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An Investigation of Ru(II) Complexes Containing
Sterically Demanding Imido Ligands

A thesis presented to Massey University in
partial fulfilment of the requirements for the degree of

MASTER OF SCIENCE

by

Andrew John Steedman
1995
This is dedicated to the Steedman and Turei ancestors, including present members, and to the dynamic duo, D.M. and Penfold.
I would like to thank sincerely my supervisor, Dr. A.K. Burrell, for his guidance and care free attitude shown through all of it.

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Most of all I want to thank Cujo.
Abstract

Monomeric, low oxidation state, ruthenium imido compounds, \((\eta^6\text{-arene})\text{RuN-Ar}^\prime\) (arene= p-cymene and \(\text{C}_6\text{Me}_6\); \(\text{Ar}^\prime = 2,4,6\text{-tri-tert-butyphenyl}\)) have been synthesized from \([((\eta^6\text{-arene})\text{RuCl}_2)_2\] and 4 equiv of LiNHAr' in THF. An X-ray crystal structure of \((\eta^6\text{-p-cymene})\text{Ru=NAr}^\prime\) showed a short Ru-N distance (1.753(3)Å) and a near linear Ru-N-C angle (177.8(4)°) consistent with ruthenium to nitrogen multiple bonding. Reaction of \([((\eta^6\text{-p-cymene})\text{RuCl}_2)_2\] with 4 equiv of LiNHR (R= 2,6-dimethylphenyl or 2,6-diisopropylphenyl) in THF afforded the dimeric ruthenium imido compounds \([((\eta^6\text{-p-cymene})\text{Ru(µ-NR)})_2\]. An X-ray crystal structure of \([((\eta^6\text{-p-cymene})\text{Ru(µ-NAr)})_2\] (\(\text{Ar} = 2,6\text{-diisopropylphenyl}\)) showed an averaged Ru-N distance of 1.974(8)Å and features characteristic of Ru(II) bridging imido complexes. Addition of 2 equiv of LiNHAr to \([((\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2)_2\] gave a HCl adduct, \((\eta^6\text{-C}_6\text{Me}_6)\text{RuClNHAr}\], characterisation of the complex was obtained by X-ray diffraction. Reaction of the HCl adduct with phenylisocyanate gave the ureylene metallacycle, \((\eta^6\text{-C}_6\text{Me}_6)\text{Ru(N(Ar)C(O)N(Ph))}\), indicating the presence of an imido intermediate. This complex was shown to have a \(\nu(\text{CO})\) band at 1596cm\(^{-1}\) and is comparable with other monomeric ureylene complexes. In addition, the complex \([((\eta^6\text{-p-cymene})\text{Ru(µ-NAr)})_2\] was made from 2 equiv of the amine, ArNH\(_2\), and \([((\eta^6\text{-p-cymene})\text{RuCl}_2)_2\] and dehydrochlorinated with \(\text{KN(SiMe}_3)_2\] providing an alternative route. Further, an X-ray crystal structure of the amine complex, \((\eta^6\text{-p-cymene})\text{RuCl}_2(\text{ArNH}_2)\] was obtained. The reaction of \((\text{bpy})_2\text{RuCl}_2\) (bpy= 2,2'-bipyridine) with LiNHAr' in THF afforded the complex, \((\text{bpy})_2\text{Ru=NAr}^\prime\], characterised by nmr and elemental analysis.
List of Figures

Figure 1  General Formulation of Oxo Complexes  page 3
Figure 2a  [(bpy)2Ru(O)(py)]2+  page 4
Figure 2b  Re(O)(η2-MeC≡CMe)2(I)  page 4
Figure 3  Cp*Re(O)3; (bpy)Mo(Et)2(O)2; CpW(Ph)(η2-PhC≡Ph)(O)  page 5
Figure 4  General Formulation of Nitrido Complexes  page 5
Figure 5  [Os(N)(O)3]−  page 5
Figure 6  Re(N)Cl2(PPh3)2  page 5
Figure 7  General Formulation of Hydrazido Complexes  page 6
Figure 8  Resonance Forms of the Hydrazido Ligand  page 7
Figure 9  [M(=NNH2)(DPPE)2X]+; M=Mo, W  page 7
Figure 10  [M(=NN=CR2)(DPPE)2X]+; M=Mo, W  page 8
Figure 11  General Formulation of Carbene/Alkylidene Complexes  page 8
Figure 12  (CO)5W=C(OCH3)(CH3)  page 9
Figure 13  β-Lactam Synthesis  page 9
Figure 14  ([BuCH2]3Ta=CtBu(H)  page 10
Figure 15  “Cp2Ti=CH2”  page 10
Figure 16  General Formulation of Carbyne/Alkylidyne Complexes  page 11
Figure 17  M(=CR)(CO)4X; M=Cr, Mo, W  page 12
Figure 18  CpTa(=CPh)(PMe3)2Cl  page 12
Figure 19  General Formulation of Terminal Imido Complexes  page 13
Figure 20  Re(=NAr)(PR3)2Cl3  page 13
Figure 21  Possible Bond Orders of the MNR Moiety  page 13
Figure 22  W(=CH(Bu)=NAr)(ORf)2  page 15
Figure 23a  (Me3SiO)4Mo(NHR)2; R=1-adamantyl  page 17
Figure 23b  (Me3SiO)2Mo(=NR)2; R=1-adamantyl  page 17
Figure 24  Transition State Involving Bridged Oxo and Imido Ligands  page 22
Figure 25  Crystal Structure of Cp*Ir(=NAr)  page 28
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>Crystal Structure of (C₆Me₆)Os(=N³Bu)</td>
</tr>
<tr>
<td>27</td>
<td>Crystal Structure of trans-Ru(=NAr)(PMe₃)₂</td>
</tr>
<tr>
<td>28</td>
<td>[Tc₂(NAr)₆] and Tc₂(NAr&quot;)₄(µ-NAr&quot;)₂</td>
</tr>
<tr>
<td>29</td>
<td>Os(NAr)₃ and [Os(N³Bu)₂(µ-N³Bu)]₂</td>
</tr>
<tr>
<td>30</td>
<td>Crystal Structure of [(cym)Ru(µ-NAr)]₂</td>
</tr>
<tr>
<td>31</td>
<td>Crystal Structure of (cym)RuCl₂NH₂Ar</td>
</tr>
<tr>
<td>32</td>
<td>Crystal Structure of (cym)Ru=NAr'</td>
</tr>
<tr>
<td>33</td>
<td>Crystal Structure of (C₆Me₆)RuClNHAr</td>
</tr>
<tr>
<td>34</td>
<td>Cp*Ir(RCCR³BuRCCR); R=CO₂Me</td>
</tr>
<tr>
<td>35</td>
<td>Sterics Versus Reactivity</td>
</tr>
</tbody>
</table>

## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1</td>
<td>Terminal Imido Functional Groups</td>
<td>27</td>
</tr>
<tr>
<td>Table 2</td>
<td>Selected Bond Lengths and Angles for ([cym]Ru(µ-NAr)]2</td>
<td>44</td>
</tr>
<tr>
<td>Table 3</td>
<td>Selected Bond Lengths and Angles for (cym)RuCl2NH2Ar</td>
<td>47</td>
</tr>
<tr>
<td>Table 4</td>
<td>Comparative 1H Chemical Shift and Coupling Constants for the Aromatic Protons of the p-Cymene Ligand</td>
<td>50</td>
</tr>
<tr>
<td>Table 5</td>
<td>Comparative 1H Chemical Shifts of the Isopropyl and Methyl Groups of the p-Cymene Ligand</td>
<td>50</td>
</tr>
<tr>
<td>Table 6</td>
<td>Comparative 13C Chemical Shifts of <em>ipso, ortho, meta</em> and <em>para</em>-carbons of the Imido Ligand</td>
<td>51</td>
</tr>
<tr>
<td>Table 7</td>
<td>Selected Bond Lengths and Angles for (cym)Ru=NAr'</td>
<td>51</td>
</tr>
<tr>
<td>Table 8</td>
<td>13C Chemical Shifts of <em>ipso, ortho, meta</em> and <em>para</em>-carbons of the Imido Ligand for (C6Me6)Ru=NAr'</td>
<td>54</td>
</tr>
<tr>
<td>Table 9</td>
<td>Selected Bond Lengths and Angles for (C6Me6)RuClNHAr</td>
<td>56</td>
</tr>
<tr>
<td>Table 10</td>
<td>Comparative Ru-N Distances</td>
<td>56</td>
</tr>
<tr>
<td>Table 11</td>
<td>Comparative Ru-Cl Distances</td>
<td>58</td>
</tr>
<tr>
<td>Table 12</td>
<td>Comparative 1H Chemical Shifts of Septets Due to the Ar Ligand</td>
<td>62</td>
</tr>
<tr>
<td>Table 13</td>
<td>Comparative 1H Chemical Shifts of the <em>tert</em>-butyl Groups</td>
<td>67</td>
</tr>
<tr>
<td>Table 14</td>
<td>Comparative 1H Chemical Shifts of the Ar Ligand, NH2 Group and I.R. Peaks of the NH2 Group for the Ru and Rh Amine Complexes</td>
<td>69</td>
</tr>
</tbody>
</table>
Abbreviations

Ac \(-\text{COCH}_3\)

Ar 2,6-diisopropylphenyl

Ar' 2,4,6-tri-vert-butylphenyl

Ar'' 2,6-dimethylphenyl

bpy 2,2'-bipyridine

Bu butyl

Cp cyclopentadienyl

Cp* pentamethylcyclopentadienyl

DMAC dimethylacetylenedicarboxylate

dme dimethoxyethane

dmtc dimethyldithiocarbamate \((R_2\text{NCS}_2^-)\)

DPPE 1,2-bis(diphenylphosphino)ethane

Et ethyl

I.R. Infra-red

Me methyl

mnt maleonitriledithiolate \([\eta^2\text{-S}_2\text{C}_2\text{(CN)}_2]^{2-}\)

nmr nuclear magnetic resonance

OTf Triflate \((\text{OSO}_2\text{CF}_3)^-\)

Ph phenyl

Pr propyl

Pr\text{} \text{iso-} \text{propyl}

py pyridine

R_f OCMe(CF_3)_2

tBu \text{vert-} \text{butyl}

thf tetrahydrofuran

tol tolyl \((4-\text{C}_6\text{H}_4\text{Me})\)

tpy 2,2':6',2''-terpyridine

X anionic ligand
# Table of Contents

## Chapter One

Introduction
- Terminal Oxo Complexes page 2
- Terminal Nitrido Complexes page 3
- Terminal Hydrazido Complexes page 5
- Carbene and Alkylidene Complexes page 6
- Carbyne and Alkylidyne Complexes page 8
- Terminal Imido Complexes page 11
- Synthetic Methods for Introducing Terminal Imido Ligands page 12
- Known Metal Terminal Imido Complexes of Os(II), Ir(III) and Ru page 16

## Chapter Two

Results and Discussion
- The Role of Sterics page 34
- Synthesis of Precursors page 34
- Synthetic Method page 36
  (i) the strategy page 40
  (ii) reactions of [(cym)RuCl2]2 page 40
  (iii) reactions of [(C6Me6)RuCl2]2 page 42
- Reactivity of the imido and amido ligand page 53
- Possible mechanisms of imido formation from LiNHR page 59
- Future work page 64
- Summary page 66
Chapter Three
Experimental Section

- General

- Compounds

# [(\eta^6-C_6Me_6)RuCl_2]_2

# (bpy)_2RuCl_2

# [(cym)Ru=NAr']_n

# [(C_6Me_6)Ru=NAr']_n

# [(cym)Ru=NAr]_n

# [(cym)Ru=NAr'']_n

# (C_6Me_6)RuClNHAr

# (C_6Me_6)RuN(Ph)C(O)N(Ar)

# (bpy)_2Ru=NAr'

# (cym)RhCl_2NH_2Ar

# (cym)RuCl_2NH_2Ar

Chapter Four

Tables of $^1$H and $^{13}$C Data

- $^1$H nmr of (cym)RhCl_2NH_2Ar

- $^1$H nmr of [(cym)Ru=NAr'']_n

- $^{13}$C nmr of [(cym)Ru=NAr'']_n

- $^1$H nmr of [(cym)Ru=NAr]_n

- $^{13}$C nmr of [(cym)Ru=NAr]_n

- $^1$H nmr of (cym)RuCl_2NH_2Ar

- $^{13}$C nmr of (cym)RuCl_2NH_2Ar

- $^1$H nmr of [(cym)Ru=NAr']_n
- $^{13}$C nmr of [(cym)Ru=NAr']$_n$
- $^1$H nmr of [(C$_6$Me$_6$)Ru=NAr']$_n$
- $^{13}$C nmr of [(C$_6$Me$_6$)Ru=NAr']$_n$
- $^1$H nmr of (C$_6$Me$_6$)RuCl$_2$NHAr
- $^{13}$C nmr of (C$_6$Me$_6$)RuCl$_2$NHAr
- $^{13}$C nmr of (cym)RhCl$_2$NH$_2$Ar
- $^1$H nmr (bpy)$_2$Ru=NAr'
- $^1$H nmr of (C$_6$Me$_6$)RuN(Ph)C(O)N(Ar)
- $^{13}$C nmr of (C$_6$Me$_6$)RuN(Ph)C(O)N(Ar)

Appendix

Crystal Structures
- [(cym)Ru=NAr]$_n$
- [(cym)Ru=NAr']$_n$
- (C$_6$Me$_6$)RuCl$_2$NHAr
- (cym)RuCl$_2$NH$_2$Ar

References
Chapter One
Introduction

In recent years few areas of inorganic chemistry have experienced the exceptional growth associated with transition metal complexes containing metal-ligand multiple bonds. Firing the growth of this field are the important chemical processes associated with multiply bonded ligands. Such species are present on the catalytic surface in a wide variety of crucial industrial processes. They constitute the “business end” of some of the most useful reagents for laboratory scale synthesis. They are involved in a fascinating array of enzymatic transformations. The oxo and nitrido moieties in particular are essential building blocks for a new generation of electronic materials.

The proliferation in the field of imido chemistry has the potential to increase our understanding of the properties pertaining to complexes containing metal-nitrogen (M=N-R) multiple bonded ligands. The imido moiety and the complex itself can embody a unique set of properties ranging from remarkable stability to extreme reactivity, which are dependent on the metal, its oxidation state, the ancillary ligands, as well as the nature of R.

The use of highly polar M-N linkages and nucleophilic imido ligands are emerging areas of future utility as sites for C-H bond activation. Also, the design of electrophilic imido ligands will be possible as more is understood about imido chemistry. Such NR transfer reagents are certain to play a role in alkene aziridination systems.

Application of imido compounds as model species in catalytic processes involving nitrogen is flourishing. Among the most important of these is propylene ammoxidation and hydrodenitrogenation (HDN) catalysis. The use of M(=NR)(=CHR)(OR)\(_2\) complexes of molybdenum and tungsten in metathesis polymerisations are extremely important. Development of technetium and rhenium compounds in radiopharmaceutical and other biological applications is an important developing area of imido chemistry.

The following discussion includes an overview of complexes containing metal-oxygen (oxo), metal-nitrogen (nitrido, hydrazido, imido) and metal-carbon (alkylidene, alkylidyne) multiple bonds. The many methods for introducing terminal imido ligands are then
covered with illustrative examples. Finally, low oxidation state osmium and iridium terminal imido complexes and the known ruthenium terminal imido compounds are discussed in detail.

Terminal Oxo Complexes:

Metal-oxo (Fig. 1) complexes were the first known compounds containing metal-ligand multiple bonds. As such their chemistry has been most extensively developed. Sodium ferrate, Na₂FeO₄, was synthesized in 1702 and compounds such as OsO₄, KMnO₄ and K₂CrO₄ were known to chemists in the early nineteenth century. The multiple bonded character of metal-oxo complexes was widely accepted by 1938.

![Figure 1](image_url)

Complexes containing terminal oxo substituents are known for all the transition metals of the vanadium through iron triads. The metals of the titanium triad tend to form bridged rather than terminal oxo structures. However, coordinative saturation of the metal enforces the terminal oxo structure and as a result several terminal oxotitanium complexes have been structurally characterised.

The vast majority of oxo complexes have d⁰, d¹ or d² configurations, giving support to the oxo ligand being best described as a closed-shell anion, O²⁻. Productive π-bonding with a metal center therefore requires that the metal d-orbitals be empty, in other words that the metal center be in a high oxidation state with a low d-electron count. Although in the last few years a handful of d⁴ oxo compounds and d⁵ species have been prepared, the d⁴ oxo species are either very reactive or adopt an unusual structure to promote multiple bonding. The d⁴ Ru oxo complex, [(bpy)₂Ru(O)(py)]²⁺ (Fig. 2a) is a very reactive oxidant and the d⁴ oxo complex, Re(O)(η²-MeC≡CMe)₂(I) (Fig. 2b) adopts an unusual tetrahedral structure.
The use of metal-oxo complexes as oxidants in organic synthesis is one important and long standing application of metal oxo derivatives.\textsuperscript{10-13}

Nature also makes use of terminal imido ligands to carry out oxidations. Enzymes of the cytochrome P-450 family contain an oxo-iron porphyrin system and are involved in a wide range of biological oxidation processes.\textsuperscript{14} A second family of oxo-metal based enzymes are the molybdenum or tungsten containing "oxo-transferases" which are involved in both oxidative and reductive processes.\textsuperscript{15}

Metal-oxo species are present on the surface of industrially important heterogeneous catalysts. For example the oxidation of propylene to acrolein\textsuperscript{16} and the oxidation of C4's to butadiene\textsuperscript{17} involve the use of bismuth molybdate catalysts. Also iron molybdate catalysts are utilised for the oxidation of methanol to formaldehyde.\textsuperscript{18} Oxo ligands are also utilised in industrial processes involving homogeneous catalysis. For example, vanadium-oxo complexes catalyse the rearrangement of allylic or propargylic alcohols in the manufacture of terpene alcohols and of vitamin A.\textsuperscript{19}

Organometallic chemists have begun to appreciate the ability of the oxo ligand to stabilise high oxidation states. This stabilisation has been applied to the synthesis of both $\sigma$ and $\pi$ organotransition metal derivatives, for example, of vanadium(V), rhenium(VII), molybdenum(VI) and tungsten(VI). Figures 3 illustrates three such complexes.\textsuperscript{20}
Terminal Nitrido Complexes:

Multiple bonded nitrido complexes (Fig. 4) are now known for all of the metals of vanadium through iron triads. However, the examples of iron, niobium and tantalum are of the bridged variety.

\[ M=\equiv N \]

Figure 4

The first nitrido complex to be synthesized was the so-called “potassium osmiamate” (Fig. 5) reported by Fritsche and Struve in 1847.\(^{21}\) However, it was not until 1901 that the presence of a nitrido ligand in the complex was recognised.\(^{22}\) The first neutral mononuclear nitrido complex did not appear until Chatt and coworkers report of \(\text{Re}(\equiv \equiv N)(\text{PPh}_3)_2\text{Cl}_2\) (Fig. 6) in 1963.\(^{23}\)

Complexes with terminal nitrido ligands are believed to contain metal-nitrogen triple bonds, or at least to be best described by that resonance structure, on the basis of crystallographic and spectroscopic data.\(^{24}\) The strong preference of nitrido ligands for the
formation of triple bonds is illustrated by the lack of dinitrido compounds, in which the ligands would have to share a metal π-orbital. As with the oxo ligand, the nitrido ligand is best described as a closed-shell anion, N$_3^-$. There is as yet no fully characterised transition metal nitrido compound with a greater than d$^2$ configuration.

The ability of the nitrido ligand to stabilise organotransition metal species was recognised by Chatt, who reported a series of aryl rhenium nitrido complexes, Re(≡N)Ar$_2$(PR$_3$)$_2$.25

The field of electronic materials is an emerging area of application of nitrido compounds. The ability of niobium(III) nitride to form films that are strong, stable and superconducting$^{26}$ has been of interest for some time. A recent theoretical study by Hoffman et al. pointed out a number of parallels between transition metal nitrides and such organic conductors as polyenes and phosphazenes$^{27}$ has fueled current interest in the electronic properties of transition metal nitrides.

**Terminal Hydrazido Complexes:**

Terminal hydrazido complexes (Fig. 7) are now known for the metals of vanadium, niobium, tantalum, titanium, tungsten and rhenium.

$$M≡N-···NR_2$$

Figure 7

A variety of structural types and resonance forms are possible for the hydrazido ligand (Fig 8). The conjugation of a substituent lone pair with a metal-ligand triple bond splits the degeneracy of the p-orbitals of the triple bond. Calculations on hydrazido$^{28}$ complexes, indicate that the amino lone pair is very involved in the bonding and that there is significant multiple bond character to the N-N bond.
The chemistry of hydrazido complexes in general and their role in nitrogen fixation in particular have been the subject of several reviews. Hydrazido ligands are of particular importance because of their suggested intermediacy in the reduction of dinitrogen by metal complexes and metalloenzymes. As such the focus of activity on hydrazido compounds has been the Institute for Nitrogen Fixation at Sussex University. In 1972 this organisation reported the synthesis of $M(=NNH_2)(DPPE)_2X$ ($M=Mo, W$; Fig. 9) hydrazido complexes accomplished by protonation of tungsten or molybdenum dinitrogen complexes.

Such complexes, it was shown, undergo a number of C-N bond-forming reactions. A simple example being formation of the diazoalkane complex ($M=Mo, W$; Fig. 10), ultimately allowing the direct conversion of dinitrogen to organonitrogen derivatives.
Carbene and Alkylidene Complexes:

Complexes that contain M=C double bonds (Fig. 11) can be termed loosely into two divisions; carbene and alkylidene complexes. They were first prepared by Fischer by the interaction of acylate anions with electrophiles.\textsuperscript{31b} These compounds were 18-electron species in low oxidation states and have been called \textit{carbene complexes}. Subsequently, compounds in high oxidation states with 10 to 16 electron counts have been made and these have been termed \textit{alkylidene complexes}.

\[
M═CRR'
\]

Figure 11

Alkylidene ligands are best described as CR\textsubscript{2}\textsuperscript{2−} only when they lact heteroatom substituents and are bound to high-oxidation state metal centers.\textsuperscript{31c} The CR\textsubscript{2} group is also often treated as a neutral ligand (a carbene) in particular when the carbon bears a substituent with lone pairs such as alkoxy or an amino group (Fischer carbene complexes).\textsuperscript{31d}

\textit{Ab initio} calculations support earlier results\textsuperscript{31d,e} that the metal-carbon interaction consists of a $\sigma$ and a $\pi$ bond. Recent calculations using high levels of theory\textsuperscript{31f} suggests that Schrock alkylidenes form ethylene-like covalent double bonds, but Fischer carbenes bond to a metal center via donor-acceptor interactions.
The first carbene complex reported was by Fischer and Maasboel in 1964 (Fig. 12). The carbene moiety in these compounds has a pronounced tendency to behave as a carbon electrophile and it has become evident that such electrophilic properties are shared by other carbene complexes, some of which do not contain a heteroatom substituent.

\[ \text{(OC)}_5\text{W} \rightleftharpoons \text{C} \begin{array}{c} \text{OCH}_3 \\ \text{CH}_3 \end{array} \]

Figure 12

Fischer carbene complexes are of considerable importance as key intermediates in catalysis. Iron methylene species are finding use as stoichiometric cyclopropanation agents and chromium analogues of \((\text{CO})_5\text{W} = \text{CCH}_3(\text{OCH}_3)\) (Fig. 12) are used increasingly in organic chemistry as reagents for two powerful synthetic transformations; the \(\beta\)-lactam synthesis (Fig. 13) and the Dötz naphthoquinone synthesis.

\[ \begin{array}{c} \text{(OC)}_5\text{Cr} \rightleftharpoons \text{C} \begin{array}{c} \text{OMe} \\ \text{R}^1 \end{array} \\ + \end{array} \rightarrow \begin{array}{c} \text{(CO)}_x\text{Cr} \rightleftharpoons \text{C} \begin{array}{c} \text{OMe} \\ \text{R}^1 \end{array} \\ \text{R}^2 \end{array} \rightarrow \begin{array}{c} \text{MeO} \\ \text{R}^1 \end{array} \rightarrow \begin{array}{c} \text{C} \begin{array}{c} \text{N} \\ \text{R}^3 \end{array} \begin{array}{c} \text{N} \\ \text{R}^4 \end{array} \end{array} \]

Figure 13

In 1973 the field of transition metal alkylidene chemistry was born. In the course of an attempted synthesis of pentakisneopentyl tantalum(V), Schrock instead isolated the complex \((\text{tBuCH}_2)_3\text{Ta} = \text{CtBu}(\text{H})\) (Fig. 14), a tantalum neopentylidene derivative.
While at the same time Fred Tebbe found that treatment of \( \text{Cp}_2\text{TiCl}_2 \) with trimethylaluminium afforded a "masked" form of the titanium methylene complex, \( \text{Cp}_2\text{Ti}≡\text{CH}_2 \) (Fig. 15). Indeed, in its reaction chemistry this adduct behaves as though it were a free methylene complex and it is because of this that "the Tebbe-Grubbs reagent" has assumed considerable importance in synthetic organic chemistry.

In contrast to the Fischer carbenes, the alkylidene ligands behave chemically as carbon nucleophiles. A feature of alkylidene reactivity is the tendency to undergo "Wittig-like" olefination reaction with organic carbonyl compounds. In a pioneering study, Schrock demonstrated that the tantalum neopentylidene complex of figure 14 would promote carbonylolefination of aldehydes and ketones in direct analogue to phosphorus ylides (Equ. 1).

Significantly, several types of carbonyl compounds that do not react readily with Wittig reagents would undergo Wittig-like reactions with the tantalum reagent. These include esters, amides and \( \text{CO}_2 \).
Alkylidene catalysts are proposed to be involved in the olefin metathesis reaction (Equ. 2),\textsuperscript{41} and ring-opening polymerisation, utilising a homogeneous catalyst (Equ. 3).\textsuperscript{42} It has been suggested by Green, Rooney and coworkers\textsuperscript{43} that Ziegler-Natta olefin polymerisation may in some cases proceed via the intermediacy of alkylidene species.

\[ 2 \text{CH}_3\text{CH} \equiv \text{CH}_2 \xrightleftharpoons{\text{cat}} \text{H}_2\text{C} \equiv \text{CH}_2 + \text{CH}_3\text{CH} \equiv \text{CHCH}_3 \]

Equation 2

\[ \uparrow \text{cat} \]

\[ (\equiv \text{CH(CH}_2)_2\text{C} \equiv \text{CH})_n \]

Equation 3

Carbyne and Alkylidyne Complexes:

Although there seems to be a chemical basis for distinguishing between the low-valent carbynes on the one hand and the d\textsuperscript{0} alkylidyines on the other, the distinction is less clear cut than in the case of the carbene/alkylidene dichotomy. One complication arises in assigning the oxidation state of these species. Alkylidyne ligands (Fig. 16) have been described as CR\textsuperscript{3-}, CR neutral and CR\textsuperscript{+}, so there is often an ambiguity in assigning oxidation states in alkylidyne compounds. The description of the alkylidyne ligand as CR\textsuperscript{3-}, is most accurate in high oxidation state complexes of electropositive metals such as tantalum or tungsten. As CR\textsuperscript{3-}, the alkylidyne ligand is a better π-donor than N\textsuperscript{3-}, NR\textsuperscript{2-} and O\textsuperscript{2-}; when taken as CR\textsuperscript{+} it is a better π-acceptor than CO.\textsuperscript{44}

\[ M \equiv \text{C} \rightleftharpoons \text{R} \]

Figure 16
The first carbyne complex reported were the complexes \( \text{M(=CR)(CO)}_4X \) (\( \text{M=Cr, Mo, W; Fig. 17} \)) in 1973 by Fischer et al.\(^4\) Five years later, Schrock\(^4\) reported the synthesis of the neutral d\(^0\) alkylidyne complex shown in figure 18.

![Figure 17](image17.png)  
![Figure 18](image18.png)

Studies of alkylidyne complexes have afforded the first well-defined catalysts for acetylene metathesis and suggest that known catalysts for this reaction may be converted to alkylidyne species under the right conditions.\(^4\) Equation 4 shows the reaction of \( \text{W(=CtBu)(dme)(OR)}_3 \) with 3-hexyne to give a tungstenacyclobutadiene complex, \( \text{W(C}_3\text{Et}_3)(\text{OR})_3 \), which can act as a catalyst for the metathesis of disubstituted acetylenes.

![Equation 4](image4.png)

**Terminal Imido Complexes:**

Terminal imido complexes (Fig. 19) are currently known for all the metals of vanadium through iron triads plus iridium.
In 1956 the first organoimido transition metal complex, t-butylimidotrioxo osmium(VIII), was reported by Clifford and Kobayashi. By 1962 an extensive series of arylimido rhenium complexes (Fig. 20) was known. A review surveying organoimido chemistry through to 1994 has been published.

The imido ligand can be considered to bond to a transition metal with one σ and either one or two π interactions. Simple valence bond descriptions suggest that the metal-nitrogen bond order can be inferred from the position of the substituent, at least to a first approximation. A linear M-N-R unit implies that there is a metal-nitrogen triple bond (A; Fig. 21), while substantial bending of the M-N-R linkage (B; Fig. 21) indicates the presence of a lone pair on the nitrogen and is usually taken as evidence for a reduced bond order. However, a linear M-N-R unit with a bond order between 2 and 3 (C; Fig. 21) cannot be ruled out and as such reference to the bond order based on the M-N-R angle must be viewed with caution.
Most structurally characterised M-N-R moieties are near linear suggesting A and C of figure 21. In C, the M=N double bond is maintained if symmetry restrictions (or perhaps a severe energetic mismatch with available metal orbitals) do not allow lone-pair donation. However, in most systems, lone-pair p(\(\pi\))\(\rightarrow\)M(d) donation is very effective leading to the linear structure depicted in A with a M–N bond order approaching 3.

The t-butylimidotrioxoosmium(VIII) complex and its analogues effect the cis vicinal oxyamination (Equ. 5) of a variety of alkenes in either a stoichiometric or catalytic manner.\(^{52}\) Subsequently the synthesis of di, tri and even tetra-imido analogues of osmium tetraoxide have been reported that promote the corresponding vicinal diamination reaction.\(^{53}\)

\[
\begin{align*}
&\text{CH}_2=\text{CHCH}_3 + 1.5 \text{O}_2 + \text{NH}_3 \xrightarrow{\text{cat} \ 450^\circ\text{C}} \text{CH}_2=\text{CHC}≡\text{N} + 3 \text{H}_2\text{O}
\end{align*}
\]

Equation 6
Weiss and coworkers\textsuperscript{54} have utilised imido complexes to catalyse the exchange of imide groups in carbodiimides (Equ. 8). This “aza analogue” of olefin metathesis appears to proceed by a four-center mechanism as shown in equation 9.

\[
RN\equiv C\equiv NR + R'N\equiv C\equiv NR' \quad \xrightarrow{\text{Cl}_4W\equiv NR} \quad 2\ RN\equiv C\equiv NR'
\]

Equation 8

\[
\begin{array}{c}
\text{Q} \\
\text{M}
\end{array} + \begin{array}{c}
\text{X} \\
\text{Y}
\end{array} \xrightarrow{} \begin{array}{c}
\text{Q} \\
\text{X} \\
\text{M} \\
\text{Y}
\end{array} \xrightarrow{} \begin{array}{c}
\text{Q} = \text{X} \\
+ \\
\text{M} = \text{Y}
\end{array}
\]

Equation 9

Organoimido ligands have come into their own as ancillary ligands in organometallic chemistry and homogeneous catalysis. Of particular interest is Schrock’s use of the arylimido ligand in figure 22. The tungsten complex in figure 22 (R\textsubscript{f}=OCMe[CF\textsubscript{3}]\textsubscript{2}) is a highly active, neutral olefin metathesis catalyst.\textsuperscript{54c}

\[
\begin{array}{c}
\text{ArN} \equiv \text{W} \equiv \text{CH}^\text{Bu} \\
\text{R_fO} \quad \text{OR_f}
\end{array}
\]

Figure 22
Synthetic methods for introducing terminal imido ligands

There are numerous methods for the synthesis of terminal imido complexes. The most common are listed below.

1) N-H bond cleavage in amines/amides
2) N-Si bond cleavage in silylamines/silylamides
3) from isocyanates, phosphinimines, sulfinylamines, carbodiimides, organoimines and related reagents that contain element=N double bonds
4) with organic azides, N$_3$R
5) from transition metal-imido species
6) methods of limited synthetic use;
   (i) with azo compounds, RN=NR
   (ii) reaction involving nitriles
   (iii) electrophilic attack on a nitrido ligand
   (iv) from a metallaaziridine precursor
   (v) from cleavage of hydrazines and
   (vi) from arylnitroso compounds.

Methods 1 and 2 involve cleavage of a nitrogen α-substituent single bond, 3 and 5 are imido metathesis via net [2+2] reaction with no change in metal oxidation state, 4 and 6(i) involve reagents that can transfer NR with oxidation of the metal center. Each of the above methods is discussed briefly below.

1) N-H bond cleavage in amines/amides:
   These can be considered amine or amido deprotonation reactions with a chloride, amide, oxide or alkyl ligand serving as the proton acceptor, or as a formal α-H “abstraction” or “elimination”.
Typical strongly basic leaving groups have been σ alkyl substituents or dialkylamido ligands as shown in equations 10-12.\textsuperscript{57}

\[
\text{Ta(NMe}_2\text{)}_5 + \text{tBuNH}_2 \rightarrow \text{Me}_2\text{NH} \quad \text{Equation 10}
\]

\[
\text{Cp}^*\text{TaMe}_3\text{Cl} + \text{LiNH}^\text{Bu} \rightarrow \text{Cp}^*\text{Ta(NBu)}\text{Me}_2 \quad \text{Equation 11}
\]

\[
\text{W(=NAr)(NEt}_2\text{)Cl}_3(\text{thf}) + \text{LiNHAr} \rightarrow \text{W(=NAr)}_2\text{Cl}_2(\text{thf})_2 \quad \text{Equation 12}
\]

Steric congestion is frequently a critical factor in promoting formation of ligand-metal multiple bonds. For example the complex Mo(NHR)$_2$(OSiMe$_3$)$_4$ (R=1-adamantyl, Fig. 23a) is robust and has been characterised structurally.\textsuperscript{58} Efforts to prepare the complex with R=t-butyl have instead afforded Mo(=NR)$_2$(OSiMe$_3$)$_2$ (Fig. 23b).
Synthesis involving the interconversion of a terminal oxo ligand to the imido ligand with loss of H$_2$O is illustrated in equations 13 (L=PEt$_2$Ph)$^{49}$ and 14.$^{59}$

\[
\begin{align*}
\text{Cl-Re=O} + \text{PhNH}_2 & \rightarrow \text{Cl-Re=NPh} \\
\text{Cl-Re=O} + \text{LiNHPh} & \rightarrow \text{Cl-Re=NPh} \\
\end{align*}
\]

Equation 13

\[
\begin{align*}
\text{OsO}_4 + \text{tBuNH}_2 & \rightarrow \text{Os(NtBu)} \\
\end{align*}
\]

Equation 14

The d$^2$ complex Cp$^*$$_2$TaCl(thf) has proven to be a useful precursor for d$^0$ imido complexes by replacement of chloride by [NHR]$^-$, followed by α-H elimination from d$^2$ “Cp$^*$$_2$TaNHR” to form the complexes Cp$^*$$_2$Ta(=NR)H (Equ. 15).$^{60}$

\[
\begin{align*}
\text{Cp}^*\text{TaCl(thf)} + \text{LiNHPh} & \rightarrow \text{Cp}^*\text{Ta(=NPh)H} \\
\end{align*}
\]

Equation 15

A special case among α-H transfer reactions is that in which the proton (or hydrogen) acceptor is itself another multiply bonded ligand. For example the tungsten alkylidyne complex (Equ. 16) can be converted to the imido/alkylidene complex.$^{61}$

Equation 16
2) N-Si bond cleavage in silylamines/silylamides:

The strong bonds that form between silicon and oxygen or halides makes these ligands the most common acceptor in a SiR₃ group transfer that effects cleavage of a N-Si bond. The typical side-products from such reactions are volatile species such as Me₃SiCl or Me₃SiOSiMe₃, which can simply be distilled away with the solvent. The silicon based approach has been particularly productive for synthesis of imido compounds. An early example was Winfields synthesis of a tungsten methylimido species shown in equation 17. The reaction of Me₃SiNHtBu with NH₄VO₃ affords V(=NtBu)(OSiMe₃)₃ and reaction of (Me₃Si)₂NMe with CpNbCl₄ forms the imido complex CpNb(=NMe)Cl₂. A further example with Me₃SiNHtBu is shown in equation 18.

\[
\text{WF}_6 + (\text{Me}_3\text{Si})_2\text{NMe} \xrightarrow{\text{MeCN}} \text{MeC≡N} \quad \xrightarrow{\text{2 Me}_3\text{SiF}} \quad \text{MeC≡N} \quad \xrightarrow{\text{W≡NMe}}
\]

Equation 17

\[
\text{CrO}_2\text{Cl}_2 + \text{Me}_3\text{SiNHtBu} \rightarrow \text{Cr(=NtBu)₂(OSiMe₃)₂}
\]

Equation 18

3) from reagents that contain element=N double bonds:

These reactions involve the direct replacement of an existing multiply bonded ligand by another upon treatment with an unsaturated reagent, as shown in equation 19. Isocyanates (RN=C=O), phosphinimines (R₃P=NR), sulfinylamino (RN=S=O), carbodiimides (RN=C=NR), organoimines (RN=CHR) and related reagents that contain element=N double bonds have all been observed to react with metal-ligand double bonds (especially M=O) in metathesis reactions.
A most intriguing application of this method was in the synthesis of di- and tri-imido analogues of osmium tetraoxide by Sharpless and coworkers.\textsuperscript{53} Triphenylphosphinimines were sufficiently reactive to introduce two imido substituents but the third imido requires the more reactive tributylphosphinimine (Equ. 20).

\begin{equation}
\text{OsO}_4 \quad 2 \text{Ph}_3\text{P}=\text{NR} \quad -2 \text{Ph}_3\text{PO} \quad \text{OsO}_2(\text{NR})_2 \quad \text{Bu}_3\text{P}=\text{NR} \quad -\text{Bu}_3\text{PO} \quad \text{OsO}(\text{NR})_3
\end{equation}

Equation 20

The isocyanate route was first used by Soviet workers to convert $L_2\text{Cl}_3\text{Re}=\text{O}$ to $L_2\text{Cl}_3\text{Re}=\text{NPh}$ ($L=\text{PPhEt}$)\textsuperscript{65} Subsequently this has developed into an important synthetic method, since the products (Equ. 21) are themselves versatile starting materials for a wide range of other imido species.\textsuperscript{66}

\begin{equation}
\text{M(O)Cl}_n + \text{PhNCO} \quad \Delta \quad \text{M(NPh)Cl}_n + \text{CO}_2
\end{equation}

Equation 21

The conversion of alkylidene complexes into their imido analogues has been exploited by Schrock and coworkers. As shown in equation 22, treatment of group five neopentyldene complexes ($M=\text{Nb, Ta}; X=\text{Cl, Br}$) with benzylidene alkylamine, $\text{PhCH}=\text{NR}$, affords the corresponding organoimido complexes, with concomitant loss of the olefin.\textsuperscript{67}
4) with organic azides, \( \text{N}_3\text{R} \):

The decomposition of azides with formation of dinitrogen is a broadly useful synthetic route to imido complexes.\(^{68}\) The extrusion of \( \text{N}_2 \) as a side-product results in easy product isolation as well as providing a large driving force for such reactions. Equations 23 and 24 show reactions of azides with \( \text{R} \) being \( \text{Me}_3\text{Si} \) and \( p\)-tolyl respectively. This method requires the oxidation state of the metal to be increased by 2 units.

\[
\text{Cp}_2\text{V} + \text{N}_3\text{Me}_3\text{Si} \rightarrow \text{Cp}_2\text{V}(\text{NSiMe}_3) + \text{N}_2
\]

Equation 23

\[
\text{MoCl}_4(\text{thf})_2 + \text{N}_3\text{tol} \rightarrow \text{Mo}(\text{Ntol})\text{Cl}_4(\text{thf}) + \text{N}_2
\]

Equation 24

5) from transition metal-imido species:

It has recently been discovered that transition metal imides can undergo facile, bimolecular exchange with other multiply bonded ligands.\(^{50}\) The reaction can be considered to proceed in a “Wittig-like” manner as given in equation 25 (c.f. Equ. 19).

\[
\begin{array}{c}
\text{M} + \left[ \begin{array}{c}
\text{M} \\
\text{Q} \\
\text{Q} \\
\text{M}'
\end{array} \right] \\
\rightarrow \text{M} \equiv \text{Q}' + \text{Q} \equiv \text{M}'
\end{array}
\]

Equation 25
Imido ligand exchange proceeds at room temperature for the four-coordinate species $\text{Mo(}\text{N}^\text{tBu}_2\text{)(O}^\text{tBu}_2\rangle$ and $\text{Mo(NR}_2\text{)(O}^\text{tBu}_2\rangle$ (Equ. 26) and even more rapidly for the oxo-imido ligand exchange shown in equation 27.\textsuperscript{64c} The latter reaction is believed to involve an ordered transition state, involving bridged oxo and imido ligands (Fig. 24) and in general keeping with the four-center mechanism (Equ. 25).\textsuperscript{64c}

![Equation 26](image)

\textbf{Equation 26}

![Equation 27](image)

\textbf{Equation 27}

![Figure 24](image)

Figure 24

Finally the exchange of alkylidene for imido ligands has been observed according to the reaction shown in equation 28.\textsuperscript{64c}

![Equation 28](image)

\textbf{Equation 28}
6) methods with limited synthetic use:

(i) with azo compounds, RN=NR:

Azoalkanes can be cleaved by low-valent metals to give organoimido complexes. For example, equation 29 proceeds for both niobium and tantalum to give chloride-bridged imido dimers as structurally characterised products.\(^{69}\) However, the reaction is limited to the use of azobenzene in the vast majority of cases.\(^{70}\)

\[
\text{Ta}_2\text{Cl}_6(\text{SMe}_2)_3 + \text{PhN}=\text{NPh} \rightarrow -\text{Me}_2\text{S} \]

Equation 29

(ii) reaction involving nitriles:

Titanocene metallacyclobutanes react with nitriles in the presence of a lewis base such as trimethylphosphine to afford vinylimido complexes of titanocene. The reaction of \(\text{Cp}_2\text{Ti}(\mu-\text{CH}_2)(\mu-\text{Cl})\text{AlMe}_2\), \(\text{N}=\text{CR}\) (\(\text{R}=\text{tBu}, 1\text{-ad}\)) and excess \(\text{PMe}_3\), in the presence of DMAP (to scavenge \(\text{AlMe}_2\text{Cl}\)) afford the vinylimido complexes shown in equation 30.\(^{72}\) These compounds also arise from the reaction of titanacyclobutane \(\text{Cp}_2\text{Ti}[-\text{CH}_2\text{CH(tBu)}\text{CH}_2]\) with \(\text{N}=\text{CR}\) and excess \(\text{PMe}_3\).\(^{72}\)

\[
\text{Cp}_2\text{Ti}(\mu-\text{CH}_2)(\mu-\text{Cl})\text{AlMe}_2 + \text{N}=\text{CR} + \text{PMe}_3 \rightarrow \text{Cp}_2\text{Ti}[=\text{NC}(=\text{CH}_2)\text{tBu}](\text{PMe}_3)
\]

Equation 30

Tantalum alkylidene complexes have been shown to react with nitriles with formation of an imido ligand (\(\text{R}=\text{Me}, \text{Ph}; \text{Equ. 31}\)).\(^{71}\) This is however, a rare example, with no subsequent reports of other alkylidene complexes reacting in this way.
(iii) electrophilic attack on a nitrido ligand:

The complexes (dmtc)$_3$Mo=N, where dmtc is dimethyldithiocarbamate, apparently contain an unusually electron-rich nitrido ligand that can be alkylated even with methyl iodide to afford a cationic methylimido compound, [(dmtc)$_3$Mo=NMe]$^+$. A number of other alkylating and acylating agents react similarly, including PhCOCl, [R$_3$O]BF$_4$, [Ph$_3$C]BF$_4$ and even 2,4-dinitrophenyl chloride.$^{73}$

One notable example is the alkylation of the nitrido ligand in [n-Bu$_4$N][Ru(=N)(CH$_2$SiMe$_3$)$_4$]. Treatment of the complex with Me$_3$SiOTf (Et$_2$O, -30°C) affords oily, orange crystals of Ru(=NSiMe$_3$)(CH$_2$SiMe$_3$)$_4$ in 92% yield (Equ 32). This was the first characterised ruthenium-imido complex.$^{74}$

(iv) from a metallaaziridine precursor:

Takahashi et al. have reported that treatment of TaCl$_5$ with lithium diethylamide at low temperature produces an η$_2$-Schiff’s base derivative ethyliminoethyl-(C,N)tris(diethylamido)tantalum.$^{75}$ On heating to 100°C, this complex undergoes clean first order loss of ethylene to afford the ethylimido compound (Equ. 33). Although this synthetic route is rare, a recent example resulting in the formation of a metallacycle imido ligand was reported in 1992.$^{76}$
(v) from cleavage of hydrazines:

A series of organoimido complexes have been prepared by the cleavage of unsymmetrical acyl hydrazines according to equation 34 (R=alkyl, aryl; L=PMePh₂, PE₂Ph). The cleavage of symmetrical hydrazines has been used to synthesize alkylimido rhenium complexes. Although the mechanism of the reaction is unknown, the reaction is suggested to follow equation 35. This method is rare with the molybdenum and rhenium examples constituting its use to date.

\[
\text{Mo(O)Cl}_2\text{L}_3 + 2\text{RCNHNHAr} \rightarrow \begin{align*}
\text{Cl} & \text{Cl} \\
\text{O} & \\
\text{C} & \text{R} \\
\text{Ar} & \\
\text{N} & \\
\text{N} & \\
\text{L} & \\
\text{Ar} & \\
\text{N} & \\
\text{N} & \\
\text{L} & \\
\text{Ar} & \\
\text{N} & \\
\text{N} & \\
\text{L} & \\
\text{Ar} & \\
\end{align*}
\]

Equation 34

\[
\text{Re(O)Cl}_3(\text{PPh}_3)_2 + \text{MeNHNHMe.2HCl} \xrightarrow{\text{PPh}_3 - \text{PH}_3\text{PO}} \text{Re(NMe)Cl}_3(\text{PPh}_3)_2 + \text{MeNH}_3\text{Cl}
\]

Equation 35

(vi) from arylnitroso compounds:

In a paper by Cotton et al., was the first reaction of a nitroso compound, nitrosobenzene (C₆H₅NO) with W₂(OCH₃)₆ (Equ. 36). This gave a product in which a remarkable double oxidative addition has occurred leading to the formation of W≡N double
bonds with concomitant loss of the W=W bond. The arylnitroso-ligand, ONtol, of Re(ONtol)Cl$_3$(OPPh$_3$) can easily be deoxygenated by transferring the oxygen to a reducing agent such as tertiary phosphine, PPh$_3$ (Equ. 37) or cyclohexyl isocyanide. The reaction with triphenylphosphine requires acetonitrile as solvent.

\[
\text{W}_2(\text{O}^\text{Bu})_6 + \text{ONPh} \rightarrow \text{W} = \text{W} \quad \text{PhN}
\]

Equation 36

\[
\text{Re}(\text{ONtol})\text{Cl}_3(\text{OPPh}_3) + 3 \text{PPh}_3 \rightarrow \text{Re}(=\text{Ntol})\text{Cl}_3(\text{PPh}_3)_2 + 2 \text{OPPh}_3
\]

Equation 37

**Known metal terminal imido complexes of Os(II), Ir(III) and Ruthenium**

This section summaries the known imido-metal functional groups of ruthenium and emphasises complexes of d$^6$ Os=NR and d$^6$ Ir=NR. Presented in table 1 are the known terminal imido complexes of the transition metals. For descriptions of each functional group listed in table 1, refer to the excellent review “Organoimido Complexes of the Transition Metals” by David E. Wigley.
Table 1: Terminal imido functional groups

- Low valent iridium and osmium

In 1989 Bergman et al. reported the first examples of an iridium imido complex. Reacting dimeric \([\text{Cp}^*\text{IrCl}_2]\) with 4 equiv of LiNH\(_2\)Bu affords yellow crystals of monomeric \(\text{Cp}^*\text{Ir}=\text{NR}\) in high yield, along with the by-product \(\text{H}_2\text{NH}_2\)Bu.\(^{81}\) The complexes \(\text{Cp}^*\text{Ir}=\text{NR}\) \([\text{R}=\text{SiMe}_3\text{Bu}, 2,6\text{-dimethylphenyl (Ar") and 2,6-diisopropylphenyl (Ar)}]\) are all similarly prepared. Although \(\text{Cp}^*\text{Ir}=\text{NAr}"\) and \(\text{Cp}^*\text{Ir}=\text{NAr}\) have been prepared by reacting \(\text{Cp}^*\text{IrCl}_2\text{Ar"NH}_2\) and \(\text{Cp}^*\text{IrCl}_2\text{ArNH}_2\) with \(\text{K}[\text{N(SiMe}_3)_2]\) or from imido exchange between \(\text{Cp}^*\text{Ir}=\text{N}_2\)Bu and free \(\text{H}_2\text{NR (R=Ar" or Ar)}\), which also forms \(\text{H}_2\text{N}_2\)Bu.\(^{81a}\) Despite the formal oxidation state and the low coordination number of the Ir(III) compounds, they were found to be monomeric by X-ray diffraction studies. Shown in figure 25 is the crystal structure of \(\text{Cp}^*\text{Ir}=\text{NAr}\), which has a \text{Ir-N-C} angle of 174.0(6)°.
While many osmium imido complexes are known, very few examples of low valent osmium imides have been characterised. One exception is the d^6 complexes reported by Bergman in 1991. These osmium complexes resulted from an extension of the Cp^*Ir=NR chemistry, to the group 8 metals.

The known d^6 compounds are all formed from the reactions of LiNHR, where R is tBu, Ar or Ar'' with the halide precursors [(η^6-arene)OsCl_2]_2 (η^6-arene=C_6Me_6 or cym) or with imido exchange from the N^3Bu to the NAr'' imido ligand. Thus, [(η^6-arene)OsCl_2]_2 reacts with 2 equiv of LiNH^3Bu per osmium to form the d^6 compounds (η^6-arene)Os=N^tBu, which can then react with NH_2Ar'' to form (η^6-arene)Os=NAr'' and NH_2^4Bu. The complex (η^6-C_6Me_6)Os=N^3Bu was shown to be monomeric by a crystal structure determination (Fig. 26). The complexes (cym)Os=N^4Bu and (cym)Os=NR (R=Ar or Ar'') are inferred to be monomeric on the basis of spectroscopic data.
The chemistry of ruthenium imides has developed slowly compared to that of osmium, with only a handful of compounds known. A number of bridging imido ligands have been identified in clusters. But it was not until 1992 that the first X-ray structure of a terminal mononuclear imido complex of ruthenium was reported.

The first characterised ruthenium-imido complex was reported by Shapley and coworkers\(^\text{74}\) in 1988. Alkylation of the nitride ligand in \([n-\text{Bu}_4\text{N}][\text{Ru}(\equiv\text{N})(\text{CH}_2\text{SiMe}_3)_4]\) with \(\text{Me}_3\text{SiOTf}\) affords oily, orange crystals of \(\text{Ru}(\equiv\text{NSiMe}_3)(\text{CH}_2\text{SiMe}_3)_4\) in 92% yield. This complex is difficult to characterise due to its extreme air and moisture sensitivity. Both ruthenium nitride anions \([\text{Ru}(\equiv\text{N})(\text{CH}_2\text{SiMe}_3)_4]^-\) and \([\text{Ru}(\equiv\text{N})\text{Me}_4]^-\) can be methylated using MeI, \([\text{Me}_3\text{O}][\text{BF}_4]\) or MeOTf, but the resulting products are thermally unstable.

Wilkinson and coworkers\(^\text{83}\) described the reaction of \(\text{Ru}_2(\mu-\text{O})_2(\text{CH}_2\text{SiMe}_3)_6\) with \(\text{PhNCO}\) to generate brown, microcrystalline \(\text{Ru}_2(\equiv\text{NPh})_2(\text{CH}_2\text{SiMe}_3)_6\) in moderate yield. While its structure is not known, a strong I.R. band at 1132 cm\(^{-1}\) is assigned as a terminal imido \(\nu(\text{Ru}=\text{N})\) band, however, a structure containing asymmetrically bridged \(\mu\)-NPh groups cannot be ruled out in view of the problems with such I.R. assignments.\(^\text{84}\) A similar reaction
of Ru₂(µ-O)₂(CH₂SiMe₃)₆ with Me₃P=NSiMe₃ affords orange crystals of Ru₂(=NSiMe₃)₂(CH₂SiMe₃)₆ in low yield.₈³

Terminal imido complexes of Ru(IV) are proposed on the basis of only indirect evidence. Thus, electrochemical experiments in which the oxidation of ammonia to nitrate is observed lead to the proposal that unstable [Ru(NH₃)(tpy)(bpy)]³⁺ undergoes disproportionation to form the imido complexes [Ru(=NH)(tpy)(bpy)]²⁺ and [Ru(NH₃)(tpy)(bpy)]²⁺.₈⁵

Although not directly observed, there is compelling evidence for the participation of d² Ru(=NR)₂ complexes in a number of reactions. For example, the reaction of [PPh₄]-[RuO₂Cl₃] with excess tBuNCO leads to the isolation of the nitrido salt [PPh₄]-[N≡Ru(N≡BuC(O)≡Bu)Cl₂] (Equ. 38).₈⁶ This complex is proposed to arise via the intermediacy of an imido complex such as [Ru(=N≡Bu)₂Cl₃]⁻, which cycloadds another isocyanate to form the N,N'-ureato ligand (Equ. 38).

\[
\text{[RuO}_2\text{Cl}_3^- \text{] + 2 tBuNCO} \rightarrow \text{[N≡Ru(N≡BuC(O)≡Bu)Cl}_2\text{]-[HCl]+Me}_2\text{C}=\text{CH}_2}
\]

Equation 38
The only example of the $d^4 \text{Ru}(=\text{N}R)_2$ moiety was reported in 1992 by Wilkinson and coworkers.\textsuperscript{87} The reaction of trans-RuCl$_2$(PMe$_3$)$_4$ with an excess of LiNHAr in THF, afforded an orange solution containing an amido species. Upon O$_2$ oxidation, a blue-green solution forms that affords blue crystals of diamagnetic trans-Ru(=NAr)$_2$(PMe$_3$)$_2$ in 16% yield. The structure of this complex reveals a square-planar derivative in which the molecule lies on a center of symmetry with trans imido groups (Fig. 27).

![Figure 27](image_url)

In summary, only a handful of ruthenium terminal imido complexes are known, with only one fully characterised. In contrast numerous terminal imido complexes of osmium from $d^0$ to $d^6$ have been reported. Also fully characterised terminal imido complexes are known for $d^6$ Os and $d^6$ Ir. It is therefore reasonable that similar complexes should exist for ruthenium and rhodium. It appears that terminal imido complexes of rhodium are extremely reactive and as such no rhodium compounds have been reported.\textsuperscript{50} With a number of ruthenium terminal imido complexes known,\textsuperscript{50} it would seem reasonable that a terminal $d^6$ ruthenium imido complex should be stable. Thus, Schrock \textit{et al.} attempted the synthesis of "(C$_6$H$_6$)Ru=NAr" using the sterically demanding 2,6-diisopropylphenylimido (Ar) ligand. However, reaction of [(C$_6$H$_6$)RuCl$_2$]$_2$ with 4 equiv of LiNHAr in ether lead to the bridging imido complex, [(C$_6$H$_6$)Ru(µ-NAr)]$_2$, shown by X-ray diffraction.\textsuperscript{88}

This thesis presents the use of the sterically demanding imido ligands, 2,6-diisopropylphenyl (Ar) and 2,4,6-tert-butylphenyl (Ar'), to synthesize the first $d^6$ ruthenium
terminal imido complexes. The results obtained with the Ar' imido ligand has resulted in the recent publication of a paper.89