

**ALKYLIMIDO COMPLEXES OF
TRANSITION METALS**

A thesis submitted by

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ABSTRACT

The sodium/amalgam reduction of $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)$ in hexane gives the dimeric rhenium(VI) complex, $[(\text{Bu}^t\text{N})_2\text{Re}(\mu\text{-NBu}^t)]_2$, which has been structurally characterised. This represents the first full report of a homoleptic transition metal imido complex. The structures of $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)$ and $(\text{Bu}^t\text{N})_2\text{ReCl}_3$ have also been determined. The latter complex reacts with silver acetate to give $(\text{Bu}^t\text{N})_2\text{Re}(\text{OAc})_3$.

The synthesis of a range of organometallic rhenium(VII) complexes, $(\text{Bu}^t\text{N})_3\text{Re}(\text{aryl})$ ($\text{aryl} = o\text{-tol}, \text{xylyl}, \text{mes}, \text{Ph}, p\text{-Bu}^t\text{Ph}$), from $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)$ and the appropriate Grignard reagent is reported. Treatment of these complexes with HCl yields the corresponding dichloro-complexes, $(\text{Bu}^t\text{N})_2\text{ReCl}_2(\text{aryl})$. The crystal structure of $(\text{Bu}^t\text{N})_2\text{ReCl}_2(o\text{-tol})$ reveals a square pyramidal geometry with one linear and one bent imido ligand, which formally suggests a 16-electron configuration. The solid state structure of $(\text{Bu}^t\text{N})_2\text{ReCl}_2\text{Ph}$ shows a trigonal bipyramidal molecule, with equatorial imido groups.

The reaction of $(\text{Bu}^t\text{N})_2\text{ReCl}_3$ with *o*-tolylmagnesium bromide gives $(\text{Bu}^t\text{N})_2\text{Re}(o\text{-tol})_3$, whereas with mesitylmagnesium bromide reduction occurs to produce $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$. This paramagnetic d^1 species has been oxidised chemically to give $[(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2]\text{X}$ ($\text{X} = \text{PF}_6, \text{OTf}$). The results of preliminary investigations into the insertion chemistry of these complexes are presented. The cationic species undergo monoinsertion reactions with isocyanides to give η^2 -iminoacyl derivatives.

A new system for the catalytic reduction of imines using rhodium-phosphine complexes has been developed. The system is effective at room temperature under one atmosphere of hydrogen. A catalytic cycle is proposed, based on the results obtained for a range of imine substrates and solvents.

CONTENTS

ABSTRACT	2
CONTENTS	4
LIST OF FIGURES	5
LIST OF TABLES	6
LIST OF ABBREVIATIONS	7
ACKNOWLEDGEMENTS	9
DEDICATION	10
INTRODUCTION	11
CHAPTER 1: High Oxidation State <i>Tertiary</i> -butylimido Complexes of Rhenium	
Introduction	21
Results and Discussion	22
Experimental	35
CHAPTER 2: High Oxidation State <i>Tertiary</i> -butylimido Rhenium Aryl Complexes	
Introduction	39
Results and Discussion	40
Experimental	65
CHAPTER 3: The Catalytic Hydrogenation of Imines Using Rhodium-phosphine Complexes	
Introduction	74
Results and Discussion	75
Experimental	81
REFERENCES	83

LIST OF FIGURES

1.0	The four basic bonding modes for organoimido ligands	13
1.1	The molecular structure of $[(\text{Bu}^t\text{N})_2\text{Re}(\mu\text{-N}\text{Bu}^t)]_2$	25
1.2	The molecular structure of $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)$	29
1.3	The molecular structure of $(\text{Bu}^t\text{N})_2\text{ReCl}_3$	32
1.4	The molecular structure of $(\text{Bu}^t\text{N})_2\text{ReCl}_3$	33
2.1	The molecular structure of $(\text{Bu}^t\text{N})_2\text{ReCl}_2(o\text{-tol})$	43
2.2	The molecular structure of $(\text{Bu}^t\text{N})_2\text{ReCl}_2\text{Ph}$	47
2.3	The e.s.r. spectrum (X-band) of $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$	52
2.4	Cyclic voltammogram of $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$	54
3.1	Proposed cycle for catalytic hydrogenation of imines on a cationic rhodium-phosphine complex	77

LIST OF TABLES

1.1	Selected bond lengths and angles for $[(\text{Bu}^t\text{N})_2\text{Re}(\mu\text{-N}\text{Bu}^t)]_2$	26
1.2	Selected bond lengths and angles for $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)$	30
1.3	Selected bond lengths and angles for $(\text{Bu}^t\text{N})_2\text{ReCl}_3$	34
2.1	Selected bond lengths and angles for $(\text{Bu}^t\text{N})_2\text{ReCl}_2(o\text{-tol})$	44
2.2	Selected bond lengths and angles for $(\text{Bu}^t\text{N})_2\text{ReCl}_2\text{Ph}$	48
2.3	Physical properties and analytical data for $(\text{Bu}^t\text{N})_3\text{Re}(\text{aryl})$ and $(\text{Bu}^t\text{N})_2\text{ReCl}_2(\text{aryl})$	59
2.4	Physical properties and analytical data for $(\text{Bu}^t\text{N})_2\text{Re}(o\text{-tol})_3$, $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$ and oxidation and insertion products	60
2.5	^1H NMR data for $(\text{Bu}^t\text{N})_3\text{Re}(\text{aryl})$	61
2.6	^1H NMR data for $(\text{Bu}^t\text{N})_2\text{ReCl}_2(\text{aryl})$	62
2.7	^1H NMR data for $(\text{Bu}^t\text{N})_2\text{Re}(o\text{-tol})_3$ and oxidation products from $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$	63
2.8	^1H NMR data for insertion products from $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$ and $[(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2]^+$	64
3.1	Representative data for the hydrogenation of imines using rhodium-phosphine complexes	78

LIST OF ABBREVIATIONS

Å	angstrom, 10^{-8} cm
Ad	adamantyl
A_{iso}	isotropic hyperfine coupling constant
atm	$101\,325\text{ Nm}^{-2}$
B.M	Bohr Magnetons ($0.927 \times 10^{-23}\text{ Am}^2$)
bipy	2,2'-Bipyridine
Cp	π -cyclopentadienyl ($\eta^5\text{-C}_5\text{H}_5$)
Cp*	π -pentamethylcyclopentadienyl ($\eta^5\text{-C}_5\text{Me}_5$)
diop	2,3-O-isopropylidene-2,3-dihydroxy- 1,4-bis(diphenylphosphino)butane
dppe	diphenylphosphinoethane
dtc	dithiocarbamate
e.s.r.	electron spin resonance
eV	electron volts
FAB	fast atom bombardment
g	g - value
HMDS	hexamethyldisiloxane
IR	infrared
J	coupling constant in Hz
MEC	maximum electron count
mes	mesityl, 2,4,6-trimethylphenyl
Mpt.	melting point
μ_{eff}	effective magnetic moment
Np	neopentyl, $(\text{CH}_3)_3\text{CCH}_2\text{-}$
NMR	nuclear magnetic resonance
nbd	norbornadiene
OAc	acetate, CH_3COO^-

OTf	triflate, CF_3SO_3^-
p.p.m	parts per million
psi	pounds per square inch
py	pyridine
<i>o</i> - tol	2-methylphenyl
THF	tetrahydrofuran
tmed	tetramethylethylenediamine
TPP	5,10,15,20-tetraphenylporphyrinato
xylyl	2,6-dimethylphenyl

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To Quacky

INTRODUCTION

Organoimido Ligands

Transition metal imido complexes are currently the focus of considerable research activity; this reflects interest in the role played by multiply-bonded ligands in important chemical transformations.

It is instructive to consider the general nature and properties of the organoimido ligand before proceeding to describe the novel alkylimido complexes generated as part of this project. The following introduction will provide useful background for the discussion in Chapters 1 and 2.

The imido ligand, NR^{2-} , is isoelectronic with the nitrido and oxo ligands - all three share a strong π -bonding capability and are capable of stabilising metal centres in high oxidation states by virtue of this pronounced π -donation. The nitrido ligand is the strongest π -bonding ligand of the three¹ - generally metal-oxo and metal-nitrido bond lengths are very similar for a given coordination environment. Metal-imido bond lengths are usually about 0.05 Å longer; the relative bond strengths are therefore $\text{M}\equiv\text{N} > \text{M}=\text{O} > \text{M}=\text{NR}$, since the radius of multiply-bonded oxygen is 0.03 Å smaller than that of nitrogen. The *trans* influence exerted by organoimido ligands is dependent on both the electron count and the geometry of the complex². In general pseudo-octahedral and pentagonal bipyramidal complexes with MECs of 18 electrons show no *trans* influence, whereas pseudo-octahedral complexes with MECs of 16 or 20 electrons do exhibit a noticeable *trans* influence.

Organoimido complexes are often more soluble in organic solvents than their oxo counterparts, the effects of multiple-bonding tend to be more pronounced since nitrogen is less electronegative than oxygen, and the organic moiety in the imido group provides a useful measure of bonding and electron distribution *via* NMR and crystallographic studies on M-N-C bond angles.

Although many organoimido complexes are isostructural with their oxo analogues,

in general the organoimido ligands form fewer bridging complexes, fewer anionic complexes and fewer first row derivatives.

Bonding in Imido Complexes

There are four basic modes of bonding for organoimido ligands (Fig.1.0). New examples of complexes containing bonding modes (a)-(c) are included in this thesis.

The terminal linear arrangement is the most commonly observed, representing *sp* hybridisation at nitrogen and thus triple bond character in the metal-nitrogen linkage. Generally a bent M-N-R geometry is expected when a linear 4-electron donor ligand would cause the electron count of the complex to exceed 18 electrons. However, other factors can influence the geometry of these linkages, and the present work has generated an unusual complex with a bent imido ligand, but a formal electron count of only 16 electrons. Symmetry restrictions may reduce the number of π -bonds which can be formed between a metal and a group of π -bonding ligands^{2,3} - this can result in bending of the M-N-R linkages in a complex. The term 'linear' is generally used to describe the binding when the M-N-C angle is greater than 160° . There is, as yet, no structurally characterised example of a complex containing a fully bent (120°) imido ligand. The most acute M-N-C angle so far observed is 139° ².

Doubly bridging imido ligands are most often symmetric with metal-nitrogen π -bonding. When metal-metal bonding is present, the M-N-M angles fall in range $78-84^\circ$, but with no metal-metal bonding the angle is usually $>94^\circ$ ².

Reactivity of Organoimido Ligands

The nature of the reactivity of the M-N bond is, to some extent, dependent on the degree of nitrogen-metal π -bonding. The fact that imido groups sometimes show electrophilic reactivity, while in other complexes the same ligands may be nucleophilic, is not unusual for multiply-bonded ligands.

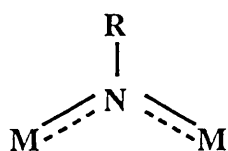
To explain this, a conceptual model has been presented⁴ based on that used for



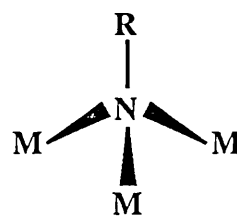
(a) Terminal Linear



(b) Terminal Bent



(c) Doubly Bridging



(d) Triply Bridging

Fig.1.0 : The Four Basic Bonding Modes for Organoimido Ligands

alkylidene ligands by Hoffman⁵. If the nitrogen *p*-orbitals are energetically well below the metal *d*-orbitals, as in the early transition metals, then the M-N π -bond will be nitrogen centred (since the high lying HOMO is heavily nitrogen *p* in character), and the imido ligand will behave as a nucleophile⁶. As one proceeds upwards and to the right across the transition series the *d*-orbitals become less diffuse and lower in energy, the π -electron density thus shifts toward the metal and the imido nitrogen becomes less nucleophilic^{7,8}. For example, the rate of protonolysis appears to decrease as we proceed from left to right along the series Ta > W > Re > Os .

¹³C NMR chemical shift data for a series of *d*⁰*tert*-butylimido derivatives have shown that decreasing the electron density on the imido nitrogen causes a downfield shift in the α -carbon resonance and an upfield shift in the β -carbon resonance⁴. The difference between these two chemical shifts, $\Delta = \delta(\alpha) - \delta(\beta)$, may thus be used as an experimental measure of electron density on the nitrogen atom.

The geometry of the M-N-C bond is obviously also important - for bent linkages less effective π -donation occurs, hence electron density on nitrogen increases and the ligand becomes more nucleophilic.

It seems likely that imido species are intermediates in several important industrial processes, *e.g.* the Haber process and the ammoxidation of propylene to acrylonitrile - models for such intermediates are currently under investigation^{9,10}. Schrock *et al* have spent several years preparing high oxidation state rhenium imido alkylidene and alkylidyne complexes. The research has been directed, with some success, towards the generation of new olefin¹¹ and acetylene¹² metathesis catalysts. Schrock has also designed a tungsten(VI) imido alkylidene complex which has shown activity as an olefin metathesis catalyst¹³. The ultimate goal of much of the study into organoimido complexes is the discovery of new synthetic routes to organic nitrogen compounds. For example, Sharpless has successfully employed OsO(NR)₃, OsO₂(NR)₂ and OsO₃(NR) as reagents for the diamination⁸ and oxyamination⁹ of olefins. The reactions are stereospecific, delivering N,N or O,N to carbon bonds *cis* to one another. However, the

intrinsic stability of the M-N bond has, in most cases, precluded the transfer of the NR group from the complex into another molecule. Research is underway to generate more complexes containing bent imido ligands, in the hope that the longer, weaker M-N bonds will be more reactive.

Recent Advances in Transition Metal Imido Chemistry

In this section the developments in transition metal imido chemistry over the past decade are briefly reviewed. The chemistry of organoimido compounds discovered prior to 1978 is covered in a comprehensive review article by Nugent and Haymore². Recent advances in rhenium imido chemistry are discussed, where appropriate, in Chapters 1 and 2, and therefore are not presented here. A large portion of the recent literature is concerned with novel Group V and Group VI organoimido complexes.

For Group V, niobium and especially tantalum have received the most attention. Schrock has used a novel reaction of the neopentylidene complex, $\text{Ta}(\text{CHBu}^t)\text{Cl}_3(\text{THF})_2$, with an imine to prepare octahedral tantalum(V) imido compounds, $\text{Ta}(\text{NR})\text{Cl}_3\text{L}_2$ ($\text{R}=\text{Me}, \text{Bu}^t, \text{Ph}$ $\text{L}=\text{THF}$, phosphine)¹⁴, one example of which has been structurally characterised¹⁵. Certain of these compounds may be reduced to give $\text{TaCl}(\text{NR})\text{L}_4$, in which one phosphine ligand is readily displaced by ethylene or styrene¹⁴. The tantalum(V) species may also be alkylated using $\text{MgNp}_2(\text{dioxane})$ to give $\text{Ta}(\text{NPh})\text{Np}_3(\text{THF})$ ¹⁶. An imidoalkylidene complex, $\text{Ta}(\text{NSiMe}_3)(\text{CHBu}^t)\text{Cl}(\text{PMe}_3)_2$, results from the oxidation of $\text{Ta}(\text{CHBu}^t)\text{Cl}(\text{PMe}_3)_4$ using trimethylsilylazide¹⁴. Complexes containing diimido bridging dinitrogen ligands are also reported, *e.g.* $[(\text{THF})_2\text{Cl}_3\text{Ta}=\text{N}]_2$ ¹⁷ in which THF may be displaced by a variety of phosphines¹⁶; here the unusual "diimido" description of the bridge is corroborated by X-ray structural data¹⁸. Several seven coordinate pentagonal bipyramidal complexes, $\text{M}(\text{NR})(\text{S}_2\text{CNR}'_2)_3$ ($\text{M}=\text{Nb}, \text{Ta}$ $\text{R}'=\text{Me}, \text{Et}$) can be synthesised

from the metal pentahalides and $\text{Me}_3\text{SiC}_2\text{CNR}'_2$ in the presence of excess amine, RNH_2 ($\text{R}=\text{Me}, \text{Pr}, \text{Pr}^i, \text{Bu}^t$)¹⁹. Analogous complexes are formed by treating $\text{TaCl}_3[\text{N}(\text{SiMe}_3)_2]_2$ with sodium dimethyldithiocarbamate, and reaction of the same starting material with lithium *t*-butylamide and with trimethylsilylbromide gave $\text{TaCl}(\text{NBu}^t)[\text{N}(\text{SiMe}_3)_2]_2$ and $\{\text{TaBr}(\mu\text{-Br})(\text{NSiMe}_3)[\text{N}(\text{SiMe}_3)_2]\}_2$ respectively²⁰. The latter complex contains unsymmetrical bromide bridges which are easily disrupted by the addition of neutral donor ligands to give $\text{TaBr}_2(\text{NSiMe}_3)[\text{N}(\text{SiMe}_3)_2]\text{L}$ ($\text{L}=\text{py}, \text{PMe}_3$)²⁰. The same research group have generated a variety of niobium(V) and tantalum(V) imido complexes containing alkoxide, amido and amino ligands, *e.g.* $[\text{TaCl}(\mu\text{-Cl})(\text{NBu}^t)(\text{NHBu}^t)(\text{NH}_2\text{Bu}^t)]_2$ ²¹ and $[\text{M}(\text{NBu}^t)(\mu\text{-OEt})\text{Cl}_2(\text{NH}_2\text{Bu}^t)]_2$ ²². Monoalkylamides react with $\text{Cp}^*\text{TaMe}_3\text{Cl}$ to form imido complexes, $\text{Cp}^*\text{TaMe}_2(\text{NR})$, which on hydrogenation in the presence of phosphine yield unusual imido hydrides, $\text{Cp}^*\text{Ta}(\text{NR})\text{H}_2\text{L}$ ($\text{R}=\text{Bu}^t, \text{Np}$ $\text{L}=\text{PMe}_3, \text{PMe}_2\text{Ph}$)²³. Preparative details for some other Group V imido compounds have been published by Nugent²⁴, *e.g.* $\text{M}(\text{NBu}^t)(\text{NMe}_2)_3$ ($\text{M}=\text{Nb}, \text{Ta}$) and $(\text{Me}_3\text{SiO})_3\text{V}(\text{NR})$ ($\text{R}=\text{Bu}^t, \text{Ad}$)²⁵. A useful vanadium starting material, $\text{V}(\text{NPh})\text{Cl}_3$, is readily prepared by the reaction of VOCl_3 with phenylisocyanate. This reacts with *t*-butyltrimethylsilylamine to give a trinuclear complex $[\text{VCl}(\text{NBu}^t)(\mu\text{-NPh})]_3(\mu_3\text{-PhNCONHBu}^t)$, which has been structurally characterised²⁶. The related complex, $(p\text{-tolN})\text{VCl}_3$, is prepared by a similar route²⁷. This 12-electron species forms monoadducts with donor ligands such as THF and PPh_3 . The chloride ligands are substituted under mild conditions to give $(\text{tolN})\text{VCl}_x(\text{OBu}^t)_{3-x}$, $\text{CpV}(\text{Ntol})\text{Cl}_2$ and $(\text{tolN})\text{VCl}_x(\text{CH}_2\text{SiMe}_3)_{3-x}$ *etc.*^{27,28}. A range of *para*-substituted

arylimido compounds (p -XC₆H₄N)VCl₃ (X=Me,CF₃,OMe,F,Cl,Br) are now known²⁸. The reaction of VCl₄ with trimethylsilylazide produces (Me₃SiN)VCl₃²⁹.

Moving on to Group VI, Wentworth *et al* have prepared a homologous series of compounds, MoO_{2-n}(NR)_n(Et₂dtc)₂ (R=aryl), in order to compare the reactivity of the oxo *versus* imido ligand^{6,30}. Oxygen atom abstraction from MoO(Ntol)(Et₂dtc)₂ using tertiary phosphines affords the oxo-bridged dimer [Mo(Ntol)(Et₂dtc)₂]₂O and Mo(Ntol)(Et₂dtc)₂³¹. Mixed oxo-imido complexes of molybdenum(VI) have also been studied by Osborn *et al* - alkylation of [MoO(NBu^t)Cl₂(MeCN)]₂ leads to the formation of various imido-alkyl and imido-carbene species³². Molybdenum(V) monoimido complexes incorporating dithiophosphate ligands are also known³³. Mo₂(OBu^t)₆ reacts with arylazides (p -tol or phenyl) to give dimeric species identified as [Mo(OBu^t)₂(NAr)(μ-NAr)]₂³⁴. Hydrazines react with MoOCl₂(PR"₃)₃ to give a range of complexes of formula [MoCl₂(NR)(RN₂COR')(PR"₃)₃]³⁵. Green has isolated a compound believed to be [Cp(NPh)Mo(μ-NPh)]₂ from the reaction of the corresponding oxo compound with excess phenylisocyanate³⁶. When the (p -tolylimido)molybdenum(VI) complex Mo(Ntol)Cl₄(THF)³⁷ is treated with tertiary phosphine reduction occurs to produce Mo(Ntol)Cl₃L₂ which has been structurally characterised for L=dppe³⁸; the orange-red PMe₃ complex may be further reduced using sodium amalgam to give green crystals of Mo(Ntol)Cl₂(PMe₃)₃^{31,38}.

A similar sequence of reactions yields the analogous W(NPh)Cl₂(PMe₃)₃³⁹ from W(NPh)Cl₄ *via* W(NPh)Cl₃(PMe₃)₂⁴⁰; W(NPh)Cl₄ also reacts with *t*-butylamine in the presence of methanol or ethanol to give dimeric species [W(NPh)(OR)₃(μ-OR)]₂; as

more crowded alcohols are used the stoichiometry of the product changes, *e.g.* $W(NPh)(OR)_4(Bu^tNH_2)$ for $R=iPr, Np$ and $W(NPh)(OR)_3Cl(Bu^tNH_2)$ for $R=Bu^t$ ^{41,42}. Treating the same starting material with *t*-butyltrimethylsilylamine gives the dimeric complex $[W(NBu^t)(\mu-NPh)Cl_2(NH_2Bu^t)]_2$ ⁴³, whereas treating tungsten hexachloride with this or *t*-butylamine gives the identical *t*-butylimido bridged dimer. A variety of such complexes has now been prepared⁴⁴. The *t*-butylimido bridged dimer is cleaved by $L=bipy$ or $tmed$ to give $W(NBu^t)_2Cl_2L$, reacts with further *t*-butylamine to give $W(NBu^t)_2(NHBu^t)_2$ and reacts with ethanol to give $[W(NBu^t)_2(OEt)_2]_x$ ⁴⁵. Similar compounds have been previously reported by Nugent and Harlow^{24,46}. $W(NBu^t)_2(NHBu^t)_2$ and $M(NBu^t)_2(OR)_2$ ($M=Cr, Mo$ $R=SiMe_3$; $M=W$ $R=Bu^t, SiPh_3$). The X-ray structures of $[(p-tolN)WCl_4(THF)]$, $[(PhN)_2WCl_2(bipy)]$ and $[(p-tolN)WCl_5]^-$ have been published⁴⁷. The tungsten(VI) tetra(amido) compound $W(NPh)(NMe_2)_4$ is produced by treating $[W(NPh)Cl_4 \cdot Et_2O]$ with one equivalent of methanol and then four equivalents of lithium dimethylamide - the compound contains a linear (180°) M-N-C bond⁴⁸. Schrock has converted a tungsten amido-neopentylidyne complex into an imido-neopentylidene complex by heating $W(CBu^t)(NHPH)Cl_2(PEt_3)_2$; also dehydrohalogenation of the latter using $Ph_3P=CH_2$ gives the alkylidyne, $W(CBu^t)(NPh)Cl(PEt_3)_2$ ⁴⁹. A large number of tungsten(VI) phenylimido alkyl and alkylidene complexes have been isolated⁵⁰. More recently $W(CHBu^t)(NR)(OR')_2$ ($R=2,6$ -diisopropylphenyl $R'=CMe(CF_3)_2$) has been shown to be an active olefin metathesis catalyst¹³. It has been found that $[Me_2W(NBu^t)(\mu-NBu^t)]_2$ ⁵¹ is isostructural with its molybdenum analogue⁵². The only other organometallic tungsten imido compound we have encountered is $[W(NPh)(\mu-O)Me_2(PMe_3)]_3$ formed in the

reaction of $\text{W}(\text{NPh})\text{Cl}_4$ with Me_2Mg and PMe_3 ⁵³ - the origin of the oxygen remains a mystery. Nitrogen-15 NMR spectra⁵⁴ and Raman spectra⁵⁵ for a range of imido tungsten and molybdenum complexes have been published.

An interesting *p*-phenylenediimido dimolybdenum complex has appeared in the literature this year⁵⁶ - $[\text{MoCl}_4(\text{THF})_2]_2(=\text{NC}_6\text{H}_4\text{N}=\text{N})$ has been prepared and reduced in a step-wise sequence through Mo(V) and Mo(IV) to $[\text{MoCl}(\text{PMe}_3)_4]_2(=\text{NC}_6\text{H}_4\text{N}=\text{N})$. Diimido complexes of tantalum have been prepared by the reductive coupling of nitriles, *e.g.* $\{\text{TaCl}_3(\text{THF})_2[=\text{NC}(\text{CH}_3)=]\}_2$ and $\{\text{Ta}(\text{Et}_2\text{dtc})_3[=\text{NC}(\text{Et})=]\}_2$ ⁵⁷.

The first imido complex of a metalloporphyrin was discovered in 1982⁵⁸ and since then several such complexes are reported for iron(IV)⁵⁹ and chromium(IV)⁶⁰.

For the Group IV metals, the structure of $[(\text{Me}_2\text{N})_2\text{Ti}(\mu\text{-NBu}^t)]_2$ ⁵¹ is identical with that of the zirconium analogue². The reaction of CpTiCl_3 with Me_3SiNHR ($\text{R}=\text{Et}, \text{Pr}^i, \text{Bu}^t$ or Ph) yields amido complexes which on thermolysis give imido bridged species, $[\text{CpClTi}(\mu\text{-NR})]_2$ - substitution of the chloride ligands by organic groups is possible⁶¹.

The alkylation of a nitrido ligand to give an imido osmium complex has also been performed⁶². The reactions of osmium oxo-imido complexes with alkenes have been further investigated by Griffith *et al*⁶³. The first *f*-metal organoimido complex was reported in 1984. This uranium species, $\text{Cp}_3\text{U}[\text{NC}(\text{Me})\text{CHP}(\text{Ph})_2\text{Me}]$ resulted from the insertion of acetonitrile into the metal-carbon bond in $[\text{Cl}_3\text{UCHP}(\text{Ph})_2\text{Me}]$ ⁶⁴. Since then, two other uranium imides have been discovered: $\text{Cp}'_3\text{U}(\text{NR})$ ($\text{R}=\text{Ph}, \text{SiMe}_3$; $\text{Cp}'=\text{C}_5\text{H}_4\text{Me}$), prepared from the reaction of RN_3 with $\text{Cp}'\text{U}(\text{THF})$ in ether⁶⁵.

All this, in addition to a wealth of publications on rhenium imido chemistry, amply demonstrates that this is a flourishing area of research.

CHAPTER 1

HIGH OXIDATION STATE *TERTIARY*-BUTYLIMIDO

COMPLEXES OF RHENIUM

CHAPTER 1

Introduction

Apart from the organometallic derivatives which will be discussed in Chapter 2, relatively few alkylimido complexes of rhenium(VII) and rhenium(VI) have been reported in the literature, and only one has been structurally characterised⁶⁶.

For rhenium(VII) the usual starting materials are $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)^{24,66}$ and $(\text{Bu}^t\text{N})_2\text{ReCl}_3$ which is prepared in high yield from the former complex by treatment with HCl ⁶⁷. When a deficiency of amine is used in the preparation of $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)$ from $\text{O}_3\text{Re}(\text{OSiMe}_3)$, a different rhenium(VII) *t*-butylimido species is formed, $[(\text{Bu}^t\text{N})_2\text{Re}(\text{OSiMe}_3)]_2\text{O}(\text{OSiMe}_3)(\text{ReO}_4)$ - this was characterised by X-ray crystallography⁶⁶. The reaction of ReO_3Cl or $\text{O}_3\text{Re}(\text{OSiMe}_3)$ with $(\text{Me}_3\text{Si})_2\text{NLi}$ gives the red, air-stable crystalline complex $(\text{Me}_3\text{SiO})_2\text{Re}[\text{N}(\text{SiMe}_3)_2](\text{NSiMe}_3)_2$ ⁶⁸. A mixture of products, believed to be $\text{Re}_2\text{O}_x(\text{NAr})_{7-x}$ ($\text{Ar} = 2,6\text{-diisopropylphenyl}$), is obtained from the reaction of $\text{O}_3\text{Re}(\text{OSiMe}_3)$ with ArNCO in toluene¹¹. One of the products, $(\text{ArN})_3\text{ReORe}(\text{O})(\text{NAr})_2$ has been isolated in 30% yield. Halonitrene complexes of rhenium(VII) are also known⁶⁹.

For rhenium(VI) the list is even shorter; $\text{Re}(\text{N-}i\text{-}p\text{-tol})\text{Cl}_4(\text{Ph}_3\text{PO})$ is thought to be one of the products from the oxygenation of $[\text{Re}(\text{N-}i\text{-}p\text{-tol})\text{Cl}_3(\text{PPh}_3)]_n$ in CCl_4 or benzene⁷⁰. The only other derivatives are N-chloroalkylated, *e.g.* $\text{Re}(\text{NR})\text{Cl}_4(\text{POCl}_3)^{71}$ and the corresponding salts $\text{Ph}_4\text{As}[\text{Re}(\text{NR})\text{Cl}_5]^{72}$ ($\text{R} = \text{CCl}_3$ or C_2Cl_5).

Octahedral rhenium(V) imido species are much more prevalent⁷³⁻⁷⁹. One such complex $\text{Re}(\text{NPh})\text{Cl}_3(\text{PMe}_3)_2$ may be reduced to give the only known rhenium(IV) imido complex, $\text{Re}(\text{NPh})\text{Cl}_2(\text{PMe}_3)_3$ ⁸⁰. Reaction of the related starting material, $\text{Re}(\text{NR})\text{Cl}_3(\text{PPh}_3)_2$ ($\text{R}=\text{Ph}$, *p*-MeO-Ph, *p*-Me-Ph), with Htipt and triethylamine (Htipt=2,4,6-triisopropylbenzenethiol) gives imido complexes of rhenium(V) containing sterically hindered thiolate ligands⁸¹.

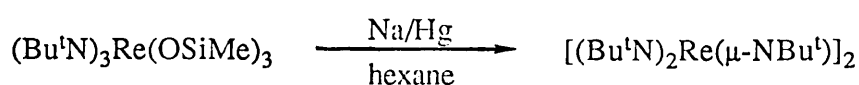
Although imido groups are isoelectronic with oxo groups, only one homoleptic imido complex of a transition metal has been previously reported, $\text{Os}(\text{NBu}^t)_3(\text{NSO}_2\text{Ar})$ ($\text{Ar} = \text{mes}$ or 2,4,6-triisopropylphenyl), but it has not been structurally characterised⁸².

This chapter reports the synthesis of several new high oxidation state rhenium imido derivatives. The most exciting is a homoleptic rhenium(VI) imido compound, $[(\text{Bu}^t\text{N})_2\text{Re}(\mu\text{-NBu}^t)]_2$. This is both the first rhenium(VI) and the first homoleptic imido complex of a transition metal to be structurally characterised. A high oxidation state acetate complex has also been prepared. The crystal structures of the two starting materials employed in this chapter, $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)$ and $(\text{Bu}^t\text{N})_2\text{ReCl}_3$, have been obtained in an effort to increase the extremely limited structural data currently available for rhenium imido species.

Results and Discussion

$[(\text{Bu}^t\text{N})_2\text{Re}(\mu\text{-NBu}^t)]_2$

The title compound is obtained in low yield from the reaction of $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)$ with an excess of sodium/mercury amalgam in hexane:

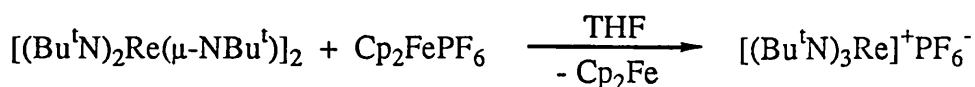


The product may be recrystallised from HMDS to yield yellow crystals which decompose slowly on exposure to air. The compound was identified initially from its ^1H NMR spectrum which shows two distinct resonances for the *t*-butyl protons in a 2:1 ratio. The terminal *t*-butylimido peak occurs at higher field (δ 1.27) than the bridging one (δ 1.82). The mass spectrum shows the parent ion (m/e 798) and accompanying peaks with the expected intensity pattern, based on isotope abundance calculations.

This represents the first full characterisation of a homoleptic transition metal imido complex. Whilst several main group elements do form homoleptic imides, *e.g.* $\text{P}_4(\text{NR})_6$, $\text{As}_4(\text{NR})_6$, $\text{S}(\text{NR})_2$ and $\text{S}(\text{NR})_3$ ⁸² all of which have oxo analogues, only one such transition metal compound, $\text{Os}(\text{NBu}^t)_3(\text{NSO}_2\text{Ar})$ where $\text{Ar}=\text{mes}$ or 2,4,6-triisopropylphenyl, has been reported⁸², but preparative details have not appeared in the open literature. This is somewhat surprising considering the ubiquity of homoleptic transition metal oxo compounds. The oxo analogue of our compound is the monomeric rhenium(VI) oxide, ReO_3 ⁸³. It is interesting that the imido compound exists as a dimer with bridging imido groups. No examples of imido bridging to rhenium were known before the present complex.

Complexes containing both bridging and terminal ligands are relatively scarce^{26,43}. The NMR spectrum of $\text{Cp}_2\text{Cr}(\text{NSiMe}_3)_4$ shows two trimethylsilyl resonances and the crystal structure reveals two bridging and two terminal imido groups⁸⁴ and Green *et al* have identified the related molybdenum complex, $[\text{Cp}(\text{NPh})\text{Mo}(\mu\text{-NPh})]_2$, from its NMR spectrum³⁶. The reaction of $(\text{Bu}^t\text{N})_2\text{W}(\text{OBu}^t)_2$ or $(\text{Bu}^t\text{N})_2\text{Mo}(\text{OSiMe}_3)_2$ with dimethyl zinc in hexane gives $[(\text{Bu}^t\text{N})_2\text{M}(\text{Me})_2]_2$. The crystal structure of the molybdenum complex reveals two terminal and two unsymmetrically bridging imido ligands⁵². Interestingly in this case the two types of imido ligands are reported to have identical shifts in the ^1H NMR spectrum at δ 1.4.

It appears that the dimeric rhenium(VI) compound may be oxidised using Cp_2FePF_6 according to the equation:



However the product has not been fully characterised, although the FAB mass spectrum of the product indicates that $[(\text{Bu}^t\text{N})_3\text{Re}]^+$ is indeed present.

Crystal Structure of $[(\text{Bu}^t\text{N})_2\text{Re}(\mu\text{-NBu}^t)]_2$

Unfortunately the crystal structure of the compound has proved difficult to solve. There are four independent molecules in the asymmetric unit. These have created a pseudo-symmetry within the unit cell, therefore the structure could not be satisfactorily refined. One of the molecules is depicted in Fig.1.1 with bond lengths and angles in Table 1.1.

The structure incorporates two tetrahedrally coordinated rhenium atoms sharing a common edge with a planar 4-membered $(\text{ReN})_2$ ring. The two terminal imido groups are symmetrically oriented above and below the $(\text{ReN})_2$ plane. The imido groups are bridging symmetrically with essentially equal Re-N distances (*ca.* 1.94Å). The terminal imido ligands are of course more tightly bound the Re-N distances being 0.3-0.4Å shorter, in accordance with the observed almost linear geometry ($\text{M-N-C}=166^\circ$ and 172°). The *t*-butylimido groups on the bridging imido functions are slightly removed from the $(\text{ReN})_2$ plane.

The $\text{Re}(1)\text{-N}(3)\text{-Re}(1')$ angle is 88° and $\text{N}(3)\text{-Re}(1)\text{-N}(3')$ is 92° . Generally M-N-M angles in the range $78^\circ\text{-}94^\circ$ occur when there is a metal-metal bond, and angles $>94^\circ$ indicate no metal-metal interaction. The $\text{Re}(1)\text{---Re}(1')$ distance in this compound is 2.7Å - this along with the intermediate M-N-M angle in the bridge suggests a weak

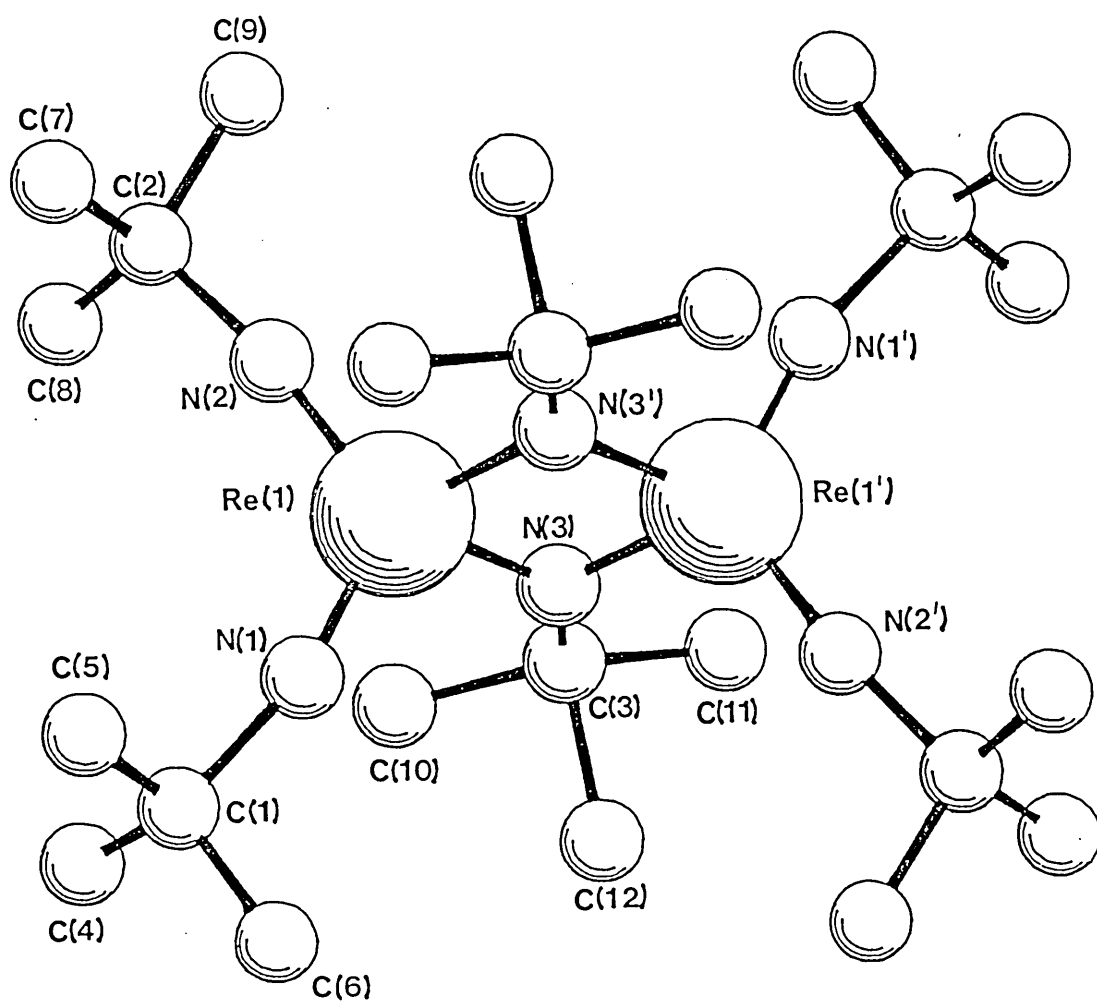


Fig.1.1 : The Molecular Structure of $[(\text{Bu}^t\text{N})_2\text{Re}(\mu\text{-NBu}^t)]_2$

Table 1.1 : Selected Bond Lengths and Angles for $[(\text{Bu}^t\text{N})_2\text{Re}(\mu\text{-NBu}^t)]_2$

Bond Lengths (Å)

Re(1)-Re(1')	2.707	Re(1)-N(1)	1.638
Re(1)-N(2)	1.726	Re(1)-N(3)	1.933
Re(1)-N(3')	1.948	N(1)-C(1)	1.596
N(2)-C(2)	1.469	N(3)-Re(1')	1.948
N(3)-C(3)	1.499	C(1)-C(4)	1.482
C(1)-C(5)	1.448	C(1)-C(6)	1.459
C(2)-C(7)	1.519	C(2)-C(8)	1.491
C(2)-C(9)	1.587		

Bond Angles (deg.)

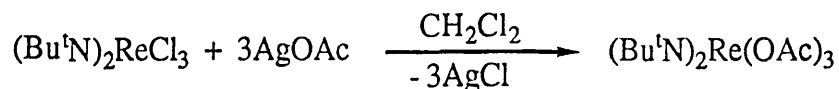
N(1)-Re-N(2)	118.54	N(1)-Re(1)-N(3)	107.84
N(2)-Re-N(3)	111.75	N(1)-Re(1)-N(3')	110.79
N(2)-Re(1)-N(3')	112.99	N(3)-Re(1)-N(3')	91.57
Re(1)-N(1)-C(1)	166.18	Re(1)-N(2)-C(2)	171.85
Re(1)-N(3)-Re(1')	88.43	Re(1)-N(3)-C(3)	136.78
Re(1')-N(3)-C(3)	134.66	N(1)-C(1)-C(4)	104.77
N(1)-C(1)-C(5)	110.00	C(4)-C(1)-C(5)	115.14
N(1)-C(1)-C(6)	106.22	C(4)-C(1)-C(6)	108.61
C(5)-C(1)-C(6)	111.54	N(2)-C(2)-C(7)	108.60
N(2)-C(2)-C(8)	107.13	C(7)-C(2)-C(8)	118.10
N(2)-C(2)-C(9)	109.00	C(7)-C(2)-C(9)	107.89
C(8)-C(2)-C(9)	105.84		

Re-Re interaction. The diamagnetism of the complex may be attributed to such interaction or to spin-pairing in the π -electron clouds of the bridging imido functions. High quality crystallographic data have been obtained for the binuclear d^1-d^1 oxo-bridged species, $[\text{Me}_2\text{ORE}(\mu\text{-O})]_2$ ⁸⁵ and $[\text{Np}_2\text{ORE}(\mu\text{-O})]_2$ ⁸⁶ - the observed Re-Re bond distances are 2.593(<1)Å and 2.606(1)Å respectively, indicating that a single metal-metal bond is present in both complexes⁸⁷.

It would be desirable to obtain better crystallographic data for a complex of type $[(\text{RN})_2\text{Re}(\mu\text{-NR})]_2$. To this end attempts have been made to prepare analogous dimers containing different alkyl groups. First of all it is necessary to make the new starting material, $(\text{RN})_3\text{Re}(\text{OSiMe}_3)$, from trimethylsilylperrhenate and the appropriate amine, RNHSiMe_3 . Several such amines were synthesised ($\text{R}=\text{Ad}, \text{Pr}^i, \text{Bu}^n, \text{Ph}$), however conversion to the tris(imido) rhenium species proved unsuccessful in all but one case. For the phenyl derivative the results look more promising - a product thought to be $(\text{PhN})_3\text{Re}(\text{OSiMe}_3)$ has been isolated. The mass spectrum shows the parent ion, m/e 549 and 547 with intensity pattern consistent with an isotope abundance calculation, and subsequent loss of two phenylimido ligands. However, the synthesis requires improvement to yield sufficient sample for reduction to the binuclear rhenium(VI) species.

$(\text{Bu}^t\text{N})_2\text{Re}(\text{OAc})_3$

The reaction of $(\text{Bu}^t\text{N})_2\text{ReCl}_3$ with silver acetate in methylene chloride gives pale orange microcrystals of the title compound according to the equation:



The product is very moisture sensitive. The mass spectrum indicates that the compound is monomeric, giving the parent ion with sequential loss of both acetate and *t*-butylimido ligands. The product also contained small amounts of both $(\text{Bu}^t\text{N})_2\text{Re}(\text{OAc})_2\text{Cl}$ and $(\text{Bu}^t\text{N})_2\text{Re}(\text{OAc})\text{Cl}_2$ impurities as evidenced by appropriate peaks in the mass spectrum. The tris(acetate) complex is thought to be trigonal bipyramidal with monodentate acetate groups. The IR spectrum shows a strong band at 1683cm^{-1} which may be assigned as $\nu_{\text{asm}}(\text{CO}_2^-)^{88}$, and the NMR spectrum shows two different methyl resonances in a 2:1 ratio ($\delta 2.02$ and $\delta 1.78$).

Substitution of halide in transition metal complexes using silver compounds is common and has recently been used to generate carbonate, sulphate and perrhenate complexes of osmium(VI)⁸⁹ and rhenium(V)⁹⁰. It appears that our starting material, $(\text{Bu}^t\text{N})_2\text{ReCl}_3$, also reacts with silver sulphate and silver carbonate, but the products have not yet been identified.

Since only one high oxidation state rhenium imido species had been structurally characterised prior to the present study, the crystal structures of the two starting materials employed in this chapter, $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)$ and $(\text{Bu}^t\text{N})_2\text{ReCl}_3$, have also been obtained.

Crystal Structure of $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)$

The molecule has a distorted tetrahedral geometry about the rhenium atom, as shown in Fig.1.2. Selected bond lengths and angles are given in Table 1.2. The angles at silicon are also approximately tetrahedral, with an average Si-C bond length of $1.8\text{\AA}$.

The Re-N-C bonds are slightly bent ($157\text{-}165^\circ$) and, as expected, the most bent imido group has the longest Re-N bond length. Taking the siloxy group as a 3-electron donor ligand², the molecule has a maximum electron count of 22 electrons, so one

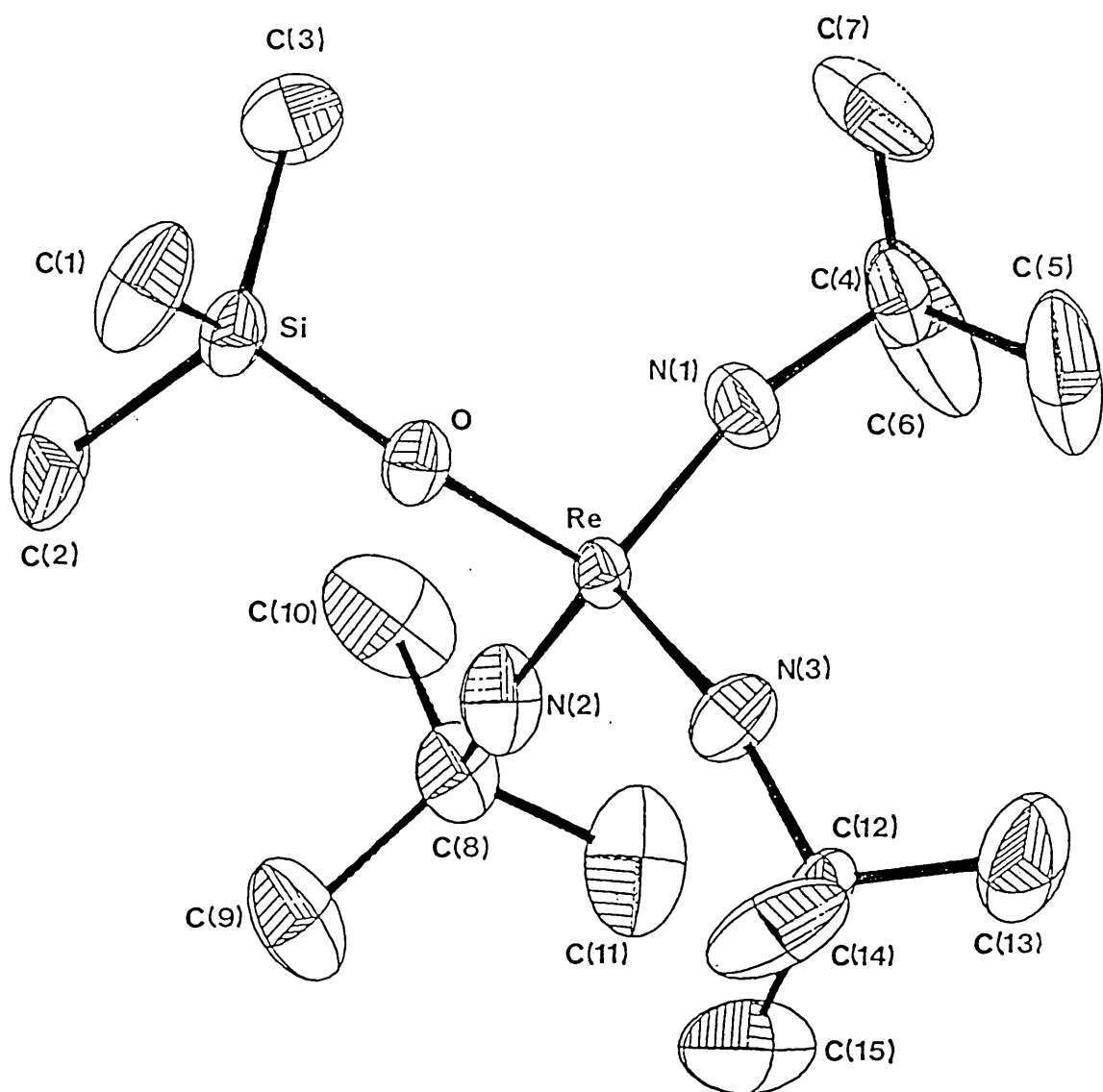


Fig.1.2 : The Molecular Structure of $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)$

Table 1.2 : Selected Bond Lengths and Angles for (Bu^tN)₃Re(OSiMe₃)

Bond Lengths (Å)

O-Re	1.899(7)	N(1)-Re	1.706(9)
N(2)-Re	1.704(11)	N(3)-Re	1.740(10)
O-Si	1.624(8)	C(1)-Si	1.852(16)
C(2)-Si	1.898(17)	C(3)-Si	1.787(16)
C(4)-N(1)	1.437(12)	C(8)-N(2)	1.469(13)
C(12)-N(3)	1.430(12)	C(5)-C(4)	1.448(22)
C(6)-C(4)	1.475(21)	C(7)-C(4)	1.414(20)
C(9)-C(8)	1.552(19)	C(10)-C(8)	1.531(24)
C(11)-C(8)	1.550(22)	C(13)-C(12)	1.465(21)
C(14)-C(12)	1.469(20)	C(15)-C(12)	1.536(20)

Bond Angles (deg.)

N(1)-Re-O	109.7(4)	N(2)-Re-O	110.4(5)
N(2)-Re-N(1)	111.1(6)	N(3)-Re-O	108.0(4)
N(3)-Re-N(1)	109.0(6)	N(3)-Re-N(2)	108.7(6)
C(1)-Si-O	105.7(6)	C(2)-Si-O	109.4(6)
C(2)-Si-C(1)	111.0(10)	C(3)-Si-O	111.2(7)
C(3)-Si-C(1)	110.7(10)	C(3)-Si-C(2)	108.8(11)
Si-O-Re	138.2(4)	C(4)-N(1)-Re	164.8(8)
C(8)-N(2)-Re	160.6(9)	C(12)-N(3)-Re	157.7(8)
C(5)-C(4)-N(1)	107.1(12)	C(6)-C(4)-N(1)	108.1(11)
C(6)-C(4)-C(5)	106.8(18)	C(7)-C(4)-N(1)	109.0(11)
C(7)-C(4)-C(5)	111.8(20)	C(7)-C(4)-C(6)	113.8(18)
C(9)-C(8)-N(2)	106.6(10)	C(10)-C(8)-N(2)	110.4(12)
C(10)-C(8)-C(9)	110.2(13)	C(11)-C(8)-N(2)	107.2(11)
C(11)-C(8)-C(9)	110.8(13)	C(11)-C(8)-C(10)	111.5(15)
C(13)-C(12)-N(3)	105.8(11)	C(14)-C(12)-N(3)	110.9(9)
C(14)-C(12)-C(13)	115.1(16)	C(15)-C(12)-N(3)	110.4(10)
C(15)-C(12)-C(13)	108.8(18)	C(15)-C(12)-C(14)	106.0(15)

would expect to observe some bending of the imido groups. The Re-O-Si bond angle is fairly acute (138°) and the Re-O bond length is $1.89\text{\AA}$, indicating that π -donation from oxygen is reduced by the presence of the imido functions. The stronger π -donating capability of imido *versus* oxo ligand is illustrated by comparison with the structure of $\text{O}_3\text{Re}(\text{OSiMe}_3)^{91}$ where the Re-O-Si angle is 164° and the Re-O bond length is $1.67\text{\AA}$. It has been suggested that silicon $3d$ orbitals may participate in the bonding in this instance. The steric effect of replacing oxo groups by *t*-butylimido ligands may also influence the Re-O-Si angle.

Crystal Structure of $(\text{Bu}^t\text{N})_2\text{ReCl}_3$

A diagram of the molecule is given in Fig.1.3, with selected bond lengths and angles in Table 1.3. The structure of the complex is a slightly distorted trigonal bipyramid with equatorial imido groups. The two axial chloride ligands are bent towards the equatorial plane, $[\text{Cl}(3)\text{-Re-Cl}(2)=165^\circ]$, in the direction of the equatorial chloride ligand. A view of the molecule looking down the $\text{Cl}(3)\text{-Re-Cl}(2)$ axis is shown in Fig.1.4.

The distribution of the angles in the equatorial plane is interesting. The N-M-N angle is smaller than both N-M-Cl angles (111° vs. 128° and 121°). This contrasts with most structures containing two neighbouring multiply-bonded functions where repulsion between the π -electron clouds in the two bonds causes an increase in the interbond angle from idealised values⁹². In this case the small N-M-N angle may perhaps be attributed to the steric demand of both the equatorial chlorine ligand and the axial chlorines which are inclined towards the equatorial plane.

The imido ligands both contain 'linear' M-N-R linkages (163° and 170°); the Re-N bond distances are in accord with these angles (1.71 and $1.68\text{\AA}$ respectively). As such the imido ligands are behaving as 4-electron donors, thus the formal electron count about rhenium is eighteen.

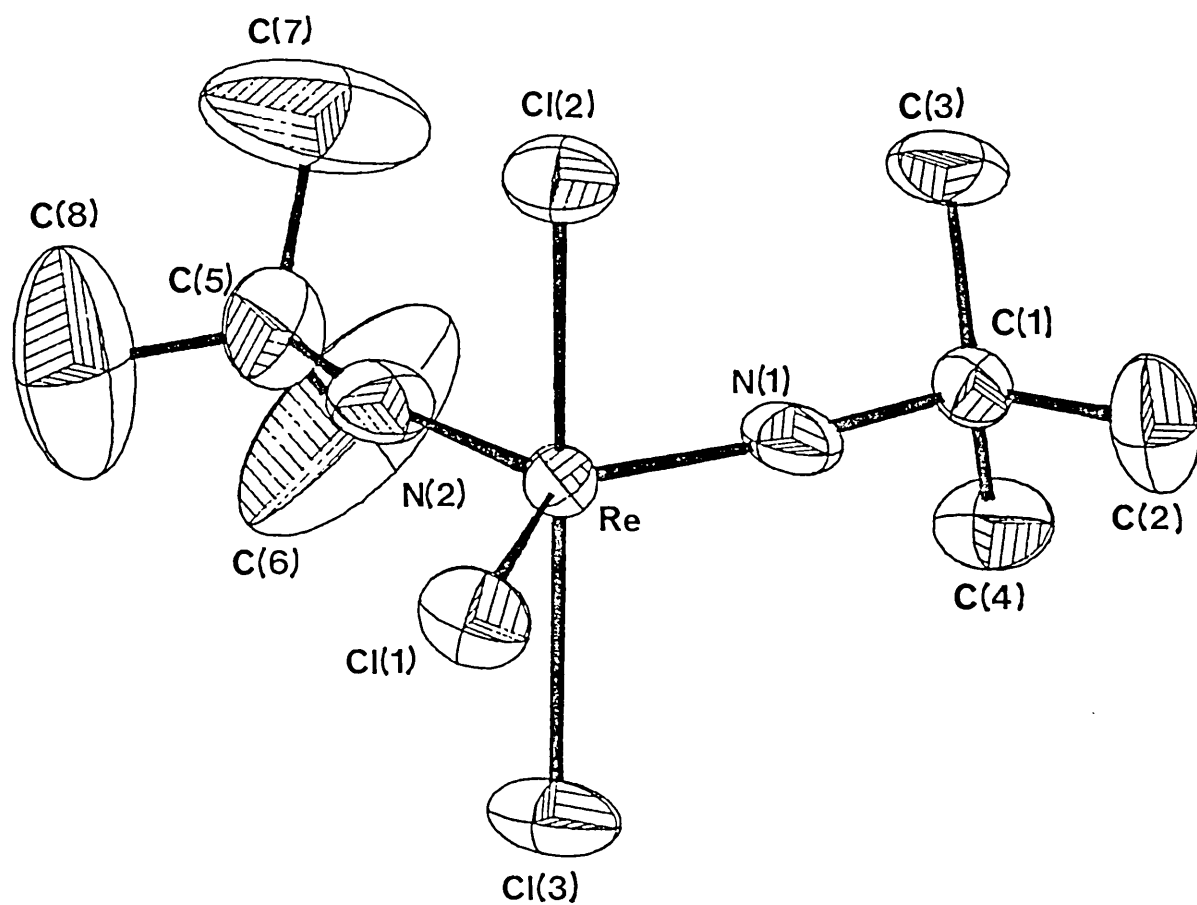


Fig.1.3 : The Molecular Structure of $(\text{Bu}^t\text{N})_2\text{ReCl}_3$

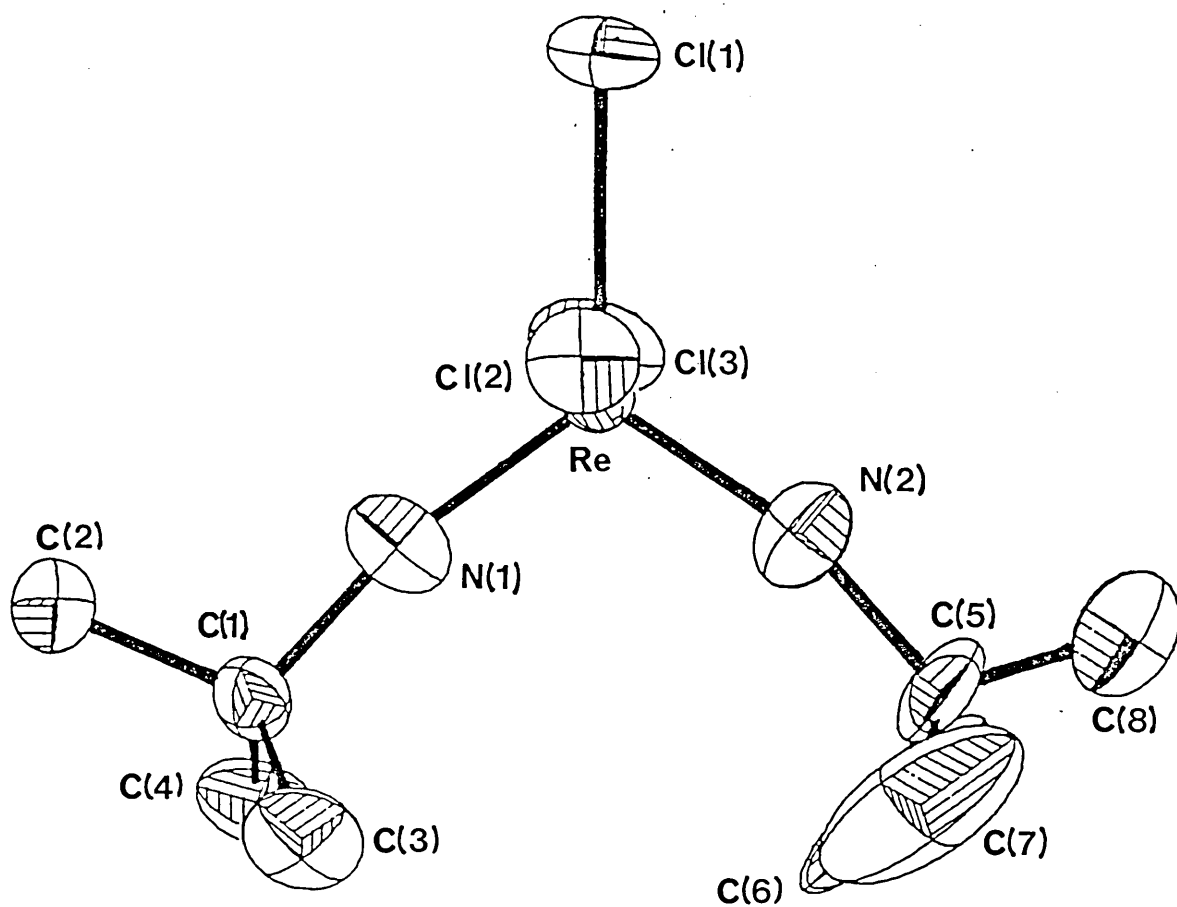


Fig.1.4 : The Molecular Structure of $(\text{Bu}^t\text{N})_2\text{ReCl}_3$

Table 1.3 : Selected Bond Lengths and Angles for (Bu^tN)₂ReCl₃

Bond Lengths (Å)

Cl(1)-Re	2.346(5)	Cl(2)-Re	2.348(5)
Cl(3)-Re	2.347(5)	N(1)-Re	1.680(12)
N(2)-Re	1.706(13)	C(1)-N(1)	1.455(15)
C(5)-N(2)	1.449(17)	C(2)-C(1)	1.537(19)
C(3)-C(1)	1.526(19)	C(4)-C(1)	1.550(18)
C(6)-C(5)	1.387(35)	C(7)-C(5)	1.432(29)
C(8)-C(5)	1.374(29)		

Bond Angles (deg.)

Cl(2)-Re-Cl(1)	82.7(2)	Cl(3)-Re-Cl(1)	83.0(2)
Cl(3)-Re-Cl(2)	165.4(1)	N(1)-Re-Cl(1)	127.8(5)
N(1)-Re-Cl(2)	91.9(4)	N(1)-Re-Cl(3)	94.4(4)
N(2)-Re-Cl(1)	121.4(5)	N(2)-Re-Cl(2)	94.5(4)
N(2)-Re-Cl(3)	95.5(4)	N(2)-Re-N(1)	110.7(7)
C(1)-N(1)-Re	169.5(9)	C(5)-N(2)-Re	163.4(12)
C(2)-C(1)-N(1)	107.5(11)	C(3)-C(1)-N(1)	107.4(11)
C(3)-C(1)-C(2)	113.0(13)	C(4)-C(1)-N(1)	109.1(11)
C(4)-C(1)-C(2)	109.6(13)	C(4)-C(1)-C(3)	110.0(11)
C(6)-C(5)-N(2)	108.3(16)	C(7)-C(5)-N(2)	107.8(17)
C(7)-C(5)-C(6)	112.8(31)	C(8)-C(5)-N(2)	111.6(18)
C(8)-C(5)-C(6)	107.7(26)	C(8)-C(5)-C(7)	108.7(27)

Experimental

Microanalyses were by Pascher, Remagen and Imperial College Microanalytical Laboratories. Melting points were determined in sealed tubes and are uncorrected.

Spectrometers: IR, Perkin Elmer 683 and 1720 (in nujol mulls, values in cm^{-1} between KBr or CsI plates); NMR, Bruker WM-250, Jeol FX 90Q, Jeol GSX 270 (data in p.p.m. relative to SiMe_4); mass spectrometers, VG Micromass 7070 and MS-9, Kratos MS902.

X-ray crystallography: crystals were sealed under argon in thin-walled glass capillaries. All crystallographic measurements were made at 293K using a CAD4 diffractometer and graphite-monochromated Mo-K_α radiation ($\lambda = 0.71069 \text{ \AA}$).

All manipulations were carried out under purified argon, dinitrogen or under vacuum. Solvents were distilled under argon from sodium-benzophenone (hexane, ether, THF), sodium (toluene), calcium hydride (dichloromethane) or phosphorus pentoxide (acetonitrile).

Both $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)^{24}$ and $(\text{Bu}^t\text{N})_2\text{ReCl}_3^{67}$ were prepared according to the literature. These were recrystallised from HMDS and ether respectively to give crystals suitable for X-ray diffraction study.

$[(\text{Bu}^t\text{N})_2\text{Re}(\mu\text{-NBu}^t)]_2$

A solution of $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)$ (0.5g, 1.0mmol) in hexane (25ml) was stirred with sodium/mercury amalgam (0.5g Na in 3cm^3 Hg) for 12h at room temperature. The resulting red-yellow solution was filtered, reduced to dryness and extracted with HMDS (10cm^3). After repeated filtration and cooling to -20°C for several days yellow crystals were obtained. Yield <20%, Mpt. sublimates at 212°C *in vacuo*

Mass spectrum: m/e 800 (87%), 798 (100%), $\text{Re}_2(\text{NBu}^t)_6^+$ (intensity pattern in agreement with isotope abundance calculations).

IR: 1455m, 1355s, 1281m, 1243s, 1214s, 1198m, 1155w, 1069(br), 1049m, 1024m, 914m, 845s, 806m, 756w, 681w, 597w, 559w, 507w, 462w.

^1H NMR: (d₈-toluene) δ 1.82 (18H, s, μ -NBu^t), 1.27 (36H, s, NBu^t)

Anal. Calcd. for $\text{Re}_2\text{C}_{24}\text{H}_{54}\text{N}_6$: C36.1, H6.8, N10.5, Found: C36.2, H6.7, N10.3.

(PhN)₃Re(OSiMe₃)

To a solution of $\text{O}_3\text{Re(OSiMe}_3)$ (0.2g, 0.62mmol) in HMDS (20cm³) was added PhNHSiMe₃ (1.5g, 8.3mmol). The solution, which became instantly red-orange then very dark, was stirred for 12h then filtered. Large dark red crystals precipitated from the filtrate. Yield *ca* 30%, Mpt. 98°C

Mass spectrum: *m/e* 549 (100%), $^{187}\text{Re(NPh)}_3(\text{OSiMe}_3)^+$; 547 (57%),

$^{185}\text{Re(NPh)}_3(\text{OSiMe}_3)^+$; 458 (26%), $^{187}\text{Re(NPh)}_2(\text{OSiMe}_3)^+$; 456 (17%),

$^{185}\text{Re(NPh)}_2(\text{OSiMe}_3)^+$; 369 (21%), $^{187}\text{Re(NPh)}(\text{OSiMe}_3)^+$; 367 (10%),

$^{185}\text{Re(PhN)}(\text{OSiMe}_3)^+$.

IR: 1619m, 1603w, 1500m, 1488w, 1349m, 1327w, 1275w, 1260w, 1243w, 1173w, 1067w, 1023w, 980w, 911m, 873w, 856w, 839w, 750m, 722m, 689m.

Anal.: Calcd. for $\text{C}_{21}\text{H}_{24}\text{N}_3\text{OSiRe}$: C46.0, H4.4, N7.7, Found: C45.6, H4.9, N7.1.

(Bu^tN)₂Re(OAc)₃

To a stirred solution of (Bu^tN)₂ReCl₃ (0.1g, 0.23mmol) in CH₂Cl₂ was added silver acetate (0.12g, 0.72mmol). The mixture was stirred for 12h, filtered and hexane added to induce precipitation of the product. Yield 0.08g, 70%, Mpt. 138°C

Mass spectrum: 506 (1%), 504 (0.5%), $\text{Re(NBu}^t)_2(\text{O}_2\text{C}_2\text{H}_3)_3^+$; 447 (76%), 445

(46%), $\text{Re}(\text{NBu}^t)_2(\text{O}_2\text{C}_2\text{H}_3)_2^+$; 375 (16%), 373 (9%), $\text{Re}(\text{NBu}^t)(\text{O}_2\text{C}_2\text{H}_3)_2^+$; 43 (100%), $(\text{OC}_2\text{H}_3)^+$.

IR: 1683s, 1652m, 1525m, 1399w, 1275m, 1249s, 1091w, 1047w, 1016m, 975w, 958w, 909s, 800m, 707m, 676m, 622m, 606m, 543w, 451m.

^1H NMR: (d_6 -benzene) δ 2.02 [6H, s, $(\text{OAc})_{\text{ax}}$], 1.78 [3H, s, $(\text{OAc})_{\text{eq}}$], 1.46 [18H, s, Bu^t]

Anal. Calcd. for $\text{ReC}_{14}\text{H}_{27}\text{N}_2\text{O}_6$: C33.3, H5.4, N5.5. Found: C32.8, H5.8, N5.5.

CHAPTER 2

HIGH OXIDATION STATE *TERTIARY*-BUTYLIMIDO

RHENIUM ARYL COMPLEXES

CHAPTER 2

Introduction

Imido aryl complexes of the transition metals are very rare. The Group VI d^0 imido aryl compounds, $(\text{Bu}^t\text{N})_2\text{M}(\text{aryl})_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$ aryl = mes, xylyl; $\text{M} = \text{Mo}$ aryl = *o*-tol) have recently been isolated by Wilkinson *et al* ^{93,94}.

Imido alkyls and other organometallic derivatives have received considerably more attention. For rhenium(V) a series of methyl derivatives has been prepared from $\text{Re}(\text{NPh})\text{Cl}_3(\text{PMe}_3)_2$ and dimethylmagnesium⁹⁵ and a novel cyclopentadienyl compound, $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Re}(\text{NBu}^t)]$ has been recently reported⁹⁶.

Schrock has generated some rhenium(VII) bisimido alkyl, alkylidene and alkylidyne complexes with a view to finding an olefin metathesis catalyst^{11,12,67,97}. The tris(alkyl) complexes, $(\text{Bu}^t\text{N})_2\text{ReR}_3$ ($\text{R} = \text{Me}, \text{CH}_2\text{Ph}, \text{CH}_2\text{SiMe}_3$) are obtained from $(\text{Bu}^t\text{N})_2\text{ReCl}_3$ ^{67,97}, and the mixed alkyl/halide species $(\text{Bu}^t\text{N})_2\text{ReClR}_2$ are also reported⁶⁷; $(\text{ArN})_2\text{ReCl}_2(\text{CH}_2\text{Bu}^t)$ ($\text{Ar} = 2,6\text{-diisopropylphenyl}$) is formed when $(\text{ArN})_2\text{ReCl}_3(\text{py})$ is treated with 0.65 equiv. of $\text{Zn}(\text{CH}_2\text{Bu}^t)_2$ ¹¹. This complex has been used in the synthesis of several four-coordinate monoimido bisalkoxide neopentylidene complexes, one of which is shown to metathesise internal acetylenes¹² - electron withdrawing groups on the alkoxide are used to render the metal sufficiently electrophilic.

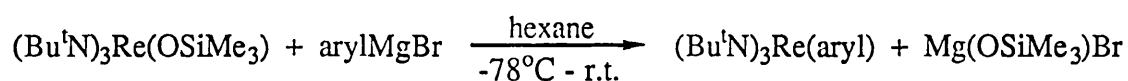
In this chapter a range of novel rhenium(VII) imido monoaryl compounds are introduced⁹⁸. The structural data obtained for one of the complexes is particularly interesting. A rhenium(VII) tris(aryl) imido complex has been prepared. We have also generated the first organometallic rhenium(VI) imido compound, $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$, investigated the redox behaviour of this species, both by cyclic voltammetry and

chemically, and conducted preliminary studies into the insertion chemistry of rhenium(VI) and rhenium(VII) bis(aryl) imido compounds.

Results and Discussion

Imido mono(aryl) complexes of rhenium

The imido aryl complexes, $(\text{Bu}^t\text{N})_3\text{Re}(\text{aryl})$ (aryl = *o*-tolyl, xylyl, mes), were prepared from $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)^{24}$ and the appropriate Grignard reagent by the reaction:



The physical and analytical data are reported in Table 2.3. The products are bright yellow, low-melting solids that are air-stable, although on prolonged exposure to the air they appear to be hygroscopic. $(\text{Bu}^t\text{N})_3\text{Re}(\textit{o}\text{-tol})$, which decomposes in halogenated solvents, may be recrystallised from ether or hexamethyldisiloxane. Crystals of $(\text{Bu}^t\text{N})_3\text{Re}(\text{xylyl})$ and $(\text{Bu}^t\text{N})_3\text{Re}(\text{mes})$ are obtained from concentrated acetonitrile solutions on cooling. The compounds are stable in hydrocarbon solutions. In contrast to the behaviour of $(\text{Bu}^t\text{N})_2\text{Cr}(\text{mes})_2^{93,94}$, they are all unreactive towards carbon monoxide even at 50 bar. This stability is presumably due to the steric protection afforded by the *ortho*-methyl groups of the arene ring and the bulky *t*-butyl groups inhibiting insertion reactions.

The room temperature ^1H NMR spectra of the compounds are reported in Table 2.5 - they show only singlets for the *t*-butylimido functions and the spectra remain unchanged on cooling to -50°C . The *ortho*-hydrogen in $(\text{Bu}^t\text{N})_3\text{Re}(\textit{o}\text{-tol})$ is shifted to low field as expected. The room temperature ^{13}C NMR spectrum for $(\text{Bu}^t\text{N})_3\text{Re}(\text{xylyl})$

also shows that the three *t*-butylimido groups are equivalent in solution, with peaks at $\delta 32.5$ (CH_3) and $\delta 69.2$ (Me_3C). It is interesting to compare the Δ -value⁴ for this complex ($\Delta = 37\text{p.p.m}$) with that for $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)$ ($\Delta = 35\text{p.p.m}$) where the siloxy group is competing for π -orbital overlap. This results in a slight decrease in M-N π -bonding, and hence the slightly lower Δ -value. The solid state structure of these compounds is thought to be similar to that of the starting material, $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)$, which has been discussed in Chapter 1, *i.e.* a distorted tetrahedral geometry about Re, with slightly bent imido ligands.

The mass spectra all show parent ions with the characteristic rhenium isotope pattern and the subsequent loss of imido and alkyl groups. The IR spectra show weak aromatic stretches at $1550\text{-}1600\text{cm}^{-1}$.

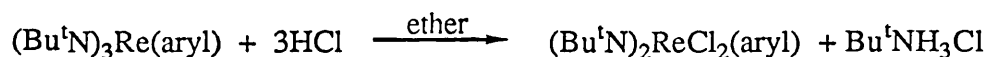
Attempts to prepare the analogous phenyl and *p*-(*t*-butyl)phenyl derivatives by the same route gave oils which could not be crystallised. It seems likely that the melting points of these complexes may be fairly close to room temperature. The NMR data for these complexes are included in Table 2.5.

One oxo analogue of these compounds has been reported⁹⁹ - $\text{O}_3\text{Re}(\text{mes})$ is obtained from the interaction of $\text{O}_3\text{Re}(\text{OSiMe}_3)$ with three equivalents of $\text{Al}(\text{mes})_3\cdot\text{THF}$.

Reaction of $\text{O}_3\text{Re}(\text{OSiMe}_3)$ with aryl Grignard reagents yields $\text{O}_2\text{Re}(\text{aryl})_2$ (aryl = *xylyl*, *mes*), although a small amount of the corresponding tris(oxo)aryl compound is observed in the mass spectrum of the product⁹⁸. The only other previously reported organometallic tris(oxo)rhenium complex is O_3ReMe , prepared by air oxidation of either OReMe_4 or *cis*- O_2ReMe_3 ¹⁰⁰.

Treatment of the tris(imido)aryl compounds with excess HCl in ether produces one equivalent of $\text{Bu}^t\text{NH}_3\text{Cl}$ and the corresponding dichloro-complexes,

$(\text{Bu}^t\text{N})_2\text{ReCl}_2(\text{aryl})$, (aryl=Ph,*o*-tolyl,xylyl,mes,):



It seems that the remaining imido functions are not susceptible to further attack by H^+ . Golden crystals are obtained on concentrating ether solutions of $(\text{Bu}^t\text{N})_2\text{ReCl}_2\text{Ph}$, $(\text{Bu}^t\text{N})_2\text{ReCl}_2(o\text{-tol})$ and $(\text{Bu}^t\text{N})_2\text{ReCl}_2(\text{mes})$; the xylyl complex was isolated as a yellow-green powder from ether.

The compounds are higher melting than their precursors (Table 2.3), and decompose slowly on exposure to air, both in the solid state and in solution. They are sparingly soluble in hexane but fairly soluble in benzene and ether, and very soluble in dichloromethane.

Again all four compounds show a parent ion in the mass spectrum, the peaks being complicated by the presence of both rhenium and chlorine isotopes. The ^1H NMR data are listed in Table 2.6.

It is interesting to note that attempts to prepare these complexes from $(\text{Bu}^t\text{N})_2\text{ReCl}_3$ ⁶⁷ and one equivalent of arylmagnesium bromide yielded a mixture of the desired product, $(\text{Bu}^t\text{N})_2\text{ReClBr}(\text{aryl})$ and $(\text{Bu}^t\text{N})_2\text{ReBr}_2(\text{aryl})$, obviously arising from halide exchange with the Grignard reagent.

Crystal Structure of $(\text{Bu}^t\text{N})_2\text{ReCl}_2(o\text{-tol})$

The crystal structure of the *o*-tolyl derivative has been determined by X-ray crystallography. A diagram of the molecule is given in Fig.2.1 and selected bond lengths and angles are listed in Table 2.1.

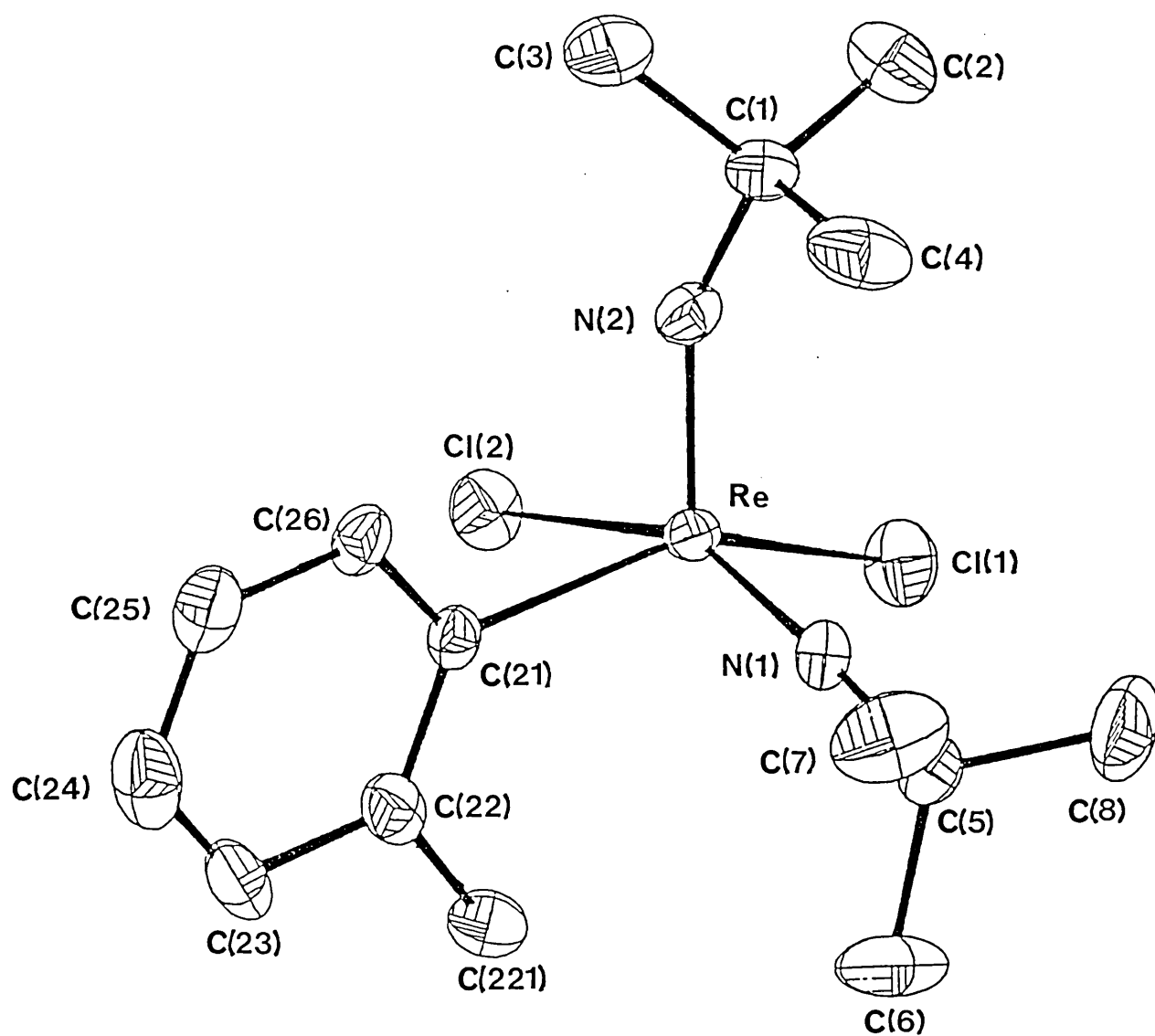


Fig.2.1 : The Molecular Structure of $(\text{Bu}^t\text{N})_2\text{ReCl}_2(o\text{-tol})$

Table 2.1 : Selected Bond Lengths and Angles for $\text{ReCl}_2(\text{NBu}^t)_2(o\text{-tolyl})$

Bond Lengths (Å)

Cl(1)-Re	2.372(5)	Cl(2)-Re	2.410(4)
N(1)-Re	1.715(9)	N(2)-Re	1.708(10)
C(21)-Re	2.148(5)	C(5)-N(1)	1.445(12)
C(2)-C(1)	1.552(18)	C(3)-C(1)	1.508(18)
C(4)-C(1)	1.536(18)	N(2)-C(1)	1.470(13)
C(6)-C(5)	1.538(18)	C(7)-C(5)	1.503(20)
C(8)-C(5)	1.521(20)	C(23)-C(22)	1.395
C(21)-C(22)	1.395	C(221)-C(22)	1.536(17)
C(24)-C(23)	1.395	C(25)-C(24)	1.395
C(26)-C(25)	1.395	C(21)-C(26)	1.395

Bond Angles (deg.)

Cl(2)-Re-Cl(1)	81.3(2)	N(1)-Re-Cl(1)	92.1(3)
N(1)-Re-Cl(2)	151.4(3)	N(2)-Re-Cl(1)	109.4(4)
N(2)-Re-Cl(2)	100.3(4)	N(2)-Re-N(1)	108.1(5)
C(21)-Re-Cl(1)	146.4(2)	C(21)-Re-Cl(2)	81.0(3)
C(21)-Re-N(1)	89.9(4)	C(21)-Re-N(2)	101.8(4)
C(5)-N(1)-Re	176.4(7)	C(3)-C(1)-C(2)	110.8(11)
C(4)-C(1)-C(2)	109.6(12)	C(4)-C(1)-C(3)	110.0(13)
N(2)-C(1)-C(2)	107.6(9)	N(2)-C(1)-C(3)	108.5(11)
N(2)-C(1)-C(4)	110.3(9)	C(1)-N(2)-Re	150.5(7)
C(6)-C(5)-N(1)	109.1(10)	C(7)-C(5)-N(1)	110.0(11)
C(7)-C(5)-C(6)	109.7(15)	C(8)-C(5)-N(1)	106.1(10)
C(8)-C(5)-C(6)	108.9(15)	C(8)-C(5)-C(7)	112.8(16)
C(21)-C(22)-C(23)	120.0	C(221)-C(22)-C(23)	117.3(7)
C(221)-C(22)-C(21)	122.7(7)	C(24)-C(23)-C(22)	120.0
C(25)-C(24)-C(23)	120.0	C(26)-C(25)-C(25)	120.0
C(21)-C(26)-C(25)	120.0	C(22)-C(21)-Re	119.2(2)
C(26)-C(21)-Re	120.8(2)	C(26)-C(21)-C(22)	120.0

The molecular geometry may be described as square-pyramidal with the *t*-butylimido group containing N(2) occupying the axial site. The *trans* angles in the basal plane are then 146.4(2)° [C(21)-Re-Cl(1)] and 151.4(3)° [N(1)-Re-Cl(2)], and the axial/equatorial angles are 100-110°.

The geometries of the imido groups, and the resulting implications for the electronic configuration of the metal are interesting. Were both imido groups to act as normal 4-electron donors with a linear M-N-R unit, the metal atom would have a formal 18-electron configuration. The imido group in the basal site containing N(1) is linear (176.4°), and typical of a 4-electron interaction, but the imido group occupying the axial site is bent (150.5°), suggesting that this group is tending to act as a 2-electron donor. If this is a true picture of the bonding, then, in the absence of any other interactions, the metal would seem to be adopting a 16-electron configuration.

Several compounds containing both linear and bent imido groups exist, but in all but two cases the complexes would have a maximum electron count of 20 or more if both NR groups behaved as 4-electron donors². Examples are Os(NBu^t)₂O₂¹⁰¹, Mo(NPh)₂(S₂CNEt₂)₂³⁰ and Re₃(NBu^t)₄O₅(OSiMe₃)₃⁶⁶. In the latter, one of the bent (154.9°) imido groups has a Re-N bond distance 0.01 Å shorter than that of the linear (167.8°) group. For this complex and for Os(NBu^t)₂O₂ the bent and linear *t*-butylimido groups are reported to be indistinguishable by NMR. Similarly, the ¹H NMR spectra for (Bu^tN)₂ReCl₂(aryl) show only a singlet for the *t*-butyl groups, even on cooling to -50°C. One example in which a bent imido ligand is bound to a metal with a formal electron count less than 18 is the complex Mo₄S₄(S₂CNBuⁱ)₂(N-*p*-tol)₄¹⁰² in which one of the four terminal imido ligands is bent to an angle of 157° (the others are 164, 170 and 173°). This geometry is explained in terms of a steric interaction involving a neighbouring molecule. The other example is the 2-(aryloxy)pyridine complex, Re(PhNNC₅H₄N)(PhN)Cl₃¹⁰³ which contains only the second discovered

bent imido ligand in Re(V) chemistry^{74,75,78,79}. For the phenylimido ligand the Re-N bond length is 1.724 Å and the angle is 159.9°. Based on idealised single- double- and triple-bonded Re^V-NR bond distances and angles⁷⁹, the bond order is estimated to be 2.7±0.1, and the hybridisation of the nitrogen $sp^{1.2}$ - the small contribution from the remaining two p -orbitals on N resulting in the observed slightly bent geometry. A brief qualitative discussion of the overall bonding concludes by saying that "the bending probably arises from optimisation of the bonding processes in the entire molecule"¹⁰³.

In our structure there are no short contacts either intra- or intermolecular involving atoms of the bent *t*-butylimido ligand. Other geometrical features of the molecule have been examined in detail, especially at the methyl group C(221) on the *o*-tolyl ligand, which is positioned below the basal plane of the square pyramid, and *trans* to the axial imido group. Although one of the methyl hydrogens is close to the metal [H(223)-Re = 2.82 Å], there does not seem to be any deformation of the CH₃ group and the *o*-tolyl ligand is bonding symmetrically (*i.e.* with approximately equal Re-C-C angles); no indication of any C-H---Re interaction was detected in the IR spectrum of the complex.

We thought it desirable to obtain the crystal structure of the analogous phenyl derivative in order to compare the two structures:

Crystal Structure of (Bu^tN)₂ReCl₂Ph

The molecule is displayed in Fig.2.2 and selected bond lengths and angles are listed in Table 2.2. In this case the molecular geometry may be described as a distorted trigonal bipyramid with the imido groups occupying equatorial positions and the phenyl ring in an axial position. In fact the structure is very similar to that of (Bu^tN)₂ReCl₃ described in Chapter 1. Again the axial chloride ligand is slightly tilted towards the equatorial plane. The phenyl ligand is also bent towards the equatorial plane, [Cl(1)-Re-C(1)=158°]; this has resulted in a widening of the N(2)-Re-Cl(2) angle (134°) in order to accommodate the phenyl ring.

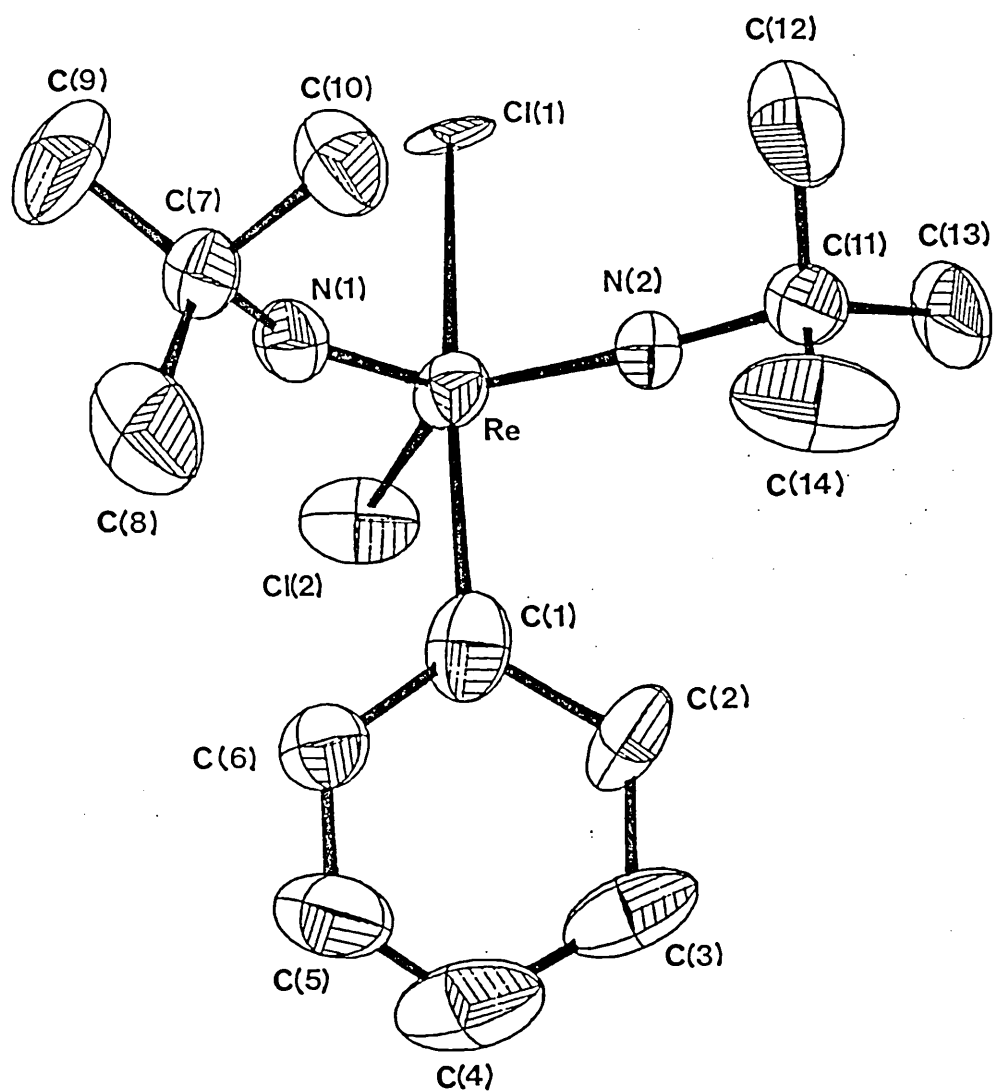


Fig.2.2 : The Molecular Structure of $(\text{Bu}^t\text{N})_2\text{ReCl}_2\text{Ph}$

Table 2.2 : Selected Bond Lengths and Angles for (Bu^tN)₂ReCl₂Ph

Bond Lengths (Å)

Cl(1)-Re	2.487(5)	Cl(2)-Re	2.417(6)
N(1)-Re	1.692(17)	N(2)-Re	1.712(15)
C(1)-Re	2.099(26)	C(7)-N(1)	1.478(23)
C(11)-N(2)	1.471(23)	C(2)-C(1)	1.438(28)
C(6)-C(1)	1.433(28)	C(3)-C(2)	1.368(31)
C(4)-C(3)	1.558(40)	C(5)-C(4)	1.219(35)
C(6)-C(5)	1.350(29)	C(8)-C(7)	1.563(32)
C(9)-C(7)	1.508(29)	C(10)-C(7)	1.646(26)
C(12)-C(11)	1.486(32)	C(13)-C(11)	1.535(30)
C(14)-C(11)	1.368(31)		

Bond Angles (deg.)

Cl(2)-Re-Cl(1)	81.1(2)	N(1)-Re-Cl(1)	100.5(6)
N(1)-Re-Cl(2)	115.5(6)	N(2)-Re-Cl(1)	95.2(6)
N(2)-Re-Cl(2)	134.1(5)	N(2)-Re-N(1)	110.2(8)
C(1)-Re-Cl(1)	158.1(5)	C(1)-Re-Cl(2)	79.1(6)
C(1)-Re-N(1)	96.5(8)	C(1)-Re-N(2)	91.8(8)
C(7)-Re-N(1)	161.1(12)	C(11)-N(2)-Re	173.1(13)
C(2)-C(1)-Re	121.5(16)	C(6)-C(1)-Re	124.2(16)
C(6)-C(1)-C(2)	114.0(21)	C(3)-C(2)-C(1)	121.1(24)
C(4)-C(3)-C(2)	119.0(23)	C(5)-C(4)-C(3)	115.5(23)
C(6)-C(5)-C(4)	127.2(28)	C(5)-C(6)-C(1)	122.6(23)
C(8)-C(7)-N(1)	107.2(17)	C(9)-C(7)-N(1)	105.8(16)
C(9)-C(7)-C(8)	118.2(19)	C(10)-C(7)-N(1)	106.5(15)
C(10)-C(7)-C(8)	107.1(17)	C(10)-C(7)-C(9)	111.4(17)
C(12)-C(11)-N(2)	114.4(19)	C(13)-C(11)-N(2)	106.3(18)
C(13)-C(11)-C(12)	112.3(21)	C(14)-C(11)-N(2)	105.5(19)
C(14)-C(11)-C(12)	99.8(25)	C(14)-C(11)-C(13)	118.7(25)

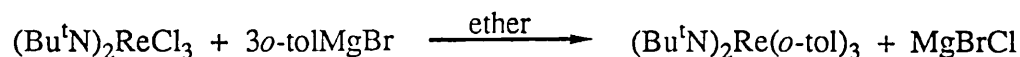
The N-M-N angle is about the same as in $(\text{Bu}^t\text{N})_2\text{ReCl}_3$ at 110° . In this case no significant bending of the imido group is observed ($161^\circ, 173^\circ$), the average M-N-R angle being approximately the same as in $(\text{Bu}^t\text{N})\text{ReCl}_3$.

It is interesting that the presence of an *ortho*-methyl group on the phenyl ring in $(\text{Bu}^t\text{N})_2\text{ReCl}_2(o\text{-tol})$ causes the molecule to adopt a different geometry with concurrent bending of an imido ligand. It seems the *o*-tolyl ligand cannot easily be accommodated in an axial site in the trigonal bipyramid. It is easy to envisage that in order to relieve such steric repulsions the axial Cl(1)-Re-C(aryl) angle would decrease, the aryl ligand moving up between N(2) and Cl(2) (in Fig.2.2) so that N(1) in Fig.2.2 would then occupy the axial site in the resultant square based pyramid. The energy difference between trigonal bipyramidal and square-based pyramidal geometries is generally quite small¹⁰⁴.

It is more difficult to account for the bending of the axial imido group in $(\text{Bu}^t\text{N})_2\text{ReCl}_2(o\text{-tol})$. If steric effects can be discounted, it may be that in this configuration appropriate orbitals for full π -bonding of both imido ligands are not available. A detailed molecular orbital analysis may reveal whether or not this is the case.

$(\text{Bu}^t\text{N})_2\text{Re}(o\text{-tol})_3$

The reaction of $(\text{Bu}^t\text{N})_2\text{ReCl}_3$ with *o*-tolyl Grignard in ether gives the expected rhenium(VII) compound:



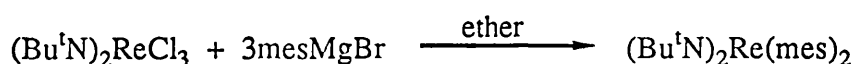
The product is soluble in hexane and may be recrystallised from this to give orange air-sensitive crystals. In the ^1H NMR spectrum there are two distinct *o*-tolyl signals in a 2:1 ratio, suggesting a trigonal bipyramidal structure, probably with equatorial imido

ligands. In this instance the axial *ortho*-methyl resonances occur at lower field (δ2.59) than the corresponding equatorial resonance (δ2.10). The mass spectrum shows only a very weak peak for the parent ion with the subsequent loss of all three *o*-tolyl ligands. Weak aromatic stretches are visible in the IR spectrum (1595-1550cm⁻¹).

Alkyl complexes of the same formulation have been prepared by Schrock - (Bu^tN)₂ReR₃ (R=Me, CH₂Ph, CH₂SiMe₃)^{67,97}. Analogous oxoaryl derivatives are also known: ReO₂R₃ (R=Me¹⁰⁵, CH₂SiMe₃¹⁰⁶) have been isolated as oils, and ReO₂(CH₂Bu^t)₃ has been prepared from O₃Re(OSiMe₃) and Al(CH₂Bu^t)₃.THF¹⁰⁷. The crystal structure of this compound reveals a trigonal bipyramidal structure with equatorial oxo groups. In both the neopentyl and trimethylsilylmethyl complex unusual α-C-H---O=Re interactions are shown to occur¹⁰⁷.

(Bu^tN)₂Re(mes)₂

The reaction of (Bu^tN)₂ReCl₃ with mesityl Grignard in ether does not give the expected rhenium(VII) tris(aryl) compound, instead a reduction occurs to give a paramagnetic rhenium(VI) species:



The product is formed in high yield (approx. 70%) and may be recrystallised from hexane to give deep red crystals.

The formulation (R^tN)₂ReR₂ is unique among known organo-rhenium imido species, and is one of the few examples of tetrahedral coordination around a rhenium(VI) centre [cf. (ReO₄²⁻)¹⁰⁸, ReO₂Cl₂¹⁰⁹ and rhenium oxoaryls -see below]. The complex is the first organometallic rhenium(VI) imido species to be discovered.

The Group VI compounds, $(\text{Bu}^t\text{N})_2\text{M}(\text{aryl})_2$ ($\text{M}=\text{Cr}, \text{Mo}, \text{W}$ aryl=mes, xylyl; $\text{M}=\text{Mo}$ aryl=*o*-tol)^{93,94} are d^0 derivatives - it will be interesting to compare both the structure and reactivity of these complexes with the neighbouring d^1 species, $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$.

Rhenium(VI) oxoaryls have been prepared in these laboratories^{92,98}. Both $\text{O}_2\text{Re}(\text{mes})_2$ and $\text{O}_2\text{Re}(\text{xylyl})_2$ have been structurally characterised. They may be prepared either *via* oxidation of the rhenium(V) magnesium solvated complexes, $(\text{aryl}_2\text{ReO}_2)_2\text{Mg}(\text{THF})_2$ ⁹² or from $\text{O}_3\text{Re}(\text{OSiMe}_3)$ and the appropriate Grignard reagent⁹⁸. Attempts to generate the bis(imido) derivatives from these by condensation of the $\text{Re}=\text{O}$ bonds with isocyanates or phosphinimines were unsuccessful¹¹⁰.

The formation of $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$, as opposed to $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_3$, may be a result of the steric demand of the mesityl group. The formation of $\text{O}_2\text{Re}(\text{aryl})_2$, as opposed to $\text{ORe}(\text{aryl})_4$ (for xylyl and mes, but not *o*-tol), has also been attributed to steric factors⁹². However the possibility of generating the rhenium(VII) trisaryl complex by appropriate selection of starting materials cannot be excluded.

Surprisingly, $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$ decomposes on prolonged exposure to air, both in the solid state and in solution. The IR spectrum shows a fairly strong aromatic stretch at 1591cm^{-1} . The mass spectrum shows both parent ions, m/e 567 and 565, and the subsequent loss of one mesityl group.

The electron spin resonance spectrum gave a simple spectrum with a six-line hyperfine structure at 295K at X-band in toluene ($g_{\text{iso}}=1.966$, $A_{\text{iso}}=0.0133\text{cm}^{-1}$) - see Fig.2.3. When the temperature of the the solution was lowered, the spectrum resolved into a complicated pattern (see Fig.2.3) showing, at 78K, more than two sets of six rhenium hyperfine lines with uneven spacing (*cf.* e.s.r. spectra of $\text{O}_2\text{Re}(\text{aryl})_2$ ^{92,98}).

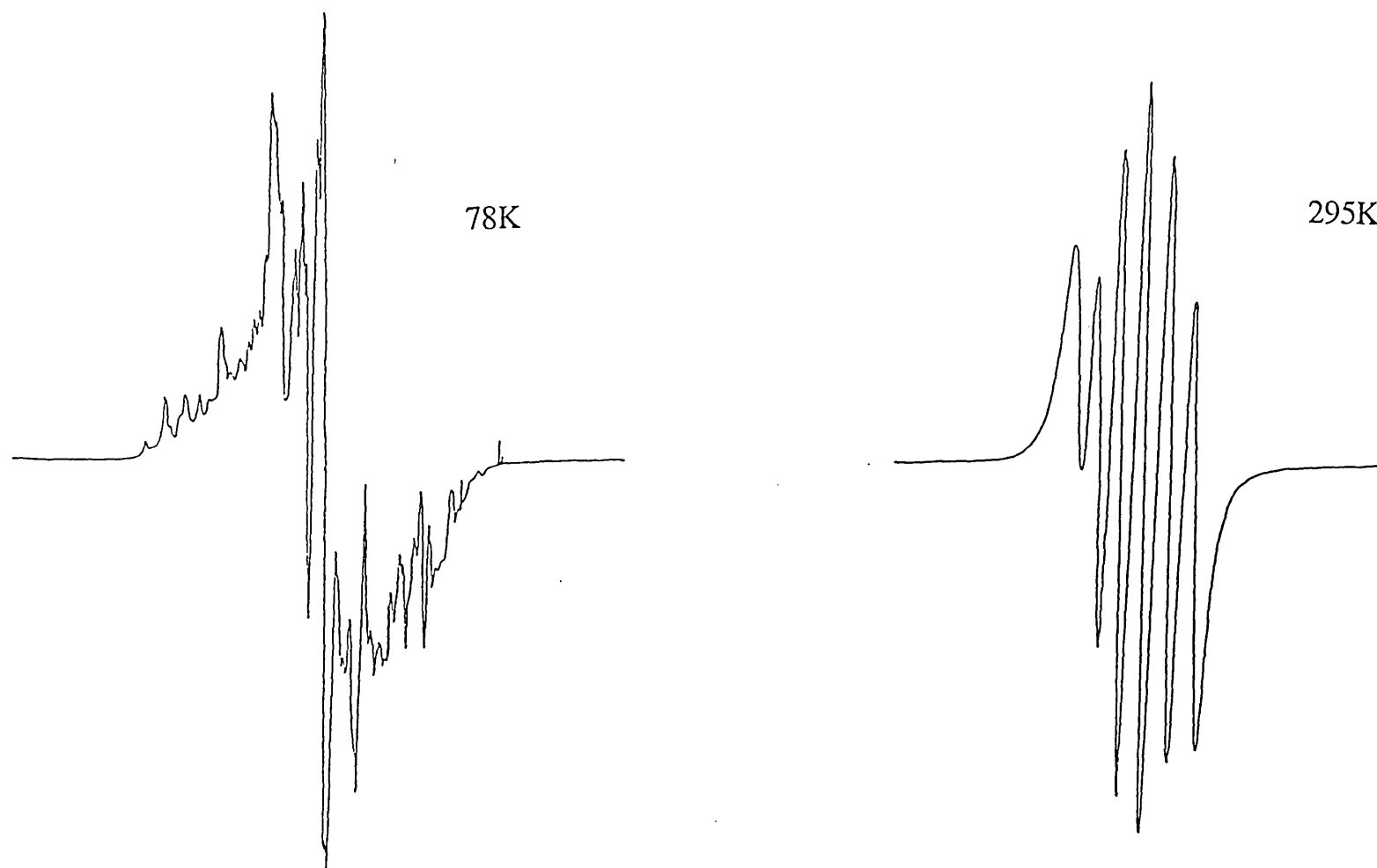
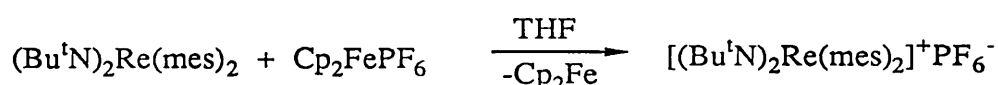


Fig.2.3 : The E.s.r. Spectrum (X-band) of $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$ in Toluene at 295K and 78K

Redox Chemistry of (Bu^tN)₂Re(mes)₂

The results of cyclic voltammetry studies on (Bu^tN)₂Re(mes)₂ are shown in Fig.2.4. Two main features were observed in THF 0.2M ⁿBu₄NPF₆ at 22°C: a reversible one-electron oxidation wave at -0.51V and a reversible one-electron reduction wave at -1.80V (relative to Cp₂Fe at 0.00V).

The complex may be readily oxidised chemically, *e.g.*



The analogous oxidation may be performed using AgOTf, AgPF₆ and AgBF₄. The oxidised species are bright red-orange crystalline materials which are air stable in the solid state, but decompose slowly in solution. They are soluble in THF, acetone, CH₂Cl₂ and acetonitrile, and are insoluble in hexane, ether and toluene.

The compounds are diamagnetic (*d*⁰). The NMR spectra are simple (see Table 2.7), and show that there is free rotation about the metal-carbon bond at room temperature. The IR spectrum exhibits a very strong aromatic stretch at 1591cm⁻¹ (for the PF₆⁻ salt).

The crystal structure determination of [(Bu^tN)₂Re(mes)₂]PF₆ is underway - it will be interesting to compare the structure of this complex with isoelectronic Group VI imido aryls prepared in these laboratories^{93,94}. It is anticipated that the positive charge on the metal will be stabilised by increased π-donation from the imido ligands, resulting in more nearly linear M-N-C angles in the cationic complex. Such π-donation may increase the electrophilicity of the coordinated imido ligands. Reactions of these cationic species with unsaturated hydrocarbons are currently under investigation.

Attempts to reduce (Bu^tN)₂Re(mes)₂ to give [(Bu^tN)₂Re(mes)₂]⁻ have not been so successful. The compound is not reduced by cobaltocene, a moderately potent reducing

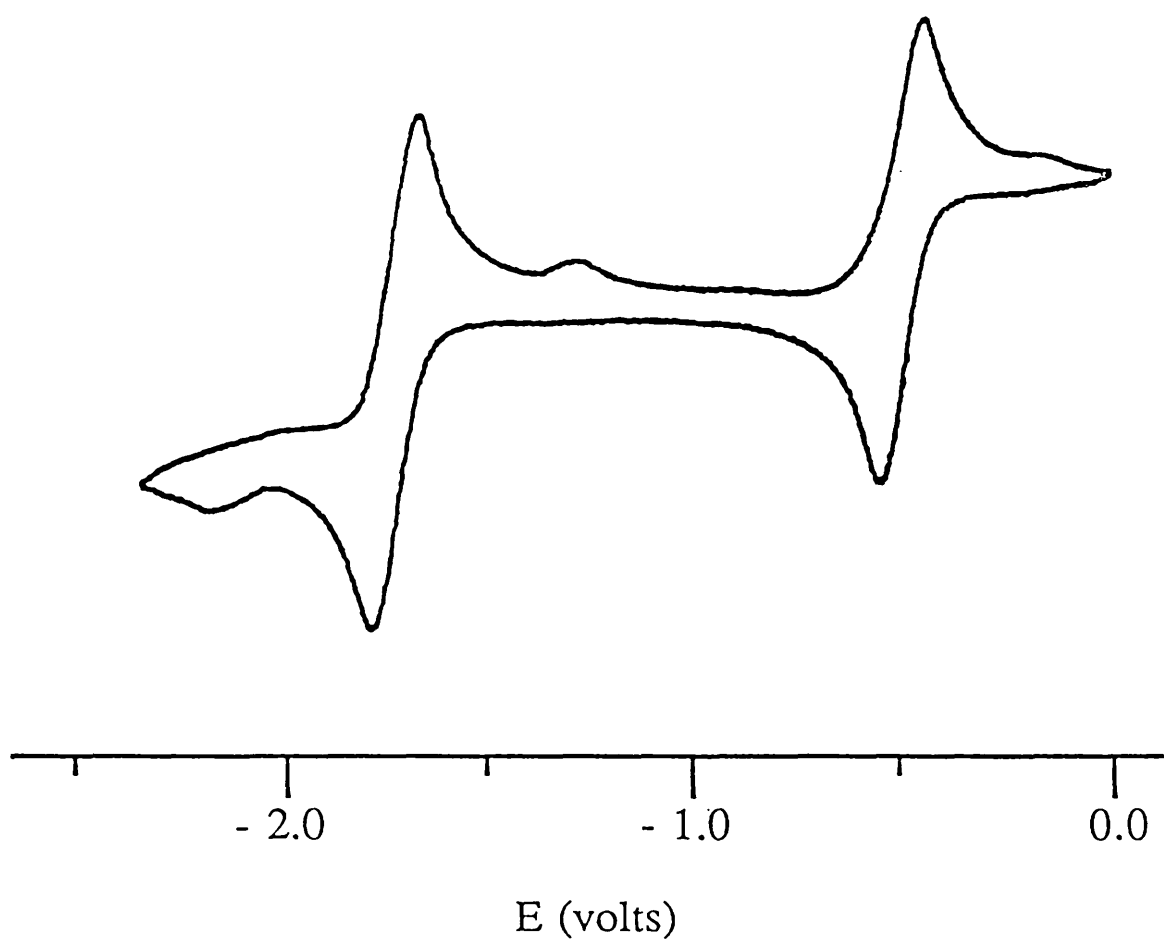


Fig.2.4 : Cyclic Voltammogram of $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$ in THF 0.2M $[\text{nBu}_4\text{N}][\text{PF}_6]$ at 50 mVs^{-1} , referenced to Cp_2Fe at 0.00V.

agent, in THF. A purple, very air-sensitive solution is produced on stirring the complex with sodium/mercury amalgam in THF, but no solid material has been isolated so far. The corresponding rhenium(V) oxo-aryl species $[\text{ReO}_2(\text{aryl})_2]^-$ (aryl=xylyl,mes) have been prepared by Wilkinson *et al*^{92,98}. Analogous oxo-alkyl anions are known⁸⁶; $[\text{ReO}_2\text{Np}_2]^-$ is formed from the sodium or lithium amalgam reduction of the binuclear complex $[\text{Np}_2\text{ORe}(\mu\text{-O})]_2$. Cyclic voltammetry on these complexes reveals an "ill-defined" oxidation wave for oxidation to rhenium(VII), indicating that chemical oxidation to $[\text{ReO}_2\text{Np}_2]^+$ is probably not feasible, (*cf.* for our complex generation of $[(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2]^+$ is straightforward). These slight differences in redox behaviour may be attributed to the difference in electronegativity, and hence π -donating capability, of the oxo *versus* imido ligand.

Attempted Insertion Reactions of $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$

The paramagnetic rhenium(VI) complex reacts with nitric oxide (3-4 equivalents) at room temperature in hexane to give a pale orange solution from which small pale yellow crystals may be isolated. These were found to be diamagnetic. We had anticipated a monoinsertion reaction to give a η^2 -nitrosoaryl group^{111,112} - a peak at 998cm^{-1} in the IR spectrum supported this suggestion. However, the NMR spectrum (see Table 2.8) shows the two mesityl groups in the product to be equivalent, with the *ortho*-methyl hydrogens shifted to low field. The IR spectrum is considerably different from that of the starting material. A peak at 1597cm^{-1} is presumably due to the aromatic stretch [*cf.* 1591cm^{-1} in $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$], however three new peaks have appeared in this region: one at 1532cm^{-1} with two weak absorptions at 1564cm^{-1} and 1511cm^{-1} . The stretching frequencies for terminal nitrosyls, $\nu(\text{NO}^+)$, generally fall in the range $1950\text{-}1600\text{cm}^{-1}$, whereas for terminal bent nitrosyls $\nu(\text{NO}^-)$ occurs between 1721 and 1520cm^{-1} ¹¹¹.

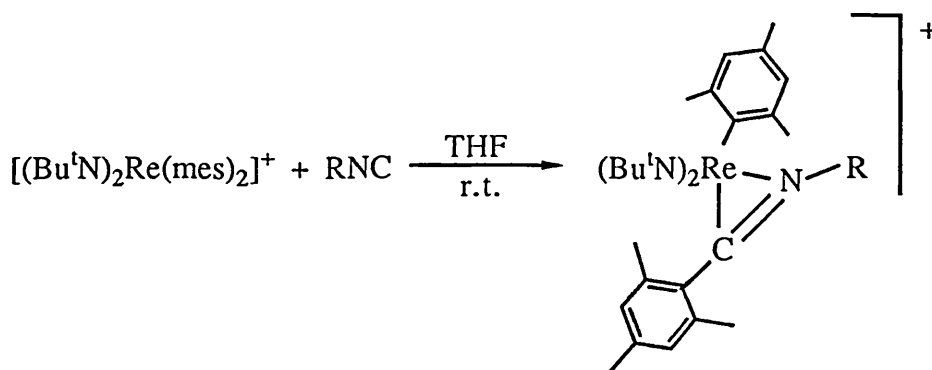
The interaction of nitric oxide with transition metal organometallic compounds has not received much attention - for diamagnetic d^0 alkyls the product is generally a chelate complex containing the $[-ONN(R)O]$ ligand^{113,114}, whereas paramagnetic alkyls give nitrosoalkane complexes which may decompose to give metal-oxo species^{115,112}. Metal-carbon bond cleavage does not always occur; $ReMe_6$ forms an adduct with nitric oxide at low temperature¹¹⁵ and $Cp_2TiClMe$ is unreactive towards nitric oxide, even at elevated temperatures¹¹³.

It is not all together clear what is happening in the case of $(Bu^tN)_2Re(mes)_2$. From the data collected so far it seems the product may contain one terminal bent nitrosyl group - this would be in accord with the IR and NMR spectra for the product. Also, in the mass spectrum the highest mass peak observed corresponds to $(Bu^tN)_2Re(mes)_2^+$ indicating that insertion into a metal-carbon is unlikely to have occurred. Such a complex would have a MEC of 20 electrons, it would not therefore be surprising if the NO ligand were to adopt a bent configuration. Work is in progress to identify the product with more certainty.

No reaction is observed between $(Bu^tN)_2Re(mes)_2$ and ethylene (80psi) at room temperature nor does the complex react with xylyl isocyanide. Other insertion reactions with this complex are under investigation. Some preliminary results on the insertion chemistry of the oxidised species have also been obtained:

Insertion Reactions of $[(Bu^tN)_2Re(mes)_2]^+$

The d^0 rhenium species, $[(Bu^tN)_2Re(mes)_2]^+X^-$ ($X = OTf^-$, PF_6^-), react rapidly with both *t*-butyl isocyanide and xylyl isocyanide at room temperature to give the monoinsertion product, even in the presence of excess isocyanide:



R = *t*-butyl, xylyl

The products are pale yellow crystalline materials which are air stable in the solid state. The IR spectra show bands in the range 1705-1595cm⁻¹ suggesting η^2 -coordination of the iminoacyl group. The aromatic stretches occur at lower frequency and are visible in the range 1610-1595cm⁻¹. The FAB mass spectra all show a parent ion with subsequent loss of the iminoacyl function and mesityl group.

The ¹H NMR spectra (see Table 2.8) all show two sets of resonances for the mesityl groups, but again there is free rotation about the Re-C bond at room temperature. For the xylyl isocyanide products the *ortho*-methyl resonances on the xylyl ring attached to nitrogen occur at the highest field (δ 1.82). The resonances for the mesityl group which remains attached to rhenium have changed relative to the starting complex, such that the *ortho*-methyl resonances fall at higher field than the *para*-methyl resonance.

This reactivity is mirrored by the isoelectronic Group VI imidoaryls, (Bu^tN)₂M(aryl)₂^{93,94}, which also undergo monoinsertion reactions with isocyanide⁹⁴. High oxidation state iminoacyl derivatives are also known for titanium¹¹⁶, zirconium¹¹⁷, uranium¹¹⁸ and tantalum¹¹⁹, but there are no *d*⁰ iminoacyls previously known for any Group VII metals.

No reaction was observed between [(Bu^tN)₂Re(mes)₂]PF₆ and an excess of carbon disulphide at room temperature. Neither did the complex react with ethylene (80psi) at room temperature. It was also unreactive towards CO (80psi) at room temperature, but on heating, the red-orange solution became pale orange - characterisation of the product

is underway.

Whilst the insertion reactions discussed above are well-known for other elements, these represent the first insertions into high oxidation state rhenium-carbon bonds. The reaction chemistry of all the imido aryl complexes presented in this chapter must be further investigated. It would also be interesting to study the comparative redox behaviour and insertion chemistry of the corresponding oxo aryl species. Clearly there is still a considerable amount of research to be done in this area.

Table 2.3 : Physical Properties and Analytical Data for (Bu^tN)₃Re(aryl)
and (Bu^tN)₂ReCl₂(aryl)

<u>Compound</u>	<u>Mpt</u> (°C)	C	Analysis (%) ^a		Cl
			H	N	
(Bu ^t N) ₃ Re(<i>o</i> -tol)	47-8	46.3 (46.7)	6.3 (6.6)	8.4 (8.6)	
(Bu ^t N) ₃ Re(xylyl)	65	47.5 (47.6)	7.3 (7.1)	8.2 (8.3)	
(Bu ^t N) ₃ Re(mes)	69	48.8 (48.6)	7.3 (7.3)	7.9 (8.1)	
(Bu ^t N) ₂ ReCl ₂ (<i>o</i> -tol)	135	36.9 (36.7)	5.2 (5.1)	5.8 (5.7)	14.5 (14.5)
(Bu ^t N) ₂ ReCl ₂ (xylyl)	122	37.2 (38.1)	5.7 (5.4)	5.4 (5.6)	
(Bu ^t N) ₂ ReCl ₂ (mes)	125-7	39.3 (39.4)	5.7 (5.6)	5.4 (5.4)	
(Bu ^t N) ₂ ReCl ₂ Ph	163	34.9 (35.3)	4.8 (4.8)	5.6 (5.9)	

^a Found (required)

Table 2.4 : Physical Properties and Analytical Data for (Bu^tN)₂Re(mes)₂ and Oxidation and Insertion products

<u>Compound</u>	<u>Mpt(°C)</u>	Analysis (%) ^a		
		C	H	N
(Bu ^t N) ₂ Re(<i>o</i> -tol) ₃	103	(57.9)	(6.5)	(4.7)
(Bu ^t N) ₂ Re(mes) ₂	128	55.0 (55.1)	7.1 (7.1)	5.0 (4.9)
(Bu ^t N) ₂ Re(mes) ₂ PF ₆	158(dec)	43.6 (43.9)	5.7 (5.6)	3.9 (3.9)
(Bu ^t N) ₂ ReR(CR=NR')PF ₆ R=mes, R'=xylyl	208	50.7 (49.9)	5.9 (5.8)	5.0 (5.0)
(Bu ^t N) ₂ ReR(CR=NR')PF ₆ R=mes, R'=Bu ^t	190	46.3 (46.9)	6.1 (6.2)	5.0 (5.3)
(Bu ^t N) ₂ ReR(CR=NR')OTf R=mes, R'=xylyl	184	51.6 (51.1)	6.1 (5.8)	4.7 (5.0)

^a Found (required)

Table 2.5 : ^1H Nuclear Magnetic Resonance Data for $(\text{Bu}^t\text{N})_3\text{Re}(\text{aryl})$

<u>Compound</u>	<u>δ/ppm</u>	<u>Assignment</u>
$(\text{Bu}^t\text{N})_3\text{Re}(o\text{-tol})^a$	8.05(dd)	1H $o\text{-H-C}_6\text{H}_3$
	7.10(m)	3H $m,p\text{-H}_3\text{C}_6\text{H}_2$
	2.44(s)	3H $o\text{-CH}_3$
	1.41(s)	27H CCH_3
$(\text{Bu}^t\text{N})_3\text{Re}(\text{xylyl})^b$	7.25(d)	2H $m\text{-H}_2\text{-C}_6\text{H}_1$
	7.07(t)	1H $p\text{-H-C}_6\text{H}_2$
	2.68(s)	6H $o\text{-CH}_3$
	1.36(s)	27H CCH_3
$(\text{Bu}^t\text{N})_3\text{Re}(\text{mes})^a$	7.06(br. s)	2H $m\text{-H}_2\text{-C}_6$
	2.65(s)	6H $o\text{-CH}_3$
	2.21(s)	3H $p\text{-CH}_3$
	1.41(s)	27H CCH_3
$(\text{Bu}^t\text{N})_3\text{Re}(p\text{-Bu}^t\text{Ph})^a$	7.45(dd)	4H $\text{C}_6\text{H}_4\text{ Bu}^t$
	$J_{\text{ortho}} = 112.7\text{Hz}$	
	$J_{\text{para}} = 8.4\text{Hz}$	
	1.42(s)	27H NCCH_3
$(\text{Bu}^t\text{N})_3\text{Re}(\text{Ph})^a$	1.31(s)	9H $\text{C}_6\text{H}_4\text{CCH}_3$
	7.74(m)	2H $o\text{-H}_2\text{ C}_6\text{H}_3$
	7.25(m)	3H $m,p\text{-H}_3\text{ C}_6\text{H}_2$
	1.41(s)	27H CCH_3

^a in CDCl_3

^b in C_6D_6

Table 2.6 : ^1H Nuclear Magnetic Resonance Data for $(\text{Bu}^t\text{N})_2\text{ReCl}_2(\text{aryl})^{\text{a}}$

<u>Compound</u>	<u>δ/ppm</u>	<u>Assignment</u>
$(\text{Bu}^t\text{N})_2\text{ReCl}_2(o\text{-tol})$	7.92(m)	1H $o\text{-HC}_6\text{H}_3$
	7.07(m)	3H $m,p\text{-H}_3 \text{C}_6\text{H}_2$
	2.47(s)	3H $o\text{-CH}_3$
	1.10(s)	18H CCH_3
$(\text{Bu}^t\text{N})_2\text{ReCl}_2(\text{xylyl})$	7.10(m)	3H $m,p\text{-H}_3 \text{C}_6$
	2.37(s)	6H $o\text{-CH}_3$
	1.10(s)	18H CCH_3
$(\text{Bu}^t\text{N})_2\text{ReCl}_2(\text{mes})$	6.94(m)	2H $m\text{-H}_2 \text{C}_6$
	2.38(s)	6H $o\text{-CH}_3$
	2.10(s)	3H $p\text{-CH}_3$
	1.12(s)	18H CCH_3
$(\text{Bu}^t\text{N})_2\text{ReCl}_2\text{Ph}$	7.90(d)	2H $o\text{-H}_2\text{C}_6\text{H}_3$
	7.3-7.1(m)	3H $m,p\text{-H}_3\text{C}_6\text{H}_2$
	1.15(s)	18H CCH_3

^a in C_6D_6

Table 2.7 : ^1H Nuclear Magnetic Resonance Data for $(\text{Bu}^t\text{N})_2\text{Re}(o\text{-tol})_3$ and Oxidation Products from $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$

<u>Compound</u>	<u>δ/ppm</u>	<u>Assignment</u>
$(\text{Bu}^t\text{N})_2\text{Re}(o\text{-tol})_3^{\text{a}}$	8.07(dd)	2H $(o\text{-H})_{\text{ax}}$
	7.23(d)	1H $(o\text{-H})_{\text{eq}}$
	7.15-6.62(m)	9H $m,p\text{-H}$
	2.59(s)	6H $(o\text{-CH}_3)_{\text{ax}}$
	2.10(s)	3H $(o\text{-CH}_3)_{\text{eq}}$
	1.21(s)	18H CCH_3
$\{(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2\}\text{PF}_6^{\text{b}}$	7.32(s)	4H $m\text{-H}_2\text{-C}_6$
	2.54(s)	12H $o\text{-CH}_3$
	2.38(s)	6H $p\text{-CH}_3$
	1.86(s)	18H CCH_3
$\{(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2\}\text{OTf}^{\text{b}}$	7.34(s)	4H $m\text{-H}_2\text{-C}_6$
	2.53(s)	12H $o\text{-CH}_3$
	2.38(s)	6H $p\text{-CH}_3$
	1.84(s)	18H CCH_3

^a in C_6D_6

^b in $\text{d}_6\text{-acetone}$

Table 2.8 : ^1H Nuclear Magnetic Resonance Data for Insertion Products
from $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$ and $[(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2]^+$

<u>Compound</u>	<u>δ/ppm</u>	<u>Assignment</u>
$\{(\text{Bu}^t\text{N})_2\text{ReR}(\text{CR}=\text{NR}')\}\text{PF}_6^{\text{a}}$ R=mes, R'=Bu ^t	7.19(s)	2H NCC ₆ H ₂
	7.12(s)	2H C ₆ H ₂
	2.45(s)	3H <i>p</i> -Me (mes)
	2.39(s)	6H <i>o</i> -Me (mes)
	2.35(s)	3H <i>p</i> -Me (N=Cmes)
	3.26(s)	6H <i>o</i> -Me (N=Cmes)
	1.59(s)	18H NCCCH ₃
	1.14(s)	9H C=NCCH ₃
$\{(\text{Bu}^t\text{N})_2\text{ReR}(\text{CR}=\text{NR}')\}\text{OTf}^{\text{a}}$ R=mes, R'=xylyl	7.23(t)	1H <i>p</i> -H (xylyl)
	7.14(s)	2H <i>m</i> -H (N=mes)
	7.07(d)	2H <i>m</i> -H (xylyl)
	6.98(s)	2H <i>m</i> -H (mes)
	2.44(s)	3H <i>p</i> -Me (mes)
	2.26(s)	3H <i>p</i> -Me (N=Cmes)
	2.23(s)	6H <i>o</i> -Me (mes)
	2.15(s)	6H <i>o</i> -Me (N=Cmes)
	1.82(s)	6H <i>o</i> -Me (xylyl)
	1.54(s)	18H NBu ^t
$\{(\text{Bu}^t\text{N})_2\text{ReR}(\text{CR}=\text{NR}')\}\text{PF}_6^{\text{a}}$ R=mes, R'=xylyl	7.32(t)	1H <i>p</i> -H (xylyl)
	7.18(s)	2H <i>m</i> -H (N=Cmes)
	7.04(s)	2H <i>m</i> -H (xylyl)
	6.96(s)	2H <i>m</i> -H (mes)
	2.44(s)	3H <i>p</i> -Me (mes)
	2.25(s)	3H <i>p</i> -Me (N=Cmes)
	2.23(s)	6H <i>o</i> -Me (mes)
	2.15(s)	6H <i>o</i> -Me (N=Cmes)
	1.81(s)	6H <i>o</i> -Me (xylyl)
	1.54(s)	18H NBu ^t
$(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2 + \text{NO}^{\text{b}}$	6.95(s)	4H <i>m</i> -C ₆ H ₂
	2.89(s)	12H <i>o</i> -CH ₃
	2.04(s)	6H <i>p</i> -CH ₃
	1.14(s)	18H CCH ₃

^a in CDCl₃

^b in C₆D₆

Experimental

E.s.r.: Varian E-12 (X-band in toluene at 22°C). Cyclic voltammetry: OE-PP2 instrument in 0.2M $^n\text{BuNPF}_6$ in THF at 22°C with platinum working, tungsten auxiliary and silver pseudo-reference electrode. Under these conditions, Cp_2Fe was oxidised at 0.46V with $\Delta E_p = 110\text{mV}$. This rather high value (theoretical = 59mV) is presumably due to uncompensated resistance in solution¹²⁰. Other details on the spectrometers used and experimental procedures are given in the experimental section of Chapter 1.

$(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)^{24}$ and $(\text{Bu}^t\text{N})_2\text{ReCl}_3^{67}$ were prepared as before. Physical and analytical data and ^1H NMR data for complexes discussed in this chapter are presented in Tables 2.3-2.8.

Tris(*t*-butylimido)(2-methylphenyl)rhenium(VII)

To a stirred solution of $(\text{Bu}^t\text{N})_3\text{Re}(\text{OSiMe}_3)$ (1g, 2.05mmol) in hexane (50cm³) was added *o*-tolylmagnesium bromide (1.1cm³ of a 1.9mol dm⁻³ solution in ether, 2.1mmol) at -78°C. The solution was allowed to warm up to room temperature and stirred for 2h. The solvent was removed under vacuum and the residue extracted with hexane (20cm³), the solution filtered and the clear yellow solution evaporated under reduced pressure. The residue was recrystallised from concentrated ether or hexamethyldisiloxane solution at -21°C, to give a yellow crystalline solid. Yield *ca* 45%.

Mass spectrum: *m/e* 491 (32%), $^{187}\text{Re}(\text{NBu}^t)_3(\text{C}_7\text{H}_7)^+$; 489 (18%), $^{185}\text{Re}(\text{NBu}^t)_3(\text{C}_7\text{H}_7)^+$; 420 (9%), $^{187}\text{Re}(\text{NBu}^t)_2(\text{C}_7\text{H}_7)^+$; 418 (4%), $^{185}\text{Re}(\text{NBu}^t)_2(\text{C}_7\text{H}_7)^+$.

IR: 1580w, 1366s, 1270(sh), 1260m, 1239s, 1210s, 1131m, 1090(br), 1050w, 1025(br), 935w, 915w, 824m, 805s, 738vs, 605m, 565w, 492m.

Tris(*t*-butylimido)(2,6-dimethylphenyl)rhenium(VII)

As for (Bu^tN)₃Re(*o*-tol) from (Bu^tN)₃Re(OSiMe₃) (1g, 2.05mmol) and xylylmagnesium bromide (1.8cm³ of a 1.2mol dm⁻³ solution in ether, 2.15mmol). The orange residue obtained from the hexane extract was recrystallised from acetonitrile at -21°C to give yellow needles. Yield *ca* 50%.

Mass spectrum: *m/e* 505 (100%), ¹⁸⁷Re(NBu^t)(C₈H₉)⁺; 503 (60%),

¹⁸⁵Re(NBu^t)(C₈H₉)⁺; 490 (100%), (¹⁸⁷P-Me)⁺; 488 (54%), (¹⁸⁵P-Me)⁺; 448 (55%), (¹⁸⁷P-Bu^t)⁺; 446 (16%), (¹⁸⁵P-Bu^t)⁺; 434 (51%), (¹⁸⁷P-NBu^t)⁺; 432 (39%), (¹⁸⁵P-NBu^t)⁺.

IR: 1400w, 1355s, 1265s, 1225s, 1209s, 1130m, 1021(br), 904s, 803s, 762s, 708m, 611w, 600m, 532w, 499m, 484m, 455w.

NMR: ¹³C-{¹H} (C₆D₆); 32.2 [s, CMe₃], 33.7 [s, *o*-Me], 69.2 [s, C Me₃], 126.6, 127.9, 146.3 [C₄H₄].

Tris(*t*-butylimido)(2,4,6-trimethylphenyl)rhenium(VII)

As for (Bu^tN)₃Re(xylyl) from (Bu^tN)₃Re(OSiMe₃) (1g, 2.05mmol) and mesitylmagnesium bromide (2.1cm³ of a 0.98mol dm⁻³ solution in THF, 2.06mmol). Bright yellow crystals were obtained from concentrated acetonitrile or ether solutions at -21°C. Yield *ca* 50%.

Mass spectrum: *m/e* 519 (69%), ¹⁸⁷Re(NBu^t)₃(C₉H₁₁)⁺; 517 (82%),

¹⁸⁵Re(NBu^t)₃(C₉H₁₁)⁺; 504 (44%), (¹⁸⁷P-Me)⁺; 502 (24%), (¹⁸⁵P-Me)⁺.

IR: 1595w, 1353s, 1258s, 1223s, 1205s, 1127m, 1085(br), 1025(br), 905m, 842s, 801s, 750w, 600(br), 493(br), 450w.

Di(*t*-butylimido)dichloro(2-methylphenyl)rhenium(VII)

To a stirred solution of $(\text{Bu}^t\text{N})_3\text{Re}(o\text{-tol})$ (0.5g, 1.0mmol) in ether (30cm^3) was added a solution of HCl in ether (7cm^3 of a 0.5mol dm^{-3} solution, 3.5mmol) at -78°C . The solution was allowed to warm to room temperature and stirred for *ca.* 3h, then filtered from $\text{Bu}^t\text{NH}_3\text{Cl}$, and the filtrate evaporated. The yellow-green residue was recrystallised from ether to give golden crystals. Yield 0.3g, 60%.

Mass spectrum: *m/e* 494 (4%), 492 (15%), 490 (21%), 488 (12%), $\text{Re}(\text{NBu}^t)_2\text{Cl}_2(\text{C}_7\text{H}_7)^+$ ($^{187,185}\text{Re}$ and $^{37,35}\text{Cl}$ isotopes); 457 (11%), 455 (35%), 453 (20%), $\text{Re}(\text{NBu}^t)_2\text{Cl}(\text{C}_7\text{H}_7)^+$; 421 (26%), 419 (15%), $\text{Re}(\text{NBu}^t)\text{Cl}_2(\text{C}_7\text{H}_7)^+$; 401 (8%), 399 (24%), $\text{Re}(\text{NBu}^t)_2\text{Cl}_2^+$; 366 (34%), 365 (50%), 364 (100%), 363 (31%), 362 (55%), $\text{Re}(\text{NBu}^t)_2\text{Cl}^+$; 91 (31%) C_7H_7^+ ; 57 (35%), C_4H_9^+ .

IR: 1576w, 1565w, 1450s, 1361s, 1257s, 1245s, 1215m, 1192s, 1138w, 1118w, 1090(br), 1055m, 1025(br), 950(br), 928w, 841m, 800s, 747vs, 646w, 605(br), 508w, 470w, 447w.

Di(*t*-butylimido)dichloro(2,6-dimethylphenyl)rhenium(VII)

As for $(\text{Bu}^t\text{N})_2\text{ReCl}_2(o\text{-tol})$ from $(\text{Bu}^t\text{N})_3\text{Re}(\text{xylyl})$ (0.5g, 0.99mmol) and HCl in ether (7cm^3 of a 0.5mol dm^{-3} solution, 3.5mmol). The solution, which became blue-green, was filtered from $\text{Bu}^t\text{NH}_3\text{Cl}$ and concentrated to give a yellow green precipitate which was recrystallised from ether. Yield 0.2g, 43%.

Mass spectrum: *m/e* 506 (24%), 505 (12%), 504 (61%), 502 (20%), $\text{Re}(\text{NBu}^t)_2\text{Cl}_2(\text{C}_8\text{H}_9)^+$ ($^{187,185}\text{Re}$ and $^{37,35}\text{Cl}$ isotopes); 457 (11%), 455 (35%), 453 (20%), $\text{Re}(\text{NBu}^t)_2\text{Cl}(\text{C}_8\text{H}_9)^+$; 105 (53%), C_8H_9^+ ; 57 (100%), C_4H_9^+ .
IR: 1571w, 1360s, 1250m, 1220w, 1210w, 1175(br), 1160w, 1130w, 1020(br), 905s, 800m, 771vs, 710w, 625w, 604w, 562w, 475w.

Di(*t*-butylimido)dichloro(2,4,6-trimethylphenyl)rhenium(VII)

As for (Bu^tN)₂ReCl₂(xylyl) from (Bu^tN)₃Re(mes) (0.3g, 0.58mmol) and HCl in ether (4cm³ of a 0.5mol dm⁻³ solution, 2mmol). The blue-green solution was filtered and concentrated to give a yellow powder which was recrystallised from ether. Yield 0.18g, 58%.

Mass spectrum: m/e 520 (32%), 518 (79%), 516 (30%), Re(NBu^t)₂Cl₂(C₉H₁₁)⁺ (187,185Re and ^{37,35}Cl isotopes); 485 (10%), 483 (55%), 481 (30%),

Re(NBu^t)₂Cl(C₉H₁₁)⁺; 119 (30%), C₉H₁₁⁺; 57 (98%), C₄H₉⁺.

IR: 1595w, 1360s, 1288m, 1240m, 1215m, 1173(br), 1119m, 1025(br), 995w, 855s, 700(br), 709m, 630w, 607w, 550w, 473w.

Di(*t*-butylimido)dichloro(phenyl)rhenium(VII)

To a stirred solution of (Bu^tN)₃Re(OSiMe₃) (0.5g, 1.0mmol) in hexane (30cm³) was added phenylmagnesium bromide (0.9cm³ of a 1.25mol dm⁻³ solution in ether, 1.1mmol) at -78°C. The solution was allowed to warm to room temperature and stirred for 2h, filtered and the solvent removed under vacuum. The solid was dissolved in ether (20cm³) and a solution of HCl in ether (7cm³ of a 0.5mol dm⁻³ solution, 3.5mmol) was added. The solution was stirred for 1h, filtered and the filtrate evaporated. The residue was recrystallised from ether. Yield *ca.* 30%.

Mass spectrum: m/e 477 (1%), 475 (0.6%), P⁺; 462 (0.5%), 460(0.5%), (P-Me)⁺; 441 (8%), 439 (4%), (P-Cl)⁺; 57 (100%), (Bu^t)⁺.

IR: 1643w, 1570w, 1428m, 1364s, 1303w, 1250s, 1213m, 1189s, 1138m, 1067m, 1016w, 996m, 905w, 848w, 799m, 741s, 696s, 654w, 609m, 474w, 459m, 334m, 322m, 286m.

Bis(*t*-butylimido)tris(2-methylphenyl)rhenium(VII)

A solution of $(\text{Bu}^t\text{N})_2\text{ReCl}_3$ (0.3g, 0.69mmol) in ether (30cm^3) was cooled to -20°C . *O*-tolylmagnesium bromide (2.45cm^3 of a 0.85mol dm^{-3} solution in ether, 2.08mmol) was added and the orange solution became instantly dark red. The solution was warmed to room temperature and stirred for 12h, then filtered and the residue extracted with ether ($2 \times 5\text{cm}^3$). The solvent was removed under reduced pressure and the material extracted with hexane (20cm^3), filtered and the volume reduced (5cm^3). After further filtration clumps of orange-red crystals were obtained on cooling the hexane solution (-20°C). Yield 0.17g, 40%.

Mass spectrum: m/e 602 (1%), $^{187}\text{Re}(\text{NBu}^t)_2(\text{C}_7\text{H}_7)_3^+$; 600 (0.5%), $^{185}\text{Re}(\text{NBu}^t)_2(\text{C}_7\text{H}_7)_3^+$; 511 (22%), $^{187}\text{Re}(\text{NBu}^t)_2(\text{C}_7\text{H}_7)_2^+$; 509 (13%), $^{185}\text{Re}(\text{NBu}^t)_2(\text{C}_7\text{H}_7)_2^+$; 420 (3%), $^{187}\text{Re}(\text{NBu}^t)_2(\text{C}_7\text{H}_7)^+$; 418 (3%), $^{185}\text{Re}(\text{NBu}^t)_2(\text{C}_7\text{H}_7)^+$; 278 (2%), $^{187}\text{Re}(\text{C}_7\text{H}_7)^+$; 276 (1%), $^{185}\text{Re}(\text{C}_7\text{H}_7)^+$; 182 (9%), $(\text{C}_7\text{H}_7)_2^+$; 91 (100%), $(\text{C}_7\text{H}_7)^+$.

IR: 1594w, 1575w, 1557w, 1359s, 1256s, 1204s, 1155m, 1141w, 1131m, 1056m, 1026w, 1014w, 804w, 768w, 745s, 731s, 708w, 638w, 578w, 447w, 408w.

Bis(*t*-butylimido)bis(2,4,6-trimethylphenyl)rhenium(VI)

A solution of $(\text{Bu}^t\text{N})_2\text{ReCl}_3$ (0.41g, 0.94mmol) in ether (30cm^3) was cooled to -20°C . Mesitylmagnesium bromide (2.8cm^3 of a 1.0M solution in THF, 2.8mmol) was added and the orange solution became instantly deep red. The solution was warmed to room temperature and stirred for 12h, then filtered and the residue washed with ether ($2 \times 5\text{cm}^3$). The solvent was removed under reduced pressure and the material was extracted with hexane (20cm^3), filtered and the volume reduced (10cm^3). After another filtration large deep red crystals were obtained on cooling the hexane solution (-10°C). Yield 0.38g, 71%.

Magnetic moment: 1.46 B.M. (Evans' method¹²¹ in toluene).

Cyclic voltammetry: see text

E.s.r.: 6 line pattern at 295K $g_{\text{iso}}=1.966$, $A_{\text{iso}}=0.0133\text{cm}^{-1}$

Mass spectrum: m/e 567 (100%), 565 (71%), $\text{Re}(\text{NBu}^t)_2(\text{C}_9\text{H}_{11})_2^+$; 511 (19%), 509 (9%), $(\text{P-Bu}^t)^+$; 447 (21%), 445 (11%), $(\text{P-C}_9\text{H}_{11})^+$; 119 (8%), $\text{C}_9\text{H}_{11}^+$.

IR: 1591m, 1357s, 1279w, 1258s, 1235w, 1210s, 1153m, 1028(br), 913(br), 847s, 806m, 705m, 593w, 541w.

Reaction of $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$ with nitric oxide

$(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$ (0.2 g, 0.35mmol) was dissolved in hexane (15cm^3). Nitric oxide (25cm^3 , 1.1mmol) was syringed into the red solution, which rapidly became pale orange. The solution was filtered, reduced in volume and cooled to -12°C to give small pale yellow crystals. Mpt. 158°C .

IR: 1597m, 1564w, 1532m, 1511w, 1363s, 1284m, 1229s, 1209s, 1189s, 1139m, 1036(br), 998w, 920w, 883m, 845s, 806w, 758w, 709m, 584w, 558w, 474m.

$[(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2]\text{PF}_6$

a) To a stirred solution of $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$ (0.5g, 0.88mmol) in THF (20cm^3) was added Cp_2FePF_6 (0.29g, 0.88mmol). The deep red solution became bright orange and was stirred for 1h. The solvent was removed under vacuum and the residue washed with hexane ($2 \times 5\text{cm}^3$) (to remove Cp_2Fe). The remaining orange powder was recrystallised from THF-ether to give bright red-orange crystals. Yield 0.6g, 95%.

b) To a stirred solution of $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$ (0.3g, 0.53mmol) in THF (20cm^3) was added AgPF_6 (0.31g, 0.53mmol). The solution was stirred for 1h, filtered (from Ag), the volume reduced (5cm^3) and a few drops of ether added to induce crystallisation of the product. Yield 0.35g, 95%

Mass spectrum (FAB): m/e 567 (90%), $^{187}\text{P}^+$; 565 (53%), $^{185}\text{P}^+$; 511(4%), $^{187}\text{P-Bu}^t]^+$; 509 (3%), $^{185}\text{P-Bu}^t]^+$; 448 (6%), $^{187}\text{P-C}_9\text{H}_{11}]^+$; 446 (4%), $^{185}\text{P-C}_9\text{H}_{11}]^+$.

IR: 3123w, 1591s, 1366s, 1280s, 1229s, 1214m, 1179s, 1160m, 1140m, 1070w, 1032(br), 1002m, 955w, 901m, 876s, 839(br), 804m, 701m, 589m, 558s, 474w, 374w, 349w.

$[(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2]\text{OTf}$

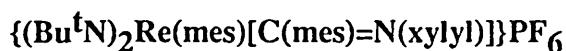
To a solution of $(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2$ (0.1g, 0.18mmol) in THF (10cm^3) was added AgOTf (0.05g, 0.19mmol). The deep red solution became bright orange and was stirred for 1h. The solvent was removed under vacuum and the residue washed with hexane ($2 \times 5\text{cm}^3$). The remaining orange powder was recrystallised from THF-ether to give bright red-orange crystals. Yield 0.1g, 85%.

$\{(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})[\text{C}(\text{mes})=\text{N}(\text{xylyl})]\}\text{OTf}$

A solution of $[(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2]\text{OTf}$ (0.3g, 0.42mmol) in THF (10cm^3) was treated with xylyl isocyanide (0.06g, 0.45mmol). The solution changed colour instantly from red-orange to pale yellow. The product was precipitated as pale yellow needles by the slow addition of hexane. Yield 0.3g, 85%.

Mass spectrum (FAB): m/e 698 (52%), $^{187}\text{P}^+$; 696 (31%), $^{185}\text{P}^+$; 448 (3%), $^{187}\text{Re}(\text{NBu}^t)_2(\text{C}_9\text{H}_{11})^+$; 446 (2%), $^{185}\text{Re}(\text{NBu}^t)_2(\text{C}_9\text{H}_{11})^+$.

IR: 1667m, 1652w, 1608m, 1586w, 1364s, 1267s, 1224m, 1191w, 1150s, 1068m, 1032s, 925w, 895m, 879w, 835w, 794m, 753w, 705w, 638s, 572m, 517m.



As above, using $[(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2]\text{PF}_6$ (0.3g, 0.42mmol) and xylyl isocyanide (0.06g, 0.45mmol) in THF (10cm³). Yield 0.32g, 90%.

Mass spectrum (FAB): m/e 698 (30%), ¹⁸⁷P⁺; 696 (16%), ¹⁸⁵P⁺; 579 (1%), (¹⁸⁷P-C₉H₁₁)⁺; 577 (0.5%), (¹⁸⁵P-C₉H₁₁)⁺; 448 (2%), ¹⁸⁷Re(NBu^t)₂(C₉H₁₁)⁺; 446 (1%), ¹⁸⁵Re(NBu^t)₂(C₉H₁₁)⁺.

IR: 1671s, 1609s, 1598m, 1364s, 1302m, 1289m, 1248s, 1224s, 1215s, 1193s, 1176m, 1168m, 1066s, 1034m, 960w, 941w, 893m, 877m, 840vs, 788m, 740w, 705m, 685w, 660w, 629m, 586w, 557s, 512w, 497w, 477w, 457w.



A solution of $[(\text{Bu}^t\text{N})_2\text{Re}(\text{mes})_2]\text{PF}_6$ (0.1g, 0.14mmol) in THF (10cm³) was treated with *t*-butyl isocyanide (0.016cm³, 0.14mmol). The red-orange solution turned pale yellow. The product was precipitated as pale yellow needles by the addition of ether. Yield 0.1g, 90%.

Mass spectrum (FAB): m/e 650 (100%), ¹⁸⁷P⁺; 648 (60%), ¹⁸⁵P⁺; 474 (20%), ¹⁸⁷Re(NBu^t)₂NC(C₉H₁₁)⁺; 472 (12%), ¹⁸⁵Re(NBu^t)₂NC(C₉H₁₁)⁺; 448 (14%), ¹⁸⁷Re(NBu^t)₂(C₉H₁₁)⁺; 446 (8%), ¹⁸⁵Re(NBu^t)₂(C₉H₁₁).

IR: 1703s, 1607m, 1597m, 1397w, 1365s, 1299w, 1286m, 1244s, 1216s, 1171s, 1144s, 1119w, 1066s, 1035w, 956w, 927w, 899m, 877m, 840vs, 735m, 705w, 667w, 654w, 582w, 558s, 526w, 468w.

CHAPTER 3

THE CATALYTIC HYDROGENATION OF IMINES

USING RHODIUM-PHOSPHINE COMPLEXES

CHAPTER 3

Introduction

Rhodium-phosphine complexes have long been used in the reduction of carbon-carbon and carbon-oxygen double bonds by molecular hydrogen¹²², however the catalytic reduction of carbon-nitrogen double bonds has received comparatively little attention^{122,123}.

The majority of systems reported for catalytic reduction of imines or Schiff bases involve metal carbonyl compounds. For example, N-benzylideneaniline is reduced to N-benzylaniline by synthesis gas (1:1, 100bar) with $\text{Co}_2(\text{CO})_8$ as a catalyst precursor at 95°C in toluene¹²⁴. A study of the kinetics of the hydrogenation has revealed $\text{HCo}(\text{CO})_4$ as the actual reducing agent. Group VI metal carbonyls $[\text{M}(\text{CO})_6]$ (M = Cr, Mo, W) have also been used in the hydrogenation of Schiff bases by molecular hydrogen (100bar) in methanol (60-160°C)¹²⁵. The rate of this hydrogenation is significantly increased by the addition of NaOMe which increases the concentration of the active catalyst *e.g.* $[\text{HCr}(\text{CO})_5]^-$. Analogous reductions may also be performed using $\text{Fe}(\text{CO})_5$ in alcohols at 150°C and 100bar H_2 ¹²⁶. In this case the substrate itself is sufficiently basic to produce $\text{HFe}(\text{CO})_4^-$ which reacts rapidly with the protonated imine *via* an Fe-C bonded species. In the former case the proposed intermediate contains a M-N σ -bond, hence the protonated imine is deactivated for reaction with $\text{HCr}(\text{CO})_5^-$.

Rhodium-phosphine complexes have been used to reduce imines *via* catalytic hydrosilylations¹²⁷, and also by Markó¹²⁸ at temperatures greater than 40°C and hydrogen pressures greater than 100bar, whilst $[\text{Rh}(\text{diop})(\text{nbd})]^+$ has been employed without great success for asymmetric reduction¹²⁹. Grigg *et al*¹³⁰ have proposed a hydride transfer mechanism for the reduction of imines by a $\text{RhCl}(\text{PPh}_3)_3/\text{Na}_2\text{CO}_3$

mixture in refluxing propan-2-ol, where $\text{RhH}(\text{PPh}_3)_4$ was the proposed effective catalyst.

This chapter concerns the development of a new catalytic cycle for the reduction of aldimines which is effective under only 1 atmosphere of hydrogen at room temperature, provided that the solvent used is an alcohol¹³¹. Wilkinson's catalyst $\text{RhCl}(\text{PPh}_3)_3$ or the cationic derivatives $[\text{Rh}(\text{PPh}_3)_2(\text{diene})]^+$ are used as catalyst precursors.

Results and discussion

The hydrogenation of $\text{RhCl}(\text{PPh}_3)_3$ or $[\text{Rh}(\text{PPh}_3)_2(\text{nbd})]\text{PF}_6$ in methanol, ethanol or higher alcohols gave pale yellow or colourless solutions respectively. On addition of an imine the solutions became deep orange. On stirring under 1 atmosphere of hydrogen at room temperature a stoichiometric amount of gas was absorbed (gas burette). Reduction was observed for several different imines in a range of alcohols (Table 3.1).

For $\text{RhCl}(\text{PPh}_3)_3$ the orange solution reverted to yellow on completion of the reduction, but for the cationic species a brown solution resulted; such solutions tended to decompose and deposit rhodium especially if fresh imine was added.

Interestingly no reduction occurred in acetonitrile or dimethylformamide, and the addition of even small amounts (<5%) of benzene to the alcohol severely inhibited the reduction. Reductions using these rhodium-phosphine catalysts in hexane-diethyl ether required temperatures higher than 50°C and hydrogen pressures greater than 40bar (*cf.* Ref. 128 where benzene-methanol (1:1) was used).

Although solvent effects in homogeneous hydrogenation are well-known¹²², the requirement for pure alcohols was unusual and the fact that other polar but non-hydrogen bonding solvents were unsuitable suggested that hydrogen bonding could be an important feature in the catalytic cycle. Support was provided by the observation of effective reduction even in aqueous alcohols.

A proposed cycle is shown in Fig.3.1. It would normally be the nitrogen atom of the imine which would act as donor, but intramolecular hydrogen-bonding as in **A** in Fig.3.1 could lead to η^2 -C,N bonding of the substrate. Protonation of the imine nitrogen might be expected to have the same effect; however attempts to reduce $[\text{RNH}=\text{CHR}]^+$ failed presumably because such a cationic substrate would have little tendency to bind to a cationic metal species. H-transfer to the imine in Fig.3.1 would produce the dialkylamido species **B**. This corresponds to the alkoxide species proposed in the reduction of ketones¹³². A second hydride-transfer to N would then give the coordinated amine complex **C** which on oxidative addition of H_2 eliminates amine. The details of the cycle could, of course, differ from those in Fig.3.1. The imine could coordinate to a rhodium(I) species which could then undergo oxidative addition of H_2 , some of the species need not be solvated and the amine could be displaced by solvent *etc..*

The rate of reduction was affected by the nature of the solvent alcohol, as illustrated in Table 3.1. For example, reduction was faster in propan-1-ol than in propan-2-ol, probably because steric crowding around the hydroxyl group in the latter restricts hydrogen bonding to the imine.

The formation of a dialkylamido intermediate $[\text{PhCH}_2\text{N(Ph)Cr(CO)}_5]^-$ has also been proposed by Markó *et al* in the hydrogenation of imines using $[\text{HCr(CO)}_5]^-$ ¹²⁵; for $[\text{HFe(CO)}_4]^-$ it was suggested that interaction with $[\text{PhCH}=\text{NHPH}]^+$ gave an Fe-C σ -bonded species $[\text{Fe}(\overline{\text{PhCHNHPH}})\text{H(CO)}_4]$ ¹²⁶.

The hydrogenolysis of a model dialkylamido complex was illustrated by the interaction of hydrogen with the complex $\text{Rh}[\text{N(SiMe}_3)_2](\text{PPh}_3)_2$ ¹³³. A green solution of the complex became immediately yellow-brown on exposure to hydrogen, and $(\text{Me}_3\text{Si})_2\text{NH}$ was formed quantitatively along with rhodium-hydride species.

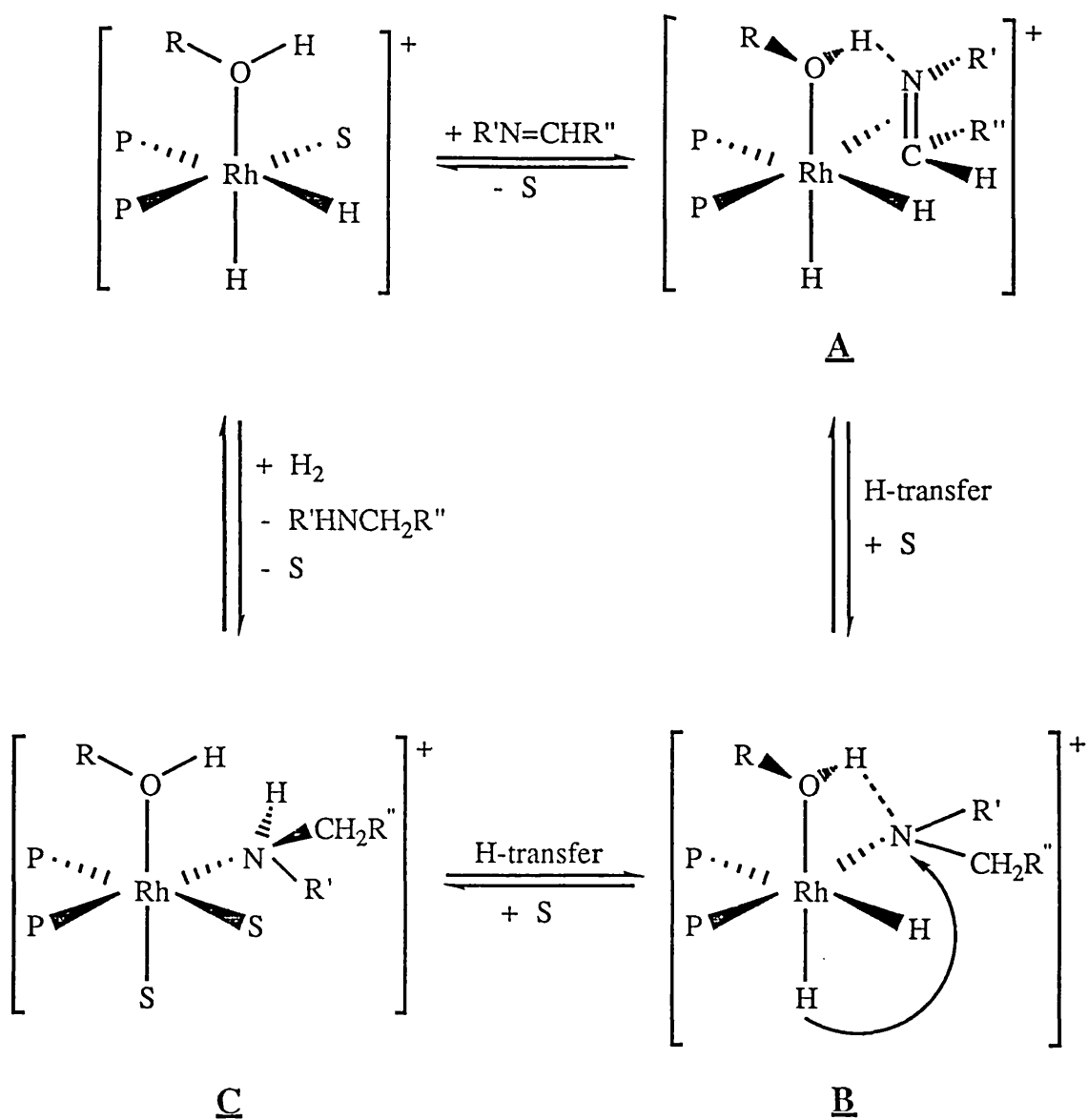


Fig.3.1 : Proposed Cycle for the Hydrogenation of an Imine on a Cationic Rhodium Phosphine Complex. S = alcohol.

Table 3.1: Representative Data for the Hydrogenation of Imines with Rhodium-phosphine Complexes.

<u>Precursor</u>	<u>Substrate</u>	<u>Time^a</u> (min.)
RhCl(PPh ₃) ₃ ^b	PhCH=NMe	160
	PhCH=N ⁱ Pr	500
	PhCH=NCH ₂ Ph	865
	PhCH=Ph	1250
	PhCH=NMe ^c	125
	PhCH=NMe ^d	1300
	PhCH=NMe ^e	2195
[Rh(PPh ₃) ₂ (nbd)]PF ₆ ^f	PhCH=NMe	105
	PhCH=N ⁱ Pr	210
	PhCH=NCH ₂ Ph	270
	PhCH=NPh	360
	PhCH=NPh ^c	315
	PhCH=NMe ^c	95
	PhCH=NMe ^d	465
	PhCH=NMe ^e	610

^a Time for complete hydrogenation. Average of 3 runs, error <10%.

^b Reaction conditions: Rh/substrate ratio = 1:50, *ca.* 1mmol of catalyst in ethanol (50cm³) at 25°C, 1 atm. H₂.

^c In methanol. ^d In propan-1-ol. ^e In propan-2-ol.

^f Reaction conditions: Rh/substrate ratio = 1:120, *ca.* 1mmol catalyst in ethanol (50cm³) at 25°C, 1 atm. H₂.

Metal-nitrogen bond cleavage resulting in amine elimination has been established in reactions of the type:



but not previously with dihydrogen.

Attempts to confirm the proposed mechanism (Fig.3.1) by performing the reduction under deuterium were not very successful. Only about 50% incorporation of D at the α -carbon atom in the product amine was observed; also the proportion of ROD in the solvent increased. This was due to ROH-D₂ exchange processes like those encountered by Schrock and Osborn in ketone hydrogenation¹³². Indeed, such exchange was observed on stirring alcohol solutions of the catalyst under D₂ in the absence of imine.

The results in Table 3.1 show that the rate of reduction decreased with increased steric crowding around the C=N bond. The higher activity of the cationic species relative to RhCl(PPh₃)₃ may be due to the possibility in the former of generating intramolecular hydrogen-bonded intermediates where both imine and alcohol are bound to the metal (as in **A**), whereas for [RhCl(PPh₃)₃H₂(imine)] hydrogen bonding is most likely to be intermolecular. Also cationic species are known to have greater ability to reduce unsaturated linkages.

RhH(CO)(PPh₃)₃, which has been used as a homogeneous hydrogenation catalyst in the selective reduction of carbon-carbon multiple bonds¹³⁴, was effective in the reduction of imines under synthesis gas (1:1, 70bar) in hot ethanol or toluene (95°C). Hydrogen alone was ineffective under these conditions, even in the presence of excess PPh₃.

Asymmetric Hydrogenation

The use of chiral catalysts for the production of optically active compounds is very important in the generation of biologically active molecules. Transition metal catalysts incorporating one or more chiral centres have already been used successfully in many aspects of asymmetric organic synthesis.

It is not easy to devise a chiral catalyst system because often the configuration-determining step is not known. It is also very difficult to predict how a chiral ligand will be oriented in the coordination sphere of the metal and what the chances of good chiral discrimination at the key steps of the catalysis are.

The most common approach is to employ a transition metal complex with a chiral phosphine ligand. Such a ligand may be asymmetric at phosphorus or may carry a chiral carbon moiety. Generally such complexes are expensive to produce and are only available in small quantities. It would be valuable if a chiral auxiliary could be generated from cheap natural products.

It was proposed to extend the new catalytic system described in this chapter to the asymmetric reduction of prochiral imines. Since the solvent molecule appeared to be involved in the reaction intermediates it was suggested that the use of a chiral solvent might produce some chiral discrimination within the catalyst-substrate intermediate and thereby induce an asymmetric transformation of the substrate.

Preliminary results using $\text{Ph(Me)C=NCH}_2\text{Ph}$ as the prochiral imine and solvents such as butan-2-ol, diethyltartrate and molten menthol showed the reduction to be extremely slow, even at increased hydrogen pressures and temperatures, presumably because of steric crowding.

Imine reduction using $\text{RhCl(PPh}_3)_3/\text{Na}_2\text{CO}_3$ in propan-2-ol is reported to proceed *via* hydride transfer from the solvent¹³⁰. The analogous reduction was performed using $\text{Ph(Me)C=NCH}_2\text{Ph}$ and (+)-butan-2-ol as solvent, but unfortunately no enantioselectivity was observed.

Experimental

$\text{RhCl}(\text{PPh}_3)_3$ ¹³⁶, $[\text{Rh}(\text{PPh}_3)_2(\text{diene})]\text{PF}_6$ (diene = cod or nbd)¹³⁷, $\text{Rh}[\text{N}(\text{SiMe}_3)_2](\text{PPh}_3)_2$ ¹³³ and $\text{RhH}(\text{CO})(\text{PPh}_3)_2$ ¹³⁵ were prepared by literature methods. N-benzylidenemethylamine and N-benzylideneisopropylamine were from Lancaster Synthesis Ltd.. N-benzylideneaniline and N-benzylidenebenzylamine were prepared by condensation of benzaldehyde with the appropriate amine in ethanol. Hydrogen was purified using an Engelhard "Deoxo" catalyst. Other details of experimental procedures are given in the experimental section of Chapter 1.

Typical Hydrogenation of Imine in Alcohols

$[\text{Rh}(\text{PPh}_3)_2(\text{nbd})]\text{PF}_6$ (0.06g, 0.07mmol) in absolute ethanol was stirred vigorously under 1 atm. hydrogen for 1h. N-benzylidenemethylamine (1g, 8.4mmol) was added and the stirring continued until hydrogen uptake was complete (gas burette). Concentrated HCl (0.8cm³, 10mmol) was added and the solution reduced to dryness. The solid was dissolved in the minimum amount of ethanol (*ca* 5cm³) and diethyl ether was added dropwise until precipitation of the amine hydrochloride was complete; the white solid was collected, washed sparingly with ethanol-ether (1:1) and ether and air-dried. Yield 1.2g, 91%.

Free N-benzylmethylamine was liberated from the hydrochloride by dissolution in the minimum amount of 5M NaOH (*ca* 5cm³) and extraction with ether. The extracts were dried over Na₂SO₄ and the ether removed under reduced pressure to give the amine. Yield 0.91g, 89%.

Hydrogenation using $\text{RhH}(\text{CO})(\text{PPh}_3)_2$

$\text{RhH}(\text{CO})(\text{PPh}_3)_2$ (0.06g, 0.065mmol) and N-benzylideneaniline (1g, 5.52mmol)

were stirred in toluene (or ethanol) at 95°C under CO + H₂ (1:1, 70bar) in a Berghof thermostatted autoclave for *ca* 48h. The product amine could be separated by distillation or by isolation of the hydrochloride salt as above.

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