridyl](image)

Upon addition of strong reducing agents such as \(\text{Na}[\text{BHEt}_3]\) in THF, the ligand appears to dissociate and the solution turns dark purple which appears to indicate formation of the dimer \([\text{Fp*}_2]\) (Scheme 3.17); the free ligand is observed by \(^1\text{H} \text{NMR analysis. Clearly these ligands}
are not suitable for reductions employing strong hydride donors. Given the presence of a π system it is likely they readily accept an electron and as such reduction on the metal is facilitated resulting in dissociation of the ligand. For future studies of N-donor complexes of the [Fe(CO)₂(Cp*)]⁺ moiety, it could be advisable to attempt use of a stronger donor e.g. (Me₂NCH₂)₂. However, these are pure σ donor ligands so could be more labile in the presence of reduced, electron-rich intermediates e.g. [Fe(CHO)(L)₂(Cp*)] (L = 2-electron donor).

Scheme 3.30: Reactivity seen on reduction of a bipyridyl carbonyl complex when using a strong hydride donor Na[BHEt₃]

3.5 Conclusion

It has been shown that suitable electronics are essential for the success of carbonyl conversion i.e. the electron density and π acid properties of the ancillary ligands. However sterics have also been shown to play a significant role. In the case of the family of bisalkylphosphines first investigated here, formyl complexes are observed for all reductions using the strong hydride donor Na[BHEt₃]. The complexes 3 and 4 produce stable equilibria between singly reduced species when treated with 1 equivalent of Na[BHEt₃] at room temperature (Scheme 3.31), while the Cp analogue 6 undergoes hydride attack solely at the Cp ring producing only one product (Scheme 3.32).

Scheme 3.31: Reactivity of complexes 3 and 4 when treated with 1 equivalent of Na[BHEt₃]
Chapter 3  

Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

Scheme 3.32: Reactivity of complex 6 when treated with 1 equivalent of Na[BHEt₃]

The complexes 5 and 7 containing larger phosphines display different reduction behaviour with a tendency for the formation of the carbonyl hydride species, and only trace conversions to formyls are observed. A possible ET mechanism may be attributable for the different behaviour shown by complex 7 as reported by Astruc with LiAlH₄ (Scheme 3.33). Time did not allow for our own EPR studies on the reduction of 7 with Na[BHEt₃].

Scheme 3.33: Reactivity of complexes 5 and 7 when treated with 1 equivalent of Na[BHEt₃]

The disproportionation of these species to further reduced products has been shown to rely on the presence of a strong Lewis acid. The results provided in this chapter highlight the ineffectiveness of BEt₃ in facilitating further reduction. Not only is a strong Lewis acid required for the activation of a formyl complex but a strong Lewis acid is also needed to prompt hydrogen cleavage. Na[BHEt₃] is the only borohydride that has been shown to reduce any of the newly investigated bisphosphine complexes discussed in this chapter. BEt₃ has recently been shown to activate hydrogen with the strong Brønsted bases [C(SiMe₂OCH₂CH₂OMe)₃]Na and Verkade’s superbase (2,8,9-Triisopropyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane) [pKₐ (ACN) 33.4]. It was envisaged that P₁ could activate hydrogen with BEt₃ and deliver hydride however this was not found experimentally. Attempted use of Bercaw’s FLP₃³ employing use of the electron-rich borane ¹BuCH₂CH₂B(C₈H₁₄) and P₁ also failed to prompt hydrogenation; in this case is likely attributable to the low concentration of borohydride in solution. It has been shown that the delivery of hydride from [HBEt₃]⁻ to [Fe(CO)(Cp*)(κ²-dmpe)]⁺ is reversible prompting an equilibrium that lies towards the
Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

borohydride. Although it seemed promising that the FLP system P₁/BE₃ could activate hydrogen and deliver a hydride to the less electron-rich species 6, this was not found experimentally. This can now be attributed to the insufficient Brønsted basicity of P₁.

The results in this chapter highlight the stabilising power of electron-rich bisphosphines to aid characterisation of homogenous CO conversion intermediates such as the formyl. However, ultimately their electron density renders reduced intermediates difficult to access when employing hydrogenation directly from hydrogen, using an FLP. A strong hydride donor is essential to reduce the carbonyl and produce a stable, electron-rich metal formyl. A strong Lewis acid or strong protonated Lewis base [LBH]⁺ is needed for activation of the resulting metal formyl to allow for further reduction. A weak Lewis acid needs a strong Lewis base to activate H₂ which will generate a weak conjugate acid which in turn will not interact with the metal formyl sufficiently. In addition, a strong Lewis acid necessary for hydrogen activation is likely to accept hydride from a strong hydride donor such as the formyl which would sequester the hydride available to access further reduced intermediates. These combined factors render this system fundamentally incompatible. Chapter 4 will explore a new approach; the use of a neutral carbonyl substrate containing strong π-acceptor ligands in order to attempt the synthesis of a more basic, anionic formyl species.
3.6 References

Chapter 3  Reduction studies of bisphosphine substituted cationic iron carbonyl complexes

11874–11875.
Chapter 4

Reduction studies of neutral iron carbonyl complexes

4.1 Introduction

Collman and Winter characterised the first anionic formyl complex on iron using the reaction of Na$_2$Fe(CO)$_4$ with acetic formic anhydride.$^1$ Casey characterised the second formyl complex from the reduction of the neutral complex [Fe(CO)$_4$P(OPh)$_3$] with 6 equivalents of K[BH(O$i$Pr)$_3$] and used a cation exchange with [Et$_4$N]Br to isolate [Et$_4$N]$^+$[((PhO)$_3$P)(CO)$_2$Fe(CHO)]$^-$. Gladysz has synthesised a host of anionic formyl complexes using 1 equivalent of M[HBEt$_3$], (M = alkali metal) on neutral carbonyl complexes and measured the decomposition rates of these formyls, reporting their slightly increased stability in comparison with neutral analogues.$^3,^4$ Winter et al. have demonstrated strong ion pairing effects (with Group 1 alkali metals) in the formation and stabilisation of anionic transition metal formyls, which has been likened to the cooperative effect of hydrogen bonding in facilitating ketone reduction.$^5$ Like their neutral analogues anionic formyls have a tendency to disproportionate and concomitantly deliver hydride to other species making them ideal candidates in a reduction cycle. In one example Gladysz reports the disproportionation of the monoanionic formyl Li[[(CO)$_4$Mn(COC$_6$H$_5$)(CHO)]$^-$(a) by intramolecular hydride transfer, forming Li[Mn(CO)$_5$] and C$_6$H$_5$CHO. Further reduction of benzaldehyde, by the formyl a results in formation of C$_6$H$_5$CH$_2$OLi and (CO)$_2$MnCOC$_6$H$_5$ and coupling of these species produces Li[Mn(CO)$_5$] and (C$_6$H$_5$)CO(OCH$_2$C$_6$H$_5$) (Scheme 4.1). Others have characterised anionic formyls on chromium and tungsten.$^2,^6,^7$ Much work has also focused on the hydride affinity of some neutral carbonyl complexes which form anionic formyls upon addition of a hydride.$^8,^9$
The results discussed in Chapter 3 demonstrate that adding electron density to a metal centre increases the metal-carbon bond strength, thereby decreasing the tendency for decarbonylation and production of unreactive metal-hydrides. Another approach to stabilise an electron-rich formyl complex would be to add a π-acceptor ligand to the iron centre. The investigations into reduction of [Fp*CO][BArF$_{24}$] discussed in Chapter 2 show more facile hydride addition; this complex was reduced by the trisarylborohydrides [H-B(2,4,6-(C$_6$H$_2$F$_3$)$_3$)]$^-$ ([HBArF$_9$]$^-$) and [H-B(C$_6$H$_5$)$_3$]$^-$ ([HBPh$_3$]$^-$) both stoichiometrically from their sodium salts, and directly from hydrogen in tandem with a base. In contrast no reduction from hydrogen was reported when the complex was stabilised with bisphosphine ligands, in the family of complexes [Fe(CO)(Cp*)(κ$_2$-P$_2$)][BArF$_{24}$]. However, the presence of these ligands allow the production of formyl complexes that are stable indefinitely at room temperature.

These observations led to the investigation of a new approach, the use of cyanide as an ancillary substituent on the [Fe(CO)$_2$(Cp$^R$)]$^+$ (Fp$^R$)$^+$ moiety. This ligand presented a number of attractive possibilities. The negative charge of the cyanide ligand (CN$^-$) would render the resulting complex neutral, whilst being isoelectronic with [Fp*CO]$^+$. With this complex we anticipated more facile reduction with greater thermodynamic formyl stability. This was indicated by comparison of the CO stretching frequencies of [Fp*CN] (9) which at 2032 and 1983 cm$^{-1}$ indicate significantly stronger C-O bonds when compared to the bisphosphine complex 3 which has a much lower stretching frequency of 1947 cm$^{-1}$ (vide infra Table 4). It was envisaged that with an anionic charge in tandem with strong π-acceptor ligands, [Fe(CHO)(CN)(CO)(Cp*)]$^-$ (9a) should possess a greater thermodynamic stability when compared to Fp*CHO (2).
was attributed to a likely increased M-CO bond strength which would prevent dissociation which likely preceeds M(CHO) decarbonylation to M-H (Scheme 4.2).

Scheme 4.2: Hydride addition to [Fp'CO]+ results in a neutral formyl complex 2 whereas hydride addition to 9 results in an anionic formyl 9a

Anionic formyl complexes will possess significantly different charge localisation and as such potentially offer different reaction pathways. Scheme 4.3 shows the different ways in which we can consider how the initial steps in carbonyl reduction could occur. With a negatively charged formyl, it could be assumed that it may be more likely to react with a source of protons.
Scheme 4.3: (i) pathway (a) shows the reactivity expected with a cationic starting carbonyl complex - addition of hydride to a neutral formyl leads to hydroxymethyl and subsequent protonation leads to the formation of potential useful C1+ products (ii) pathway (b) shows protonation of a neutral formyl leading to a hydroxycarbene species (iii) pathway (c) highlights how the presence of an anionic formyl complex could prompt more facile protonation stemming from more favourable electrostatics and reactivity.

Pathway (a) shows the initial steps we presumed likely when designing the complexes in Chapters 2 and 3. The use of 2 L type ligands in addition to a Cp* and the carbonyl itself renders the complex cationic which we assumed would promote attack by a nucleophilic hydride reagent. Although reasonably successful reduction of the less electron-rich complex [Fp*CO]+ was reported, the addition of electron density using bisphosphine substituents renders the system much more unfavourable to accept hydride; the only reduction we, and others, have seen has been in using the strong hydride donors Na[BHET3] and LiAlH4.10,11 It is likely that in putting electron-rich ligands on the metal centre (complexes 3-8), we localise a high electron density on the carbonyl carbon, thereby causing significant repulsion for an incoming nucleophile. If the first step of pathway (a) is achieved, further increasing the electron density of the starting complex, it is unsurprising that the second hydride attack is energetically very demanding. This therefore requires significant electron density to be withdrawn via Lewis acid activation, without which further reduction is hampered. We have already shown in
Chapter 3 that the reaction of a Brønsted proton source at this point results in formation of hydrogen. Pathway (b) shows another possible interpretation of how the initial steps of reduction may proceed – protonation to give a hydroxycarbene relieves electron density, resulting in a second hydride attack. Pathway (c) presents a new approach, the results of which will be discussed in this chapter. It seemed plausible that a π acceptor CN⁻ ligand would not only facilitate nucleophilic hydride attack but render the resultant anionic system more reactive towards a proton source which via a transient hydroxycarbene could produce an anionic hydroxymethyl, which again should be more reactive towards protons and therefore loss of H₂O. This reactivity could lead to the key intermediate methylidene [Fe(=CH₂)(CO)(CN)(Cp*)], analogous to the cationic complex [Fp*=CH₂]⁺. [Fp*=CH₂]⁺ has been reported to produce uncoordinated ethylene postulated to occur via a biscationic metallocycle.¹²,¹³ Additionally the dimerisation of a neutral methylidene such as [Fe(=CH₂)(CO)(CN)] would involve more favourable electrostatics (Scheme 4.4).

**Scheme 4.4:** Possible electrostatic interactions in the dimerisation of electrophilic Fe methylidenes.
4.2 Synthesis of FpR\textsuperscript{CN} complexes

To investigate the reduction of cyano substituted [Fp\textsuperscript{R}][+] complexes, [Fe(CN)(CO)\textsubscript{2}(Cp*)] (9) and [Fe(CN)(CO)\textsubscript{2}(Cp)] (10) were synthesised via literature procedures. 9 \[ ^{1}H \text{ (CD}_{3}\text{OD) } \delta 1.93, s \] has been synthesised by Daresbourg et al.\textsuperscript{14} and involves reaction of Fp*Br with one equivalent of KCN in methanol. This synthesis was problematic due to typically 10 \% impurity of K[Cp*Fe(CN)\textsubscript{2}CO] \[ ^{1}H \text{ (CD}_{3}\text{OD) } \delta 1.79, s \] formed from over-substitution. The compound was purified using sublimation \( 1 \times 10^{-2} \text{ mbar, 50 } ^{\circ}\text{C} \). Fp*Br is readily obtained by the oxidation of Fp*\textsubscript{2} using Br\textsubscript{2} (Scheme 4.5).\textsuperscript{15} The synthesis of 10 was carried using a similar procedure, also published by Daresbourg.\textsuperscript{16,17} FpBr was stirred at room temperature with KCN in methanol and any over-substituted products removed by sublimation. Both 9 and 10 are obtained as dark yellow/mustard solids in 65 \% and 60 \% yields respectively, their characterisation data agrees with the published details.

\begin{center}
\textbf{Scheme 4.5:} Synthesis of [Fp*CN] via substitution of Fp*Br using KCN.
\end{center}

The CO stretching frequencies for 9 and 10 are compared to those of the cationic carbonyl complexes discussed in previous chapters (Table 4). The level of metal-carbon back donation present in 9 and 10 is significantly less than in the bisphosphine substituted complexes and are closer to that observed in [Fp*CO][+]. Complexes 9 and 10 should hence also possess stronger M-C bonds which was envisaged to suppress the problem of decarbonylation. As expected, the permethylated analogue 9 has lower stretching frequencies \( 2032, 2014 \text{ cm}^{-1} \) compared to the Cp substituted complex 10 \( 2056, 2009 \text{ cm}^{-1} \) reflecting the decreased C-O bond strength in 9 as a result of the increased electron density on the metal, conferred by the methyl groups on the Cp* ring.
Table 4: Comparison of IR stretching frequencies for various carbonyl complexes

<table>
<thead>
<tr>
<th>Carbonyl Compound</th>
<th>CO ν/cm⁻¹</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(CO)₃(Cp*)]⁺ (1)</td>
<td>2072, 2135¹⁸</td>
<td>CH₂Cl₂</td>
</tr>
<tr>
<td>[Fe(CO)₂(CN)(Cp)]⁻ (10)</td>
<td>2056, 2009</td>
<td>CH₃CN</td>
</tr>
<tr>
<td></td>
<td>2059, 2014¹⁰</td>
<td>CH₂Cl₂</td>
</tr>
<tr>
<td>[Fe(CO)₂(CN)(Cp)]⁻ (9)</td>
<td>2032, 1983¹⁴</td>
<td>CH₃CN</td>
</tr>
<tr>
<td>[Fe(CO)(Cp*)(κ²-dmpe)]⁺ (3)</td>
<td>1947</td>
<td>CH₂Cl₂</td>
</tr>
<tr>
<td>[Fe(CO)(Cp*)(κ²-depe)]⁺ (4)</td>
<td>1944</td>
<td>CH₂Cl₂</td>
</tr>
<tr>
<td>[Fe(Cp*)(CO)(κ²-dippe)]⁺ (5)</td>
<td>1940</td>
<td>CH₂Cl₂</td>
</tr>
</tbody>
</table>

4.3 Reductions of Fp⁷CN complexes

In order to investigate the reduction behaviour of 9 and 10, a series of stoichiometric reactions were carried out. As with previous studies, before attempting hydrogenations directly from H₂, an understanding of the reduction behaviour of each complex was desired.

4.3.1 Stoichiometric reductions of Fp⁷CN complexes using NaBH₄

When beginning the investigation of 9 and 10 it was an initial aim to attempt reduction with the mild reducing agent NaBH₄. NaBH₄ was calculated by Heiden to be 15 kcal/mol more reducing than the borohydride of the archetypal FLP borane [HB(C₆F₅)₃⁻ ([HBArF₁₅]⁻).²⁰ It is known that [Fp*CO]⁺ is reduced by NaBH₄²¹ and we have shown NaBH₄ is not capable of reducing any of the bisphosphine substituted complexes 3-7. When 1 equivalent of NaBH₄ is reacted with 9 in methanol, immediately at room temperature the formyl proton resonance of 9a is observed at ¹H (CD₃OD) 14.4 ppm at trace (< 5 %) conversion; methanol was chosen because of the high solubility of NaBH₄ in this solvent. If this reaction is gently heated at 45 °C for 3 hours the conversion to 9a reaches 50 % (Scheme 4.6 & Figure 4.1).
Scheme 4.6: Reactivity of [Fp*CN] with NaBH₄ in CD₃OD.

Figure 4.1: ¹H NMR in CD₃OD at room temperature, of the reduction of [Fp*CN] (9) with 1 equivalent of NaBH₄ to form the formyl [Fe(CHO)(CN)(CO)(Cp*)] (9a) at 50 % conversion - formyl proton observed at δ 14.4 ppm

Conversion stops at this point due to the competing consumption of NaBH₄ by reaction with the solvent at higher temperatures. The reduction appears relatively facile in MeOH however methanolysis of NaBH₄ results in NaB(OCH₃)₄ (¹¹B δ 3.41, s) via transient hydrido-borates NaBH₄(OCH₃)₄ₓ and H₂ (Scheme 4.7). The reaction with MeOH is relatively slow at room temperature but if heated, H₂ is evolved rapidly.

NaBH₄ + 4CH₃OH → NaB(OCH₃)₄ + 4H₂

Scheme 4.7: Competing methanolysis when NaBH₄ reduction carried out in MeOH or MeOD.
Given that NaBH₄ reacts with MeOH relatively quickly at higher temperatures, subsequent equivalents of NaBH₄ would be necessary to achieve full conversion to the formyl Na[Fe(CHO)(CN)(CO)(Cp*)] (9a). It was also recognised that the reduction being observed is likely to be as a result of the more strongly reducing intermediate hydrido-borate species and does not conclusively show if NaBH₄ is capable of reducing 9. This hypothesis is also supported by the result that Bu₄NBH₄, which is readily soluble in THF at room temperature, will not reduce [Fp*CN] even after 12 hours at 45 °C. However, this does eliminate the possibility of the Na⁺ cation playing a favourable role in the NaBH₄ reduction of [Fp*CN]. The limited solubility of NaBH₄ in a range of suitable solvents limited the scope for using a non-alcoholic solvent. Instead reduction was attempted in the solvent 2-butanol, which is unreactive with NaBH₄ at room temperature. The lack of reduction in this solvent at room temperature confirmed that the reductant was in fact likely to be the much stronger hydride donor, a substituted hydrido-borate (NaBHₓ(OR)₄₋ₓ) (Scheme 4.8).

Scheme 4.8: Reaction of NaBH₄ with alcoholic solvents produces strongly reducing hydrido-borate species
Despite the likely action of a strong hydride donor, the facile observation of the seemingly thermodynamically stable formyl species 9a was still an interesting discovery. It was envisaged that full conversion and attempted isolation of the formyl 9a could aid study of the appropriate acid strength to prompt further proton mediated reduction. Using 2-butanol as solvent and 2 equivalents of NaBH₄, 80 % conversion of formyl is easily achieved after 24 hours at 45 °C (Scheme 4.9 & Figure 4.2). The reaction does not tolerate higher temperatures given the tendency for nucleophilic ligand scrambling of the cyanide ligand in 9; the impurities [[Fp*H]] and Na[Fe(CN)₂(CO)(Cp*)] (¹H δ 1.79 ppm, s) were therefore always observed in the product mixture. The ready loss of the nucleophilic CN⁻ leads to vacant sites on the Fp*- fragment and hydride attack on the metal to produce [[Fp*H]] (Scheme 4.10). There is the possibility of [[Fp*H]] arising from decarbonylation of the formyl 9a, prompting loss of the most nucleophilic ligand CN⁻. However, this pathway seems unlikely since it has already been shown that the formyl 9a is stable at room temperature and up to at least 45 °C.

Scheme 4.9: Optimised reaction conditions for the reduction of 9 with NaBH₄ in 2-butanol

Scheme 4.10: Ligand scrambling of the nucleophilic cyanide ligand in complex 9 is observed with prolonged heating
Figure 4.2: $^1$H NMR spectrum in CD$_3$OD at room temperature, after heating the reduction of 9 with NaBH$_4$ for 24 hours at 45 °C in 2-butanol - bicineanide complex produces singlet resonance at δ 1.79 ppm

Before attempting purification and crystallisation of the species 9, we aimed to unequivocally determine, via labelling experiments, that it was the presumed formyl species 9a. Complex 9 was labelled with $^{13}$CO gas administered via a Toepler line. The complex was irradiated for several hours at 254 nm to prompt exchange of the $^{12}$CO ligands with $^{13}$CO (Scheme 4.11).

![Scheme 4.11: $^{13}$CO enrichment of complex 9 in THF](image)

Presumably due to the presence of strong π acceptor ligands CO and CN, the complex is very difficult to label and prolonged irradiation led to significant ligand scrambling. A cleanly 10% labelled sample was achieved and subsequent reduction gave rise to a doublet resonance at $^1$H δ 14.4 ppm with coupling $J = 128$ Hz (Figure 4.3). This coupling is in good agreement for what
we would expect from a $^{13}$C-$^1$H formyl splitting; Astruc reported a $^1J_{CH}$ coupling of 127 Hz for the species Fe(CHO)(CO)(Cp*)(PMe$_3$)$_2$.$^{21}$

![Figure 4.3: $^1$H NMR spectrum at room temperature in CD$_3$OD, the doublet at $\delta$ 14.4 ppm arises from the coupling between the formyl proton in [Fe(CHO)(CN)(Cp*)] and the $^{13}$C of the isotopically labelled formyl carbon.](image)

NaBD$_4$ is commercially available and can be incorporated into a NaBD$_4$/2-butanol reduction to demonstrate deuteride delivery to the carbonyl (Scheme 4.12).

![Scheme 4.12: Reduction of 9 using NaBD$_4$.](image)

After addition of NaBD$_4$ in 2-butanol and heating at 45 °C a $^2$H NMR experiment can be run and a singlet at the distinctive formyl shift is observed [$^2$H (2-butanol) $\delta$ 14.77 ppm]. The other peaks ($\delta$ 0-2 ppm and ca. 5 ppm) observed occur from exchange of proteo 2-butanol with deuterium in NaBD$_4$ (Figure 4.4).
Figure 4.4: $^2$D NMR spectrum in 2-butanol at room temperature, of the reduction of [Fp*CN)] using NaBD$_4$; the spectrum shows [Cp*FeCO(CN)CDO] at $\delta$ 14.77 ppm

$^{13}$C\{$^1$H} NMR analysis was carried out to observe coupling in 9a-d, between the carbonyl carbon and the new deuteride functionality –CDO. The $^{13}$C\{$^1$H} resonance is observed as a triplet at $^{13}$C\{$^1$H} $\delta$ 296 ppm with a coupling constant of $^1J_{CD} = 20$ Hz (Figure 4.5). The coupling of $^{13}$C-2D is related to the coupling constant of $^{13}$C-1H through the equation $J_{C-D} = (\gamma_H/\gamma_D)J_{C-H}$. From $^{13}$CO labelling experiments and the $^{13}$C-1H coupling constant was determined to be 128 Hz. This gives a theoretical value for the $^{13}$C-2D coupling constant of 19.6 Hz which gives excellent agreement with what is found experimentally.
Attempts to optimise the synthesis and isolate the formyl 9a were made. The complex can be extracted with Et$_2$O and washed with pentane to give a crude 40 % yield. However, attempts to remove borate salt NaB(Obu)$_4$ $[^{11}\text{B} (\text{CD}_3\text{OD}) \delta 2.93$ ppm, s] and over-substituted Na[Fe(CN)$_2$(CO)(Cp*)] impurities were unsuccessful. Multiple attempts were made to fractionally crystallise the majority formyl product and/or precipitate using non-polar solvents e.g. pentane. The use of alcoholic solvents generated a high yield of inseparable impurities. However, reduction attempts of 9 using NaBH$_4$ in THF at elevated temperatures (heating at 60 °C for 2-12 hours) never produce a formyl resonance and solely result in the formation of the products of ligand scrambling 10 % [[Fp*H]] ($^1\text{H} (\text{THF}) \delta -11.8$ ppm, s) and 10 % Na[Fe(CN)$_2$(CO)(Cp*)] ($^1\text{H} (\text{THF}) \delta 1.79$ ppm, s) (Scheme 4.13). These results highlight the incompatibility of complex 9 with elevated temperatures indicating a poor potential choice for incorporation into a catalytic cycle.
Complex 9 can be reduced, however, with 1 equivalent of Na[BHEt₃] in THF, producing 76% conversion to the formyl 9a (¹H (THF) δ 14.50 ppm). The complex 9a is stable indefinitely at room temperature but was not heated due to potential ligand scrambling. These results highlight the greater ease of reduction of 9 vs. the bisphosphine complexes (3-7) discussed in Chapter Three, in addition to the notable thermodynamic stability of the formyl 9a. However, it may be concluded that once again reduction is only achieved with strong hydride donors (Scheme 4.14).

Attempts to crystallise the formyl from alcoholic solvents, using pentane as an anti-solvent, met with failure given immiscibility of pentane and alcoholic solvents. Crude 9a was extracted and dissolved in THF to attempt crystallisation, however this only ever resulted in co-precipitation of 9a and borate salt impurities. Unfortunately, a crystalline sample of the formyl was never obtained. The results discussed show that none of the alcoholic solvents \([pK_a 15.5-16.1]\) used for reactions were capable of protonating the anionic formyl species. Protonation attempts were also carried out with acids typically formed in FLP systems such as...
[TMPH][BArF$_{20}$] and [HPBu$_3$][BArF$_{20}$], showing no reaction in any case as evidenced by a lack of change in the $^1$H and $^{31}$P NMR spectra.

### 4.3.2 Stoichiometric reduction of [Fe(CO)$_2$(CN)(Cp*)]

The less electron-rich complex 10 is reduced at room temperature in CH$_3$OD and appears to decarbonylate rapidly, as evidenced by the immediate observation of [[FpH]] $^\delta$ (CH$_3$OD) −12.2 ppm, s] in the $^1$H NMR spectrum. Upon heating at 45 °C no formyl resonance was observed and the signal for [[FpH]] grows in, in the $^1$H NMR spectrum. Analogous results are seen if 10 is reduced with Na[BHEt$_3$]. Rapid reduction was expected given the higher CO stretching frequencies reported for the Cp analogue, however reduction results in the generation of a highly unstable formyl species.$^{14}$ It is also the case that ligand scrambling appears to occur more rapidly for the Cp analogue; if the reaction mixture is heated for 1 hour at 45 °C [[FpH]] is observed in the $^1$H NMR spectrum. The rapid ligand scrambling producing [[FpH]] undermines any attempt to reduce complex 10. Analogous results to 9 are observed with NaBH$_4$ in THF however the formation of [[FpH]] ($^1$H $\delta$ −12.2 ppm, s) and Na[Fe(CN)$_2$(CO)(Cp)] ($^1$H $\delta$ 4.36 ppm, s) occurs more rapidly (both 15 % conversion, 2 hours 60 °C) (Scheme 4.15).

![Scheme 4.15](image)

Scheme 4.15: Ligand scrambling occurs rapidly for complex 10 when heated at 60 °C

### 4.3.3 Frustrated Lewis pairs and hydrogen: Reactivity with [Fe(CN)(CO)$_2$(Cp*)]

In Chapter Two we reported hydride delivery to [Fp*CO]$^+$ using a FLP and hydrogen. So far there are no reports of the delivery of a proton from hydrogen to a reduced carbonyl. This was attributed to both concentrations of borohydride in solution, which prevents [MCHO] formation, and an inertness of the formyl [Fe(CHO)(CO)$_2$(Cp*)] with relatively weak proton sources such as [Et$_3$NH]$^+$ ($pK_a$ DMSO 9.0). It was anticipated that an anionic formyl would be much more reactive to a H$^+$ source thereby facilitating H$^+$ mediated reduction. Reduction of complex 9 has been demonstrated with electron-rich borohydrides Na[HB(OMe)$_3$], Na[HB(OBu)$_3$] and Na[BHEt$_3$]
To investigate the reactivity of 9 with a FLP and hydrogen a reaction was prepared using the electron-rich borane 1BuCH2CH2B(C8H14) and tert-Butylimino-tri(pyrrolidino)phosphorane (P1) (Scheme 4.16); Bercaw observed reduction of a rhenium carbonyl complex to the formyl using the aforementioned system.\(^\text{22,23}\) Hydride delivery (9 %) occurs immediately at room temperature (< 0.5 hours) as evidenced by the characteristic formyl resonance for 9a at \(^1\)H (THF) \(\delta\) 14.50 ppm. Unfortunately, even with heating for 12 hours at 60 °C no further conversion to formyl 9a or further reduced species was observed demonstrating that [P1H]\(^+\) [pK\(_a\) (MeCN) 28.4] is not a sufficiently strong acid to protonate the anionic formyl complex 9a. A second hydride equivalent is not delivered either, which is not unexpected since this would lead to a dianionic species, in the absence of protonation occurring. Instead the formyl concentration reaches a steady state (9 % conversion), which then loses CN\(^-\) to form [[Fp*H]] (−11.8 ppm).

\[\begin{align*}
\text{BR}_3 + \text{P}_1 & \rightarrow [\text{HBR}_3]^− + [\text{HP}_1]^+ \\
\end{align*}\]

\[\begin{align*}
\text{Fe}^\text{II} & \rightarrow \text{Fe}^\text{III} \\
\text{CN}^− & \rightarrow \text{CH} \\
\end{align*}\]

\textbf{Scheme 4.16:} Attempted FLP hydrogenation using a system developed by Bercaw \textit{et al.}
In order to utilise a stronger acid source to attempt protonation of the formyl complex, FLP hydrogenations were attempted with more Lewis acidic boranes. A range of experiments were carried out with the *tris*arylboranes BPh$_3$, BArF$_9$, B(mes)(C$_6$F$_5$)$_2$ and BArF$_{15}$. These boranes can be used in conjunction with weaker bases (*cf*. P$_1$) such as lutidine $[\text{pK}_\text{aq}(\text{aq}) 6.6]$ collidine $[\text{pK}_\text{aq}(\text{aq}) 7.4]$, 2,2,6,6-tetramethylpiperidine (TMP) $[\text{pK}_\text{aq}(\text{aq}) 11.0]$. These bases form stronger conjugate acids and therefore may provide proton transfer. Given the presence of a nucleophilic cyanide ligand on the carbonyl complex, potential adduct formation was foreseen but not expected to be problematic due to the assumed low nucleophilicity of coordinated cyanide.

Initial $^{11}$B NMR spectroscopic analysis was used to determine whether adduct formation occurred with the cyanide substituent of 9. The chosen solvent for FLP investigations was 1,2-difluorobenzene (DFB), given its suitability in the hydrogenation results detailed in Chapter Two. The polarity of DFB not only stabilises charged [LAH]$^+$ and [LBH]$^+$ species formed form hydrogen activation, but was also anticipated to stabilise a charged formyl 9a.

The FLP Et$_3$N, BPh$_3$ and 9 are added together in DFB. 9–BPh$_3$ adduct formation occurs immediately, observed as a broad singlet in the $^{11}$B NMR (DFB) $\delta$ $-$3.2 ppm. Addition of hydrogen at room temperature does not affect the mixture; even when the reaction is heated at 60 ºC and 90 ºC for 2-12 hours, the $^{11}$B NMR spectra stay constant throughout with only the broad singlet for the adduct being observed, and no evidence for reduced species in the $^1$H NMR spectrum. Despite the increased steric protection afforded by the *ortho*-fluorine substituents in the more Lewis acidic BArF$_9$, it also forms an adduct with the cyanide ligand ($^{11}$B $\delta$ -12.51 ppm, br s) in the presence of 2,4,6-collidine as base. Upon addition of hydrogen (4 bar) at room temperature, no change was evident by $^{11}$B NMR spectroscopic analysis indicating no significant reactivity with hydrogen (Figure 4.6). Again there is no evidence for hydrogen activation or hydride delivery to 9 at room temperature or above (60 – 90 ºC) using this FLP and hydrogen.
Figure 4.6: $^{11}$B NMR analysis at room temperature in DFB, of the reaction mixture: 9, BArF$_9$ and 2,4,6-collidine

Analogous irreversible adduct formation is observed when hydrogenation is attempted with the FLP B(mes)(C$_6$F$_5$)$_2$ and DABCO. The 9-B(mes)(C$_6$F$_5$)$_2$ adduct is observed as a broad singlet at $^{11}$B (DFB) $\delta$ −8.8 ppm and remains unchanged upon addition of hydrogen. The increased nucleophilicity of cyanide in these systems is possibly due to the significant addition of electron density imparted by the Cp* substituent in the complex creating a highly electron-rich species. This observed adduct formation renders 9 unsuitable for hydrogenation using FLPs.

4.4 Conclusion for Fp$^R$CN reduction studies

Despite the formation of a thermodynamically stable formyl 9a from the reduction of carbonyl 9, complex 9 remains unsuitable as a CO hydrogenation catalyst for two significant reasons. Firstly, the complex is not compatible with elevated temperatures since ready scrambling of the cyanide ligand leads to formation of [[Fp*H]] which is not conducive to FLP hydrogenation of CO. Secondly, complex 9 readily forms adducts with Lewis acidic boranes, which are commonly utilised in FLP hydrogenation chemistry (Scheme 4.17). Unfortunately irreversible
adduct formation with 9 and trisarylboranes was not foreseen due to the poor nucleophilicity normally seen with cyanide.

**Scheme 4.17:** Irreversible adduct formation prevents FLP hydrogenation studies
4.5 Reduction studies of the neutral carbonyl complex \([\text{Fe(CO)}_5]\)

Following on from the reduction studies of cyanide substituted complexes 9 and 10 it was deemed wise to investigate a neutral carbonyl complex which will not present nucleophilic ligand scrambling. One such complex is the commercially available iron pentacarbonyl. This complex has been widely studied stoichiometrically and there are several reports of the isolation of the formyl \([\text{Fe(CHO)}(\text{CO})_4]\)^\(^{1,2}\). Our attention therefore focused on synthesising this formyl species directly from hydrogen. The reported isolation of the complex \([\text{Fe(CHO)}(\text{CO})_4][\text{N(PPh}_3)_2]\) indicates the kinetic and thermodynamic stability of this species. \([\text{Fe(CO)}_5]\) is the first species to be investigated which does not contain the electron-rich \(\text{Cp}\) or \(\text{Cp}^*\) ancillary ligand. Possessing only strong \(\text{CO}\) \(\pi\)-acceptor ligands, this complex was anticipated to have a higher hydride affinity when compared to complexes 9 and 10.

4.5.1 FLP hydrogenation studies of \([\text{Fe(CO)}_5]\)

In order to probe the solution phase hydride affinity of \([\text{Fe(CO)}_5]\), a series of reactions was carried out with pre-formed sodium trisarylborohydrides derived from the target FLP boranes (\(\text{BArF}_{15}\), \(\text{BArF}_9\) and \(\text{BPh}_3\)). The salts \(\text{Na}[\text{HBArF}_{15}]\), \(\text{Na}[\text{HBArF}_9]\) and \(\text{Na}[\text{HBPh}_3]\) were reacted stoichiometrically with \([\text{Fe(CO)}_5]\) in order to probe the feasibility of this carbonyl in a FLP CO hydrogenation system (Scheme 4.18).

**Scheme 4.18:** Addition of pre-formed trisarylborohydride salts to \([\text{Fe(CO)}_5]\) in DFB and TBME

Partial conversion to \(\text{Na}[\text{Fe(CHO)}(\text{CO})_4]\) is observed when \([\text{Fe(CO)}_5]\) is reacted with one equivalent of \(\text{Na}[\text{HBPh}_3]\) in tert-butylmethylether (TBME). Unfortunately, it is not possible to determine an accurate conversion to the formyl given the lack of proton environment in the starting carbonyl complex. However, after 1 hour at room temperature the formyl resonance is
observed at $^1$H (TBME) $\delta$ 15.4 ppm along with the B-H doublet resonance in the $^{11}$B NMR spectrum at $\delta$ – 7.1 ppm indicating incomplete addition of hydride (Figure 4.7 & 4.8); there is no resonance indicating BPh$_3$ coordination in the $^{11}$B NMR spectrum.

![Figure 4.7](image1.png)

**Figure 4.7**: $^1$H NMR spectrum of the formyl Na[Fe(CHO)(CO)$_4$] formed in the reduction of [Fe(CO)$_5$] with one equivalent of Na[BHPh$_3$] in TBME at room temperature

![Figure 4.8](image2.png)

**Figure 4.8**: $^{11}$B NMR analysis in DFB at room temperature after the addition of Na[BHPh$_3$] to [Fe(CO)$_5$]
The reaction does not occur when carried out in DFB, this is most likely attributable to the lack of interaction between the two reactants in this solvent. TBME appears to offer better stabilisation of the formyl Na[Fe(CHO)(CO)₄]. From the favourable reduction of [Fe(CO)₅] using Na[HBPh₃] it was anticipated that the carbonyl could be reduced directly from hydrogen using the parent borane BPh₃ in tandem with a base. Given the favourable hydrogen activation and subsequent hydride delivery observed in Chapter Two with the FLP BPh₃/Et₃N, this system was once again used for the attempted hydrogenation of [Fe(CO)₅]. Unfortunately no observable NMR spectroscopy evidence for hydrogen activation or hydride delivery at room temperature or after heating for 12 hours at 60 °C (Scheme 4.19).

Although partial hydride formation was observed from the pre-formed salt Na[HBPh₃] and [Fe(CO)₅], the reduction did not occur in 100 % conversion as evidenced by significant presence of borohydride in solution after addition to [Fe(CO)₅]. This implies that there is perhaps an equilibrium between [Fe(CO)₅] and the parent borane BPh₃. The addition of hydride is kinetically slow and as such when attempting the FLP hydrogenation, the concentration of borohydride in solution is too low to observe any hydride delivery to [Fe(CO)₅]. The reaction was also carried out in THF and in this case [(CO)₄FeH] ¹H δ -14.8 ppm is observed after 30 minutes at room temperature. THF appears to allow for faster hydride attack but does not provide stabilisation for the resulting formyl species Na[Fe(CHO)(CO)₄]. It is likely that the stronger interaction between the counterion Na⁺ and the donor solvent THF destabilises the complex [Fe(CHO)(CO)₄]Na. This interaction would be diminished in the non-coordinating solvent TBME therefore allowing for a stronger Na⁺ cation interaction with the anionic formyl complex. In order to probe the effect of an alkali metal to facilitate reduction, a FLP hydrogenation was carried out with the addition of NaBArF₂₄. Surprisingly, this does not facilitate any observed hydrogenation at room temperature or after heating for 1 – 2 days at 80 °C (Scheme 4.20), despite the positive influence seen by the presence of NaBArF₂₄ in Chapter Two.
In order to investigate the effects of hydrogen activation a range of experiments using BPh$_3$ and a variety of strengths of bases including TMP [$pK_{a(aq)}$ 11], Barton base (2-tert-Butyl-1,1,3,3-tetramethylguanidine) [$pK_{a(aq)}$ 14] and pyrrolidine [$pK_{a(aq)}$ 11.27] were carried out at 4 bar and 9 bar of hydrogen. No FLP hydrogenation of [Fe(CO)$_5$] was observed in any case. With prolonged heating 2-12 hours at 80 °C under H$_2$ (4 - 9 bar), BPh$_3$ is observed to decompose to [BPh$_4^-$] ($^{11}$B δ −6.2) and BHPh$_2$ ($^{11}$B δ 53.3 ppm). This highlights a separate problem when using electron-rich trisarylborohydrides; using heat to prompt hydrogen activation results in decomposition of the borane itself via aryl migration and ligand scrambling which is favoured when using a more electron-rich borane containing nucleophilic aryl groups.

4.6 Conclusion for [Fe(CO)$_5$] reduction studies

Partial reduction of [Fe(CO)$_5$] has been demonstrated stoichiometrically only with the most electron-rich trisarylborohydride Na[HBPh$_3$] in TBME. The observation of the formyl Na[Fe(CHO)(CO)$_4$] has not been recorded in any other solvent. In attempting FLP hydrogenations directly from hydrogen, there is clearly no favourable hydride delivery in TBME, presumably due to a low concentration of borohydride in solution as a direct consequence of the use of an electron-rich borane. In the case of THF, hydrogen activation appears to occur at a faster rate resulting in a higher concentration of borohydride in solution and therefore hydride addition to the carbonyl. The interaction of THF and the Na$^+$ counterion, however, renders the formyl destabilised and rapid decarbonylation results, forming [Fe(CO)$_4$(H)]. The results show [Fe(CO)$_5$] has no potential for carbonyl conversion within the particular FLP systems studied. Recent developments have been reported by Krempner, in the activation of hydrogen, using BEt$_3$ and Verkade’s Superbase, which occurred after the work discussed here was carried out. Use of the electron-rich BEt$_3$ and an adequate base would be a worthwhile future investigation for the reduction of [Fe(CO)$_5$], directly from hydrogen. Many electronic issues have been highlighted in this and previous chapters with regards to
homogeneous syngas conversion via hydride attack on a carbonyl. The following chapter aims to look at the prospect of electrophilic activation of carbonyl substrates to facilitate hydride addition.
4.7 References

Chapter 5

Further work & preliminary results:
Carbonyl reduction using Bu$_3$SnNTf$_2$ and Bu$_3$SnH

5.1 Introduction

So far this project has discussed syngas conversion chemistry using the most commonly encountered mechanism starting with hydride addition to a carbonyl, with no additional activation on the carbonyl other than the transition metal-ligand framework. In Chapter Two we reported homogeneous hydrogenation directly from hydrogen to give the formyl complex [Fp*CHO] (2), as well as its decomposition products [Fp*$_2$] and [Fp*H]. In Chapter Three, we demonstrated the use of bisphosphine ligands to increase electron density at the Fe centre and consequently stabilise the formyl produced upon hydride delivery. Chapter 4 discussed hydride addition to the neutral carbonyl [Fe(CO)$_2$CN(Cp*)]; however, scrambling of the cyanide ligand and adduct formation with trisarylboranes make this complex unsuitable for further investigation. Despite several success in achieving the initial hydride transfer needed for formyl generation, each system thus far has lacked sufficient activation or stabilisation for reduction past the formyl oxidation state.

Throughout our work and others’ it has been shown that without a relatively powerful Lewis acid present (e.g. AlH$_3$ or BH$_3$), reduction past the formyl is extremely difficult.$^{1,2,3}$ The necessity of a strong Lewis acid fundamentally undermines our ability to hydrogenate a carbonyl ligand from an FLP and hydrogen: it has been shown on numerous occasions that a strong hydride donor is necessary for mild homogenous reduction of a carbonyl.$^{4,5,2}$ However, to generate such a reagent from heterolytic H$_2$ cleavage, a weak Lewis acid is necessary. The only homogeneous conversion of a carbonyl using a reasonably mild hydride donor is the reduction of [Fp*CO][PF$_6$] to Fp*CH$_3$ using NaBH$_4$ in THF/H$_2$O.$^6$ Heiden et al. have used computational calculations to show that NaBH$_4$ is still 15 kcal/mol more reducing than the borohydride of the most commonly used borane in FLP chemistry, [HB(C$_6$F$_5$)$_3$]$^-$. The full reduction of [Fp*CO][PF$_6$] has been shown to fail when no BH$_3$ is present resulting in 100% conversion to [Fp*H]. These results can in part be attributed to the lack of electrophilic
activation of the carbonyl rendering it inert to weak proton sources thereby allowing decomposition of the formyl.

Given our results and the results of others we decided that it seemed wise to investigate a new route to carbonyl reduction, namely involving electrophilic activation rather than hydride transfer in the first step. This would be akin to the recently reported successes in the FLP-catalysed hydrogenations of conceptually-related organic carbonyls.\textsuperscript{8,9,10} Scheme 5.1 shows the well documented approach of nucleophilic hydride attack on a carbonyl. In this strategy an electron-rich metal center can be used to stabilise the resulting formyl, generated from hydride addition to the carbonyl. However, as we have shown this requires a potent hydride donor, which upon hydride delivery cannot bind to the formyl resulting in no electron withdrawal from the formyl species for further hydride attack or protonation, as demonstrated by the results of reduction of the bisphosphine carbonyl complexes in Chapter 3. If a less electron-rich species is used, a less potent hydride donor may be employed however the resulting formyl species is unreactive towards weak sources of proton or Lewis acid, again hampering further reactivity past the formyl. Without further reactivity the less electron-rich formyl species tends to decarbonylate, as demonstrated by the results discussed in Chapter 2. Both of these approaches rely on attack from a hydride source, followed by activation from a Lewis acid or proton. An alternative mechanism is to activate the carbonyl with an electrophile (E\textsuperscript{+}), prior to any hydride addition thereby creating a new O-E covalent bond which facilitates hydride addition from a neutral hydride source. For this approach to be successful, the electrophile must not be too oxophilic or a strong O-E bond will hamper catalysis. The carbonyl complex itself must also be neutral to allow for increased back bonding from the metal to the C-O ligand creating a nucleophilic oxygen primed for attack of an incoming electrophile.
Recently the groups of Stephan and Ashley have demonstrated reduction of simple aldehydes and ketones using ethereal solvents as weak Brønsted bases which form strong proton sources ($pK_a < -2$) when combined with the Lewis acid $\text{B(C}_6\text{F}_5)_3\text{(BARF}_{15})$ under $\text{H}_2$ (Scheme 5.2).\textsuperscript{11,9,10} This approach involves activation of the substrate by the strong Brønsted acid and subsequent transfer of the relatively weak hydride addition to the C=O bond. The Ashley group have shown that this route can even be employed in the presence of water utilising 1,4-dioxane as solvent, again as Lewis base in tandem with BARF$_{15}$.\textsuperscript{8} Stephan et al. have further extended this method to afford the hydrogenation of ketones and aldehydes in toluene with the addition of heterogeneous oxygen containing Lewis bases such as $\alpha$-cyclodextrin and molecular sieves.\textsuperscript{12} In addition, the Stephan group have reported hydrosilylation of ketones, imines and nitriles using electrophilic phosphonium cations.\textsuperscript{13}
**Scheme 5.2:** The use of a weak Brønsted base such at Et₂O provides a strong proton source on activation of H₂. The C=O bond is polarised by interaction with a strong acid, allowing for hydride donation from the weak hydride source [HBArF₁₅⁻]

This FLP mediated hydrogenation can also be compared to the BArF₁₅ catalysed hydrosilylation of carbonyl compounds developed earlier by Piers.¹⁴,¹⁵,¹⁶ In this reaction, BArF₁₅ activates the silane R₃SiH to produce a powerful Si-centred Lewis acid, behaving formally as R₃Si⁺. This species is responsible for activation of the weakly basic C=O moiety, which again polarises the C=O bond, facilitating hydride transfer from [HBArF₁₅⁻] (Scheme 5.3).
This methodology could be of use when designing a syngas conversion cycle; however hard Lewis acids such as electron-deficient Ar₃B compounds and [R₃Si]⁺ present the problem of strong B-O and Si-O bond formation which is likely to hamper catalytic activity, which previously proved a major hurdle to the development of FLP catalysed organic C=O hydrogenation. In such cases where borane Lewis acids have been shown to activate carbonyls and their corresponding formyls, subsequent equivalents of preformed reductant are always necessary to facilitate further reactivity.⁶,¹⁷ The necessary subsequent equivalents of reductant are a direct result of the strong interaction between the borane and formyl oxygen. Catalytic reduction of transition metal bound CO using silane has limited scope due to the inevitable formation of a strong Si-O bonds. Stoichiometric reduction of CO ligands is however known on both Fe and Ru; Akita et al.¹⁸ reported the use of excess of silanes to form monomeric bridging ‘CH₂’ fragments at temperatures of 150 °C (Scheme 5.4). This example highlights the limits of using highly oxophilic Si, which on Si-O bond formation cannot regenerate Si-H preventing catalytic activity. The Si-O bond is also too poorly basic to accept a proton, preventing loss of H₂O and potential FLP type hydrogen activation. If the same transformation could be performed with an electrophile that forms a weaker O-E bond, the process could potentially become catalytic.
5.1.1 Developing a Sn based FLP

In order to employ the mechanism of electrophilic C-O bond activation followed by hydride addition to a CO bound to a transition metal, a neutral, electron-rich complex should be used in tandem with a ‘softer’ electrophile or Lewis acid. One type of species which have the scope to act as an increasingly reactive hydride source are organic tin hydrides of the type $R_3SnH$. On hydride delivery from this already more polarised E-H bond (cf. Si-H), a strongly coordinating Lewis acid $R_3Sn^+$ is formed. Existing work in the Ashley group has shown promise for the use of tributyltin hydrides ($Bu_3SnH$) and tributyltin cation ($Bu_3Sn^+$) equivalents as the reductant system to afford stoichiometric conversion of $CO_2$ via $HCO_2SnBu_3$ to eventually liberate methyl formate, without the need for an activating borane or base.\(^{19,20}\) This system is postulated to begin with insertion of $CO_2$ into a bridging hydride species $[H-(SnBu_3)_2]^+$ ($^1H$ ($C_6D_6$) $\delta$ 4.8 ppm) with concomitant coordination of the $Bu_3Sn^+$ Lewis acid.

The Lewis acid $R_3Sn^+$ is isolobal with $Ar_3B$ and Sn has a comparable electronegativity to B ($\chi_B$ = 2.04, $\chi_{Sn}$ = 1.96). It is possible that CO reduction could be facilitated with coordination of a cationic Lewis acid $Bu_3Sn^+$ to the O in a CO ligand, with concomitant hydride delivery from $Bu_3SnH$. The development of a catalytic hydrogenation cycle involving $R_3SnH/R_3Sn^+$ is promising. Unlike previous examples of CO reduction using silanes, which produce poorly basic siloxanes on C-O bond cleavage, a Sn system would produce the cation tristannyl oxonium $[O(SnBu_3)_3]^+$ upon C-O cleavage.\(^{19,20}\) It is envisaged that FLP $H_2$ activation should be possible with either of these species and gratifyingly under HD this has been reported to form a 1:1:1 mixture of $H_2$:HD:D$_2$, indicating its ability to activate $H_2$ (Scheme 5.4).\(^{19}\) The
mechanism of CO reduction and C-O bond cleavage would necessarily produce H₂O, Sn-R bonds are stable to hydrolysis.

Scheme 5.5: Scrambling of HD using basic stannyl oxonium cations; observed previously in the Ashley group

5.2 Preliminary results

5.2.1 Synthesis of Bu₃SnNTf₂

Previous work in the Ashley group has focused on the conversion of CO₂ using the stannyl cation [Bu₃Sn]⁺ and Bu₃SnH under H₂. It seemed wise to take this chemistry and investigate its use for carbonyl hydrogenation as a model for syngas conversion. Three coordinate stannyl cations have been previously reported to complex to weakly nucleophilic non-coordinating counterions such as hydrotris(pentafluorophenyl)borate, tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate (BArF₂⁻) and more recently tetrakis(pentafluorophenyl)borate. ¹⁹,²¹,²² Previously successful CO₂ conversion chemistry has been carried out in the Ashley group using stannyl cations stabilised by tetrakis(pentafluorophenyl)borate (BArF₂⁰⁻). The complex [Bu₃Sn][BArF₂⁰] was synthesised using the trityl species [Ph₃C][B(C₆F₅)₄] to prompt a Bartlett-Condon-Schneider type hydride abstraction in situ in an identical manner to the procedure reported by Kira et al.²² Although much work was developed using this cation synthesis, results using this salt proved capricious and difficult to reproduce – perhaps due to an inefficient stabilisation of the reactive stannyl cation with the weakly coordinating borate anions. In the following preliminary investigations of CO reduction, an alternative stannyl complex equivalent has therefore been pursued.

Other possible forms of anion stabilisation include species such as the triflate anion (OTf⁻) and bistriﬂimide (NTf₂⁻), Tf⁻ = F₃CSO₂⁻. Although both Manners’ and Stephan reported
dehydrogenation of amino-boranes using Bu₃SnOTf and TMP, further work has found that Bu₃SnOTf is not capable of FLP H₂ activation with TMP. Ghosez et al. discovered a surprising inverse correlation between the the Brønsted acidity for HX acids (X = OTf⁻, NTf⁻) and the Lewis acidity of their R₃SiX derivatives. This discovery has been attributed to the size of the anion, X⁻, ([NTf]⁻ > [OTf]⁻). The synthesis of Bu₃SnNTf₂ was therefore pursued due to its increased Lewis acidity when compared to Bu₃SnOTf. The complex was found to be easily synthesised via the reaction of HNTf₂ and Bu₃SnH in C₆D₆ giving a quantitative yield of Bu₃SnNTf₂ as a colourless, extremely viscous oil (Scheme 5.6). HNTf₂ is inexpensive and readily available starting material meaning Bu₃SnNTf₂ can be readily made with very little synthetic effort. In C₆D₆, Bu₃SnNTf₂ gives a broad singlet at δ 254 ppm in the \(^{119}\text{Sn}\{\text{¹H}\}\) NMR spectrum and a sharp singlet at δ −78.6 ppm in the \(^{19}\text{F}\) NMR spectrum. This shift is relatively low for a `true` three coordinate Sn species indicating significant stabilisation from NTf₂⁻ and/or the solvent C₆D₆ (Figure 5.1). Many attempts have been made to generate a truly three-coordinate stannylium cation, one notable example from Lambert et al is the cation Tip₃Sn⁺ which produces a resonance at δ 714 ppm. However empirical chemical shift values for an unstabilised three coordinate stannylium can be as high as δ 1500 ppm, as has been calculated for tributylstannylium CB₁₁Me₁₂⁻. The shift reported for [Bu₃Sn][BARF₂₄] is \(^{119}\text{Sn}\{\text{¹H}\}\) δ 360 ppm in CD₂Cl₂, indicating a weaker interaction than when NTf₂⁻ and C₆D₆ are present.

\[
\begin{align*}
\text{Bu}_3\text{SnH} & \quad + \quad \text{HNTf}_2 \\
\text{C}_6\text{D}_6 & \quad \text{Bu}_3\text{Sn[NTf}_2] \quad + \quad \text{H}_2
\end{align*}
\]

**Scheme 5.6:** Synthesis of stannyl cations stabilised by bistriflimide anion
In order to test the hypothesis of electrophilic activation followed by hydride addition the carbonyl substrate scope was altered compared to those used in previous chapters. In order to facilitate nucleophilic hydride attack we, and others, have focused on cationic carbonyl complexes to promote favourable electrostatics. However, in the case of electrophilic activation of a carbonyl, an electron-rich, neutral carbonyl should show favourable electrostatics and the most reactivity towards an electrophile. For this preliminary investigation a number of readily prepared neutral carbonyls have been used, synthesised according to literature procedures ([Fe(CO)₅] is commercially available): [Co(CO)₂(Cp*)]₃⁰ [Mn(CO)₃(Cp*)]₃¹ and [Fe(CO)₂(Cp*)]₂₃² (Figure 5.2).

**Figure 5.1:** $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum at room temperature of Bu₃SnNTf₂ in C₆D₆

**Figure 5.2:** Neutral metal carbonyls which were used to explore reduction using electrophilic activation with Bu₃Sn⁺ and hydride transfer from R₃SnH
5.2.2 Neutral transition metal carbonyl complexes with Bu₃Sn⁺ and Bu₃SnH

The aim of the following set of preliminary results was to establish the feasibility of Bu₃SnH as the reductant for CO conversion and in turn the feasibility of a [M]-CO/R₃Sn⁺/base/H₂ catalytic cycle. A plausible mechanism for neutral methylidene [M]=CH₂ synthesis is postulated in Scheme 5.7; such species are widely accepted as key intermediates in homogeneous CO conversion cycles.³³

![Scheme 5.7: A plausible mechanism by which Bu₃SnH and Bu₃Sn⁺ could reduce a transition metal bound carbonyl to produce a neutral methylidene [M]=CH₂.][3]

It was envisaged that the carbonyl complex itself could act as the Lewis base for FLP type chemistry whether via initial activation by stannyl cations or simply via the carbonyl itself. If the carbonyl oxygen was sufficiently basic it could activate H₂ in tandem with the stannyl cation (Scheme 5.8).
Scheme 5.8: Potential role of an electron-rich neutral carbonyl in FLP activation of hydrogen using 
Bu$_3$SnNTf$_2$ as a strong Lewis acid, [Bu$_3$Sn]$^+$ = Bu$_3$SnNTf$_2$

In either case a strong interaction between the carbonyl and the stannyl cation was of interest
given its potential to indicate activation of the carbonyl for hydride addition. To investigate
whether there is any observable interaction or binding of the stannyl cation to the carbonyl
ligand, one equivalent of Bu$_3$SnNTf$_2$ was added to each carbonyl complex and monitored by
$^{119}$Sn{$_1^1$H} and $_1^1$H NMR in C$_6$D$_6$. 
Figure 5.3: $^{119}$Sn $^1$H NMR in at room temperature C$_6$D$_6$, after the addition of one equivalent of Bu$_3$SnNTf$_2$ to the neutral carbonyl complexes shown

Figure 5.3 shows that on addition of the Bu$_3$SnNTf$_2$ to the neutral carbonyl complexes in C$_6$D$_6$, a shift in the $^{119}$Sn $^1$H NMR signal for the Sn species is seen in all cases. Each signal has remained diamagnetic suggesting no electron transfer mechanisms. It was initially anticipated that upon Bu$_3$Sn$^+$ [M]-CO binding we would observe the $^{119}$Sn $^1$H resonance to shift upfield reflecting a more shielded, four coordinate Sn centre; however this is only the case for [Co(CO)$_2$(Cp*)] and Bu$_3$SnNTf$_2$. The results do indicate a change in Sn environment and instead the downfield shift may be indicative of a weakening of the Bu$_3$Sn$^+$-NTf$_2^-$ interaction and/or formation of a new complex [M-CO-SnBu$_3$]$^-$NTf$_2^-$. Importantly, no new species are observed in the $^1$H NMR at this point aside from a slight shifting downfield of the butyl peaks (of Bu$_3$SnNTf$_2$) in each case. Infrared spectroscopy studies would confirm carbonyl binding via change in the CO stretching frequency however time did not allow for this investigation.

To each of these reaction mixtures 1 equivalent of Bu$_3$SnH was added in order to probe if hydride transfer would occur. Figure 5.4 shows a stack plot of the $^1$H NMR results after 30 minutes at room temperature after addition of Bu$_3$SnH.
Figure 5.4: $^1$H NMR spectra of each of the reactions of [M]-CO/Bu$_3$Sn$^+$/Bu$_3$SnH after 30 minutes at room temperature. In each case the spectra show the bridging hydride species (*) [Bu$_3$Sn—H—Bu$_3$Sn]$^+$ at δ 5.05, (▲) H$_2$ at δ 4.5 and a new species in the –CH$_2$O region at (●) Cp*Mn(CO)$_3$, δ 3.47, Cp*Co(CO)$_2$, δ 3.87, [Fe(CO)$_5$] δ 3.46 and Fp* $^2$ δ 3.55.

In each case a broad signal, indicating hydride exchange, is observed at $^1$H δ 5.05 ppm for the species [Bu$_3$Sn-H-SnBu$_3$]$^+$NTf$_2^-$, which has been characterised previously with BArF$_{20}$ as the counterion.$^{19}$ In the case of [Co(CO)$_2$(Cp*)] the peak is relatively sharp indicating the least exchange, possibly due to this reaction having the lowest available concentration of stannylium equivalents, due to coordination or the oiling out of stannylium cation equivalents from solution. This is supported by the $^{119}$Sn{$^{1}$H} NMR spectra (vide supra) in which the stannylium cation moves upfield on addition of the carbonyl, possibly indicating a strong carbonyl-Sn interaction. On addition of Bu$_3$SnH, the Cp*Co(CO)$_2$ reaction also separated into two immiscible oils which means the analysis of this particular reaction is hindered; this separation is indicated in the $^1$H NMR spectrum which shows a very low concentration of new species. The sharper Bu$_3$SnH signal indicates that perhaps the Bu$_3$SnNTf$_2$ species and any products of hydride addition are concentrated in the separate oil, which did not dissolve upon decanting C$_6$D$_6$ and attempted dissolution in more polar solvents e.g. CH$_2$Cl$_2$. In each case a new species has been produced, giving rise to peaks in the region δ 3.47 – 3.87 ppm. These peaks are at a
slightly different chemical shift for each complex, suggesting that a reduced product remains coordinated to the metal centre rather than being a transition metal free by-product of reaction between Bu3SnH/Bu3SnNTf2 and the carbonyl. Although it was not possible to thoroughly characterise this species from the 1H NMR spectra alone, the chemical shift range is indicative of a Sn bound methoxide species.19 It is reasonable to postulate that this resonance arises from a reduced carbonyl fragment. The particular chemical shift is indicative of a –CH2 containing functional group that is still bound to the transition metal.6 Scheme 5.9 postulates possible structures and the mechanism of formation for a species derived from a methylidene fragment [M]=CH2, the mechanism of formation of the methylidene is shown in Scheme 5.7 (vide infra).

Scheme 5.9: Possible products from reduction of [M]-CO by Bu3SnNTf2 and Bu3SnH

The insertion of CO into metal-alkyl and metal-methylidene bonds is known34; numerous examples on Fe have been reported by Cutler et al. including of CO insertion (under 1 atm CO) into a Fe-CH3 bond to give the acetyl functional group as shown in product b in Scheme 5.9.35 Although conceptually similar Sn alkyl enolates are known (119Sn{1H} δ 100-120 ppm)36, none bound to a transition metal has been synthesised previously. The 1H NMR resonances for the postulated, new reduced species are fairly broad perhaps indicating some exchange with [Bu3Sn]+ which could be expected given the evident exchange with Bu3SnH, resulting in the very broad peak at δ 5.05 ppm ([Bu3Sn-H-SnBu3][NTf2]). Coupling (1H-119Sn) of J = 6 Hz can be observed in one case, for the new species arising from the reaction of [Fe(CO)5], Bu3SnNTf2 and Bu3SnH.119Sn{1H} NMR analysis of the same reaction mixtures shows Bu3SnNTf2 δ 254 ppm and Bu3SnH at -90 ppm.19,37 While a peak at δ -13.3 ppm is due to Bu4Sn,37 the product
of decomposition and peaks seen at δ 179-186 ppm could be attributed to the coordination of Bu₃Sn⁺ fragment to a reduced carbonyl species (Figure 5.5).

Figure 5.5: ¹¹⁹Sn{¹H} NMR spectra at room temperature of the reactions of [M]-CO/Bu₃SnNTf₂/Bu₃SnH after 24 hours at room temperature – the peaks at δ 179-186 ppm could be attributed to reduced carbonyl fragments bound to the transition metals.

If the reaction is repeated with 2 equivalents of Bu₃SnH, the results are analogous with observation of the new species at ¹H 3.47-3.87. Each of the reactions with 1 and 2 equivalents of Bu₃SnH were heated gently at 40 °C for 1.5 to 4 hours; higher temperatures see rapid decomposition of Sn species. Even with gentle heating, significant increases in the presence of the decomposition product Bu₄Sn are observed as evidenced by a sharp increase in the resonance at ¹¹⁹Sn{¹H} δ -13.3 ppm, however the peaks that are presumed to correspond to reduced carbonyl ligands still remain, as do the corresponding ¹H peaks. In most cases after 4 hours the ¹H NMR spectra remain mainly unchanged. In the case of Fp*₂ however there are markedly different resonances in the ¹H NMR spectrum. After heating for only 1.5 hours, the spectrum contains two unusual new peaks: a 1:1 doublet at δ 6.25 (Figure 5.6) along with two new singlets at δ 3.60 and 3.02.
Figure 5.6: $^1$H NMR spectrum at room temperature: new product peaks in the reaction of Fp*$_2$/Bu$_3$Sn'/Bu$_3$Sn' in C$_6$D$_6$. These new species appear after 4 days at room temperature or after 1.5 hours if the reaction is heated gently at 40 °C.

The same peaks start to appear if the reaction mixture is left at room temperature for 4 days and appear to grow in with the consumption of the peak initially reported after 30 minutes at room temperature at δ 3.55. This indicates that they are a new product dependent on the specific reaction mixture and metal carbonyl present. No new peaks are observed in the reactions with the other metal carbonyls [Co(CO)$_2$(Cp*)], [Mn(CO)$_3$(Cp*)] and [Fe(CO)$_3$]. Unfortunately time only permitted a preliminary investigation into this chemistry and as such these new species remain uncharacterised; however they warrant further investigation. It was envisaged that [Fp*$_2$] should show the greatest reactivity given that it is the only complex containing bridging CO ligands, which are known to be more basic due to increased back bonding from two metal centers, and as such are likely to show an enhanced tendency towards [M$_2$CO-SnBu$_3$]$^+$ activation and concomitant H-SnBu$_3$ reduction.
5.3 Conclusion

This chapter aimed to preliminarily investigate the possibility of carbonyl reduction using [Sn]-hydride species. The brief set of results presented here show there is a metal dependent reaction in each case with the addition of 1 equivalent of Bu$_3$SnNTf$_2$ and Bu$_3$SnH to a series of neutral carbonyls [Co(CO)$_2$(Cp*)], [Mn(CO)$_3$(Cp*)], [Fe(CO)$_5$] and [Fp*$_2$]. The species formed in these reactions have not been unambiguously characterised however the $^1$H resonances could be attributed to a [Bu$_3$Sn]$^+$ coordinated ‘CH$_2$’ or ‘CH$_3$’ moiety. Work is currently underway in the Ashley group to investigate various R$_3$Sn$^+$ and R$_3$SnH of differing R groups, in particular the more sterically encumbered stannyl cation ‘Pr$_3$SnNTf$_2$ which in tandem with ‘Pr$_3$SnH shows increased stability towards R migration, circumventing the production of R$_4$Sn decomposition products. A stabilised R$_3$Sn$^+$ species may prove suitable for an FLP type catalytic cycle. Fp*$_2$ appears to show increased reactivity with a lack of observation [Fe]-H resonances and the indication that several new metal dependent species are forming in the stoichiometric reduction. This highlights a potentially interesting system for investigation upon the design of a suitable catalytic [Sn]/base/H$_2$ FLP system.
5.4 References

Chapter 6

Experimental Details & Characterising Data

6.1 General procedures

Unless stated otherwise, all reactions and compounds, were manipulated under N₂ using either a MBraun Labmaster DP glovebox or using standard Schlenk line techniques on a dual manifold vacuum/inert gas line. For the manipulation of moisture sensitive compounds, all glassware was heated to 170°C before use for at least four hours. Solvents and solutions were transferred using a positive pressure of nitrogen through stainless steel or Teflon cannulae, or via plastic syringes for volumes less than 20 ml. Filtrations were performed using either glassware containing sintered glass frits or modified stainless steel cannulae fitted with glass microfibre filters.

Reaction solvents (pentane, heptane, hexane, toluene, CH₂Cl₂) were dried using an Innovative Technology Pure Solv SPS-400; whereas Et₂O and THF were distilled from purple Na/benzophenone diketyl; all except CH₂Cl₂ and THF were stored over K-mirrored ampoules. PhCl₂ (Anhydrous) was thoroughly dried and distilled over CaH₂. CHCl₃ and methanol were thoroughly dried over pre-activated 4 Å and 3 Å molecular sieves respectively. (CH₃)₂CO was distilled from B₂O₃. H₂ was purchased from BOC (research grade) and dried by passage through Matheson Tri-Gas Weldassure™ Purifier drying columns. 3:1 H₂:CO was purchased from BOC (research grade) and used as purchased.

Deuterated NMR solvents were dried and freeze-thaw degassed over the appropriate drying agent: CD₂Cl₂, CDCl₃, THF (4 Å molecular sieves) and C7D₈ (K). All were purchased from Goss Scientific (99.8, 99.6 and 99.6 % D respectively).
6.2 Elemental Analyses

Elemental analyses were conducted by Mr. S. Boyer of the London Metropolitan University.

6.3 Mass Spectrometry

High resolution mass spectrometry samples (HRMS; EI & ESI) were recorded by Dr. L. Haigh using either a Micromass Autospec Premier or a Micromass LCT Premier spectrometer.

6.4 NMR Spectroscopy

NMR spectra were recorded using Bruker AV-400 (400 MHz), DRX-400 (400 MHz) and AV-500 (500 MHz) spectrometers at room temperature unless otherwise stated. Chemical shifts, $\delta$, are reported in parts per million (ppm). $^1$H and $^{13}$C {$^1$H} chemical shifts are given relative to Me$_4$Si and referenced internally to the residual proton shift of the deuterated solvent employed. $^{11}$B, $^{19}$F, $^{31}$P {$^1$H} and $^{119}$Sn {$^1$H} chemical shifts were referenced externally in CDCl$_3$ to BF$_3$·OEt$_2$, CFCl$_3$, 85% H$_3$PO$_4$(aq) and Me$_4$Sn, respectively.

6.5 IR Spectroscopy

IR spectra were recorded on a Perkin Elmer GX FT-IR spectrometer (range 4000-400 cm$^{-1}$, resolution 0.5 cm$^{-1}$) as solutions. All air sensitive samples were loaded into an air-tight Specac$^\text{TM}$ Omni Cell$^\text{TM}$ at ca. 0.01M concentrations using a syringe in an N$_2$ glove box.

6.6 X-Ray Crystallography

Single crystal X-ray data for both compounds was collected by Dr Laurence Doyle and refined by Andrew Crawford.

6.6.1 Chapter Three: [Fe(CO)(Cp*)($\kappa^2$-dmpe)][BArF$_{24}$]

Single crystals of C$_{49}$H$_{43}$BF$_{24}$FeOP$_{2}$ were obtained from slow diffusion of an Et$_2$O/pentane layer at room temperature. A suitable crystal was selected and mounted on a glass fibre using
perfluoropolyether oil. Data was collected on an Oxford Diffraction Xcalibur Eos diffractometer. The crystal was kept at 172.95(10) K during data collection. Using Olex2, the structure was solved with the Superflip\(^2,3,4\) structure solution program using Charge Flipping and refined with the ShelXL\(^5\) refinement package using Least Squares minimisation.

**Crystal Data** for \(\text{C}_{49}\text{H}_{43}\text{BF}_{24}\text{FeOP}_{2} (M = 1232.43 \text{ g/mol})\): triclinic, space group P-1 (no. 2), \(a = 13.2968(9) \ \text{Å}, b = 14.5079(10) \ \text{Å}, c = 15.0867(9) \ \text{Å}, \alpha = 102.482(5)^\circ, \beta = 108.996(6)^\circ, \gamma = 97.823(6)^\circ\), \(V = 2618.8(3) \ \text{Å}^3, Z = 2, T = 172.95(10) \ \text{K}, \mu(\text{MoK}) = 0.472 \ \text{mm}^{-1}, D_{\text{calc}} = 1.563 \ \text{g/cm}^3\), 15014 reflections measured (4.672\(^\circ \leq 2\Theta \leq 56.456\(^\circ\)), 10255 unique \((R_{\text{int}} = 0.0387, R_{\text{sigma}} = 0.0803)\) which were used in all calculations. The final \(R_1 = 0.0673 \ (I > 2\sigma(I))\) and \(wR_2 = 0.1922 \ \text{(all data)}\).

### 6.6.2 Chapter Three: [Fe(CO)(Cp\*)(κ\(^2\)-depe)][BArF\(_{24}\)]

Single crystals of \(\text{C}_{53}\text{H}_{51}\text{BF}_{24}\text{FeOP}_{2}\) were obtained from slow diffusion of an Et\(_2\)O/pentane layer at room temperature. A suitable crystal was selected and mounted on a glass fibre with polyfluorether oil on an Oxford Diffraction Xcalibur diffractometer. The crystal was kept at 173.00(14) K during data collection. Using Olex2, the structure was solved with the olex2.solve\(^3,4,2\) structure solution program using Charge Flipping and refined with the ShelXL\(^5\) refinement package using Least Squares minimisation.

**Crystal Data** for \(\text{C}_{53}\text{H}_{51}\text{BF}_{24}\text{FeOP}_{2} (M = 1288.54 \ \text{g/mol})\): monoclinic, space group P2\(_1\) (no. 4), \(a = 12.45311(9) \ \text{Å}, b = 54.6911(3) \ \text{Å}, c = 12.62253(10) \ \text{Å}, \beta = 97.4213(7)^\circ, V = 8524.87(11) \ \text{Å}^3, Z = 6, T = 173.00(14) \ \text{K}, \mu(\text{CuK}) = 3.720 \ \text{mm}^{-1}, D_{\text{calc}} = 1.506 \ \text{g/cm}^3\), 36099 reflections measured (6.464\(^\circ \leq 2\Theta \leq 147.564\(^\circ\)), 24260 unique \((R_{\text{int}} = 0.0293, R_{\text{sigma}} = 0.0432)\) which were used in all calculations. The final \(R_1 = 0.0527 \ (I > 2\sigma(I))\) and \(wR_2 = 0.1404 \ \text{(all data)}\).

### 6.7 Experimental details for Chapter Two

The bases TMP (> 99 %), 2,4,6-collidine (> 99 %), 2,6-lutidine (> 99 %) and Et\(_3\)N (> 99 %) were purchased from sigma, distilled and dried over 4 Å molecular sieves. DABCO was purchased from Sigma Aldrich and vacuum dried overnight. \(^{t}\)PrMgCl, 1-bromo-2,4,6-trifluorobenzene and BF\(_3\).OEt\(_2\) were purchased from Sigma Aldrich and used as received. The
following chemicals were synthesised according to literature procedures Fp*₂, [Cp₂Fe][BF₄],
NaBArF₂₄, P'Bu₃, BPh₃, and Fp*Cl is adapted from a literature synthesis for FpCl.

**6.7.1 Synthesis of [Fp*CO][BArF₂₄]**

This synthesis is adapted from a literature procedure. A 100 ml greaseless ampoule was
charged with a magnetic stirrer bar, Fp*₂ (0.64 g, 1.3 mmol), [Fe(Cp)₂][BF₄] (0.71 g, 2.6 mmol)
and a 1:1 mixture of CH₂Cl₂/THF (50 ml), before being thoroughly degassed and sealed under
a pressure of CO (1 atm) for 12 hours. Removal of the volatiles in vacuum followed by washing
of the purple solid with pentane (2 x 20 ml) and ether (2 x 20 ml) gave an analytically pure
sample (0.75 g, 80%, 2.1 mmol). [Fp*CO][BF₄] (0.70 g, 1.9 mmol), NaBArF₂₄ (1.71 g, 1.9
mmol), CH₂Cl₂ (50 ml) and finally a magnetic stirrer bar were added to a 100 ml greaseless
ampoule. The vessel was sealed and left to stir overnight by which point an insoluble tan
precipitate NaBF₄ was visible. The volatiles were filtered off and removed under vacuo to yield
a vermilion solid. Recrystallisation from Et₂O at -78 °C, followed by washing with pentane
afforded a spectroscopically pure peach solid (1.74 g, 79%, 1.5 mmol).

**¹H NMR (400 MHz, CD₂Cl₂) δ (ppm):** 7.72 (s, 8H, B-(mAr-H)₄), 7.57 (s, 4H, B-(pAr-H)₄),
2.02 (s, 15H, C₅(CH₃)₅), **¹B (128.4 MHz, CD₂Cl₂) δ (ppm):** δ -6.0, s

**6.7.2 Synthesis of BArF₉**
This synthesis was previously reported but has been modified.\textsuperscript{12,13} \textsuperscript{1}PrMgCl (2.0 M in Et\textsubscript{2}O, 4.8 mL, 9.6 mmol) was added dropwise to a solution of 1-bromo-2,4,6-trifluorobenzene (1.14 mL, 9.6 mmol) in THF (200 mL) at \(-20\) °C. The reaction mixture was allowed to warm slowly to 0 °C and left to stir for 1 hour. After stirring for 1 hour, the reaction was cooled to \(-50\) °C and BF\textsubscript{3}.OEt\textsubscript{2} (0.4 mL, 3.2 mmol) was added. After stirring for 1 hour at \(-50\) °C, the cooling bath was removed and the reaction left to warm slowly to room temperature. The reaction is left to stir at room temperature for 12 hours. Solvent is removed \textit{in vacuo} and the residue is refluxed for 12 hours in heptane (200 mL). The Mg salts are removed by filtration and solvent removed \textit{in vacuo}. To remove any THF adduct impurity, the crude product is stirred in neat Me\textsubscript{2}SiClH for 3 hours at room temperature. After removing volatiles, the product is crystallised from a heptane/dichloromethane layer to give white needles. Crystals are spectroscopically pure and characterisation agrees with literature (2.15 g, 55 %).\textsuperscript{12}

6.7.3 General synthesis of \textit{trisarylborylborohydride} salts: Na[HBP\textsubscript{3}], Na[HBArF\textsubscript{9}], Na[HBArF\textsubscript{15}]

This procedure has been adapted from literature and used to make two new borohydride salts.\textsuperscript{14} A colourless solution of Na[BHet\textsubscript{3}] (1.0 M, THF) in toluene (3 mL) is added to the borane 1.1:1 slight excess. The reaction is stirred at room temperature for 1 hour and the product salts [HBAr\textsubscript{3}]Na will precipitate from solution. The toluene is decanted and the resulting white solid is washed with pentane and dried \textit{in vacuo} to give spectroscopically pure samples.

\begin{itemize}
    \item Na[HBP\textsubscript{3}] \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) (ppm): \(\delta\) 7.00-7.15, m, 15 H, \textsuperscript{11}B (128.4 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) (ppm): \(\delta\) -9.4, d
    \item Na[HBArF\textsubscript{9}] \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) (ppm): \(\delta\) 6.33-6.37 (m, 6 H) \textsuperscript{11}B (128.4 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) (ppm): \(\delta\) -25.3, (d, B-H) \textsuperscript{19}F (376.8 MHz) \(\delta\) -100.0 (2 F, s), 119.8 (1 H, septet)
    \item Na[HBArF\textsubscript{15}] \textsuperscript{11}B (96.3 MHz, DMSO): \(\delta\) -21.1 (d, B-H)
\end{itemize}

6.7.4 General procedure for FLP hydrogenations of [Fp*CO][BArF\textsubscript{24}]

At \textit{4 bar}:

Inside an N\textsubscript{2} glovebox, the chosen borane (0.018 mmol) is placed in a J. Young sealed NMR tube followed by base (10 eq., 0.18 mmol) and 1,2-difluorobenzene (0.5 mL). The solution is then monitored by \textsuperscript{1}H, \textsuperscript{31}P{\textsuperscript{1}H} and \textsuperscript{11}B NMR to assess any adduct formation. Again in a glovebox, [Fp*CO][BArF\textsubscript{24}] (20 mg, 0.018 mmol) is added to the same J. Young sealed NMR tube. Following this the solution is monitored again by \textsuperscript{1}H, \textsuperscript{31}P{\textsuperscript{1}H} and \textsuperscript{11}B NMR. To emit H\textsubscript{2},
the solution was degassed once using the freeze-thaw method and sealed under 1 bar pressure of \( \text{H}_2 \) at 77 K (to ensure reproducible pressures all tubes were immersed in liquid \( \text{N}_2 \) to a control depth of 10 cm and backfilled for 10 seconds); this results in an equivalent internal NMR tube pressure of 4 bar at room temperature. Reactions are then monitored by \(^1\text{H}, ^{31}\text{P} \{^1\text{H}\}\) and \(^{11}\text{B}\) NMR.

- For 1:3 \( \text{CO}/\text{H}_2 \) reactions at 4 bar same procedure as \( \text{H}_2 \) (4 bar).

At 10 bar:

Same procedure as 4 bar but in place of a J. Young NMR tube, a Norell Inc. High Pressure Valve NMR tube is charged with reactants. \( \text{H}_2 \) is admitted at room temperature through high pressure Swagelock\(^\circ\) fittings. The pressure is adjusted to 10 bar at room temperature and the reactions are then monitored by \(^1\text{H}, ^{31}\text{P} \{^1\text{H}\}\) and \(^{11}\text{B}\) NMR analysis.

### 6.8 Experimental details for Chapter Three

The bisphosphine ligands 1,2-\( \text{bis} \)(dimethylphosphino)ethane (dmpe), 1,2-\( \text{bis} \)(diethylphosphino)ethane (depe), 1,2-\( \text{bis} \)(diisopropylphosphino)ethane (dippe) were synthesised according to the procedure developed in the Ashley group.\(^{16}\) The base tert-butylimino-tri(pyrrolidino)phosphorane was purchased from sigma and used as received. The borane \( \text{^1BuCH}_2\text{CH}_2\text{B(C}_8\text{H}_14) \) was synthesised according to literature.\(^{17}\)

#### 6.8.1 Synthesis of \([\text{Fe(CO)}(\text{Cp}^*)(\kappa^2\text{dmpe})][\text{BArF}_{24}]\)

![Diagrams](image.png)

In a sealed schlenk bomb, 1,2-\( \text{bis} \)(dimethylphosphino)ethane (0.21 g, 1.42 mmol) and \( \text{Cp}^*\text{Fe(CO)}_2\text{Cl} \) (0.40 g, 1.42 mmol) are dissolved in toluene (20 mL), the reaction mixture immediately turns from red to yellow/orange. The reaction is refluxed overnight and toluene removed in vacuo to give yellow solids. The yellow solids are dissolved in THF and NaBArF\(_{24}\) (1.26 g, 1.42 mmol) is added. The reaction mixture is stirred for 1h at RT, the solution is then
filtered to remove NaCl and THF removed in vacuo to give yellow solid. This solid is extracted with CHCl$_3$ and the product is obtained as a dark yellow solid. The product can be recrystallized from an Et$_2$O/pentane layer to give yellow/orange crystals, (1.0 g, yield 57%).

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm): $\delta$ 7.70 (s, 8H, B-(mAr-H)$_4$), 7.53 (s, 4H, B-(pAr-H)$_4$), 1.76 (s, 15H, C$_5$(CH$_3$)$_5$), 1.73 (m, 4H, -PCH$_2$CH$_2$P-), 1.51 (m, 6H, -P(CH$_3$)$_2$), 1.38 (m, 6H, -P(CH$_3$)$_2$); $^{31}$P$^1$H NMR (162 MHz, CDCl$_3$) $\delta$ (ppm): $\delta$ 70.2; $^{13}$C$^1$H NMR (101 MHz, CDCl$_3$) $\delta$ (ppm): $\delta$ 161.8, 134.7, 129.1, 125.6, 123.4, 121.3, 117.5, 94.4, 29.9, 18.0, 16.1, 10.0. MS (ES/m/z): for [C$_{17}$H$_{31}$FeOP$_2$]$^+$ calcd: 369.22. Found 369.00. IR (CD$_2$Cl$_2$, cm$^{-1}$): ν/CO 1947.

Anald. Calcd. for C$_{49}$H$_{43}$BF$_{24}$FeOP$_2$: C, 47.47; H, 3.52. Found: C, 47.68; H, 3.82.

6.8.2 Synthesis of [Fe(CO)(Cp*)(κ$^2$-depe)][BArF$_{24}$]

In a sealed schlenk bomb 1,2-bis(diethylphosphino)ethane (0.14 g, 0.69 mmol), Cp*Fe(CO)$_2$Cl (0.19 g, 0.69 mmol) and NaBArF$_{24}$ (0.61 g, 0.69 mmol) are added together in toluene (20 mL). The reaction is refluxed overnight and the yellow solid product is obtained by filtration. The product is re-dissolved in THF and filtered to remove NaCl, followed by removal of THF in vacuo to give a pale yellow solid and was recrystallized from an Et$_2$O/pentane layer to give yellow crystals, (0.4 g, yield 45%).

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm): $\delta$ 7.70 (s, 8H, B-(mAr-H)$_4$), 7.53 (s, 4H, B-(pAr-H)$_4$), 1.92 (m, 8H, -PCH$_2$), 1.76 (s, 15H, C$_5$(CH$_3$)$_5$), 1.61 (m, 4H, -PCH$_2$CH$_2$P-), 1.10 (br s, 12H, -PCH$_2$CH$_3$); $^{31}$P$^1$H NMR (162 MHz, CDCl$_3$) $\delta$ (ppm): $\delta$ 84.7; $^{13}$C$^1$H NMR (101 MHz, CDCl$_3$) $\delta$ (ppm): $\delta$ 161.1, 134.8, 128.8, 125.6, 123.5, 117.45, 67.9, 34.1, 24.4, 22.33, 21.7, 14.1, 10.5, 8.4, 7.9. MS (ES/m/z): for [C$_{21}$H$_{39}$FeOP$_2$]$^+$ calcd: 425.33. Found 425.00. IR (CD$_2$Cl$_2$, cm$^{-1}$): (ν/CO) 1944. Anald. Calcd. for C$_{53}$H$_{51}$BF$_{24}$FeOP$_2$: C, 49.40; H, 3.99. Found C, 49.78; H, 4.10.

6.8.3 Synthesis of [Fe(CO)(Cp*)(κ$^2$-dippe)][BArF$_{24}$]
In a sealed schlenk bomb 1,2-bis(diethylphosphino)ethane (0.13 g, 0.5 mmol), Cp*Fe(CO)$_2$Cl (0.14 g, 0.496 mmol) and NaBArF$_{24}$ (0.44 g, 0.5 mmol) are added together in THF (20 mL). The reaction is heated at 60°C overnight. The solution is filtered to remove NaCl and the THF removed in vacuo to yield the product as a yellow powder which was recrystallized from Et$_2$O to give orange/yellow crystals, (0.3 g, yield 45%).

$^1$H NMR (CDC$_3$, 400 MHz) δ (ppm): δ 7.70 (s, 8H, B-(m-Ar)-H$_4$), 7.53 (s, 4H, B-(p-Ar)-H$_4$), 2.39 (m, 2H, -PCH(i-C$_3$H$_2$)$_2$), 2.26 (m, 2H, -PCH(i-C$_3$H$_2$)$_2$), 1.83 (m, 2H, -PCH$_2$CH$_2$P-), 1.54 (m, 2H, -PCH$_2$CH$_2$P-), 1.24-1.05 (m, 24H, -PCH(i-C$_3$H$_2$)$_2$)); $^{31}$P$^{1}$H NMR (162 MHz, CDC$_3$) δ (ppm): δ 91.6

$^{13}$C$^{1}$H (101 MHz, CDCl$_3$) δ (ppm): δ 161.5, 134.8, 129.0, 127.7, 125.8, 123.5, 117.5, 94.6, 34.12, 28.5, 24.7, 22.3, 20.1, 19.5, 19.3, 18.9, 17.8, 14.05, 10.7. MS (ES/m/z): for [C$_{21}$H$_{39}$FeOP$_2$]$^+$ calcld: 481.43. Found 481.00, 425.33. IR (CD$_2$Cl$_2$, cm$^{-1}$): (ν/CO) 1940. Anal. Calcd. for C$_{57}$H$_{59}$BF$_{24}$FeOP$_2$: C, 50.91; H, 4.42. Found: C, 50.74; H, 4.38.

### 6.8.4 Synthesis of [Fe(CO)(Cp)(κ$^2$-dmpe)][BArF$_{24}$]

Follows the same procedure as detailed for [Fe(CO)(Cp)(κ$^2$-dmpe)][BArF$_{24}$]. A previously published synthesis by Davies et al. does not include spectroscopic data.

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz) δ (ppm): δ 7.72 (s, 8H, B-(m-Ar)-H$_4$), 7.56 (s, 4H, B-(p-Ar)-H$_4$), 4.78 (s, 5 H, C$_5$H$_5$), 1.91 (m, 4 H, -PCH$_2$CH$_2$P-), 1.70 (m, 6 H, -PCH$_3$); $^{31}$P$^{1}$H NMR (162 MHz, CDCl$_3$) δ (ppm): δ 75.1 (s)

### 6.8.5 Synthesis of [Fe(CO)(Cp)(κ$^2$-dppe)][BArF$_{24}$]

Follows the same procedure as detailed for [Fe(CO)(Cp)(κ$^2$-dppe)][BArF$_{24}$]. A previously published synthesis by Davies et al. does not include spectroscopic data.
1H NMR (CDCl₃, 400 MHz) δ (ppm): δ 7.70 (s, 8H, B-(mAr-H)₄), 7.50 (s, 4H, B-(pAr-H)₄), 7.59-7.46 (m, Ph), 7.3-7.2 (m, Ph), 2.58 (m, 2 H, -PCH₂CH₂P-); 2.28 (m, 2 H, -PCH₂CH₂P-), 1.48 (C₅Me₅), 31P{¹H} NMR (162 MHz, CDCl₃) δ (ppm): δ 75.1

6.8.6 Hydrogenation of bisphosphine complexes
The FLP hydrogenations of the bisphosphine complexes were all carried out at 4 bar H₂ and using the same procedure as described in Section 6.7.4.

6.9 Experimental details for Chapter Four

[Fe(CO)₅] and KCN were both purchased from Sigma Aldrich and used as received. The following chemicals were synthesised according to literature procedures [Fp*Br], [FpCN] and [Fp*CN].

6.9.1 ¹³CO labelling of Fp*CN

Figure 6.1: Toepler Pump

[19] [20]

6.10 Experimental details for Chapter Five

Bu₃SnH was purchase from Sigma Aldrich and dried over 4 Å molecular sieves and stored at -30 °C. [Fe(CO)₅] and HNTf₂ were purchased from Sigma Aldrich and used as received. The
following chemicals were synthesised according to literature procedure [Co(CO)\textsubscript{2}(Cp*)]\textsuperscript{21} and [Mn(CO)\textsubscript{3}(Cp)].\textsuperscript{22}

\textbf{6.10.1 Synthesis of [Bu\textsubscript{3}Sn][NTf\textsubscript{2}]}

Bu\textsubscript{3}SnH (1.53 g, 5.26 mmol) and HNTf\textsubscript{2} (1.48 g, 5.26 mmol) are added together in C\textsubscript{6}D\textsubscript{6} (100 mL). The reaction is stirred for 20 minutes at room temperature or when H\textsubscript{2} evolution has stopped. The solvent is then removed \textit{in vacuo} to obtain a colourless viscous oil, isolated yield 78%.

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta\) (ppm): 1.75 (m, 2H, Sn(CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3})), 1.59 (m, 2H, Sn(CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3})), 1.43 (sextet, 2H, Sn(CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3})), 0.97 (sextet, 3H, Sn(CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3})). \(\delta\) \textsuperscript{119}Sn\textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}) \(\delta\) (ppm): \(\delta\) 254 (br s) \textsuperscript{19}F\textsuperscript{1}H (C\textsubscript{6}D\textsubscript{6}) \(\delta\) (ppm): \(\delta\) -78.5
6.11 References

APPENDIX
(i) Crystal structure and refinement for complex 3, [Fe(CO)(Cp*)(κ²-dmpe)][BArF₂₄]

Table 1 Crystal data and structure refinement for ASH1538

<table>
<thead>
<tr>
<th>Identification code</th>
<th>ASH1538</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₄₉H₄₃BF₂₄FeOP₂</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1232.43</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>172.95(10)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>a/Å</td>
<td>13.2968(9)</td>
</tr>
<tr>
<td>b/Å</td>
<td>14.5079(10)</td>
</tr>
<tr>
<td>c/Å</td>
<td>15.0867(9)</td>
</tr>
<tr>
<td>α/°</td>
<td>102.482(5)</td>
</tr>
<tr>
<td>β/°</td>
<td>108.996(6)</td>
</tr>
<tr>
<td>γ/°</td>
<td>97.823(6)</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>2618.8(3)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>ρ calc/g/cm³</td>
<td>1.563</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.472</td>
</tr>
<tr>
<td>F(000)</td>
<td>1244.0</td>
</tr>
</tbody>
</table>
Crystal size/mm$^3$ 0.381 × 0.2886 × 0.1372

Radiation MoKα ($\lambda = 0.71073$)

2Θ range for data collection/° 4.672 to 56.456

Index ranges $-15 \leq h \leq 17, -13 \leq k \leq 17, -19 \leq l \leq 13$

Reflexions collected 15014

Independent reflexions 10255 [R$_{int}$ = 0.0387, R$_{sigma}$ = 0.0803]

Data/restraints/parameters 10255/0/712

Goodness
- of fit on F$^2$ 1.026

Final R indexes [I$\geq$2σ (I)]
- R$_1$ = 0.0673, wR$_2$ = 0.1692

Final R indexes [all data]
- R$_1$ = 0.0943, wR$_2$ = 0.1922

Largest diff. peak/hole / e Å$^{-3}$ 1.00/-0.55

Table 2 Bond Lengths for ASH1538

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Length/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(1) P(6)</td>
<td>C(23) C(28)</td>
<td>1.932 (5)</td>
</tr>
<tr>
<td>Fe(1) P(3)</td>
<td>C(23) C(24)</td>
<td>1.900 (5)</td>
</tr>
<tr>
<td>Fe(1) C(71)</td>
<td>C(23) B(16)</td>
<td>1.645 (5)</td>
</tr>
<tr>
<td>Fe(1) C(70)</td>
<td>C(15) C(10)</td>
<td>1.409 (5)</td>
</tr>
<tr>
<td>Fe(1) C(67)</td>
<td>C(34) C(29)</td>
<td>1.393 (5)</td>
</tr>
<tr>
<td>Fe(1) C(73)</td>
<td>C(34) C(33)</td>
<td>1.392 (5)</td>
</tr>
<tr>
<td>Fe(1) C(69)</td>
<td>C(29) C(30)</td>
<td>1.406 (5)</td>
</tr>
<tr>
<td>Fe(1) C(72)</td>
<td>C(29) B(16)</td>
<td>1.638 (5)</td>
</tr>
<tr>
<td>P(6) C(7)</td>
<td>C(10) C(11)</td>
<td>1.387 (5)</td>
</tr>
<tr>
<td>P(6) C(5)</td>
<td>C(10) B(16)</td>
<td>1.632 (5)</td>
</tr>
<tr>
<td>P(6) C(8)</td>
<td>C(21) C(22)</td>
<td>1.381 (5)</td>
</tr>
<tr>
<td>P(3) C(2)</td>
<td>C(21) C(51)</td>
<td>1.499 (5)</td>
</tr>
<tr>
<td>P(3) C(4)</td>
<td>C(21) C(20)</td>
<td>1.385 (5)</td>
</tr>
<tr>
<td>P(3) C(9)</td>
<td>C(28) C(27)</td>
<td>1.389 (5)</td>
</tr>
<tr>
<td>F(56) C(55)</td>
<td>C(18) C(19)</td>
<td>1.383 (5)</td>
</tr>
<tr>
<td>F(60) C(59)</td>
<td>C(24) C(25)</td>
<td>1.387 (5)</td>
</tr>
<tr>
<td>F(52) C(51)</td>
<td>O(68) C(67)</td>
<td>1.053 (5)</td>
</tr>
<tr>
<td>F(40) C(39)</td>
<td>C(33) C(35)</td>
<td>1.488 (5)</td>
</tr>
<tr>
<td>F(41) C(39)</td>
<td>C(33) C(32)</td>
<td>1.382 (6)</td>
</tr>
<tr>
<td>F(57) C(55)</td>
<td>C(19) C(20)</td>
<td>1.386 (5)</td>
</tr>
<tr>
<td>F(53) C(51)</td>
<td>C(19) C(55)</td>
<td>1.499 (6)</td>
</tr>
<tr>
<td>F(54) C(51)</td>
<td>C(30) C(31)</td>
<td>1.389 (5)</td>
</tr>
<tr>
<td>F(61) C(59)</td>
<td>C(11) C(12)</td>
<td>1.384 (5)</td>
</tr>
<tr>
<td>F(44) C(43)</td>
<td>C(31) C(32)</td>
<td>1.392 (5)</td>
</tr>
<tr>
<td>F(64) C(63)</td>
<td>C(31) C(39)</td>
<td>1.486 (6)</td>
</tr>
<tr>
<td>F(45) C(43)</td>
<td>C(12) C(13)</td>
<td>1.391 (5)</td>
</tr>
<tr>
<td>F(42) C(39)</td>
<td>C(12) C(63)</td>
<td>1.505 (5)</td>
</tr>
<tr>
<td>F(38) C(35)</td>
<td>C(25) C(26)</td>
<td>1.372 (6)</td>
</tr>
<tr>
<td>F(58) C(55)</td>
<td>C(25) C(47)</td>
<td>1.488 (6)</td>
</tr>
<tr>
<td>F(65) C(63)</td>
<td>C(71) C(70)</td>
<td>1.420 (7)</td>
</tr>
<tr>
<td>Atom</td>
<td>Atom</td>
<td>Atom</td>
</tr>
<tr>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>P(6)</td>
<td>Fe(1)</td>
<td>P(3)</td>
</tr>
<tr>
<td>C(71)</td>
<td>Fe(1)</td>
<td>P(6)</td>
</tr>
<tr>
<td>C(71)</td>
<td>Fe(1)</td>
<td>P(3)</td>
</tr>
<tr>
<td>C(71)</td>
<td>Fe(1)</td>
<td>C(70)</td>
</tr>
<tr>
<td>C(71)</td>
<td>Fe(1)</td>
<td>C(73)</td>
</tr>
<tr>
<td>C(71)</td>
<td>Fe(1)</td>
<td>C(69)</td>
</tr>
<tr>
<td>C(71)</td>
<td>Fe(1)</td>
<td>C(72)</td>
</tr>
<tr>
<td>C(70)</td>
<td>Fe(1)</td>
<td>P(6)</td>
</tr>
<tr>
<td>C(70)</td>
<td>Fe(1)</td>
<td>P(3)</td>
</tr>
<tr>
<td>C(70)</td>
<td>Fe(1)</td>
<td>C(69)</td>
</tr>
<tr>
<td>C(67)</td>
<td>Fe(1)</td>
<td>P(6)</td>
</tr>
<tr>
<td>C(67)</td>
<td>Fe(1)</td>
<td>P(3)</td>
</tr>
<tr>
<td>C(67)</td>
<td>Fe(1)</td>
<td>C(71)</td>
</tr>
<tr>
<td>C(67)</td>
<td>Fe(1)</td>
<td>C(70)</td>
</tr>
<tr>
<td>C(67)</td>
<td>Fe(1)</td>
<td>C(73)</td>
</tr>
<tr>
<td>C(67)</td>
<td>Fe(1)</td>
<td>C(69)</td>
</tr>
<tr>
<td>C(67)</td>
<td>Fe(1)</td>
<td>C(72)</td>
</tr>
<tr>
<td>C(73)</td>
<td>Fe(1)</td>
<td>P(6)</td>
</tr>
<tr>
<td>C(73)</td>
<td>Fe(1)</td>
<td>P(3)</td>
</tr>
<tr>
<td>C(73)</td>
<td>Fe(1)</td>
<td>C(70)</td>
</tr>
<tr>
<td>C(73)</td>
<td>Fe(1)</td>
<td>C(69)</td>
</tr>
<tr>
<td>C(69)</td>
<td>Fe(1)</td>
<td>P(6)</td>
</tr>
<tr>
<td>C(69)</td>
<td>Fe(1)</td>
<td>P(3)</td>
</tr>
<tr>
<td>C(72)</td>
<td>Fe(1)</td>
<td>P(6)</td>
</tr>
<tr>
<td>C(72)</td>
<td>Fe(1)</td>
<td>P(3)</td>
</tr>
<tr>
<td>C(72)</td>
<td>Fe(1)</td>
<td>C(70)</td>
</tr>
<tr>
<td>C(72)</td>
<td>Fe(1)</td>
<td>C(73)</td>
</tr>
<tr>
<td>C(72)</td>
<td>Fe(1)</td>
<td>C(69)</td>
</tr>
<tr>
<td>C(7)</td>
<td>P(6)</td>
<td>Fe(1)</td>
</tr>
<tr>
<td>------</td>
<td>------</td>
<td>-------</td>
</tr>
<tr>
<td>C(7)</td>
<td>P(6)</td>
<td>C(5)</td>
</tr>
<tr>
<td>C(5)</td>
<td>P(6)</td>
<td>Fe(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>P(6)</td>
<td>Fe(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>P(6)</td>
<td>C(7)</td>
</tr>
<tr>
<td>C(8)</td>
<td>P(6)</td>
<td>C(5)</td>
</tr>
<tr>
<td>C(2)</td>
<td>P(3)</td>
<td>Fe(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>P(3)</td>
<td>C(4)</td>
</tr>
<tr>
<td>C(2)</td>
<td>P(3)</td>
<td>C(9)</td>
</tr>
<tr>
<td>C(4)</td>
<td>P(3)</td>
<td>Fe(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>P(3)</td>
<td>Fe(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>P(3)</td>
<td>C(4)</td>
</tr>
<tr>
<td>C(15)</td>
<td>C(14)</td>
<td>C(59)</td>
</tr>
<tr>
<td>C(13)</td>
<td>C(14)</td>
<td>C(15)</td>
</tr>
<tr>
<td>C(13)</td>
<td>C(14)</td>
<td>C(59)</td>
</tr>
<tr>
<td>C(18)</td>
<td>C(17)</td>
<td>C(22)</td>
</tr>
<tr>
<td>C(18)</td>
<td>C(17)</td>
<td>B(16)</td>
</tr>
<tr>
<td>C(22)</td>
<td>C(17)</td>
<td>B(16)</td>
</tr>
<tr>
<td>C(28)</td>
<td>C(23)</td>
<td>C(24)</td>
</tr>
<tr>
<td>C(28)</td>
<td>C(23)</td>
<td>B(16)</td>
</tr>
<tr>
<td>C(24)</td>
<td>C(23)</td>
<td>B(16)</td>
</tr>
<tr>
<td>C(14)</td>
<td>C(15)</td>
<td>C(10)</td>
</tr>
<tr>
<td>C(33)</td>
<td>C(34)</td>
<td>C(29)</td>
</tr>
<tr>
<td>C(34)</td>
<td>C(29)</td>
<td>C(30)</td>
</tr>
<tr>
<td>C(34)</td>
<td>C(29)</td>
<td>B(16)</td>
</tr>
<tr>
<td>C(30)</td>
<td>C(29)</td>
<td>B(16)</td>
</tr>
<tr>
<td>C(15)</td>
<td>C(10)</td>
<td>B(16)</td>
</tr>
<tr>
<td>C(11)</td>
<td>C(10)</td>
<td>C(15)</td>
</tr>
<tr>
<td>C(11)</td>
<td>C(10)</td>
<td>B(16)</td>
</tr>
<tr>
<td>C(22)</td>
<td>C(21)</td>
<td>C(31)</td>
</tr>
<tr>
<td>C(22)</td>
<td>C(21)</td>
<td>C(20)</td>
</tr>
<tr>
<td>C(20)</td>
<td>C(21)</td>
<td>C(31)</td>
</tr>
<tr>
<td>F(60)</td>
<td>C(59)</td>
<td>F(62)</td>
</tr>
<tr>
<td>F(60)</td>
<td>C(59)</td>
<td>C(14)</td>
</tr>
<tr>
<td>F(61)</td>
<td>C(59)</td>
<td>F(60)</td>
</tr>
<tr>
<td>F(61)</td>
<td>C(59)</td>
<td>F(62)</td>
</tr>
<tr>
<td>F(61)</td>
<td>C(59)</td>
<td>C(14)</td>
</tr>
<tr>
<td>F(62)</td>
<td>C(59)</td>
<td>C(14)</td>
</tr>
<tr>
<td>C(27)</td>
<td>C(28)</td>
<td>C(23)</td>
</tr>
<tr>
<td>C(19)</td>
<td>C(18)</td>
<td>C(17)</td>
</tr>
<tr>
<td>C(25)</td>
<td>C(24)</td>
<td>C(23)</td>
</tr>
<tr>
<td>C(34)</td>
<td>C(33)</td>
<td>C(35)</td>
</tr>
<tr>
<td>C(32)</td>
<td>C(33)</td>
<td>C(34)</td>
</tr>
<tr>
<td>C(32)</td>
<td>C(33)</td>
<td>C(35)</td>
</tr>
<tr>
<td>C(18)</td>
<td>C(19)</td>
<td>C(20)</td>
</tr>
</tbody>
</table>
C(18) C(19) C(55) 119.3(4) C(4) C(5) P(6) 108.2(3)
C(20) C(19) C(55) 119.9(4) C(5) C(4) P(3) 111.9(3)
C(31) C(30) C(29) 122.2(3) F(48) C(47) F(49) 99.0(5)
C(12) C(11) C(10) 123.2(3) F(48) C(47) C(25) 113.0(4)
C(30) C(31) C(32) 120.4(4) F(49) C(47) C(25) 111.6(5)
C(30) C(31) C(39) 121.2(4) F(50) C(47) F(48) 109.8(6)
C(32) C(31) C(39) 118.5(3) F(50) C(47) F(49) 107.0(5)
C(11) C(12) C(13) 120.3(3) F(50) C(47) C(25) 115.1(5)
C(11) C(12) C(63) 119.7(3) C(71) C(72) Fe(1) 70.6(2)
C(13) C(12) C(63) 120.0(3) C(71) C(72) C(73) 107.9(4)
C(24) C(25) C(47) 119.0(4) C(71) C(72) C(76) 127.1(5)
C(26) C(25) C(24) 120.6(4) C(73) C(72) Fe(1) 70.4(2)
C(26) C(25) C(47) 120.4(4) C(73) C(72) C(76) 124.9(6)
C(21) C(22) C(17) 123.0(3) C(76) C(72) Fe(1) 127.5(3)
F(38) C(35) F(37) 104.8(4)
(i) Crystal structure and refinement for complex 4, $\text{[Fe(CO)(Cp*)}(\kappa^2$-depe)]$\text{[BArF}_{24}]$
Index ranges
-13 ≤ h ≤ 15, -46 ≤ k ≤ 67, -15 ≤ l ≤ 15

Reflections collected
36099

Independent reflections
24260 \[ R_{int} = 0.0293, \ R_{sigma} = 0.0432 \]

Data/restraints/parameters
24260/1/2242

Goodness-of-fit on \( F^2 \)
1.031

Final R indexes [I>=2σ (I)]
\( R_1 = 0.0527, \ wR_2 = 0.1364 \)

Final R indexes [all data]
\( R_1 = 0.0565, \ wR_2 = 0.1404 \)

Largest diff. peak/hole / e Å\(^3\)
-0.89/-0.49

Flack parameter
-0.0026(19)

Table 2 Bond Lengths for ASH1537.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Length/Å</th>
<th>Atom</th>
<th>Atom</th>
<th>Length/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(0A)</td>
<td>P(3AA)</td>
<td>2.2195(17)</td>
<td>C(2CA)</td>
<td>C(8NA)</td>
<td>1.495(8)</td>
</tr>
<tr>
<td>Fe(0A)</td>
<td>P(5AA)</td>
<td>2.2260(17)</td>
<td>F(8DA)</td>
<td>C(2KA)</td>
<td>1.308(8)</td>
</tr>
<tr>
<td>Fe(0A)</td>
<td>C(3DA)</td>
<td>2.128(5)</td>
<td>C(4CA)</td>
<td>C(0DA)</td>
<td>1.393(7)</td>
</tr>
<tr>
<td>Fe(0A)</td>
<td>C(5DA)</td>
<td>2.131(5)</td>
<td>C(4CA)</td>
<td>C(1DA)</td>
<td>1.385(7)</td>
</tr>
<tr>
<td>Fe(0A)</td>
<td>C(5FA)</td>
<td>2.101(6)</td>
<td>C(5CA)</td>
<td>B(6AA)</td>
<td>1.630(7)</td>
</tr>
<tr>
<td>Fe(0A)</td>
<td>C(1IA)</td>
<td>1.738(7)</td>
<td>C(5CA)</td>
<td>C(7EA)</td>
<td>1.403(7)</td>
</tr>
<tr>
<td>Fe(0A)</td>
<td>C(4JA)</td>
<td>2.120(6)</td>
<td>C(5CA)</td>
<td>C(5LA)</td>
<td>1.403(7)</td>
</tr>
<tr>
<td>Fe(0A)</td>
<td>C(0KA)</td>
<td>2.140(5)</td>
<td>C(6CA)</td>
<td>C(2FA)</td>
<td>1.395(7)</td>
</tr>
<tr>
<td>Fe(2A)</td>
<td>P(0AA)</td>
<td>2.2311(16)</td>
<td>C(6CA)</td>
<td>C(0GA)</td>
<td>1.406(7)</td>
</tr>
<tr>
<td>Fe(2A)</td>
<td>P(4AA)</td>
<td>2.2085(16)</td>
<td>C(7CA)</td>
<td>C(7)</td>
<td>1.491(7)</td>
</tr>
<tr>
<td>Fe(2A)</td>
<td>C(8CA)</td>
<td>2.118(5)</td>
<td>F(39A)</td>
<td>C(36A)</td>
<td>1.310(8)</td>
</tr>
<tr>
<td>Fe(2A)</td>
<td>C(2DA)</td>
<td>2.115(5)</td>
<td>C(8CA)</td>
<td>C(2DA)</td>
<td>1.410(8)</td>
</tr>
<tr>
<td>Fe(2A)</td>
<td>C(4DA)</td>
<td>2.139(5)</td>
<td>C(8CA)</td>
<td>C(4DA)</td>
<td>1.425(8)</td>
</tr>
<tr>
<td>Fe(2A)</td>
<td>C(2GA)</td>
<td>2.134(5)</td>
<td>C(8CA)</td>
<td>C(0PA)</td>
<td>1.500(8)</td>
</tr>
<tr>
<td>Fe(2A)</td>
<td>C(3IA)</td>
<td>2.127(5)</td>
<td>F(57A)</td>
<td>C(58A)</td>
<td>1.324(13)</td>
</tr>
<tr>
<td>Fe(2A)</td>
<td>C(3KA)</td>
<td>1.749(6)</td>
<td>C(6A)</td>
<td>C(7A)</td>
<td>1.422(8)</td>
</tr>
<tr>
<td>Fe(1A)</td>
<td>P(14A)</td>
<td>2.2330(15)</td>
<td>C(6A)</td>
<td>C(5A)</td>
<td>1.433(8)</td>
</tr>
<tr>
<td>Fe(1A)</td>
<td>P(18A)</td>
<td>2.2041(16)</td>
<td>C(6A)</td>
<td>C(11A)</td>
<td>1.497(8)</td>
</tr>
<tr>
<td>Fe(1A)</td>
<td>C(6A)</td>
<td>2.137(5)</td>
<td>C(0DA)</td>
<td>C(12)</td>
<td>1.485(7)</td>
</tr>
<tr>
<td>Fe(1A)</td>
<td>C(2A)</td>
<td>1.732(6)</td>
<td>C(0DA)</td>
<td>C(0HA)</td>
<td>1.395(8)</td>
</tr>
<tr>
<td>Fe(1A)</td>
<td>C(7A)</td>
<td>2.138(5)</td>
<td>C(1DA)</td>
<td>B</td>
<td>1.634(7)</td>
</tr>
<tr>
<td>Fe(1A)</td>
<td>C(4A)</td>
<td>2.112(5)</td>
<td>C(1DA)</td>
<td>C(5HA)</td>
<td>1.409(7)</td>
</tr>
<tr>
<td>Fe(1A)</td>
<td>C(5A)</td>
<td>2.140(5)</td>
<td>C(2DA)</td>
<td>C(2GA)</td>
<td>1.427(9)</td>
</tr>
<tr>
<td>Fe(1A)</td>
<td>C(8A)</td>
<td>2.099(5)</td>
<td>C(2DA)</td>
<td>C(3NA)</td>
<td>1.506(8)</td>
</tr>
<tr>
<td>P(0AA)</td>
<td>C(1NA)</td>
<td>1.823(7)</td>
<td>C(3DA)</td>
<td>C(5DA)</td>
<td>1.436(9)</td>
</tr>
<tr>
<td>P(0AA)</td>
<td>C(8OA)</td>
<td>1.890(9)</td>
<td>C(3DA)</td>
<td>C(4)</td>
<td>1.488(9)</td>
</tr>
<tr>
<td>P(0AA)</td>
<td>C(1K)</td>
<td>1.801(10)</td>
<td>C(3DA)</td>
<td>C(0KA)</td>
<td>1.423(8)</td>
</tr>
<tr>
<td>P(14A)</td>
<td>C(19A)</td>
<td>1.829(6)</td>
<td>C(4DA)</td>
<td>C(3)</td>
<td>1.500(7)</td>
</tr>
<tr>
<td>P(14A)</td>
<td>C(15A)</td>
<td>1.873(7)</td>
<td>C(4DA)</td>
<td>C(31A)</td>
<td>1.435(8)</td>
</tr>
<tr>
<td>P(14A)</td>
<td>C(21A)</td>
<td>1.828(7)</td>
<td>C(5DA)</td>
<td>C(5FA)</td>
<td>1.407(10)</td>
</tr>
<tr>
<td>P(14A)</td>
<td>C(17A)</td>
<td>1.834(6)</td>
<td>C(5DA)</td>
<td>C(1MA)</td>
<td>1.497(9)</td>
</tr>
<tr>
<td>P(14A)</td>
<td>C(25A)</td>
<td>1.842(7)</td>
<td>C(32A)</td>
<td>C(33A)</td>
<td>1.396(8)</td>
</tr>
</tbody>
</table>
P(18A) C(23A) 1.821(7)  C(32A)  C(31A) 1.394(7)
P(3AA) C(0JA) 1.831(9)  C(32A)  C(40A) 1.484(9)
P(3AA) C(00A) 1.852(9)  B(6AA)  C(3EA) 1.632(7)
P(3AA) C(1F) 1.817(7)  C(8DA)  C(5) 1.493(8)
P(4AA) C(4KA) 1.848(7)  C(8DA)  C(7EA) 1.386(7)
P(4AA) C(5NA) 1.834(9)  C(8DA)  C(1GA) 1.389(8)
P(5AA) C(15) 1.824(9)  F(2EA)  C(9MA) 1.324(8)
P(5AA) C(0IA) 1.812(8)  C(9DA)  C(9EA) 1.383(9)
P(5AA) C(1LA) 1.871(8)  C(9DA)  C(4EA) 1.395(7)
P(4AA) C(50A) 1.270(8)  C(10A)  B(27A) 1.634(8)
P(4AA) C(40A) 1.339(9)  C(0GA)  C(5JA) 1.405(7)
P(5AA) C(12A) 1.339(9)  C(0GA)  C(5JA) 1.498(8)
C(2AA)C(7CA) 1.389(7) C(12) F(17) 1.281(9)
C(3AA)C(3CA) 1.377(7) C(1GA) C(1KA) 1.388(8)
C(3AA)C(6) 1.494(7) C(19A) C(20A) 1.515(9)
C(3AA)C(8FA) 1.405(7) C(2GA) C(3HA) 1.505(8)
C(4AA)C(5AA) 1.407(7) C(2GA) C(3IA) 1.415(8)
C(4AA)C(1BA) 1.390(7) C(15) C(18) 1.486(13)
C(5AA)B 1.629(7) C(5GA) F(1A) 1.204(10)
C(6AA)C(6BA) 1.390(8) B C(8HA) 1.635(7)
C(6AA)C(3EA) 1.392(8) C(8GA) C(9HA) 1.399(8)
C(7AA)C(9AA) 1.399(7) C(1HA) C(4HA) 1.498(9)
C(7AA)C(0CA) 1.393(7) C(1HA) F(6) 1.258(9)
C(8AA)C(0HA) 1.377(8) C(1HA) F(10) 1.292(10)
C(8AA)C(51A) 1.382(7) C(1HA) F(18) 1.257(9)
C(8AA)C(2KA) 1.499(8) F(15) C(5MA) 1.248(11)
C(9AA)C(2BA) 1.395(7) C(0IA) C(1J) 1.528(10)
C(9AA)B 1.645(7) C(17A) C(15A) 1.490(11)
C(41A)C(40A) 1.330(8) C(3IA) C(17) 1.502(8)
C(41A)C(4IA) 1.305(8) C(5IA) F(13) 1.310(8)
C(1)C(2FA) 1.483(8) C(47A) C(46A) 1.392(10)
C(44A)C(45A) 1.411(7) C(47A) C(54A) 1.376(9)
C(44A)C(49A) 1.406(8) F(7IA) C(4NA) 1.374(11)
C(44A)B(27A) 1.630(8) C(0JA) C(7OA) 1.489(13)
C(1BA)C(3CA) 1.398(7) F(3JA) C(4NA) 1.266(9)
C(1BA)C(5IA) 1.471(8) C(4JA) C(0KA) 1.414(8)
F(1)C(12) 1.303(8) C(4JA) C(6LA) 1.492(9)
C(2BA)C(3BA) 1.399(7) C(5JA) C(9JA) 1.393(8)
O(2)C(3KA) 1.139(8) C(6JA) C(0KA) 1.492(8)
C(3BA)C(6DA) 1.388(8) C(35A) C(36A) 1.499(9)
C(3BA)C(10) 1.495(8) C(9JA) C(4NA) 1.498(8)
C(4BA)B(6AA) 1.641(7) C(1KA) C(5LA) 1.396(7)
C(4BA)C(0FA) 1.398(6) C(4KA) C(9OA) 1.519(9)
C(5BA)C(7CA) 1.393(7) F(16) C(5MA) 1.170(11)
C(6BA)C(4GA) 1.379(10) F(12) C(8NA) 1.285(9)
C(6BA)C(0MA) 1.494(9) C(1LA) C(1F) 1.463(12)
F(43A)C(40A) 1.316(8) C(25A) C(26A) 1.520(9)
Table 3 Bond Angles for ASH1537

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle/°</th>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(3AA)</td>
<td>Fe(0A)</td>
<td>P(5AA)</td>
<td>83.96(7)</td>
<td>F(4CA)</td>
<td>C(5)</td>
<td>C(8DA)</td>
<td>113.5(5)</td>
</tr>
<tr>
<td>C(3DA)</td>
<td>Fe(0A)</td>
<td>P(3AA)</td>
<td>108.39(16)</td>
<td>C(9DA)</td>
<td>C(4EA)</td>
<td>C(0AA)</td>
<td>121.7(5)</td>
</tr>
<tr>
<td>C(3DA)</td>
<td>Fe(0A)</td>
<td>P(5AA)</td>
<td>106.74(17)</td>
<td>F(2AA)</td>
<td>C(6)</td>
<td>F(6AA)</td>
<td>107.1(5)</td>
</tr>
<tr>
<td>C(3DA)</td>
<td>Fe(0A)</td>
<td>C(5DA)</td>
<td>39.4(2)</td>
<td>F(2AA)</td>
<td>C(6)</td>
<td>F(8AA)</td>
<td>107.4(5)</td>
</tr>
<tr>
<td>C(3DA)</td>
<td>Fe(0A)</td>
<td>C(0KA)</td>
<td>39.0(2)</td>
<td>F(2AA)</td>
<td>C(6)</td>
<td>C(3AA)</td>
<td>113.6(5)</td>
</tr>
<tr>
<td>C(5DA)</td>
<td>Fe(0A)</td>
<td>P(3AA)</td>
<td>93.71(17)</td>
<td>F(6AA)</td>
<td>C(6)</td>
<td>F(8AA)</td>
<td>105.9(5)</td>
</tr>
<tr>
<td>C(5DA)</td>
<td>Fe(0A)</td>
<td>P(5AA)</td>
<td>143.12(19)</td>
<td>F(6AA)</td>
<td>C(6)</td>
<td>C(3AA)</td>
<td>111.0(5)</td>
</tr>
<tr>
<td>C(5DA)</td>
<td>Fe(0A)</td>
<td>C(0KA)</td>
<td>65.1(2)</td>
<td>F(8AA)</td>
<td>C(6)</td>
<td>C(3AA)</td>
<td>111.4(5)</td>
</tr>
<tr>
<td>C(5FA)</td>
<td>Fe(0A)</td>
<td>P(5AA)</td>
<td>114.31(18)</td>
<td>C(8BA)</td>
<td>C(5EA)</td>
<td>C(1EA)</td>
<td>121.4(5)</td>
</tr>
<tr>
<td>C(5FA)</td>
<td>Fe(0A)</td>
<td>P(3AA)</td>
<td>161.53(18)</td>
<td>C(8LA)</td>
<td>C(6EA)</td>
<td>C(8HA)</td>
<td>122.0(6)</td>
</tr>
<tr>
<td>C(5FA)</td>
<td>Fe(0A)</td>
<td>C(3DA)</td>
<td>66.2(2)</td>
<td>C(8DA)</td>
<td>C(7EA)</td>
<td>C(5CA)</td>
<td>122.6(5)</td>
</tr>
<tr>
<td>C(5FA)</td>
<td>Fe(0A)</td>
<td>C(5DA)</td>
<td>38.8(3)</td>
<td>C(28A)</td>
<td>C(33A)</td>
<td>C(32A)</td>
<td>122.8(6)</td>
</tr>
<tr>
<td>C(5FA)</td>
<td>Fe(0A)</td>
<td>C(4JA)</td>
<td>39.8(2)</td>
<td>F(7DA)</td>
<td>C(7)</td>
<td>C(7CA)</td>
<td>115.4(5)</td>
</tr>
<tr>
<td>C(5FA)</td>
<td>Fe(0A)</td>
<td>C(0KA)</td>
<td>65.7(2)</td>
<td>F(7DA)</td>
<td>C(7)</td>
<td>F(11)</td>
<td>101.8(6)</td>
</tr>
<tr>
<td>C(1IA)</td>
<td>Fe(0A)</td>
<td>P(3AA)</td>
<td>92.3(2)</td>
<td>F(4)</td>
<td>C(7)</td>
<td>F(7DA)</td>
<td>110.6(7)</td>
</tr>
<tr>
<td>C(1IA)</td>
<td>Fe(0A)</td>
<td>P(5AA)</td>
<td>89.3(2)</td>
<td>F(4)</td>
<td>C(7)</td>
<td>C(7CA)</td>
<td>113.7(5)</td>
</tr>
<tr>
<td>C(1IA)</td>
<td>Fe(0A)</td>
<td>C(3DA)</td>
<td>154.7(3)</td>
<td>F(4)</td>
<td>C(7)</td>
<td>F(11)</td>
<td>101.8(8)</td>
</tr>
<tr>
<td>C(1IA)</td>
<td>Fe(0A)</td>
<td>C(5DA)</td>
<td>127.6(3)</td>
<td>F(11)</td>
<td>C(7)</td>
<td>C(7CA)</td>
<td>112.1(6)</td>
</tr>
<tr>
<td>C(1IA)</td>
<td>Fe(0A)</td>
<td>C(5FA)</td>
<td>92.4(3)</td>
<td>C(9DA)</td>
<td>C(9EA)</td>
<td>C(1FA)</td>
<td>118.7(5)</td>
</tr>
<tr>
<td>C(1IA)</td>
<td>Fe(0A)</td>
<td>C(4JA)</td>
<td>89.2(3)</td>
<td>O(3A)</td>
<td>C(2A)</td>
<td>Fe(1A)</td>
<td>174.3(5)</td>
</tr>
<tr>
<td>C(1IA)</td>
<td>Fe(0A)</td>
<td>C(0KA)</td>
<td>121.1(3)</td>
<td>C(1AA)</td>
<td>C(0FA)</td>
<td>C(4BA)</td>
<td>122.5(4)</td>
</tr>
<tr>
<td>C(4JA)</td>
<td>Fe(0A)</td>
<td>P(3AA)</td>
<td>154.13(18)</td>
<td>C(0EA)</td>
<td>C(1FA)</td>
<td>C(1B)</td>
<td>120.3(5)</td>
</tr>
<tr>
<td>C(4JA)</td>
<td>Fe(0A)</td>
<td>P(5AA)</td>
<td>121.89(17)</td>
<td>C(9EA)</td>
<td>C(1FA)</td>
<td>C(0EA)</td>
<td>120.3(5)</td>
</tr>
<tr>
<td>C(4JA)</td>
<td>Fe(0A)</td>
<td>C(3DA)</td>
<td>65.8(2)</td>
<td>C(9EA)</td>
<td>C(1FA)</td>
<td>C(1B)</td>
<td>119.3(5)</td>
</tr>
<tr>
<td>C(4JA)</td>
<td>Fe(0A)</td>
<td>C(5DA)</td>
<td>65.5(2)</td>
<td>C(9BA)</td>
<td>C(2FA)</td>
<td>C(1)</td>
<td>119.5(5)</td>
</tr>
<tr>
<td>C(4JA)</td>
<td>Fe(0A)</td>
<td>C(0KA)</td>
<td>38.8(2)</td>
<td>C(9BA)</td>
<td>C(2FA)</td>
<td>C(6CA)</td>
<td>120.6(5)</td>
</tr>
<tr>
<td>C(0KA)</td>
<td>Fe(0A)</td>
<td>P(3AA)</td>
<td>146.50(16)</td>
<td>C(6CA)</td>
<td>C(2FA)</td>
<td>C(1)</td>
<td>119.8(5)</td>
</tr>
<tr>
<td>C(0KA)</td>
<td>Fe(0A)</td>
<td>P(5AA)</td>
<td>97.75(15)</td>
<td>C(2CA)</td>
<td>C(3FA)</td>
<td>C(8BA)</td>
<td>117.9(5)</td>
</tr>
<tr>
<td>Compound</td>
<td>Bond Lengths (Å)</td>
<td>Bond Angles (°)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>------------------</td>
<td>-----------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4A) Fe(2A) P(0AA)</td>
<td>84.16 (7) C(5A) C(49A) C(44A)</td>
<td>122.7 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8CA) Fe(2A) P(0AA)</td>
<td>122.29 (16) C(5DA) C(5FA) Fe(0A)</td>
<td>71.8 (3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8CA) Fe(2A) P(4AA)</td>
<td>153.51 (16) C(5DA) C(5FA) C(4J)</td>
<td>107.8 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8CA) Fe(2A) P(4DA)</td>
<td>39.1 (2) C(5DA) C(5FA) C(1D)</td>
<td>126.0 (7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8CA) Fe(2A) C(2GA)</td>
<td>65.2 (2) C(4I) C(5FA) Fe(0A)</td>
<td>70.8 (3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8CA) Fe(2A) C(3JA)</td>
<td>65.6 (2) C(4I) C(5FA) C(1D)</td>
<td>125.6 (8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2DA) Fe(2A) P(0AA)</td>
<td>160.97 (17) C(1D) C(5FA) Fe(0A)</td>
<td>129.5 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2DA) Fe(2A) P(4AA)</td>
<td>114.59 (17) C(8LA) C(6FA) C(4HA)</td>
<td>117.5 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2DA) Fe(2A) C(8CA)</td>
<td>38.9 (2) F(4AA) C(9) C(1KA)</td>
<td>113.4 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2DA) Fe(2A) C(4DA)</td>
<td>65.7 (2) F(2CA) C(9) F(4AA)</td>
<td>105.4 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2DA) Fe(2A) C(2GA)</td>
<td>39.2 (2) F(2CA) C(9) C(1KA)</td>
<td>113.3 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2DA) Fe(2A) C(3JA)</td>
<td>65.8 (2) F(6EA) C(9) F(4AA)</td>
<td>105.2 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4DA) Fe(2A) P(0AA)</td>
<td>97.12 (14) F(6EA) C(9) F(2CA)</td>
<td>106.7 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4DA) Fe(2A) P(4AA)</td>
<td>146.50 (16) F(6EA) C(9) C(1KA)</td>
<td>112.2 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2GA) Fe(2A) P(0AA)</td>
<td>142.31 (18) F(5AA) C(10) C(3BA)</td>
<td>112.1 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2GA) Fe(2A) P(4AA)</td>
<td>93.50 (15) F(0BA) C(10) F(5AA)</td>
<td>105.6 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2GA) Fe(2A) C(4DA)</td>
<td>65.3 (2) F(0BA) C(10) F(3DA)</td>
<td>107.8 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3IA) Fe(2A) P(0AA)</td>
<td>106.56 (16) F(0BA) C(10) C(3BA)</td>
<td>112.8 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3IA) Fe(2A) P(4AA)</td>
<td>108.15 (17) F(3DA) C(10) F(5AA)</td>
<td>105.3 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3IA) Fe(2A) C(4DA)</td>
<td>39.3 (2) F(3DA) C(10) C(3BA)</td>
<td>112.7 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3IA) Fe(2A) C(2GA)</td>
<td>38.8 (2) C(6A) C(7A) Fe(1A)</td>
<td>70.5 (3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3KA) Fe(2A) P(0AA)</td>
<td>89.9 (2) C(6A) C(7A) C(8A)</td>
<td>108.6 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3KA) Fe(2A) P(4AA)</td>
<td>92.7 (19) C(6A) C(7A) C(12A)</td>
<td>126.1 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3KA) Fe(2A) C(8CA)</td>
<td>89.4 (2) C(8A) C(7A) Fe(1A)</td>
<td>68.9 (3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3KA) Fe(2A) C(2DA)</td>
<td>92.4 (3) C(8A) C(7A) C(12A)</td>
<td>124.4 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3KA) Fe(2A) C(4DA)</td>
<td>121.1 (2) C(12A) C(7A) Fe(1A)</td>
<td>134.5 (4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3KA) Fe(2A) C(2GA)</td>
<td>127.7 (3) C(5AA) C(8FA) C(3AA)</td>
<td>122.1 (4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3KA) Fe(2A) C(3JA)</td>
<td>154.7 (2) C(29A) C(28A) B(27A)</td>
<td>119.7 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(18A) Fe(1A) P(14A)</td>
<td>84.66 (6) C(33A) C(28A) C(29A)</td>
<td>115.8 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6A) Fe(1A) P(14A)</td>
<td>107.32 (16) C(33A) C(28A) B(27A)</td>
<td>124.3 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6A) Fe(1A) P(18A)</td>
<td>107.89 (16) F(53A) C(50A) C(46A)</td>
<td>112.8 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6A) Fe(1A) C(7A)</td>
<td>38.8 (2) F(51A) C(50A) F(53A)</td>
<td>103.9 (7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6A) Fe(1A) C(5A)</td>
<td>39.2 (2) F(51A) C(50A) C(46A)</td>
<td>112.6 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2A) Fe(1A) P(14A)</td>
<td>90.3 (2) F(52A) C(50A) F(53A)</td>
<td>105.1 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2A) Fe(1A) P(18A)</td>
<td>92.3 (2) F(52A) C(50A) F(51A)</td>
<td>107.6 (7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2A) Fe(1A) C(6A)</td>
<td>154.0 (2) F(52A) C(50A) C(46A)</td>
<td>113.9 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2A) Fe(1A) C(7A)</td>
<td>126.3 (3) C(6CA) C(0GA) B(27A)</td>
<td>122.3 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2A) Fe(1A) C(4A)</td>
<td>88.8 (2) C(5JA) C(0GA) C(6CA)</td>
<td>115.4 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2A) Fe(1A) C(5A)</td>
<td>121.4 (2) C(5JA) C(0GA) B(27A)</td>
<td>122.2 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2A) Fe(1A) C(8A)</td>
<td>91.0 (3) F(I) C(12) C(0DA)</td>
<td>114.2 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7A) Fe(1A) P(14A)</td>
<td>143.36 (18) F(9) C(12) F(I)</td>
<td>103.2 (7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7A) Fe(1A) P(18A)</td>
<td>93.38 (16) F(9) C(12) C(0DA)</td>
<td>112.8 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7A) Fe(1A) C(5A)</td>
<td>65.1 (2) F(17) C(12) F(I)</td>
<td>106.7 (8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4A) Fe(1A) P(14A)</td>
<td>121.29 (17) F(17) C(12) C(0DA)</td>
<td>114.4 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4A) Fe(1A) P(18A)</td>
<td>154.03 (18) F(17) C(12) F(9)</td>
<td>104.5 (9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>C-01A</td>
<td>P(5AA)</td>
<td>C(1LA)</td>
<td>101.5 (4)</td>
<td>C(1CA)</td>
<td>C(4HA)</td>
<td>C(6FA)</td>
</tr>
<tr>
<td>----------</td>
<td>-------</td>
<td>--------</td>
<td>--------</td>
<td>-----------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td></td>
<td>C(1LA)</td>
<td>P(5AA)</td>
<td>Fe(0A)</td>
<td>108.5 (3)</td>
<td>C(1CA)</td>
<td>C(4HA)</td>
<td>C(1HA)</td>
</tr>
<tr>
<td></td>
<td>C(0EA)</td>
<td>C(0AA)</td>
<td>B(6AA)</td>
<td>119.3 (4)</td>
<td>C(6FA)</td>
<td>C(4HA)</td>
<td>C(1HA)</td>
</tr>
<tr>
<td></td>
<td>C(4EA)</td>
<td>C(0AA)</td>
<td>B(6AA)</td>
<td>124.2 (4)</td>
<td>C(8AA)</td>
<td>C(5HA)</td>
<td>C(1DA)</td>
</tr>
<tr>
<td></td>
<td>C(4EA)</td>
<td>C(0AA)</td>
<td>C(0EA)</td>
<td>116.3 (4)</td>
<td>C(1CA)</td>
<td>C(8HA)</td>
<td>C(6EA)</td>
</tr>
<tr>
<td></td>
<td>C(5BA)</td>
<td>C(1AA)</td>
<td>C(2)</td>
<td>120.7 (4)</td>
<td>C(1CA)</td>
<td>C(8HA)</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>C(5BA)</td>
<td>C(1AA)</td>
<td>C(0FA)</td>
<td>120.5 (4)</td>
<td>C(6EA)</td>
<td>C(8HA)</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>C(0FA)</td>
<td>C(1AA)</td>
<td>C(2)</td>
<td>118.8 (4)</td>
<td>C(3EA)</td>
<td>C(9HA)</td>
<td>C(8GA)</td>
</tr>
<tr>
<td></td>
<td>C(7CA)</td>
<td>C(2AA)</td>
<td>C(4BA)</td>
<td>121.9 (4)</td>
<td>C(1J)</td>
<td>C(0IA)</td>
<td>P(5AA)</td>
</tr>
<tr>
<td></td>
<td>C(3CA)</td>
<td>C(3AA)</td>
<td>C(6)</td>
<td>120.3 (5)</td>
<td>O(4)</td>
<td>C(1IA)</td>
<td>Fe(0A)</td>
</tr>
<tr>
<td></td>
<td>C(3CA)</td>
<td>C(3AA)</td>
<td>C(8FA)</td>
<td>120.7 (4)</td>
<td>C(15A)</td>
<td>C(17A)</td>
<td>P(18A)</td>
</tr>
<tr>
<td></td>
<td>C(8FA)</td>
<td>C(3AA)</td>
<td>C(6)</td>
<td>119.0 (5)</td>
<td>C(4DA)</td>
<td>C(3IA)</td>
<td>Fe(2A)</td>
</tr>
<tr>
<td></td>
<td>C(1BA)</td>
<td>C(4AA)</td>
<td>C(5AA)</td>
<td>122.6 (4)</td>
<td>C(4DA)</td>
<td>C(3IA)</td>
<td>C(17)</td>
</tr>
<tr>
<td></td>
<td>F(5CA)</td>
<td>C</td>
<td>F(2)</td>
<td>103.0 (7)</td>
<td>C(2GA)</td>
<td>C(3IA)</td>
<td>Fe(2A)</td>
</tr>
<tr>
<td></td>
<td>F(5CA)</td>
<td>C</td>
<td>C(9DA)</td>
<td>113.1 (5)</td>
<td>C(2GA)</td>
<td>C(3IA)</td>
<td>C(4DA)</td>
</tr>
<tr>
<td></td>
<td>F(2)</td>
<td>C</td>
<td>C(9DA)</td>
<td>113.8 (5)</td>
<td>C(2GA)</td>
<td>C(3IA)</td>
<td>C(17)</td>
</tr>
<tr>
<td></td>
<td>F(1B)</td>
<td>C</td>
<td>F(5CA)</td>
<td>106.9 (7)</td>
<td>C(17)</td>
<td>C(3IA)</td>
<td>Fe(2A)</td>
</tr>
<tr>
<td></td>
<td>F(1B)</td>
<td>C</td>
<td>F(2)</td>
<td>105.1 (8)</td>
<td>F(2BA)</td>
<td>C(4IA)</td>
<td>C(8BA)</td>
</tr>
<tr>
<td></td>
<td>F(1B)</td>
<td>C</td>
<td>C(9DA)</td>
<td>114.1 (6)</td>
<td>F(9CA)</td>
<td>C(4IA)</td>
<td>F(2BA)</td>
</tr>
<tr>
<td></td>
<td>C(4AA)</td>
<td>C(5AA)</td>
<td>B</td>
<td>122.5 (4)</td>
<td>F(9CA)</td>
<td>C(4IA)</td>
<td>C(8BA)</td>
</tr>
<tr>
<td></td>
<td>C(8FA)</td>
<td>C(5AA)</td>
<td>C(4AA)</td>
<td>115.7 (4)</td>
<td>F(4DA)</td>
<td>C(4IA)</td>
<td>F(2BA)</td>
</tr>
<tr>
<td></td>
<td>C(8FA)</td>
<td>C(5AA)</td>
<td>B</td>
<td>121.6 (4)</td>
<td>F(4DA)</td>
<td>C(4IA)</td>
<td>F(9CA)</td>
</tr>
<tr>
<td></td>
<td>C(6BA)</td>
<td>C(6AA)</td>
<td>C(3EA)</td>
<td>123.4 (6)</td>
<td>F(4DA)</td>
<td>C(4IA)</td>
<td>C(8BA)</td>
</tr>
<tr>
<td></td>
<td>C(0CA)</td>
<td>C(7AA)</td>
<td>C(9AA)</td>
<td>122.2 (5)</td>
<td>F(9BA)</td>
<td>C(5IA)</td>
<td>C(1BA)</td>
</tr>
<tr>
<td></td>
<td>C(9HA)</td>
<td>C(8AA)</td>
<td>C(5HA)</td>
<td>121.2 (5)</td>
<td>F(9BA)</td>
<td>C(5IA)</td>
<td>F(13)</td>
</tr>
<tr>
<td></td>
<td>C(9HA)</td>
<td>C(8AA)</td>
<td>C(2KA)</td>
<td>118.2 (5)</td>
<td>F(5EA)</td>
<td>C(5IA)</td>
<td>F(9BA)</td>
</tr>
<tr>
<td></td>
<td>C(5HA)</td>
<td>C(8AA)</td>
<td>C(2KA)</td>
<td>120.6 (5)</td>
<td>F(5EA)</td>
<td>C(5IA)</td>
<td>C(1BA)</td>
</tr>
<tr>
<td></td>
<td>C(7AA)</td>
<td>C(9AA)</td>
<td>C(2BA)</td>
<td>116.2 (5)</td>
<td>F(5EA)</td>
<td>C(5IA)</td>
<td>F(13)</td>
</tr>
<tr>
<td></td>
<td>C(7AA)</td>
<td>C(9AA)</td>
<td>B</td>
<td>121.9 (4)</td>
<td>F(13)</td>
<td>C(5IA)</td>
<td>C(1BA)</td>
</tr>
<tr>
<td></td>
<td>C(2BA)</td>
<td>C(9AA)</td>
<td>B</td>
<td>121.6 (5)</td>
<td>C(54A)</td>
<td>C(47A)</td>
<td>C(46A)</td>
</tr>
<tr>
<td></td>
<td>F(3AA)</td>
<td>C(1)</td>
<td>C(2FA)</td>
<td>112.5 (5)</td>
<td>C(70A)</td>
<td>C(0JA)</td>
<td>P(3AA)</td>
</tr>
<tr>
<td></td>
<td>F(4BA)</td>
<td>C(1)</td>
<td>F(3AA)</td>
<td>106.1 (5)</td>
<td>C(5FA)</td>
<td>C(4JA)</td>
<td>Fe(0A)</td>
</tr>
<tr>
<td></td>
<td>F(4BA)</td>
<td>C(1)</td>
<td>C(2FA)</td>
<td>113.4 (5)</td>
<td>C(5FA)</td>
<td>C(4JA)</td>
<td>C(6LA)</td>
</tr>
<tr>
<td></td>
<td>F(0CA)</td>
<td>C(1)</td>
<td>F(3AA)</td>
<td>105.6 (5)</td>
<td>C(0KA)</td>
<td>C(4JA)</td>
<td>Fe(0A)</td>
</tr>
<tr>
<td></td>
<td>F(0CA)</td>
<td>C(1)</td>
<td>F(4BA)</td>
<td>106.8 (5)</td>
<td>C(0KA)</td>
<td>C(4JA)</td>
<td>C(5FA)</td>
</tr>
<tr>
<td></td>
<td>F(0CA)</td>
<td>C(1)</td>
<td>C(2FA)</td>
<td>111.9 (4)</td>
<td>C(0KA)</td>
<td>C(4JA)</td>
<td>C(6LA)</td>
</tr>
<tr>
<td></td>
<td>C(45A)</td>
<td>C(44A)</td>
<td>B(27A)</td>
<td>118.6 (5)</td>
<td>C(6LA)</td>
<td>C(4JA)</td>
<td>Fe(0A)</td>
</tr>
<tr>
<td></td>
<td>C(49A)</td>
<td>C(44A)</td>
<td>C(45A)</td>
<td>114.3 (5)</td>
<td>C(9JA)</td>
<td>C(51A)</td>
<td>C(0GA)</td>
</tr>
<tr>
<td></td>
<td>C(49A)</td>
<td>C(44A)</td>
<td>B(27A)</td>
<td>127.1 (5)</td>
<td>C(29A)</td>
<td>C(35A)</td>
<td>C(36A)</td>
</tr>
<tr>
<td></td>
<td>C(4AA)</td>
<td>C(1BA)</td>
<td>C(3CA)</td>
<td>120.1 (5)</td>
<td>C(31A)</td>
<td>C(35A)</td>
<td>C(29A)</td>
</tr>
<tr>
<td></td>
<td>C(4AA)</td>
<td>C(1BA)</td>
<td>C(51A)</td>
<td>120.7 (5)</td>
<td>C(31A)</td>
<td>C(35A)</td>
<td>C(36A)</td>
</tr>
<tr>
<td></td>
<td>C(3CA)</td>
<td>C(1BA)</td>
<td>C(51A)</td>
<td>119.1 (5)</td>
<td>C(9BA)</td>
<td>C(9JA)</td>
<td>C(5JA)</td>
</tr>
<tr>
<td></td>
<td>C(9AA)</td>
<td>C(2BA)</td>
<td>C(3BA)</td>
<td>122.3 (5)</td>
<td>C(9BA)</td>
<td>C(9JA)</td>
<td>C(4NA)</td>
</tr>
<tr>
<td></td>
<td>C(2BA)</td>
<td>C(3BA)</td>
<td>C(10)</td>
<td>119.6 (5)</td>
<td>C(5JA)</td>
<td>C(9JA)</td>
<td>C(4NA)</td>
</tr>
<tr>
<td></td>
<td>C(6DA)</td>
<td>C(3BA)</td>
<td>C(2BA)</td>
<td>120.3 (5)</td>
<td>C(3DA)</td>
<td>C(0KA)</td>
<td>Fe(0A)</td>
</tr>
<tr>
<td>C(6DA) C(3BA) C(10)</td>
<td>120.0 (5)</td>
<td>C(3DA) C(0KA) C(6JA)</td>
<td>126.4 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------</td>
<td>----------------------</td>
<td>-----------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2AA) C(4BA) B(6AA)</td>
<td>122.9 (4)</td>
<td>C(4JA) C(0KA) Fe(0A)</td>
<td>69.9 (3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2AA) C(4BA) C(0FA)</td>
<td>116.0 (4)</td>
<td>C(4JA) C(0KA) C(3DA)</td>
<td>108.8 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(0FA) C(4BA) B(6AA)</td>
<td>120.8 (4)</td>
<td>C(4JA) C(0KA) C(6JA)</td>
<td>123.9 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(1AA) C(5BA) C(7CA)</td>
<td>118.2 (4)</td>
<td>C(6JA) C(0KA) Fe(0A)</td>
<td>134.4 (4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(6AA) C(6BA) C(0MA)</td>
<td>118.7 (6)</td>
<td>C(1GA) C(1KA) C(9)</td>
<td>119.2 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(4GA) C(6BA) C(6AA)</td>
<td>119.8 (6)</td>
<td>C(1GA) C(1KA) C(5LA)</td>
<td>121.0 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(4GA) C(6BA) C(0MA)</td>
<td>121.5 (6)</td>
<td>C(5LA) C(1KA) C(9)</td>
<td>119.7 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(46A) C(45A) C(44A)</td>
<td>123.1 (5)</td>
<td>F(1BA) C(2KA) C(8AA)</td>
<td>112.0 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5EA) C(8BA) C(3FA)</td>
<td>121.3 (5)</td>
<td>F(3CA) C(2KA) F(1BA)</td>
<td>102.6 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5EA) C(8BA) C(4IA)</td>
<td>118.6 (5)</td>
<td>F(3CA) C(2KA) C(8AA)</td>
<td>112.6 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(3FA) C(8BA) C(4IA)</td>
<td>119.9 (5)</td>
<td>F(8DA) C(2KA) F(1BA)</td>
<td>105.0 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(9JA) C(9BA) C(2FA)</td>
<td>117.9 (5)</td>
<td>F(8DA) C(2KA) F(3CA)</td>
<td>109.6 (7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7AA) C(0CA) C(9MA)</td>
<td>120.0 (5)</td>
<td>F(8DA) C(2KA) C(8AA)</td>
<td>114.2 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(6DA) C(0CA) C(7AA)</td>
<td>120.7 (5)</td>
<td>O(2) C(3KA) Fe(2A)</td>
<td>176.3 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(6DA) C(0CA) C(9MA)</td>
<td>119.3 (5)</td>
<td>C(9OA) C(4KA) P(4AA)</td>
<td>116.6 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(4HA) C(1CA) C(8HA)</td>
<td>123.1 (5)</td>
<td>C(44A) B(27A) C(1EA)</td>
<td>103.8 (4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(3FA) C(2CA) C(9KA)</td>
<td>121.1 (5)</td>
<td>C(44A) B(27A) C(28A)</td>
<td>110.8 (4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(3FA) C(2CA) C(8NA)</td>
<td>119.0 (5)</td>
<td>C(44A) B(27A) C(0GA)</td>
<td>115.0 (4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(9KA) C(2CA) C(8NA)</td>
<td>119.9 (5)</td>
<td>C(28A) B(27A) C(1EA)</td>
<td>112.0 (4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(1AA) C(2) F(9AA)</td>
<td>105.9 (4)</td>
<td>C(0GA) B(27A) C(1EA)</td>
<td>109.7 (4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(1AA) C(2) C(1AA)</td>
<td>113.2 (4)</td>
<td>C(0GA) B(27A) C(28A)</td>
<td>105.7 (4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(7AA) C(2) F(1AA)</td>
<td>107.4 (4)</td>
<td>C(2CA) C(9KA) C(1EA)</td>
<td>121.9 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(7AA) C(2) F(9AA)</td>
<td>106.2 (5)</td>
<td>C(45A) C(46A) C(50A)</td>
<td>119.2 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(7AA) C(2) C(1AA)</td>
<td>112.5 (4)</td>
<td>C(45A) C(46A) C(47A)</td>
<td>120.6 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(9AA) C(2) C(1AA)</td>
<td>111.1 (4)</td>
<td>C(47A) C(46A) C(50A)</td>
<td>120.2 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(3AA) C(3CA) C(1BA)</td>
<td>118.7 (5)</td>
<td>C(1F) C(1LA) P(5AA)</td>
<td>111.6 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(1DA) C(4CA) C(0DA)</td>
<td>122.6 (5)</td>
<td>C(26A) C(25A) P(18A)</td>
<td>117.4 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7EA) C(5CA) B(6AA)</td>
<td>121.9 (4)</td>
<td>F(38A) C(36A) C(35A)</td>
<td>112.5 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5LA) C(5CA) B(6AA)</td>
<td>121.9 (4)</td>
<td>F(39A) C(36A) F(38A)</td>
<td>107.1 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5LA) C(5CA) C(7EA)</td>
<td>116.0 (4)</td>
<td>F(39A) C(36A) C(35A)</td>
<td>112.3 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2FA) C(6CA) C(0GA)</td>
<td>122.5 (5)</td>
<td>C(37A) C(36A) F(38A)</td>
<td>105.3 (7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2AA) C(7CA) C(5BA)</td>
<td>120.9 (5)</td>
<td>F(37A) C(36A) F(39A)</td>
<td>106.0 (8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2AA) C(7CA) C(7)</td>
<td>120.5 (5)</td>
<td>F(37A) C(36A) C(35A)</td>
<td>113.1 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5BA) C(7CA) C(7)</td>
<td>118.6 (5)</td>
<td>C(1KA) C(5LA) C(5CA)</td>
<td>121.6 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2DA) C(8CA) Fe(2A)</td>
<td>70.5 (3)</td>
<td>C(6EA) C(8LA) C(5GA)</td>
<td>118.9 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2DA) C(8CA) C(4DA)</td>
<td>108.9 (5)</td>
<td>C(6FA) C(8LA) C(6EA)</td>
<td>121.8 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2DA) C(8CA) C(0PA)</td>
<td>125.5 (6)</td>
<td>C(6FA) C(8LA) C(5GA)</td>
<td>119.3 (6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(4DA) C(8CA) Fe(2A)</td>
<td>71.3 (3)</td>
<td>C(6A) C(5A) Fe(1A)</td>
<td>70.3 (3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(4DA) C(8CA) C(0PA)</td>
<td>125.4 (5)</td>
<td>C(6A) C(5A) C(10A)</td>
<td>125.1 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(0PA) C(8CA) Fe(2A)</td>
<td>128.9 (4)</td>
<td>C(10A) C(5A) Fe(1A)</td>
<td>135.3 (4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7A) C(6A) Fe(1A)</td>
<td>70.6 (3)</td>
<td>C(4A) C(5A) Fe(1A)</td>
<td>69.4 (3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7A) C(6A) C(5A)</td>
<td>107.4 (5)</td>
<td>C(4A) C(5A) C(6A)</td>
<td>108.2 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7A) C(6A) C(11A)</td>
<td>126.4 (6)</td>
<td>C(4A) C(5A) C(10A)</td>
<td>125.5 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5A) C(6A) Fe(1A)</td>
<td>70.5 (3)</td>
<td>F(7CA) C(0MA) C(6BA)</td>
<td>113.9 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
C(5A) C(6A) C(11A) 125.3 (5) F(7CA) C(0MA) F(19) 106.0 (7)
C(11A) C(6A) Fe(1A) 132.5 (4) F(14) C(0MA) F(7CA) 106.3 (9)
C(4CA) C(0DA) C(12) 120.2 (5) F(14) C(0MA) C(6BA) 113.4 (6)
C(4CA) C(0DA) C(0HA) 120.2 (5) F(14) C(0MA) F(19) 103.3 (10)
C(0HA) C(0DA) C(12) 119.6 (5) F(19) C(0MA) C(6BA) 113.0 (7)
C(4CA) C(1DA) B 124.8 (4) C(49A) C(54A) C(58A) 118.7 (6)
C(4CA) C(1DA) C(5HA) 115.9 (4) C(47A) C(54A) C(49A) 121.7 (6)
C(5HA) C(1DA) B 119.2 (4) C(47A) C(54A) C(58A) 119.6 (6)
C(8CA) C(2DA) Fe(2A) 70.6 (3) F(15) C(5MA) C(8GA) 116.1 (6)
C(8CA) C(2DA) C(2GA) 107.6 (5) F(15) C(5MA) F(1D) 98.9 (11)
C(8CA) C(2DA) C(3NA) 125.7 (6) F(16) C(5MA) C(8GA) 116.0 (8)
C(2GA) C(2DA) Fe(2A) 71.1 (3) F(16) C(5MA) F(15) 109.3 (13)
C(2GA) C(2DA) C(3NA) 126.3 (6) F(16) C(5MA) F(1D) 100.1 (13)
C(3NA) C(2DA) Fe(2A) 129.1 (4) F(1D) C(5MA) C(8GA) 114.1 (10)
C(5DA) C(3DA) Fe(0A) 70.4 (3) F(3BA) C(9MA) F(8BA) 106.8 (5)
C(5DA) C(3DA) C(4) 126.2 (6) F(3BA) C(9MA) C(0CA) 113.6 (5)
C(4) C(3DA) Fe(0A) 132.7 (4) F(3BA) C(9MA) F(2EA) 105.7 (6)
C(0KA) C(3DA) Fe(0A) 71.0 (3) F(8BA) C(9MA) C(0CA) 112.7 (5)
C(0KA) C(3DA) C(5DA) 106.9 (5) F(8BA) C(9MA) F(2EA) 106.1 (6)
C(0KA) C(3DA) C(4) 125.8 (6) F(2EA) C(9MA) C(0CA) 111.4 (5)
C(8CA) C(4DA) Fe(2A) 69.6 (3) C(17A) C(15A) P(14A) 110.5 (5)
C(8CA) C(4DA) C(3) 126.2 (5) C(6MA) C(1NA) P(0AA) 116.2 (6)
C(8CA) C(4DA) C(3IA) 107.1 (5) C(22A) C(21A) P(14A) 115.5 (5)
C(3) C(4DA) Fe(2A) 133.6 (4) F(8) C(4NA) F(7IA) 97.8 (8)
C(3IA) C(4DA) Fe(2A) 69.9 (3) F(8) C(4NA) C(9JA) 114.5 (6)
C(3IA) C(4DA) C(3) 125.8 (5) F(7IA) C(4NA) C(9JA) 109.4 (7)
C(3DA) C(5DA) Fe(0A) 70.2 (3) F(3JA) C(4NA) F(8) 114.8 (8)
C(3DA) C(5DA) C(1MA) 125.7 (7) F(3JA) C(4NA) F(7IA) 102.0 (7)
C(5FA) C(5DA) Fe(0A) 69.4 (3) F(3JA) C(4NA) C(9JA) 115.6 (6)
C(5FA) C(5DA) C(3DA) 108.7 (5) C(7NA) C(5NA) P(4AA) 115.6 (6)
C(5FA) C(5DA) C(1MA) 124.9 (7) F(8CA) C(8NA) C(2CA) 113.7 (6)
C(1MA) C(5DA) Fe(0A) 133.6 (5) F(4EA) C(8NA) F(8CA) 103.9 (7)
C(3BA) C(6DA) C(0CA) 118.3 (5) F(4EA) C(8NA) C(2CA) 113.9 (6)
C(33A) C(32A) C(40A) 121.3 (6) F(12) C(8NA) F(8CA) 104.6 (7)
C(31A) C(32A) C(33A) 119.9 (6) F(12) C(8NA) C(2CA) 112.5 (6)
C(31A) C(32A) C(40A) 118.7 (5) F(12) C(8NA) F(4EA) 107.4 (8)
C(4BA) B(6AA) C(0AA) 110.7 (4) C(8OA) C(9NA) P(4AA) 107.3 (5)
C(5CA) B(6AA) C(0AA) 104.9 (4) C(19) C(00A) P(3AA) 117.5 (7)
C(5CA) B(6AA) C(4BA) 112.9 (4) C(7A) C(8A) Fe(1A) 71.9 (3)
C(5CA) B(6AA) C(3EA) 114.2 (4) C(7A) C(8A) C(4A) 107.7 (5)
C(33A) B(6AA) C(0AA) 111.7 (4) C(7A) C(8A) C(13A) 126.6 (6)
C(33A) B(6AA) C(4BA) 102.7 (4) C(4A) C(8A) Fe(1A) 70.6 (3)
C(7EA) C(8DA) C(5) 120.1 (5) C(4A) C(8A) C(13A) 125.2 (6)
C(7EA) C(8DA) C(1GA) 120.5 (5) C(13A) C(8A) Fe(1A) 129.7 (4)
C(1GA) C(8DA) C(5) 119.3 (5) C(9NA) C(8OA) P(0AA) 113.1 (6)
<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
<th>Bond</th>
<th>Angle (°)</th>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(4EA) - C(9DA) - C</td>
<td>119.1(5)</td>
<td>C(24A) - C(23A) - P(18A)</td>
<td>115.2(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(9EA) - C(9DA) - C</td>
<td>120.1(5)</td>
<td>F(6BA) - C(1B) - F(0DA)</td>
<td>105.7(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(9EA) - C(9DA) - C(4EA)</td>
<td>120.9(5)</td>
<td>F(6BA) - C(1B) - C(1FA)</td>
<td>113.8(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(1FA) - C(0EA) - C(0AA)</td>
<td>122.1(5)</td>
<td>F(0DA) - C(1B) - C(1FA)</td>
<td>111.5(7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5EA) - C(1EA) - B(27A)</td>
<td>118.5(5)</td>
<td>F(2DA) - C(1B) - F(6BA)</td>
<td>109.7(7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(9KA) - C(1EA) - C(5EA)</td>
<td>116.2(5)</td>
<td>F(2DA) - C(1B) - F(0DA)</td>
<td>102.8(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(9KA) - C(1EA) - B(27A)</td>
<td>125.2(4)</td>
<td>F(2DA) - C(1B) - C(1FA)</td>
<td>112.6(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(35A) - C(29A) - C(28A)</td>
<td>121.8(5)</td>
<td>F(57A) - C(58A) - C(54A)</td>
<td>113.0(7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(6AA) - C(3EA) - B(6AA)</td>
<td>120.0(4)</td>
<td>F(57A) - C(58A) - F(56A)</td>
<td>103.1(8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(6AA) - C(3EA) - C(9HA)</td>
<td>115.8(5)</td>
<td>F(55A) - C(58A) - F(57A)</td>
<td>109.4(12)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(9HA) - C(3EA) - B(6AA)</td>
<td>123.6(5)</td>
<td>F(55A) - C(58A) - C(54A)</td>
<td>113.4(8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(0AA) - C(5) - C(8DA)</td>
<td>112.9(5)</td>
<td>F(55A) - C(58A) - F(56A)</td>
<td>105.6(11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(5BA) - C(5) - F(0AA)</td>
<td>104.8(5)</td>
<td>F(56A) - C(58A) - C(54A)</td>
<td>111.7(11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(5BA) - C(5) - C(8DA)</td>
<td>111.9(5)</td>
<td>C(1LA) - C(1F) - P(3AA)</td>
<td>107.5(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(4CA) - C(5) - F(0AA)</td>
<td>104.9(5)</td>
<td>C(1I) - C(1K) - P(0AA)</td>
<td>112.8(7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(4CA) - C(5) - F(5BA)</td>
<td>108.3(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
$^1$H NMR spectrum for Chapter 2

HD scrambling experiment using the FLP BPh$_3$/Et$_3$N at 298 K in 1,2-difluorobenzene:

$^1$H NMR spectrum of the reaction after 24 hours at room temperature in 1,2-difluorobenzene. The red spectrum is at 0 hours and the blue spectrum is at 24 hours; indicating the consumption of H$_2$ via scrambling to produce HD over time.
$^1$H-$^{31}$P HMBC NMR spectrum: The reaction of [Fe(CO)(Cp*)($\kappa_2$-dmpe)][BARF$_{24}$] (3) with one equivalent of Na[BHE$_3$] in THF-$d_8$ at 289 K
$^{1}H-^{31}P$ HMBC NMR spectrum: The reaction of $[\text{Fe(CO)}(\text{Cp}^*)(\kappa^2-\text{dmpe})][\text{BARF}_{24}]$ (3) with 10 equivalents of NaH and 3 equivalents of BEt$_3$ in THF-$d_8$ at 289 K
$^1$H NOESY NMR spectrum: The reaction of $[\text{Fe(CO)}(\text{Cp}^*)(\kappa^2-\text{dmpe})][\text{BArF}_{24}]$ (3) with 10 equivalents of NaH and 3 equivalents of BEt$_3$ in THF-$d_8$ at 289 K