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Synthesis, Characterization and Reactivity of Molybdenum and Tungsten Imido Complexes of Relevance to Alkene Dimerization

Thesis submitted for the Degree of Doctor of Philosophy

By

William R.H. Wright, M.Chem. (Durham)

In the Department of Chemistry
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January 2009
Statement

This thesis is based on work conducted by the author, in the Department of Chemistry at Durham University, during the period October 2005 to September 2008.

All work described in this thesis is original, unless otherwise acknowledged in the text or in the references. None of this work has been submitted for another degree in this or any other University.

Signed: William Wright

Date: 03/04/2009

William Wright
Abstract

Title: Synthesis, Characterization and Reactivity of Molybdenum and Tungsten Imido Complexes of Relevance to Alkene Dimerization

Author: William Wright

This thesis describes a range of investigations undertaken with the aim of increasing insight into alkene dimerization systems formed via reaction of WCl₆ and an aniline.

Chapter 1 introduces alkene dimerization systems based on reaction of WCl₆ with an amine and an Et₃AlCl₃-x co-initiator. As imido complexes are postulated to form in situ in such WCl₆-based dimerization systems, the imido chemistry of group VI has briefly been reviewed. Finally the aims of this work are outlined.

Chapter 2 outlines a comparative investigation, examining the capacity of a range of discrete molybdenum and tungsten imido pre-catalysts to initiate ethylene dimerization. This has enabled for the first time direct comparison as to the relative activities of each type of imido complex. With the aim of establishing the nature of the initiator complex formed in situ, a range of discrete imido complexes were reacted with the co-initiators EtAlCl₂ and Et₃Al₂Cl₃ in the absence of any alkenes. Furthermore, the relative capacities of EtAlCl₂, Et₃Al₂Cl₃ and EtMgCl to activate mono(imido) complexes for propylene and ethylene dimerization were assessed. Lastly, WCl₆ was reacted with an aniline using similar conditions to those employed in the preparation of WCl₆-based initiator solutions.

Chapter 3 outlines the reactions of discrete bis(imido) chloride complexes with Me₄AlCl₃-x reagents. This study was undertaken with the aim of clarifying the mode by which bis(imido) complexes are activated for ethylene dimerization by the co-initiator EtAlCl₂. During this investigation a new class of complexes, with the general formula M[N(Ar)AIMe(x-1)Cl(3-x)(μ-Cl)](NAr)Me₂ (M = Mo or W) were discovered. These dimethyl compounds result from coordination of a Me₄AlCl₃-x (x ≥ 1) fragment to an imido ligand. Furthermore, the reactivity of these new complexes with both Lewis bases and Lewis acids was examined. Finally, a number of ethylene dimerization systems were identified based on bis(imido) complexes.

Chapter 4 examines the reactivity of discrete mono(imido) chloride complexes with Me₄AlCl₃-x reagents. It was determined that in contrast to the bis(imido) complexes examined in Chapter 3, coordination of Me₄AlCl₃-x groups to mono(imido) ligands was disfavoured. Instead, a range of adducts were formed via coordination of Me₄AlCl₃-x fragments to tungsten chloride ligands. Next, attention turned to assessing the capacity of Me₄AlCl₃-x reagents to activate mono(imido) complexes for ethylene dimerization.

All the experimental details and supporting information and data for this thesis are presented in Chapter 5. In Chapter 6 further possible investigations are outlined.
Acknowledgements

I wish to thank my supervisor Dr. P.W. Dyer for his help, encouragement and patience. Thanks must also be extended to my collaborators Dr. M.J. Hanton and Professor R.P. Tooze of Sasol Technology UK Ltd for practical input and financial support. I also would like to thank Dr A.K. Hughes and Dr K.B. Dillon for helpful discussions. Furthermore, I must acknowledge Dr. A.S. Batsanov for obtaining molecular structures. I am also grateful for the assistance of Dr. A. Kenwright, Mr I. McKeag and Mrs C. Heffernan (NMR) as well Mrs L. Turner and Dr. M. Jones (MS). In addition I am indebted to Mrs J. Dorstal and Mrs J. Magee for providing combustion analysis.

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## Abbreviations used in the text

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<td>C3D4</td>
<td>Trideuterocyclopropane</td>
</tr>
<tr>
<td>C2H4</td>
<td>Ethylene</td>
</tr>
<tr>
<td>C2D4</td>
<td>Dideuterocyclopropane</td>
</tr>
<tr>
<td>WCl6</td>
<td>Hexachloro-Wolframium (VI)</td>
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Abbreviations used in the text

Ar = 2,6-Diisopropylphenyl
Bu’ = tert-Butyl
Bz = Benzyl
COSY = Correlated Spectroscopy
CP MAS NMR = Cross-Polarised Magic Angle Spinning NMR
Cp = C₅H₅
Cp⁺ = C₅Me₅
CSD = Cambridge Structural Database
Cy = Cyclohexyl
DCM = Dichloromethane
DEPT = Distortionless Enhancement by Polarisation Transfer
DME = 1,2-Dimethoxyethane
DPPE = Diphenyl Phosphino Ethane
EI = Electron Ionisation
ES = Electrospray
Et = Ethyl
FMES = 2,4,6 tris(trifluoromethyl) phenyl
GC = Gas Chromatography
GCMS = Gas Chromatography Mass Spectrum
h = hour
hh = head-to-head olefin dimerization product
HOMO = Highest occupied Molecular Orbital
ht = head-to-tail olefin dimerization product
LUMO = Lowest Unoccupied Molecular Orbital
M = Generic transition metal, unless otherwise stated.
MAO = Methylaluminoxane
MAS = Magic Angle Spinning
Me = Methyl
MMAO = Modified Methylaluminoxane
MMA = Methyl Methacrylate
MO = Molecular Orbital
MS = Mass Spectrometry
m/z = Mass/charge ratio
NMR = Nuclear Magnetic Resonance
NOESY = Nuclear Overhauser Effect Spectroscopy
OTf = Triflate
Ph = Phenyl
ppm = parts per million
'Pr= isopropyl
Py = Pyridine
R = Generic alkyl, aryl group
SHOP = Shell Higher Olefin Process
STUK = Sasol Technology UK Ltd
THF = Tetrahydrofuran
th = tail-to-head olefin dimerization product
TMEDA = N,N,N',N'-Tetramethylethylenediamine
TOF = Turnover Frequency
TON = Turnover Number
Tos = Tosylate
tt = tail-to-tail olefin dimerization product
VT NMR = Variable Temperature Nuclear Magnetic Resonance Spectroscopy
wt = weight %
XPS = X-ray photoelectron Spectroscopy

NMR Abbreviations

δ = chemical shift (in ppm)
b = broad signal
(s) = singlet
(d) = doublet
(t) = triplet
(m) = complex multiplet
Chapter 1 Introduction

1.0 The Significance of α-Olefin Manufacture and Dimerization

The production of α-olefins is of great industrial significance providing the raw materials for a range of applications, including, the manufacture of synthetic lubricants and surfactants. Furthermore, α-olefins have found application as monomers (particularly as co-monomers in polyethylene), with $10^8$ tons of polyolefins being consumed world wide per year.$^1$ α-Olefins are produced in a number of ways: the cracking and dehydrogenation of paraffins; from CO and H$_2$ via the Fischer-Tropsch process; dehydration of alcohols; electrolysis of straight chain C$_3$-C$_{30}$ carboxylic acids; dimerization and metathesis of olefins; and oligomerization of ethylene, the latter being the main method used for the production of C$_9$-C$_{30}$ olefins.$^2$

One important industrial processes by which linear α-olefins are produced via ethylene oligomerization is the Shell Higher Olefin Process (SHOP), in which nickel-based homogeneous catalysts are employed (Scheme 1.1).$^3$

Scheme 1.1 Ethylene oligomerization via SHOP-type nickel-based pre-initiators

Of significance is that ethylene oligomerization, via the SHOP and related processes, exclusively produces olefins containing even numbers of carbon atoms. This is in contrast to the Fischer-Tropsch process (Scheme 1.2) in which olefins are obtained from a C$_1$ unit ("syn-gas"), resulting in the formation of both odd- and even-numbered olefin products.$^4,^5$

Scheme 1.2 The Fisher-Tropsch process
The conversion of CO and H$_2$ into hydrocarbons via the Fischer-Tropsch reaction requires that the C-O bond of carbon monoxide is first broken, which occurs upon the surface of a heterogeneous catalyst. This is followed by C-H and C-C bond formation steps. Next, hydrogenolysis occurs, followed by hydrogenation forming a hydrocarbon which then dissociates from the metal surface (Scheme 1.3).^6

**Scheme 1.3 Simplified mechanism of hydrocarbon formation in the Fischer-Tropsch process**

Fischer-Tropsch synthesis is of great commercial importance, with South Africa alone using the process to manufacture approximately four million tonnes of hydrocarbon products a year.^[7] Depending on the reaction conditions, up to 25% of the material produced by Fischer-Tropsch synthesis can be comprised of C$_2$-C$_4$ olefins. Often the uses of these light products is restricted, for instance there is a limit to the amount of short chain hydrocarbons that can be accommodated in motor gasoline (which consists mainly of C$_5$-C$_{10}$ molecules). As such olefin dimerization or oligomerization provides a means to convert C$_2$-C$_4$ olefins into heavier products that can be included in liquid fuels.^[8]

Significantly, industrial processes, optimised to convert even-numbered olefins, into commercial products cannot readily utilize the odd-numbered olefins produced via Fischer-Tropsch synthesis. This is because odd-numbered olefins tend to have lower boiling points than those found for related even-number olefins.^[9] Hence, for a given process switching from an even-numbered to an odd-numbered olefin feedstock could potentially require significant plant re-engineering (e.g. the redesigning of distillation columns). Thus, dimerization of odd-numbered olefins has
the potential to produce heavier even-numbered olefins, compatible with optimised industrial processes that are based on the more common even-numbered olefins derived from ethylene.

1.1 Alternate Mechanisms of Transition Metal-initiated Olefin Dimerization

Dimerization of olefins by transition metal catalysts can proceed via one of three general mechanisms: degenerate polymerization, concerted coupling, or reductive dimerization. Degenerate polymerization, also referred to as the hydride cycle, (Scheme 1.4) is initiated by coordination of an olefin to a metal hydride, followed by formation of a metal–alkyl species via migratory insertion. Propagation and termination are achieved by sequential coordination and insertion (into the newly formed metal–carbon bond) of a second olefin, followed by reformation of the metal-hydride species by β-hydride elimination. Dissociation of the newly formed olefin then regenerates the metal initiator complex. A catalyst selective for olefin dimerization, not oligomerization, is obtained when the rate of termination exceeds the rate of propagation.

Scheme 1.4 General mechanism for ethylene dimerization via a hydride cycle
An example of an initiator known to dimerize α-olefins via a hydride cycle has been published by Small et al.\textsuperscript{11} In Small's dimerization system pyridine bis(imine) ligands are coordinated to FeCl\textsubscript{2}, giving a family of complexes, which when treated with excess MMAO (800 equivalents)\textsuperscript{1} can initiate but-1-ene or hex-1-ene dimerization, in high activity and selectivity for linear head-to-head products (Scheme 1.5).

**Scheme 1.5 Pyridine bis(imine) Fe\textsuperscript{II}-based hex-1-ene dimerization systems**

![Scheme 1.5](image)

An alternative means of achieving olefin dimerization is through reductive dimerization (Scheme 1.6). This process is observed when a metal alkyl complex is exposed to a pressure of H\textsubscript{2} gas or a reducing agent.\textsuperscript{12} It is reasoned that reductive dimerization occurs via one of two potential pathways, with the reducing agent acting as either a chain transfer agent (Scheme 1.6, Pathway A) or as a hydride source (Scheme 1.6, Pathway B).

**Scheme 1.6 Proposed mechanisms of reductive dimerization (R or R' = alkene moieties)**

**Pathway A**

\[
M-\text{R} + R' + H_2 \rightleftharpoons M-H + \text{Me-}R'
\]

**Pathway B**

\[
2 \left[ M-\text{R} \right] + 2 R' + \text{H}_2 \rightarrow M-M + 2R-\text{R'} + \text{H}_2 \rightarrow 2 \left[ M-H \right]
\]

\textsuperscript{1} MMAO = Modified metalumoxane (25% of methyl groups replaced by isobutyl)
Chapter 1: Introduction

The third olefin dimerization methodology commonly used is concerted coupling. Here, dimerization is initiated by coordination of two olefins to a electronically and coordinatively unsaturated metal centre and is followed by the generation of a metallacycle via oxidative coupling. Termination results from $\beta$-hydride elimination, followed by reductive elimination of the olefin (Scheme 1.7).

**Scheme 1.7 General mechanism of concerted coupling - via metallacycle formation**

One potential advantage associated with olefin dimerization *via* a concerted coupling mechanism, when contrasted with many degenerate polymerization initiators, would be no observable isomerization, which would enable both high selectivity and activity. Also, for processes that operate *via* a concerted coupling mechanism, high selectivity for the dimerization product is often obtained (although trimerization of ethylene proceeds *via* a related mechanism, the formation of metallacyclo-heptane intermediates is disfavoured in many systems).

In order for the concerted coupling mechanism to be effective, for dimerization there must be a sufficiently low energy barrier for a five-membered metallacycle to undergo $\beta$-hydride elimination. This is often believed to be disfavoured since five-membered rings are considered to be stabilized due to the chelate effect. Furthermore, the conformation of a five membered ring tends to orientate the $\beta$-hydrogen away from the metal, disfavouring $\beta$-hydride elimination. However, recent B3LYP density functional calculations on 16-electron ruthenium metallacycle complexes indicate that $\beta$-hydride eliminations from a five membered ring can in fact occur relatively readily. Indeed, many examples of early transition metal systems that are believed to catalyze the dimerization of olefins *via* a
concerted coupling mechanism are known, including those based on titanium butadiene (1) and tantalocyclopentate (2) complexes (Figure 1.1).

**Figure 1.1 Early transition metal dimerization initiators operating via a concerted coupling pathway**

Variations of complex 2 have been reported such as (Cp*)Cl₂Ta(cyclooctene) (3) (Cp* = η⁵-C₅Me₅), which also readily dimerizes olefins. Of significance is that when complex 3 initiates dimerization of 4,4-dimethyl-1-pentene, complete selectivity for the head-to-tail (ht) dimerization product 2,2,7,7-tetramethyl-3-methyleneoctane is obtained (Scheme 1.8).

**Scheme 1.8 Dimerization of 4,4-dimethyl-1-pentene**

The mechanism by which the tantalum based pre-catalysts 2 and 3 initiate olefin dimerization has been examined through the use of deuterium labelling study on model systems. This determined that olefin dimerization is initiated by the formation of a tantalacyclopentane ring, which then contracts via a hydride intermediate to give a metallocyclobutane. Fast degradation of the metallocyclobutane then liberates the product olefin (Scheme 1.9).
**Scheme 1.9 Concerted coupling via a Ta metallocyclobutane**

![Scheme 1.9 Concerted coupling via a Ta metallocyclobutane](image)

The formation of head-to-tail products in dimerization systems based upon complexes 2 and 3 is attributed to catalysis proceeding via formation of α,β-disubstituted metallacycles in preference to the α,α-analogues, which would result in tail-to-tail products. Thus, selectivity for the head-to-tail dimerization product can be attributed to carbon-carbon bond formation via a metallacycle intermediate, characteristic of a concerted coupling mechanism.

### 1.2 Recently Developed Ethylene Dimerization Systems

A number of ethylene dimerization systems in which nickel complexes are employed as pre-catalysts have recently been reported. Le Floch et al. has synthesised a new family of N-P ligands containing a phosphino group and an iminophosphorane moiety. These ligands readily react with NiBr₂.DME to give a family of complexes (4-5) which when treated with MAO give highly active ethylene dimerization initiators (Figure 1.2 and Table 1.1)

**Figure 1.2 P-N Nickel(II) ethylene dimerization pre-catalysts**

![Figure 1.2 P-N Nickel(II) ethylene dimerization pre-catalysts](image)

4a: R = CH₂-t-Bu  
4b: R = p-CH₂-C₆H₄OMe  
5a: R = CH₂-t-Bu  
5b: R = iPr
Table 1.1 Ethylene Oligomerization by complexes 4-5

<table>
<thead>
<tr>
<th>Pre-Catalyst</th>
<th>TOF x 10^3(b)</th>
<th>C_4 (%)</th>
<th>[1-C_4 (%)]</th>
<th>C_6 (%)</th>
<th>[1-C_6 (%)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>45.3</td>
<td>93.9 [83.4]</td>
<td>6.1 [32.7]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td>65.8</td>
<td>92.8 [77.0]</td>
<td>7.2 [29.4]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5a</td>
<td>96.7</td>
<td>96.3 [67.5]</td>
<td>3.7 [39.8]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5b</td>
<td>106.5</td>
<td>97.7 [61.4]</td>
<td>2.3 [73.9]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Conditions: T = 45°C, 30 bar ethylene, 1 h reaction time, 0.02 mmol Ni complex, 6 mmol MAO, solvent: toluene (30 mL). b) TOF = mol ethylene consumed per mol of Ni per hour (mol \('\text{mol}^{-1}\'\ h^{-1}\').

Of note is that for all four systems outlined in Table 1.1, high selectivity for C_4 dimerization products were obtained. Also of significance are the high activities of the initiator solutions, particularly those of 5a and 5b. Indeed, Le Floch states that 5b gives one of the most active dimerization systems that have currently been reported. In a related study, Braunstein et al. have also mixed donor P-N ligands to synthesise nickel complexes with oxazoline (6) or pyridine-phosphonite (7) donors (Figure 1.3).^{20}

Figure 1.3 Nickel-based ethylene dimerization pre-catalysts

The ability of the pre-catalysts 6 and 7 to dimerize ethylene after treatment with EtAlCl_2 or MAO was assessed. It was determined that increasing the moles of co-initiator (EtAlCl_2 or MAO) in the systems based on 6 and 7 simultaneously resulted in a marked increase in initiator activity, but a significant decrease in initiator selectivity (Table 1.2). A higher selectivity for C_4 products was obtained when MAO was
employed as a co-initiator. In contrast, the highest TOFs were obtained when 
EtAlCl₂ was used.

**Table 1.2 Ethylene dimerization using the pre-catalysts 6 and 7**

<table>
<thead>
<tr>
<th>Pre-Catalyst</th>
<th>Activator [eq]</th>
<th>Selectivity C₄ (%)</th>
<th>TOF (mol C₂H₄/mol Ni h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>EtAlCl₂ [2]</td>
<td>76</td>
<td>12,700</td>
</tr>
<tr>
<td>6</td>
<td>EtAlCl₂ [6]</td>
<td>70</td>
<td>31,400</td>
</tr>
<tr>
<td>7</td>
<td>EtAlCl₂ [2]</td>
<td>82</td>
<td>21,100</td>
</tr>
<tr>
<td>7</td>
<td>EtAlCl₂ [6]</td>
<td>75</td>
<td>27,400</td>
</tr>
<tr>
<td>7</td>
<td>MAO [400]</td>
<td>94</td>
<td>7,400</td>
</tr>
<tr>
<td>7</td>
<td>MAO [800]</td>
<td>90</td>
<td>13,200</td>
</tr>
</tbody>
</table>

a) General conditions: T = 30°C, 10 Bar C₂H₄, 35 min, 4.0 x 10⁻² mmol Ni complex, solvent 
15 mL toluene b) General conditions: T = 30°C, 10 Bar C₂H₄, 35 min, 4.0 x 10⁻² mmol Ni 
complex, solvent 20 mL toluene

The P-N nickel complexes employed by both Le Floch (**Table 1.1**) and Braunstein 
(**Table 1.2**) give both high selectivity and activity for ethylene dimerization. However, 
related nickel systems have been reported for which the selectivity for ethylene 
dimerization is even higher. Dyer *et al.* have reported the bis(pyrrolatoimine) 
complex [Ni{2-(mes-N-CH)C₄H₃N}₂] (8) which when activated by EtAlCl₂ generates 
an initiator complex that gives exclusively ethylene dimerization (**Scheme 1.10**).²¹

Though the dimerization system based on complex 8 is highly selective for butenes, 
the activity obtained was low (1g ethylene/mmol Ni/ h/ bar).

**Scheme 1.10 Synthesis and reactivity of complex 8**

![Scheme 1.10 Synthesis and reactivity of complex 8](image-url)
One novel nickel-based dimerization initiator, which combines both high activities with excellent selectivity stems from the use of diphosphinated calix[4]arenes by Matt et al. (Figure 1.4).  

**Figure 1.4 Nickel-base diphosphinated calix[4]arenes pre-catalysts**

Both complexes 9 and 10 (Figure 1.4) can be activated for ethylene dimerization by EtAlCl₂. Although the initiator systems based around 9 and 10 were examined under a range of conditions it was stated that the selectivity for butenes always exceeded 95%. Furthermore, the selectivity for but-1-ene specifically could be enhanced by modification of the reaction conditions, with low pre-catalyst concentrations resulting in outstanding selectivity for but-1-ene (91% for entry 1, Table 1.3) as well as favouring higher TOF (Table 1.3).

**Table 1.3 Ethylene dimerization with nickel calix[4]arene pre-catalysts**

| Entry | Precursor | n(Ni) [μmmol] | Pressure | T°C | ΔT°C | MAO [equiv/Ni] | TOF c)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>0.09</td>
<td>20</td>
<td>25</td>
<td>3</td>
<td>400</td>
<td>83.53</td>
</tr>
<tr>
<td>2</td>
<td>9</td>
<td>4.5</td>
<td>20</td>
<td>25</td>
<td>57</td>
<td>400</td>
<td>11.74</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0.09</td>
<td>20</td>
<td>25</td>
<td>3</td>
<td>400</td>
<td>120.54</td>
</tr>
</tbody>
</table>

*a) The solvent toluene (22 mL) was employed in all runs. b) Maximum temperature increase during the catalytic run. c) TOF reported in mol of C₂H₄ converted per mol of Ni per hour (mol C₂H₄/mol Ni/h).*
For runs in which relatively high pre-catalyst concentrations of 9 and 10 were employed (Table 1.3 entry 2) rapid rises in the temperature of the initiator solutions occurred, as ethylene dimerization is an exothermic process. In contrast, when lower concentrations of both 9 and 10 were used better temperature control was obtained. This data suggests that it is tighter temperature control which leads to higher TOF and greater selectivity for but-1-ene (Table 1.3, entries 2 and 3). Also of note, is that the highest TOF was attained from the pre-initiator 10 (Figure 1.4 R = Br). It is suggested that the bulky bromine atoms present in the ligand backbone of 10, will be able to interact with intermediate formed Ni-butyl moieties, a steric interaction which will favour fast reductive elimination of butenes. Significantly, the TOF obtained with either complexes 9 or 10 are reported as exceeding the activities of any currently known nickel diposphine catalysts. As such, the use of a diphosphinated calix[4]arene ligand backbone provides an alternative, yet attractive, approach to developing new ethylene dimerization systems.

1.3 Ethylene Trimerization Initiated by Homogeneous Chromium-based Initiators

Although this thesis concerns the use of molybdenum and tungsten dimerization systems, it should be noted that chromium based pre-catalysts are arguably more widely used to initiate alkene dimerization and oligomerization reactions. Indeed, the use of chromium complexes to initiate ethylene trimerization is especially prominent. The importance of ethylene trimerization stems from the Schulz-Flory (or Poisson) distribution of linear α-olefins obtained from ethylene oligomerization systems. Often this Schulz-Flory product distribution does not match the market demand for linear α-olefins in the valued co-monomer range (1-C₆ and 1-C₈). As such an immense emphasis has been placed on developing ethylene trimerization systems which offer an atom efficient route to hex-1-ene, which is widely utilized as a co-monomer in polyethylene manufacture. An important development in the field of ethylene trimerization concerns the use of diphosphazane (or “PNP”) ligands (Scheme 1.11).

Scheme 1.11 Ethylene trimerization using orthomethoxy-substituted diphosphazanes

\[
\text{CrCl}_3(\text{THF})_2 \rightarrow \text{MAO} \rightarrow \text{Toluene} \rightarrow 80\text{°C}, 20 \text{ Bar Ethylene} \rightarrow 1,033,200 \text{ g/g Cr/h}
\]
The most active trimerization systems were obtained when the diphosphazane backbone contained \textit{ortho}-methoxy moieties as in Scheme 1.11. Indeed the ethylene trimerization system illustrated in Scheme 1.11 gives an activity that is two orders of magnitude higher than those previously reported.\textsuperscript{24} Furthermore, this initiator system was highly selective, producing 90\% C\textsubscript{6} products of which 99.9\% was hex-1-ene (giving an overall selectivity of 89.9\% for the 1-C\textsubscript{6} product). This high selectivity for hex-1-ene makes this initiator system particularly attractive for commercial application.

1.4 Determining the Mechanism of a Chromium-based Ethylene Trimerization by Reaction of C\textsubscript{2}D\textsubscript{4} and C\textsubscript{2}H\textsubscript{4}

In Section 1.2 the range of mechanisms by which olefin dimerization can be achieved was discussed. Particularly prominent are catalytic cycles that proceed via hydride or metallacyle intermediates. Similarly, trimerization of ethylene by a chromium-based initiator could also feasibly occur via a hydride (degenerate polymerization) (Scheme 1.12) or a metallacyle (oxidative coupling) (Scheme 1.13) mechanism.

\textbf{Scheme 1.12 Chromium-initiated ethylene trimerization via a hydride cycle}
Scheme 1.13 Chromium-initiated ethylene trimerization via metallacycle intermediates

With regard to gaining understanding of the trimerization mechanism, of particular significance is the potential for the hydride or metallacycle mechanisms to give different product distributions when reacted with a 1:1 mixture of $\text{C}_2\text{D}_4$ and $\text{C}_2\text{H}_4$. If a hydride regime was in operation, a $\text{C}_2\text{D}_4/\text{C}_2\text{H}_4$ mixture would undoubtedly give olefins containing both odd and even numbers of deuterium atoms (Scheme 1.14).

Scheme 1.14 Products obtainable from trimerization of a $\text{C}_2\text{D}_4/\text{C}_2\text{H}_4$ mixture via a hydride initiator

In contrast to a hydride cycle, trimerization via metallacycles can result in the exclusive production of olefins containing even numbers of deuterium and hydrogen atoms. For instance trimerization of two molecules of $\text{C}_2\text{H}_4$ with one of $\text{C}_2\text{D}_4$ via first a five, and then a seven membered ring, can only result in the formation of the “even” product $\text{C}_8\text{H}_8\text{D}_4$ (Scheme 1.15).
Bercaw et al. have employed a 1:1 C_{2}D_{4}/C_{2}H_{4} feedstock to investigate their trimerization system which is based upon complexation of the PNP ligand (o-MeOC_{6}H_{4})_{2}PN(Me)P(o-MeOC_{6}H_{4})_{2} to the Cr^{III} precursor CrCl_{3}.THF_{2}, followed by addition of the co-initiator MAO. Using these conditions Bercaw and co-workers observed the formation of C_{6} products containing exclusively even numbers of D and H atoms. This was cited as being proof of a metalacycle mechanism, as only this type of mechanism could give such a product distribution. Hence, reaction of a C_{2}D_{4}/C_{2}H_{4} mixture has been successful in identifying the mechanism of Bercaw's trimerization system. As such, similar investigations could also feasibly provide mechanistic information regarding related dimerization initiators.

1.5 Olefin Dimerization Systems Based on WCl_{6}
Processes describing the dimerization of olefins using solutions of WCl_{6} were first outlined by Goodyear in the 1970's. In the Goodyear system, an unknown initiator complex is formed in situ from reaction of WCl_{6} with two equivalents of an aniline in chlorobenzene, followed by addition of an excess of an aluminium alkyl halide, typically EtAlCl_{2}, Et_{2}AlCl or Et_{3}Al_{2}Cl_{3}. Through this procedure a highly active alkene dimerization initiator is obtained (Scheme 1.16).29

**Scheme 1.16 Ethylene dimerization based on WCl_{6}**

\[
\text{WCl}_{6} \quad \xrightarrow{\text{i) } 2\text{NH}_{2}R, \ 132^\circ\text{C}} \quad \text{but-1-ene (92 % selectivity)} \\
\text{\quad \xrightarrow{\text{ii) } 80 \text{ Et}_{2}\text{AlCl}, \text{C}_{6}\text{H}_{5}\text{Cl}} \quad \text{TOF = 176,000} \\
\quad \text{\quad \xrightarrow{\text{iii) Ethylene (27 atm)}} \quad (\text{moles C}_{2}\text{H}_{4}/\text{moles WCl}_{6}/\text{h})}
\]
Of significance, is that HCl has been found to evolve during initiator preparation. Furthermore, a patent was awarded to Exxon, specifying that it was advantageous to remove HCl from the WCl₆/2NH₂R reaction solution though the use of an N₂ gas stream. Purging the initiator solution of HCl enabled the use of lower co-catalyst loadings in the Exxon system, with W:Al molar ratios of between 3:1 to 5:1 stated as being preferable. Hence, although the identity of the actual active compound is not firmly established, the evolution of HCl in both the Exxon and Goodyear systems is suggestive of the formation of nitrogen–metal bonds (e.g. W-NR(H) or W=NR) in situ (Scheme 1.17).

**Scheme 1.17 Generation of metal imido bond through elimination of HCl**

In both the Goodyear and Exxon systems, the aniline is generally used in an excess relative to WCl₆ (two equivalents) and as such, there is the possibility that either mono or bis(imido) tungsten complexes could evolve in situ. Furthermore, there is also the potential that amido complexes are present in the initiator solution. In order to evaluate the plausibility of imido formation in situ, catalysis has been carried out by Olivier et al. using discrete pre-formed imido complexes (of the general formula W(NR)Cl₄·THF) and results directly compared to those obtained using the Goodyear catalyst system (WCl₆/ArNH₂/EADC, 1:2:11). Although the activities given by the discrete imido complexes tended to be slightly lower than that obtained using the Goodyear system, the TON and initiator selectivity were comparable, strongly suggesting that the active initiator species is a tungsten imido complex.
Although Exxon employed a flow of nitrogen to remove HCl from the initiator solution and hence enhance initiator performance, in a recent patent filed by Sasol Technology UK (STUK) a separate base (such as Et₃N) was used as a HCl scavenger. The STUK patent also outlines procedures for the dimerization of heavier olefins such as hex-1-ene (Scheme 1.18).

**Scheme 1.18 Dimerization of Hex-1-ene using the STUK WCl₆ based process**

\[ \text{WCl}_6 \xrightarrow{i) \text{ 4Et}_3\text{N, C}_6\text{H}_5\text{Cl}} \xrightarrow{\text{ii) 2H}_2\text{NPh, hex-1-ene}} \xrightarrow{\text{iii) 60°C}} \xrightarrow{\text{iv) 10 Et}_3\text{Al}_2\text{Cl}_3} \text{C}_{12} (87.8 \text{ wt }\% ) \xrightarrow{\text{C}_{18} (1.3 \text{ wt }\% )} \text{heavies (10.9\% wt }\% ) \]

\[ \text{a) heavies are defined as being hydrocarbon products containing 24 or more carbon atoms} \]

The activity obtained for the hex-1-ene dimerization system outlined in **Scheme 1.18** was 107.2 (mol hex-1-ene/mol WCl₆/h) and the TON was 428.7 (mol hex-1-ene/mol WCl₆). Analysis of the skeletal selectivity (through the use of a hydrogenating GC) of the C₁₂ product fraction indicated a high preference for the branched dimerization products, with no linear products observed (Table 1.4).

**Table 1.4 Analysis of C₁₂ skeletal selectivity obtained from hex-1-ene dimerization using the STUK WCl₆ system**

<table>
<thead>
<tr>
<th>Hydrocarbon backbone</th>
<th>Skeletal selectivity (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear product</td>
<td>0</td>
</tr>
<tr>
<td>5-methyldecenes</td>
<td>65</td>
</tr>
<tr>
<td>5,6 dimethyldecenes</td>
<td>35</td>
</tr>
</tbody>
</table>

Clearly the STUK WCl₆ hex-1-ene dimerization system exhibits good activity and the selectivity for C₁₂ dimerization products are high. As such, the WCl₆ STUK dimerization system provides a means to dimerize heavier α-olefins. Furthermore, initiator preparation using procedures outlined in the STUK patent from WCl₆ is relatively simple and does not require the timely synthesis of bi-dentate ligands. This is in contrast to many of the nickel based dimerization systems previously outlined in **Section 1.3.**
1.6 Examining the Selectivity of the WCl₆ Goodyear Dimerization System

Insights into the mechanism by which systems based on WCl₆ initiate alkene dimerization can be obtained from examination of the olefin dimerization products. From the examples provided by Goodyear (Table 1.5), it is clear that alkene dimerization results in a significant amount of both the tail-to-tail (tt) as well as the head-to-tail (ht) and tail-to-head (th) products. Conversely, linear head-to-head (hh) products are produced in trace amounts (less than 2%).

Table 1.5 Product distributions obtained from a Goodyear WCl₆-based propylene dimerization system

<table>
<thead>
<tr>
<th>Aniline used in initiator preparation.</th>
<th>C₆ (%)</th>
<th>4-methylpent-1-ene (molar % of product)</th>
<th>2,3-dimethylbut-1-ene (molar % of product)</th>
<th>2-methylpent-1-ene (molar % of product)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,6-dichloro-4-fluoroaniline</td>
<td>55</td>
<td>11</td>
<td>49</td>
<td>38</td>
</tr>
<tr>
<td>2,4-difluoroaniline</td>
<td>74</td>
<td>10</td>
<td>50</td>
<td>34</td>
</tr>
<tr>
<td>2,4,6-trichloroaniline</td>
<td>53</td>
<td>8.3</td>
<td>76</td>
<td>10</td>
</tr>
</tbody>
</table>

The evolution of both ht and th product, from the WCl₆ Goodyear (and STUK) dimerization systems can be explained by the formation of α-β-substituted metallacycles (Scheme 1.18). Indeed, dimerization of olefins to give both ht and tt products is characteristic of a concerted coupling mechanism. This is suggestive that for systems generated in situ from WCl₆ dimerization occurs via a tungsten metallacycle complex, formed from an imido/amido pro-initiator.
**Scheme 1.18** Formation of **ht** dimerization products via a concerted coupling mechanism

![Scheme 1.18](image)

**1.7 Applications and Bonding Modes of Transition Metal Imido Complexes**

Evolution of HCl during the formation of the STUK, Exxon and Goodyear WCl₆ based dimerization systems strongly suggests the *in situ* formation of an imido initiator complex. As discussed above this conclusion was confirmed by the use of *mono*(imido) pre-catalysts (W(NR)Cl₄·THF) by Olivier *et al.*[^31] The chemistry of imido systems has been extensively investigated, as such, a wide range of imido transition metal complexes are known and have been the subject of a number of reviews.[^34]

Indeed, transition metal complexes containing imido ligands (NR²) alongside use as alkene dimerization precatalysts have many other possible applications. For instance, imido complexes are viewed as potential azirinadination and amination reagents.[^35] Imido complexes have also been considered to be prospective metal nitride film growth precursors,[^36] as well as being employed as ligands in ring opening metathesis polymerization,[^37] Ziegler-Natta olefin,[^38] and MMA-polymerization initiators.[^39] The imido ligand is known to adopt one of five different bonding modes as illustrated in **Figure 1.5**, utilizing the formal 2− charge and lone pair of the nitrogen atom.
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Figure 1.5 Known imido bonding modes

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Triply bridging</td>
<td>Unsymmetrically</td>
<td>Symmetrically</td>
<td>Terminal bent</td>
</tr>
<tr>
<td></td>
<td>bridging</td>
<td>bridging</td>
<td>bridging</td>
<td>Terminal Linear</td>
</tr>
</tbody>
</table>

In the terminal linear imido bonding mode, the interaction between the metal and the nitrogen can be considered to consist of one $\sigma$- and two $\tau$-bonds, with the nitrogen being formally sp-hybridized. Thus, for linear imido ligands the ideal M-N-C bond angle is 180° and consequently the imido ligand is assigned as being a 4-electron donor (neutral ligand formalism). In practice, the M-C-N bond angle of a linear imido ligand is highly variable, with bond angles in the range of 150-180°. This is because the M-N-C bond angle associated with a given imido moiety can be heavily influenced by factors such as crystal packing forces. As such, in many systems it is the relative M-N bond lengths that are more descriptive of a given imido ligands bonding mode. The inaccuracy of assigning imido bonding modes based on the M-N-C angle is illustrated by the mixed bis(imido) complex Mo(NAr)(N'Bu)Cl_2.DME (11) (Figure 1.6). With a M-N-C bond angle of 174.3(2)° the NAr ligand of Mo(NAr)(N'Bu)Cl_2.DME (11) is seemingly adopting the linear bonding mode. However, it is the N'Bu ligand which has a shorter Mo-N contact (1.728(2) Å vs 1.753(2) Å) and it is the N'Bu imido that is observed to exert a greater trans influence on the corresponding trans Mo-O contact (Table 1.6). Thus, contrary to the apparent linear geometry of the NAr ligand, for Mo(NAr)(N'Bu)Cl_2.DME (11) it is the N'Bu ligand that has a Mo-N contact with the greatest triple bond character.

Figure 1.6 and Table 1.6 Assessing the relative trans influences of the NAr and N'Bu ligands of complex 11

<table>
<thead>
<tr>
<th></th>
<th>Bond distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-O₁</td>
<td>2.330(2)</td>
</tr>
<tr>
<td>Mo-O₂</td>
<td>2.392(1)</td>
</tr>
</tbody>
</table>
Although it is often difficult to assign a bonding mode (linear vs bent) to a given imido ligand, *bona fide* examples of truly bent terminal imido ligands (i.e. 2-electron donors, neutral formalism) with a sp$^2$ hybridized N atom have been identified. For example, the complex [Mo(NAr)$_2$(L)] (L is a tridentate pyridinediolato ligand) (12) is observed to have two inequivalent imido ligands one adopting a linear geometry (Mo-N(2)-C$_{ipso}$164.7(4)$^\circ$; Mo-N2, 1.760(4)Å) and the other a bent (Mo-N(3)-C$_{ipso}$144.8(5)$^\circ$; Mo-N3, 1.771(4)).^42 This situation arises in this "π-loaded" bis(imido) complex, to avoid the unfavourable valence electron count of twenty that would result from both imido ligands adopting the linear bonding mode and donating 4 electrons to the molybdenum atom. Instead, one imido ligand adopts the bent bonding mode and as an X$_2$ donor, donates 2 electrons to the Mo atom, enabling the more favourable electron count of eighteen (Figure 1.7). A second commonly cited example of a bent imido ligand can be found in the complex Mo(NC$_6$H$_5$)$_2$(S$_2$CN(C$_2$H$_5$)$_2$)$_2$ (13).^43 The molecular structure of complex 13 contains a distinctly bent imido ligand with a Mo-N-C bond angle of 139.4$^\circ$ and a Mo-N bond length of 1.789 Å as well as a linear imido ligand (Mo-N-C = 169.4$^\circ$ and Mo-N = 1.754 Å).

**Figure 1.7** Simplified structure of the "π-loaded" bis(imido) complex 12 (only key atoms are included for clarity)

Imido π-bonding can be considered to result from overlap of a filled nitrogen p-orbital with an empty metal d-orbitals (Figure 1.8). As empty metal d-orbitals of the correct symmetry and similar energy are required for formation of metal-nitrogen multiple bonds, linear imido complexes are favoured for high oxidation state and early transition metals.^34 However, many mid-series transition metal imido complexes have been reported, for example, those of osmium.^44 The homoleptic osmium imido complex Os(NAr)$_3$ (14) is of particular interest, as with three seemingly
linear imido ligands (verified using X-ray crystallography) 14 is outwardly a 20 electron complex (Figure 1.9).\textsuperscript{44}

\textbf{Figure 1.8 Imido $\pi$-bonding}

\begin{center}
\includegraphics{fig18.png}
\end{center}

\textbf{Figure 1.9 The tris(imido) complex Os(NAr)$_3$ (14)}

\begin{center}
\includegraphics{fig19.png}
\end{center}

It is reasoned that although all three imido ligands of complex 14 adopt a linear geometry, at least one imido ligand does not donate the maximum of four electrons to the metal. Instead, one imido N-lone pair is located in a non-bonding orbital centred on a nitrogen atom. Thus, 14 can be considered as being an 18 electron complex. Hence, characterization of the osmium complex Os(NAr)$_3$ (14) further demonstrates that a linear imido ligand does not necessarily have to act as a formal four electron donor. This again emphasises that a given imido ligands geometry is a poor indication of $\pi$-donor capacity.

Although osmium imido complexes have been reported, few structures of late transition metal complexes (beyond group 8) with terminal imido ligands are currently deposited in the Cambridge Structural data base. However, late transition metal complexes with bridging imido ligands are known,\textsuperscript{45} though this bonding mode does not require the acceptance of a nitrogen lone pair to a single metal centre. Metal nitrogen multiple bonds are not exclusive to transition metals, both lanthanide and
actinide\textsuperscript{48} imido complexes have been identified, with those of uranium-imido being particularly prevalent.\textsuperscript{47}

\section*{1.8 Attempts to Spectroscopically Distinguish between Imido Bonding Modes}
As mentioned in Section 1.8, determination of an imido fragment's bonding mode ($X_2$ vs $LX_2$) on the basis of M-N-C bond angle, is often inaccurate and requires material suitable for single crystal X-ray diffraction. Consequently, assessment of imido coordination modes has been attempted using a range of alternative techniques. For example, complexes containing imido ligands have been examined using X-ray photoelectron spectroscopy (XPS), measuring the 1s binding energy of the imido nitrogen atom.\textsuperscript{49} However, it was determined that the resulting XPS spectrum cannot be used to conclusively assign a given nitrogen atom's hybridization (sp vs sp$^2$). This indicates that XPS is unsuitable for determining a given imido ligands bonding mode.

In an alternative approach Bradley \textit{et al.} conducted a comprehensive study of complexes containing both linear and bent imido ligands using both $^{14}\text{N}$ and $^{15}\text{N}$ NMR spectroscopy.\textsuperscript{49} Again, this analysis was unsuccessful in differentiating between bent and linear bonding modes, with nitrogen chemical shifts (both $^{14}\text{N}$ and $^{15}\text{N}$) being insensitive to the deshielding observed on imido bending.

In contrast, $^{13}\text{C}$ NMR spectroscopy can be used to gain insight into the electronic environment of an imido nitrogen atom. Hogarth \textit{et al.} have used $^{13}\text{C}$ MAS-NMR to characterize a series of bis(imido) complexes with the general formula $\text{Mo(NR)}_2(S_2\text{CNET})_2$ and observed two distinct ipso carbon resonances corresponding to two different imido environments existing in the solid state.\textsuperscript{50} Strong correlation between $\Delta\delta$ (the difference between $C_{ipso}$ chemical shifts in ppm), and $\Delta^\circ$ (the difference in M-N-C bond angles) was observed, enabling quick assignment of the relative bending of the bis(imido) ligands. Notably, Hogarth and co-workers did not offer any explanation regarding the origin of the correlation that exists between $\Delta\delta$ and $\Delta^\circ$. 
1.9 Molecular Orbital Description of Imido Complexes and Resulting Isolobal Relationships

1.9.1 Molecular Orbital Description of mono(imido) Complexes

A molecular orbital description of metal-imido bonding for an mono(imido) octahedral complex can be readily defined (Figure 1.10). If the z-axis is set as being along the M-N bond, then the $d_{xz}$ (metal) combines with the $p_x$ (nitrogen) and the $d_{yz}$ (metal) with the $p_y$ (nitrogen). The final orbital of the $t_{2g}$ set, $d_{xy}$ (metal), is non-bonding. As the nitrogen atom lies along the z-axis the degeneracy of the $d_{xz}$ and $d_{yz}$ orbitals is lost, with the $d_{z}^{2}$ orbital and the $p_{z}$ (nitrogen) orbitals combining.

*Figure 1.10* Orbital energy diagram for a linear imido ligand of an octahedral metal complex.

![Orbital energy diagram for a linear imido ligand of an octahedral metal complex.](image_url)
Thus, for a mono(imido) system in an octahedral geometry, combination of the nitrogen p-orbitals with the metal d-orbitals allows for a maximum of three bonding interactions (1σ and 2π). The relative energies of the combining metal and nitrogen orbitals have been shown by Nugent et al. to influence the nucleophilicity of a given N'Bu ligand within a homologous series of d⁰ complexes (Figure 1.11).\(^{51}\)

When an N'Bu ligand is coordinating to an early transition metal (such as tantalum), then bonding occurs between a nitrogen p-orbital and a high energy d-orbital (Figure 1.11, A). This gives a HOMO with a relatively high energy and predominantly nitrogen character, resulting in an imido ligand that preferentially reacts as a nucleophile. A bonding regime such as that outlined in Figure 1.11, B is argued by Nugent to apply to an imido ligand bound to a more electronegative metal such as chromium which has d-orbitals that are less diffuse and lower in energy.\(^{51}\)

Thus, the relatively low energy of a chromium d-orbital (compaired to a tantalum) in turn gives a HOMO of reduced energy, significantly decreasing the nucleophilicity of the corresponding chromium imido ligand.\(^{51}\)

**Figure 1.11** Changes to nitrogen/metal π-interactions resulting from variation of the atomic orbital relative energies.
1.9.2. Isolobal Relationships Between $[M(NR)_2]^{2-}$ (M = Mo or W) and $[M(Cp)_2]^{2-}$ (M = Zr or Hf) Complexes

Similarities can be drawn between imido, cyclopentadienyl, cyclobutadiene and cyclopropenyl fragments, as all four ligands have two $\pi$-symmetry frontier orbitals available to interact with a given metal (Figure 1.12).

**Figure 1.12** Simplified energy level diagram denoting the frontier orbitals of $NR^2-$ and $C_nH_n$ fragments

It is clear from the energy level diagram outlined in Figure 1.12 that the imido and cyclobutadiene ligand are isonumeral with both fragments capable of donating a maximum of four electrons to a given metal.\(^52\) Strictly the imido and $C_4H_4$ fragment cannot be considered as formally isolobal, as in contrast to an imido ligand the $C_4H_4$ fragment binds to a metal via four atoms and has a $\delta$ symmetry orbital available for metal back donation. However, it is clear that $C_nH_n$ and imido moieties have similar frontier orbitals. Using this observation, and the knowledge that imido and Cp ligands have a respective formal charge of 2– and 1–, group VI $\text{bis(}imido\text{)}$ complexes can be related to group IV metalloccenes.\(^52,53\) This gives an isolobal series comprising of complexes with an identical valence metal count of sixteen (Figure 1.13).
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Figure 1.13 Isolobal relationships between Zr, Nb and Mo cyclopentadienyl and complexes

The isolobal relationship between (Cp)₂M (M = Ti, Zr or Hf) and (RN)₂M (M = Cr, Mo or W) fragments has also been investigated by Schrock et al., using SCF-XαSW calculations to examine the bonding of the hypothetical tetrahedral complex W(NH)₂(PH₃)₂. It was determined that the [W(NR)₂] core has three vacant frontier orbitals, two of a₁ and one of b₂ symmetry, which is the same configuration to that found for a (Cp)₂M (M = Ti, Zr or Hf) fragment. Hence, Schrock's analysis clearly shows that parallels can be drawn between the frontier orbital configuration and structure of the isolobal fragments W(NAr)₂Cl₂ and Cp₂HfCl₂. This isolobal relationship hints that potentially W₃(NH)₅(η₂-imido) complexes may display similar reactivity to that of established Cp₂MCl₂ (M = Ti, Zr, Hf) ethylene polymerization pre-catalysts.

1.10 Methods of Imido ligand Synthesis

There are a wide range of synthetic methods available to introduce an imido ligand into a metal complex. The most important being highlighted in Table 1.6.

Table 1.6 Synthesis of imido complexes

<table>
<thead>
<tr>
<th>Synthetic method</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-H bond cleavage-aminines/amides⁶⁶</td>
<td>W(NAr)(NEt₂)Cl₃(THF) LiNHAr W(NAr)₂Cl₂(THF)₂ + HNEt₂</td>
</tr>
<tr>
<td>N-Si bond cleavage⁵⁷</td>
<td>CrO₂Cl₂ 4Me₃SiNHBF₄ Cr(N'Bu)₂(OSiMe₃)₂ + Me₂Si-SiMe₃ + 2'BuNH₃Cl</td>
</tr>
<tr>
<td>Imido metathesis [2+2] cycloaddition⁵⁸</td>
<td>Re(OSiPh₃)O₃ → ArN=C=O Re(NAr)₃(OSiPh₃) + 3CO₂</td>
</tr>
<tr>
<td>Organic azides (elimination of N₂)⁵⁹</td>
<td>MoCl₄(THF)₂ N₂O₃ Mo(Nol)Cl₄(THF) + N₂</td>
</tr>
<tr>
<td>Azo compounds⁶⁰</td>
<td>2Ti(n²-PhN=NPh)(OAr)₂(py)₂ → 2Ti(NPh)(OAr)₂(py)₂ + PhN=NPh</td>
</tr>
<tr>
<td>Oxidizing agents⁶¹</td>
<td>MoO(S₂CNEt₂)₂ 2C₆H₆NNTs → 2Mo(NTs)(S₂CNEt₂)₂ + C₆H₆NNC₃H₅</td>
</tr>
</tbody>
</table>
Many of the synthetic routes outlined in Table 1.6 result in the evolution of an entropically favoured leaving group such as CO₂, N₂ or the formation of an enthalpically stable product such as lithium chloride or a silyl ether. The formation of such by-products provides a thermodynamic driving force for imido formation, allowing the energy cost associated with the synthesis of a multiple bond to be offset.

1.11 Synthesis and Reactivity of Group 6 Imido Complexes

Particular emphasis has been placed on the development of both low valent tungsten and molybdenum d⁰ (imido) complexes, as their derivatives can be used as precursors to Schrock-type olefin metathesis initiators of the general formula M(NAr)(CHR)(OR')₂ (M=Mo or W) which have been used widely as RCM and ROMP pre-catalysts. One advantage of using imido ligands to stabilize a M⁶⁺ centre, in preference to isoelectronic alternatives such as the oxo ligand, is the potential to alter the R group of the imido moiety. This allows for greater variation and control of the steric environment about a given metal. Typically in Schrock type metathesis initiators, bulky R groups such as 2,6-diisopropyl phenyl (Ar) are employed. The steric influence exerted by such bulky fragments, simultaneously stops the imido ligand adopting a bridging bonding mode and 'protects' the reactive alkylidene ligand, which could potentially dimerize with a second metal alkylidene moiety. Although a substantial number of investigations have been undertaken with the aim of developing and improving Schrock-type metathesis initiators, in this thesis such complexes have not been utilized and so will not be discussed in detail. Instead, a brief survey examining Group 6 imido complexes will be undertaken.

1.11.1 Synthesis of Chromium Imido Complexes

Interest in the synthesis of chromium imido complexes first stemmed from the isolobal relationship that exists between the metal fragments [Cp₂Ti] and [Cr(NR)₂] (Section 1.10.2). This isolobal link is significant as complexes such as Cp₂TiCl₂ when reacted with a suitable co-initiator (such as MAO) readily polymerize ethylene via a Ziegler-type mechanism. Although the isolobal analogy is strictly structural, and hence cannot be used to map complexes' reactivity, chromium bis(imido) complexes can indeed be used as ethylene polymerization pre-catalysts. Consequently a wide range of chromium bis(imido) complexes and their derivatives have been synthesised with the aim of developing discrete and active olefin polymerization initiators.

Reaction of the di-oxo complex CrO₂Cl₂ with tBuNHSiMe₃ provides an entry into chromium imido chemistry, with imido formation via Si-N bond cleavage giving
Cr(N'Bu)₂(OSiMe₃)₂ (15). The dichloride bis(imido) complex Cr(N'Bu)₂Cl₂ (16) can then be obtained by addition of BCl₃ (Scheme 1.19).

**Scheme 1.19 Synthesis of Cr(N'Bu)₂(OSiMe₃)₂ (15) and Cr(N'Bu)₂Cl₂ (16)**

\[
\begin{align*}
\text{CrO}_2\text{Cl}_2 + 4\text{BuNHSiMe}_3 &\rightarrow \text{Cr(N'Bu)₂(OSiMe₃)₂ (15)} \\
2\text{BCl}_3 &\rightarrow \text{Cr(N'Bu)₂Cl₂ (16)}
\end{align*}
\]

The d⁰ bis(imido) complex Cr(N'Bu)₂Cl₂ (16) can readily be converted into a range of derivatives including the d¹ mono(imido) complex Cr(N'Bu)Cl₃ (17) by reaction with Cl₂. Addition of amines to 16 results in an imido exchange. Thus, reaction of Cr(N'Bu)₂Cl₂ (16) with NH₂Ar gives the bis(imido) amido complex Cr(NAr)₂(NH'Bu)Cl (18), which can readily be transformed into Cr(NAr)₂Cl₂ by addition of BCl₃. It is proposed that Cr(NAr)₂(NH'Bu)Cl (18) is generated from complex 16 via a hydrogen transfer mechanism (Scheme 1.20).

**Scheme 1.20 Proposed hydrogen transfer mechanism of imido ligand exchange**

Chromium bis(imido) systems can readily be alkylated, with addition of PhCH₂-MgBr to Cr(N'Bu)₂Cl₂ (16) affording the complex Cr(N'Bu)₂(CHO₂Ph)₂ (19) in high yields.⁶⁸
Alternatively, \( \text{Cr}(N'^3\text{Bu})_2(\text{OSiMe}_3)_2 \) (15) can be used as a precursor for a range of dialkyi complexes, invariably isolated as red oils (Scheme 1.21).\(^{14}\)

**Scheme 1.21 Synthesis of bis(imido) dialkyi derivatives of \( \text{Cr}(N'^3\text{Bu})_2(\text{OSiMe}_3)_2 \)**

\[
\begin{align*}
\text{Cr}(N'^3\text{Bu})_2(\text{OSiMe}_3)_2 & \xrightarrow{\text{pyridine, } 2\text{Me}_3\text{SiBr}} \text{Cr}(N'^3\text{Bu})_2(\text{pyridine})\text{Br}_2 \\
(15) & \xrightarrow{2\text{RCH}_2\text{MgCl}} \text{Cr}(N'^3\text{Bu})_2(\text{CH}_2\text{R})_2 \\
R = \text{CMe}_3, \text{CMe}_2\text{Ph} & \text{or SiMe}_3
\end{align*}
\]

Exploiting the reactivity of \( \text{Cr}(N'^3\text{Bu})_2(\text{CH}_2\text{Ph})_2 \) (19) has led to the development of a new class of well defined single component ethylene polymerization initiator by Gibson et al.\(^{69}\) Addition of \([\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)]\) to complex 19 generates the ionic complex \([\text{Cr}(N'^3\text{Bu})_2(n^2-\text{CH}_2\text{Ph})][\text{B}(\text{C}_6\text{F}_5)]\) (20), which Gibson has reported to be able to initiate ethylene polymerization, on an NMR scale, without requiring a separate co-initiator. Thus, the further development of chromium \( \text{bis(imido)} \) systems ultimately may lead to well defined single-component alkene polymerization initiators.

1.11.2 Synthesis and Reactivity of Molybdenum Imido Complexes

In contrast to chromium, a wider range of precursors are known from which the corresponding molybdenum imido complexes can be generated. For example, molybdenum \( \text{mono(imido)} \) complexes have been prepared by Schrock et al. and have been used subsequently as precursors to alkyl alkylidene complexes (Scheme 1.22).\(^{70}\)
Scheme 1.22 Deriving molybdenum alkylidene complexes from mono(imido) precursors

With the aim of developing precursors to novel molybdenum-alkylidene complexes a range of molybdenum bis(imido) complexes have been synthesised, via reaction of MoO₂Cl₂ with isocyanates. For example, reaction of MoO₂Cl₂ with 'BuNCO generates Mo(N'Bu)₂Cl₂ (21) in high yields (~95%). Using a similar procedure, Mo(NAr)₂Cl₂·THF (22) can be prepared via reaction of MoO₂Cl₂ with ArNCO. Furthermore, complex 22 provides ready access to a range of bis(aryl imido) complexes. For example, reaction with both lithium alkyls and lithiated amines has been utilized to afford access to a range of bis(imido) derivatives (Scheme 1.23).
**Scheme 1.23** Reactions of Mo(NAr)₂Cl₂, THF and Mo(NAr)₂Cl₂

While the reactions between MoO₂Cl₂ and isocyanates are generally high-yielding, synthetic routes employing cheaper, air stable molybdenum starting materials such as (NH₄)₂Mo₂O₇ have been reported by Schrock et al.³³ For example, a straightforward "one-pot" reaction of (NH₄)₂Mo₂O₇ suspended in dimethoxyethane (DME), with two equivalents of a substituted aniline, in the presence of excess CISiMe₃ and Et₃N results in the formation the bis(imido) complexes Mo(NR)₂Cl₂.DME (Scheme 1.24) in near quantitative yields. Imido synthesis occurs via Si-N bond cleavage, with the (trimethylsilyl)amine believed to be generated in situ.

**Scheme 1.24** Synthesis of Mo(NR)₂Cl₂, DME from (NH₄)₂Mo₂O₇

\[
(NH_4)_2Mo_2O_7 \xrightarrow{4NH_2R, 17SiMe_3Cl, 8NEt_3} Mo(NR)_2Cl_2.DME \quad \text{DME, 65°C, 6-10hrs}
\]

R =
- 2,6-diisopropyl-phenyl
- 2,6-dimethyl-phenyl
- 2-tert-butyl-phenyl
- pentafluorophenyl
As complexes such as $\text{Mo(NAr)}_2\text{Cl}_2\text{DME (23)}$ can be prepared from $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ in large quantities (in excess of 20 g), the $\text{bis(imido)}$ complex $\text{Mo(NAr)}_2\text{Cl}_2\text{DME (23)}$ is an ideal precursor to imido alkylidene olefin metathesis initiators (Scheme 1.25). This is achieved by initial alkylation of $\text{Mo(NAr)}_2\text{Cl}_2\text{DME (23)}$ with neopentyl or neophyl Grignard reagents. Treatment of the resulting dialkyl complex (Scheme 1.25, 24) with triflic acid, simultaneously results in imido cleavage and formation of the molybdenum-carbon bond, giving an eighteen electron $\text{bis(triflate)}$ complex 25 (Scheme 1.25). Finally, addition of alkoxide or arloxide salts (Li, Na or K) gives the desired alkylidene complex via nucleophilic substitution.$^7$

**Scheme 1.25** Preparation of $\text{Mo(NAr)(CHC(CMe)_2R(O^tBu))}_2$

Using a similar procedure to that employed in Schrock's synthesis of $\text{Mo(NAr)}_2\text{Cl}_2\text{DME (23)}$ from $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$. Gibson et al., have synthesised molybdenum $\text{bis(imido)}$ complexes using the precursor $\text{Na}_2\text{MoO}_4$. Addition of two separate amines to a DME suspension of $\text{Na}_2\text{MoO}_4$ was found to be a viable route to mixed $\text{bis(imido)}$ complexes, which have also been used as intermediates in the synthesis of metathesis initiators. Alternatively mixed $\text{bis(imido)}$ complexes can be obtained by treatment of $\text{Mo(N'Bu)}_2\text{Cl}_2\text{DME (26)}$ with a substituted aniline (such as $\text{H}_2\text{NC}_6\text{F}_5$) (Scheme 1.26).
The ready availability of Mo(NR)\textsubscript{2}Cl\textsubscript{2}.DME complexes on large scales has allowed a broad number of derivatives to be synthesised containing the molybdenum bis(imido) moiety. For example, reaction with simple Grignard reagents such as MeMgBr\textsuperscript{76} or Li(fmes)\textsuperscript{77} (fmes = 2,4,6 tris(trifluoromethyl) phenyl) have shown that DME can be displaced, allowing access to the pseudo-four-coordinate dialky products Mo(NAr)\textsubscript{2}Me\textsubscript{2} (27) and Mo(NAr)\textsubscript{2}(fmes)\textsubscript{2} (28) respectively. Alternatively, similar reactions using Grignard reagents containing \( \beta \)-hydrogen atoms results in reduction of the molybdenum centre. Thus, addition of CH\textsubscript{3}CH\textsubscript{2}MgCl or CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}MgCl to Mo(NAr)\textsubscript{2}Cl\textsubscript{2}.DME (23) in the presence of PMe\textsubscript{3} has been shown, to generate bis(imido) Mo\textsuperscript{IV}-olefin complexes such as Mo(NAr)\textsubscript{2}(PMe\textsubscript{3})\textsubscript{2}(CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}) (29) (Scheme 1.27).\textsuperscript{78}
In contrast, the related 'Bu imido analogue to complex 29, Mo(N'Bu)\(_2\)(PMMe\(_3\))(\(\eta^2\)-CH\(_2\)CHCH\(_3\)) (30), is only four coordinate. It is reasoned that in the aforementioned NAr \textit{bis}(imido) system there is greater scope for the aryl imidos to alter their orientation, allowing coordinating of a second PMMe\(_3\) ligand, giving a five coordinate molybdenum centre.\(^{79}\)

As well as Grignard reagents, the chloride ligands of Mo(NR)\(_2\)Cl\(_2\).DME complexes can be readily replaced by nitrogen and silyl,\(^{80}\) oxygen,\(^{81}\) and oxygen-boron nucleophiles,\(^{82}\) to give tetrahedral Mo(NR)\(_2\)X\(_2\) complexes and a salt, typically LiCl (Scheme 1.28). The \textit{bis}(imido) molybdenum core has also been chelated by both \textit{bis}(sulphur) donors\(^{83}\) and 1,4,7-trioazacyclononane macrocycles.\(^{84}\)

\textbf{Scheme 1.28 Reaction of lithium-based reagents with Mo(NR)\(_2\)Cl\(_2\).DME (R = 'Bu or Ar)}

Thus, there is evidently a large range of synthetic procedures that can be used to modify molybdenum \textit{bis}(imido) complexes, generating a plethora of derivatives. Similarly a wide range of tungsten \textit{mono} and \textit{bis}(imido) complexes have been reported, some of which will be discussed in the following subsection.
1.11.3 Synthesis and Reactivity of Tungsten Imido Complexes

A notable recent application of tungsten imido complexes comes from the potential of thin tungsten carbonitride films as barrier layers in electronic devices. One method of preparing WC\textsubscript{N}\textsubscript{y} films is via low pressure chemical vapour deposition of tungsten imido complexes onto suitable surfaces. As for chromium and molybdenum, tungsten imido complexes can be prepared from readily available tungsten oxo compounds. For example, polymeric WOCl\textsubscript{4} can be reacted with an isocyanate (PhNCO) to give W(NPh)Cl\textsubscript{4} (31), which may upon subsequent addition of THF, be converted to the adduct W(NPh)Cl\textsubscript{4}.THF (32). The mono(imido) complex W(NPh)Cl\textsubscript{4} (31) can be used as a precursor to make a range of derivatives (Scheme 1.29). Heating a solution of W(NPh)Cl\textsubscript{4} (31) dissolved in benzene in the presence of a phosphine, results in reduction of the tungsten atom, giving the $W^V$ mono(imido) complexes W(NPh)(Cl)\textsubscript{2}L\textsubscript{2} (L= PMe\textsubscript{3} or PMe\textsubscript{2}Ph). The $W^V$ complex W(NPh)(Cl)\textsubscript{3}(PMe\textsubscript{3})\textsubscript{2} (33) can itself be further reduced by Na/Hg amalgam, again presence of a phosphine, to give the $W^V$ complex W(NPh)(Cl)\textsubscript{2}(PMe\textsubscript{3})\textsubscript{3} (34). Ethylene can then be used to displace a phosphine ligand from 34 to give the complex [WCl\textsubscript{2}(NPh)(CH\textsubscript{2}=CH\textsubscript{2})(PMe\textsubscript{3})\textsubscript{2}] (35). Using closely related procedures W(NAr)(Cl)\textsubscript{2}(PMe\textsubscript{3})\textsubscript{3} (36) can be prepared and reacted with ethylene to give [W(NAr)(CH\textsubscript{2}=CH\textsubscript{2})(PMe\textsubscript{3})\textsubscript{2}] (37).

Scheme 1.29 Synthesis of tungsten mono(imido) complexes via reduction of W(NPh)Cl\textsubscript{4}

As well as being readily reduced, mono(imido) complexes such as W(NAr)Cl\textsubscript{4}.THF (38) can be reacted with nitrogen-based reagents such as silyl amines to give both bis- and tris(imido) complexes. Alternatively, reaction of lithiated amines results in mono(imido) amidinate and guanidinate complexes (Scheme 1.30).
Reaction of the mono(imido) complexes \( \text{W(NR)}_4\text{Cl}_4 \cdot \text{THF} \) with silyl amines has become an established route to the synthesis of related bis(imido) complexes. For example, Nielsen et al. have synthesised the mixed bis(imido) complex \( \text{W(NPh)}(\text{N(C}_6\text{H}_4-p-\text{Me})\text{Cl}_2(\text{bipy}) \) (39) via reaction of \( \text{W(NPh)}_4\text{Cl}_4 \cdot \text{THF} \) (32) and \( p-\text{MeC}_6\text{H}_4\text{N(SiMe}_3)_2 \).\(^{91}\) Alternatively, bis(imido) complexes can be prepared directly, in "one-pot" procedures, without the requirement of isolating a mono(imido) intermediate. Schrock et al. has reported the synthesis of \( \text{W(NAr)}_2\text{Cl}_2 \cdot \text{DME} \) (40) directly from the precursor \( \text{WO}_2\text{Cl}_2 \) via reaction of isocyanates, amines or silyl amines.\(^ {92}\) It has also been reported that the cheap, readily available tungsten complex \( \text{W(CO)}_6 \) can be used to synthesise tosyl bis(imido) complexes such as \( \text{W(NTs)}_2\text{Cl}_2 \).\(^ {93}\)

Of relevance to \( \text{WCl}_6 \)-based dimerization systems (see Section 1.6) is that bis(imido) complexes can be prepared directly from reaction of \( \text{WCl}_6 \) with excess \( \text{NH}_2\text{Bu} \) giving the bis(imido) bis(amido) complex \( \text{W(N'Bu)}_2(\text{N'H'Bu})_2 \) (41).\(^ {94}\) Similarly the bis(imido) complex \( \text{W(N'Bu)}_2\text{Cl}_2(\text{py})_2 \) (42) can be made from reaction of \( \text{WCl}_6 \) and \( \text{NH(SiMe}_3)_3\text{Bu} \) (Scheme 1.31).\(^ {95}\) Thus, the synthesis of 41 and 42 directly from \( \text{WCl}_6 \), further indicates that imido moieties can be formed in situ in the Goodyear or STUK
dimerization processes (Section 1.6, Scheme 1.7), in which an unknown initiator complex is formed via reaction of WCl₆ with two equivalents of an aniline.

**Scheme 1.31 Direct synthesis of tungsten bis(imido) complexes from WCl₆**

![Scheme 1.31](image)

1.12 Synthesis and Reactivity of Tungsten and Molybdenum Diamine-chelated Complexes

Both tungsten and molybdenum *mono*(imido) complexes can be stabilized by a diamine to give a family of M⁶⁺ complexes with the general formula M(NPh)Cl₂(L)(o-(Me₃SiN)₂C₆H₄) (M = W or Mo, L = NH₂R or PR₃). This class of complex displays interesting reactivity with Grignard reagents and olefins, which suggest that tungsten or molybdenum imido complexes can act as dimerization initiators via a metallacycle pathway.⁹⁶,⁹⁷ Thus, the general reactivity of M(NPh)Cl₂(L)(o-(Me₃SiN)₂C₆H₄) (M = W or Mo) complexes supports the notion that in the WCl₆-based olefin dimerization systems outlined in Section 1.6 an imido initiator complex is forming *in situ*.

Boncella *et al.* synthesised the *mono*(imido) molybdenum complex Mo(NPh)Cl₂(NH₂Ph)(o-(Me₃SiN)₂C₆H₄) (43) from reaction of Mo(NPh)₂Cl₂.DME with (Me₃SiNH₂)₂.⁹⁶ The bound NH₂Ph ligand of 43 can readily be displaced by PMe₃ to give the complex Mo(NPh)Cl₂(PMe₃)(o-(Me₃SiN)₂C₆H₄) (44), which readily undergoes reaction with a range of Grignard reagents forming, for example, the complexes Mo(NPh)(CH₂CHPh)(o-(Me₃SiN)₂C₆H₄) (45) and Mo(NPh)(CH₂)₄(o-(Me₃SiN)₂C₆H₄) (46) (Scheme 1.32).⁹⁷
**Scheme 1.32** Synthesis and reactivity of chelate-stabilized mono (molybdenum) d^5 complexes from Mo(NPh) _2_ Cl_2_ DME

The formation of complex 45 undoubtedly occurs via alkylation of 44, giving a di-alkyl intermediate, which then undergoes β-hydride elimination, followed by reductive elimination (Scheme 1.33). Thus, the isolation of 45 demonstrates that a Mo^VI complex can be reduced to a Mo^IV species by reaction with an appropriate alkylation agent. It is possible to envisage a similar reaction pathway occurring in WCl_6-based dimerization systems (Section 1.6). The isolation of complex 45, suggests that alkylation of a tungsten core (by a Et_4AlCl_3-x co-initiator) could then result in reduction,
yielding a $W^V$ intermediate capable of initiating dimerization via metallacycle formation (Scheme 1.34).

**Scheme 1.33** Formation of complex 45 via $\beta$-hydride elimination

Boncella has characterized Mo(NPh)(CH$_2$CHPh)(o-(Me$_3$SiN)$_2$C$_6$H$_4$) (45) using 2D COSY NMR experiments, which indicate that 45 adopts one of two conformations in
solution, resulting from differing positions of the molybdenum \( \eta^2 \) bound styrene moiety of complex 45 relative to the "fixed" imido. It is proposed that with a large degree of back bonding from the \( d^2 \)-metal, there is a considerable barrier to olefin rotation (CH\(_2\)CHPh), forcing the olefin moiety of complex 45 to adopt one of two orientations.

Synthesis of the metallacyclic complex Mo(NPh)(CH\(_2\))\(_4\)(o-(Me\(_3\)SiN)\(_2\)C\(_6\)H\(_4\)) (46) (Scheme 1.32) is of great significance as it demonstrates that group VI metallacyclopentanes are stable; suggesting that alkene coupling via a metallacycle (or oxidative coupling) mechanism in the STUK WCl\(_6\) dimerization system is viable (Section 1.6). Indeed, complex 46 is sufficiently stable to allow investigations into its reactivity to be made. Thus, Boncella has reacted the metallacyclic complex 46 with isocyanides (resulting in displacement of the metallacycle by isocyanide ligands)\(^{98}\) and AlMe\(_3\) (Scheme 1.35).\(^{99}\)

Scheme 1.35 Reactivity of a chelate-stabilized mono(imido) complex with AlMe\(_3\)

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{Ph} \\
\begin{array}{c}
\text{N} \\
\text{Mo}
\end{array} & \quad \begin{array}{c}
\text{Si} \\
\text{Me}_3
\end{array} \\
\text{Me}_3\text{Si} & \quad \text{Al} \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{SiMe}_3 \\
\text{Ph} & \quad \text{N}
\end{align*}
\]

Addition of Me\(_3\)Al to Mo(NPh)(CH\(_2\))\(_4\)(o-(Me\(_3\)SiN)\(_2\)C\(_6\)H\(_4\)) (46) (Scheme 1.35) does not simply result in alkylation of the molybdenum centre. Instead, Me\(_3\)Al also reacts as a Lewis acid forming an aluminium-centred anion, which stabilizes the new \( d^0 \)-molybdenum centre giving complex Mo(NPh)CH\(_3\)(CH\(_2\))\(_4\)(\( \eta^2 \)-C\(_6\)H\(_4\)-o-(Me\(_3\)SiN)\(_2\)AlMe\(_2\)) (47) (Scheme 1.35). The formation of 47 via reaction of Me\(_3\)Al as a Lewis acid indicates that for the STUK WCl\(_6\) dimerization system, the EtAlCl\(_2\) co-initiator is unlikely to react only as a simple alkylation agent. Indeed, the synthesis of 47 demonstrates that aluminium based Lewis acids such as EtAlCl\(_2\) or Me\(_3\)Al, have the capacity to interact with electron-rich nitrogen donors, such as imido ligands.

Tungsten mono(imido) diamine complexes can also be readily prepared, directly from mono(imido) precursors. Thus, W(NPh)Cl\(_4\)(OEt) (48) can easily be converted into W(NPh)Cl\(_2\)(o-(Me\(_3\)SiN)\(_2\)C\(_6\)H\(_4\)) (49) (Scheme 1.36), which readily reacts with Grignard reagents to give relatively stable di-alkyl complexes (Scheme 1.36, complex 50).\(^{100}\) Although the dialkyl complex 50 is stable and does not readily
undergo reductive elimination, complex 50 can be induced to undergo α-elimination in the presence of PMe₃ to give an alkylidene product (Scheme 1.36, complex 51).

**Scheme 1.36 Synthesis of tungsten chelate-stabilized mono(imido) complexes**

The stabilized mono(imido) tungsten metallacyclic complex W(NPh)(CH₂)₄(o-(Me₃SiN)₂C₆H₄) (52) can be formed via reaction of the di-Grignard Mg(CH₂)₄ with complex 49 (Scheme 1.37). Alternatively a metallacycle moiety can be synthesised by reaction of ethylene with an alkyl¹⁰¹ (53) or hydride¹⁰² (54) complexes (Scheme 1.37).
Scheme 1.37 – Formation of $W^{6}$ metallacycles from both alkyl and hydride precursors

A mechanism rationalizing the conversion of 50 to 52 can be proposed, following identification of the reaction by-products, neohexene and $CH_{2}CH'Bu$ (Scheme 1.38).$^{101}$ Production of neohexene demonstrates that 50 initially undergoes $\alpha$-hydride elimination reaction, followed by a reductive elimination to give an alkylidene functionality (Scheme 1.38, intermediate A). Metathesis with ethylene then generates the second reaction by-product $CH_{2}CH'Bu$ and a tungsten methylidene complex (Scheme 1.38, intermediate B). Reaction of two tungsten methylidene complexes then gives a $W^{6}$ core (Scheme 1.38, intermediate C), which can readily undergo oxidative coupling with ethylene to give a metallacycle (Scheme 1.38, intermediate D).
Examination of the mechanism by which W(NPh)(CH*(Bu))₂(o-(Me₃SiN)₂C₆H₄) (53) reacts with ethylene to give W(NPh)(CH₂)₄(o-(Me₃SiN)₂C₆H₄) (52), reveals that oxidative coupling of two ethylene molecules to a W⁺⁺⁺ atom is indeed a favourable reaction pathway. This is of relevance to the STUK WC₁₆ olefin dimerization system (WC₁₆, 2NH₂R, 4Et₃N, 10EtAlCl₂), in which alkene dimerization is believed to proceed via metallacycle formation, in an oxidative coupling mechanism. Thus, the synthesis of complex 52 further suggests that metallacycle intermediates are generated in alkene dimerization systems based on WC₁₆.
Chapter 1: Introduction

1.13 Aims of this Thesis

The broad aim of this thesis is to increase understanding of the STUK WCl₆-based olefin dimerization system (WCl₆, 2H₂NR, 4Et₃N, 10 EtAlCl₂), with the view of identifying both the mechanism of alkene coupling and the nature of the active initiator complex. Evolution of HCl in the STUK system, strongly suggests that either mono or bis(imido) complexes are formed in situ from reaction of WCl₆ and H₂NR. This has been corroborated by Olivier et al. who have shown that discrete mono(imido) complexes can initiate ethylene dimerization, when co-initiated by EtAlCl₂. Significantly, reactions of EtAlCl₂ and mono(imido) complexes, e.g. W(NR)Cl₄·THF, have not been studied in the absence of olefin. Thus, a key aim of this work is to investigate the reaction of EtAlCl₂ and W(NR)Cl₄·THF complexes, with the aim of assessing the mode by which EtAlCl₂ acts as a co-initiator. It is clear that aluminium alkyl halides such as EtAlCl₂ have the capacity to interact with either the chloride or imido ligands of a W(NR)Cl₄ fragment as both types of ligands have lone pairs available to donate to a RₓAlClₓLewis acid. Hence, an endeavour of this work is to assess, through the use of model reactions, the ability of a range of RₓAlClₓ reagents to bind to tungsten mono(imido) chloride complexes. The consequence of RₓAlClₓ coordination, to the reactivity of tungsten systems with ethylene is also of general interest. It is hoped that understanding the influence of RₓAlClₓ coordination, to a given complexes reactivity with alkenes, could provide key insights into the mode by which imido chloride pre-catalysts are activated by aluminium-based co-initiators.

It is clear from the reaction stiochiometry of the STUK system, in which WCl₆ is reacted with two equivalents of H₂NR that a bis(imido) complex could readily be formed in situ. As for mono(imido) systems it is known that both M(NR)₂Cl₂·DME (M= W or Mo) complexes, when treated with EtAlCl₂ can initiate ethylene dimerization, although further clarification as to the relative activities of bis and mono(imido) systems is required. Again it is unclear as to how EtAlCl₂ activates W(NR)₂Cl₂·DME complexes for ethylene dimerization. Indeed, no previous experimental investigations assessing the reactivity of RₓAlClₓ reagents with relevant bis(imido) complexes have been made. One aspiration of this work is to clarify the reactivity of tungsten and molybdenum bis(imido) systems with a range of RₓAlClₓ reagents. It is hoped that such investigations will increase insight into how EtAlCl₂ activates bis(imido) pre-catalysts for alkene dimerization.

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1.14 References

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R. Hoffmann, Nobel Lecture, 1981.


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103 M.A. Hanton, unpublished work.
Chapter 2: Evaluating the Ethylene Dimerization Capacity of Discrete Imido Complexes

2.0 Introduction

The possibility that imido complexes are formed in situ during the preparation of alkene dimerization systems generated through reaction of WCl₆ with an aniline (Chapter 1, Section 1.5, Scheme 1.17) has led to investigation into the capacity of both discrete bis(imido) and mono(imido) tungsten complexes to initiate alkene dimerisation.¹ For example, work conducted at Sasol Technology UK Ltd (STUK) concluded that tungsten and molybdenum bis(imido) dichloride complexes, e.g. W(NPh)₂Cl₂.TMEDA and Mo(NAr)₂Cl₂,DME (23) can both readily initiate ethylene dimerization when co-initiated with EtAICl₂.² Similarly, in a related study Olivier et al. have investigated the initiator ability of a range of discrete mono(imido) pre-catalysts. Olivier and co-workers established that complexes such as W(NAr)Cl₄.THF (38), when activated by EtAICl₂ generate initiator systems capable of inducing both ethylene and propylene dimerization.³

A second conclusion of Olivier's investigation concerned the reaction of the W⁷ complex W(NPh)(Cl)₂(PMe₃)₃ (34) with AlCl₃ (in chlorobenzene or chloroaluminate ionic liquids), which was found to produce an active ethylene dimerization initiator.³ As AlCl₃ has the capacity to react as a Lewis acid, Olivier proposed that the active initiator in the W(NPh)(Cl)₂(PMe₃)₃/AlCl₃ system is formed via halide abstraction giving an AlCl₄⁻ anion. Thus, displacement of a chloride ligand by AlCl₃ is postulated to generate a coordinatively unsaturated tungsten centre, which can then react with ethylene to form a metallacycle (Scheme 2.1), enabling dimerization of ethylene via an oxidative coupling cycle. However, it should be stressed that this proposed activation pathway has not been proven experimentally as none of the intermediates suggested by Olivier have been isolated or observed spectroscopically.
Chapter 2

Scheme 2.1 Formation of a charged active initiator complex (ethylene dimerization) as proposed by Olivier et al.\textsuperscript{3}

With a view to examining the plausibility of an ionic complex forming in Olivier’s W(NPh)(Cl)\textsubscript{2}(PM\textsubscript{e}\textsubscript{3})\textsubscript{3}/AlCl\textsubscript{3} dimerization system (Scheme 2.1), in this chapter the relative capacity of the Lewis acids EtAlCl\textsubscript{2}, B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}, and Me\textsubscript{3}Al to activate W(NPh)(Cl)\textsubscript{2}(PM\textsubscript{e}\textsubscript{3})\textsubscript{3} (34) towards ethylene dimerization has been examined. Particular emphasis has been placed on assessing if abstraction of a chloride moiety from 34 is a pre-requisite for initiator formation, as activation of the W\textsuperscript{V} complex 34 may be achievable by simply displacing a PM\textsubscript{e}\textsubscript{3} ligand using a weak Lewis acid (Scheme 2.2).

Scheme 2.2 Potential activation of W(NPh)(Cl)\textsubscript{2}(PM\textsubscript{e}\textsubscript{3})\textsubscript{3} (34) by Me\textsubscript{3}Al

The investigations made by Olivier and co-workers\textsuperscript{3} and STUK\textsuperscript{2} have established that tungsten imido chloride complexes can be used as alkene dimerization pre-catalysts. However, neither study examined the relative activities given by each type of imido complex. Thus, in this Chapter the relative abilities of both mono- and bis(imido) pre-catalysts to initiate ethylene dimerization have been
assessed using directly comparable reaction conditions for the first time. In particular, attention here has focussed on any differences displayed by mono and bis(imido) pre-catalysts, in order to establish if similar active initiator complexes are operating in each system. Notably, the studies conducted by Olivier and STUK concerned exclusively the use of mono and bis(imido) chloride complexes. Hence, no previous investigations have been made into the activation of imido complexes with groups other than chloride ligands (such as amido groups). This is relevant since it is quite feasible that mixed amido/imido complexes may be formed in the STUK dimerization system during preparation of initiator solutions, which requires reaction of WCl6 with an amine. Indeed, it has previously been reported that reaction of WCl6 with 10H2N'Bu gives the bis(imido) bis(amido) complex W(N'Bu)2(N'H'Bu)2 (41). Thus, assessing the ability of EtAlCl2 to activate discrete amido complexes for ethylene dimerization is of interest and has also been examined in this Chapter.

2.1 Synthesis and Characterization of the bis(imido) Pre-catalysts W(NAr)2Cl2.DME (40) and Mo(NAr)2(N'H'Bu)2 (55)

To provide starting pre-catalysts for an ethylene dimerization study, both W(NAr)2Cl2.DME (40) and the new complex Mo(NAr)2(N'H'Bu)2 (55) have been synthesised using simple “one-pot” procedures. Both 40 and 55 have been characterized by single crystal X-ray diffraction studies; the resulting molecular structures will be discussed in this section.

2.1.1 Synthesis and Characterization of the Mixed bis(imido) bis(amido) Complex Mo(NAr)2(N'H'Bu)2 (55)

Wilkinson et al. have previously reported the synthesis of the mixed bis(alkyl imido) bis(amido) complex Mo(N'Bu)2(N'H'Bu)2 (56). However, complex 56 contains electron donating 'Bu imido ligands; this is undesirable as it has been found that pre-catalysts with 'Bu bis(imido) moieties tend to generate inactive alkene dimerization systems. Consequently, attention turned to synthesising a more appropriate mixed bis(aryl imido) bis(amido) complex containing electron withdrawing imido ligands.

Addition of two equivalents of LiNH'Bu to Mo(NAr)2Cl2.DME (23) (Ar = 2,6-diisopropylphenyl) was found to give the bis(aryl imido) bis(amido) complex Mo(NAr)2(N'H'Bu)2 (55) (Scheme 2.3). Characterization of 55 using 1H NMR spectroscopy gives a single 'Bu resonance as well as a single set of 'Pr resonances (doublet and septet). This is consistent with both imido ligands of 55 being equivalent. Recrystallization of complex 55 from hexane gave large, bright red
crystals of sufficient quality for single crystal X-ray diffraction analysis (Figure 2.1 and Table 2.1).

Scheme 2.3 Synthesis of Mo(NAr)$_2$(NH$^t$Bu)$_2$ (55)

Figure 2.1 Solid state structure of Mo(NAr)$_2$(NH$^t$Bu)$_2$ (55) with the thermal ellipsoids set at the 50% level. Two orientations of 55 have been included for clarity.

Table 2.1 Selected bond distances (Å) and bond angles (°) for Mo(NAr)$_2$(NH$^t$Bu)$_2$ (55)

<table>
<thead>
<tr>
<th></th>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-N2</td>
<td>1.7543(15)</td>
<td>N3-C7 1.476(2)</td>
</tr>
<tr>
<td>Mo-N1</td>
<td>1.7609(14)</td>
<td>N4-C17 1.476(2)</td>
</tr>
<tr>
<td>Mo-N4</td>
<td>1.9495(16)</td>
<td>N2-Mo-N1 112.32(7)</td>
</tr>
<tr>
<td>Mo-N3</td>
<td>1.9537(16)</td>
<td>N3-Mo-N4 111.88(7)</td>
</tr>
<tr>
<td>N1-C1</td>
<td>1.401(2)</td>
<td>Mo-N1-C1 155.32(13)</td>
</tr>
<tr>
<td>N2-C11</td>
<td>1.392(2)</td>
<td>Mo-N2-C11 170.28(13)</td>
</tr>
</tbody>
</table>

As discussed in Chapter 1, Section 1.7 for a given bis(imido) system it is the relative lengths of the M-N contacts that gives the most accurate indication as to the bonding mode adopted by each imido ligand. For complex (55) the Mo-N1 and Mo-N2 contacts at 1.7543(15) Å and 1.7609(14) Å respectively are similar. This indicates that both imido ligands of 55 adopt a bonding mode between that of a 2 and 4 electron donor (neutral formalism), an arrangement which is commonly associated
with terminal bis(imido) complexes.⁷ It is clear from the N2-Mo-N1 112.32(7)° and N3-Mo-N4 111.88(7)° bond angles that complex 55 is pseudo tetrahedral, a similar geometry being adopted by the closely related complex Mo(NAr)₂(NHAr)₂ (57).⁸ One notable difference between the structures adopted by the complexes 55 and 57 concerns the orientation of the 2,6-diisopropyl phenyl fragments. In the molecular structure of 55, the 2,6-diisopropyl phenyl groups lie approximately parallel to each other (Figure 2.1). In contrast, in the molecular structure adopted by Mo(NAr)₂(NHAr)₂ (57) the two diisopropylphenyl moieties adopt a perpendicular orientation, which presumably minimizes steric interactions between the bis(imido) and bulky bis(amido) NHAr ligands (Figure 2.2).

**Figure 2.2** Solid state structure of Mo(NAr)₂(NHAr)₂ (57) obtained from the Cambridge structural data base

- **2.1.2 Synthesis and Characterization of W(NAr)₂Cl₂.DME (40) by Single Crystal X-Ray Diffraction Analysis**

The complex W(NAr)₂Cl₂.DME (40) was prepared using a variation of the procedure described by Schrock et al.⁹ A suspension of WO₂Cl₂ in DME was treated with H₂NAr in the presence of excess 2,6-lutidene and C₅SiMe₃. Following work-up, complex 40 was isolated in approximately 30% yield. As reported by Schrock, W(NAr)₂Cl₂.DME (40) was found to present a single set of ¹Pr resonances in its ¹H NMR spectrum when analysed in either C₆D₆ or CDCl₃. Recrystallization of W(NAr)₂Cl₂.DME (40) from a concentrated DME solution at room temperature gave single crystals of complex 40 of sufficient quality for X-ray diffraction analysis (Figure 2.3 and Table 2.2).¹

¹ Surprisingly the molecular structure of W(NAr)₂Cl₂.DME (40) is not currently deposited in the Cambridge Structural Database.
Figure 2.3 Solid state structure of $\text{W(NAr)}_2\text{Cl}_2\cdot\text{DME}$ (40) with the thermal ellipsoids set at the 50% level. Two orientations of 40 have been included for clarity.

Table 2.2 Selected bond distances (Å) and bond angles (°) for $\text{W(NAr)}_2\text{Cl}_2\cdot\text{DME}$ (40)

<table>
<thead>
<tr>
<th></th>
<th>W-N1</th>
<th>O2-W-O1</th>
<th>70.06(6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-N2</td>
<td>1.7599(17)</td>
<td>N1-W-N2</td>
<td>103.89(8)</td>
</tr>
<tr>
<td>N2-C11</td>
<td>1.395(3)</td>
<td>N2-W-O2</td>
<td>96.69(7)</td>
</tr>
<tr>
<td>W-Cl1</td>
<td>2.3841(7)</td>
<td>W-N2-C11</td>
<td>161.47(15)</td>
</tr>
<tr>
<td>W-O1</td>
<td>2.3494(15)</td>
<td>Cl1-W-Cl2</td>
<td>154.28(2)</td>
</tr>
</tbody>
</table>

The complex $\text{W(NAr)}_2\text{Cl}_2\cdot\text{DME}$ (40) adopts a distorted octahedral structure, with the chloride ligands lying $\text{trans}$ to one another. Distortion from an ideal octahedral polyhedron is clear from the obtuse Cl-W-Cl bond angle of 154.28(2)°. A similar distortion is observed in the molecular structure of the closely related complex $\text{Mo(N(C}_6\text{H}_4\text{-o-(CN)}_2\text{)}_2\text{Cl}_2\cdot\text{DME}}$ (58),$^{10}$ which has a Cl-Mo-Cl bond angle of 159.71(5)°. Schrock has carried out SCRF-Xα-SW calculations on a $\text{W(NH)}_2\text{(PH}_3\text{)}_2$ core, concluding that minimizing of the P-W-P bond angle maximizes the stabilizing interaction between the phosphine ligand frontier orbitals and the vacant tungsten 5a1 orbital.$^{11}$ Although the $\text{W(NH)}_2\text{(PH}_3\text{)}_2$ fragment considered by Schrock was tetrahedral and the complexes 40 and 58 are both distorted octahedral, it is reasonable to speculate that a similar effect may be occurring for the complexes 40 and 58, with a bending of the Cl-M-Cl bond angle potentially occurring to increase interaction between the chloride and tungsten/molybdenum frontier orbitals.
2.2 Ethylene Dimerization Systems Produced From Reaction of Imido Halide Complexes with the co-Initiators EtAlCl₂ and B(C₆F₅)₃

As stated in Section 2.1 complexes 40 and 55 were synthesised for use as catalyst precursors in an ethylene dimerization study. To extend the range of complexes available for this study, additional mono and bis(imido) complexes have been prepared using established literature procedures. Subsequently, the capacity of each of the discrete imido complexes to initiate ethylene dimerization after reaction with a given co-initiator (typically EtAlCl₂) was assessed (Table 2.3). It should be stressed that the high pressure ethylene dimerization study reported herein, was conducted in collaboration with Dr. M.J. Hanton (Sasol Technology UK Ltd). In this study the pre-catalyst solutions were charged to an autoclave, which was then pressurized with ethylene. Through the use of a mass flow controller the pressure of the reaction vessel was kept constant throughout the catalyst test run. As ethylene uptake could be monitored, the reactions were terminated as soon as it became apparent that reaction of ethylene had ceased. This approach allows for a more accurate measure of a given initiator's activity.

Table 2.3 Ethylene dimerization using pre-formed mono and bis(imido) pre-catalysts

<table>
<thead>
<tr>
<th>run</th>
<th>Pre-Catalyst</th>
<th>Co-initiator</th>
<th>Time (mins)</th>
<th>TON&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Activity&lt;sup&gt;a&lt;/sup&gt;</th>
<th>C₄ (%)</th>
<th>1-C₄ in C₄ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>W(NAr)₂Cl₂.DME (40)</td>
<td>EtAlCl₂</td>
<td>20</td>
<td>58,043</td>
<td>174,128</td>
<td>84.1</td>
<td>57.2</td>
</tr>
<tr>
<td>2</td>
<td>Mo(NAr)₂Cl₂.DME (23)</td>
<td>EtAlCl₂</td>
<td>55</td>
<td>58,503</td>
<td>63,821</td>
<td>88.9</td>
<td>63.7</td>
</tr>
<tr>
<td>3</td>
<td>Mo(NAr)₂(NH'Bu)₂ (56)</td>
<td>EtAlCl₂</td>
<td>54</td>
<td>56,938</td>
<td>62,876</td>
<td>87.7</td>
<td>62.9</td>
</tr>
<tr>
<td>4</td>
<td>Mo(NAr)(N'Bu)Cl₂.DME (11)</td>
<td>EtAlCl₂</td>
<td>80</td>
<td>59,508</td>
<td>44,874</td>
<td>89.3</td>
<td>61.5</td>
</tr>
<tr>
<td>5</td>
<td>Mo(N'Bu)₂Cl₂.(DME) (26)</td>
<td>EtAlCl₂</td>
<td>74</td>
<td>14,028</td>
<td>11,361</td>
<td>88.9</td>
<td>63.7</td>
</tr>
<tr>
<td>6</td>
<td>W(NPh)Cl₄.THF (32)</td>
<td>EtAlCl₂</td>
<td>61</td>
<td>21,385</td>
<td>20,807</td>
<td>90</td>
<td>74.5</td>
</tr>
<tr>
<td>7</td>
<td>W(NAr)Cl₄.THF (38)</td>
<td>EtAlCl₂</td>
<td>80.0</td>
<td>46,321</td>
<td>34,857</td>
<td>88.2</td>
<td>64.2</td>
</tr>
<tr>
<td>8</td>
<td>W(NPh)(Cl)₂(PMe₃)₃ (34)</td>
<td>EtAlCl₂</td>
<td>68</td>
<td>62,632</td>
<td>55,195</td>
<td>90.5</td>
<td>63.1</td>
</tr>
<tr>
<td>9</td>
<td>W(NPh)(Cl)₂(PMe₃)₃ (34)</td>
<td>B(C₆F₅)₃</td>
<td>18.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>Ta(NAr)Cl₆(TMEDA) (59)</td>
<td>EtAlCl₂</td>
<td>75</td>
<td>26,447</td>
<td>21,158</td>
<td>86.3</td>
<td>72.4</td>
</tr>
</tbody>
</table>

<sup>a</sup> General conditions: 0.2 mmol precatalyst for all runs; 3.0 mmol EtAlCl₂ (runs 1-9 inclusive); 0.8 mmol B(C₆F₅)₃ (run 10); PhCl (solvent) 74.2 ml; 60°C; ethylene pressure (40 bar); stirrer speed 1000 rpm; nonane standard (0.5 mL).<br>b) TON is reported in mol/mol. c) Activity is reported in mol/mol/h. d) In all runs C₆ alkenes were produced (8-15%) as well as trace C₅ (2-3%).
For the range of pre-initiators screened (Table 2.3) the highest activity and TON was obtained from the system based on W(NAr)₂Cl₂,DME (40) (174,128 mol/mol/h; run 1). Notably similarly high TONs were obtained from molybdenum *bis*(imido) pre-catalysts (runs 2-4). This demonstrates that molybdenum *bis*(imido) complexes can readily be activated by EtAlCl₂ to give productive ethylene dimerization initiators. Moreover, for runs 2-4 the selectivity of these molybdenum-based ethylene dimerization systems for butenes was high ranging between 84-89%.

It is interesting to note the similarity in TONs and activities obtained in the catalyst runs 2 and 3 in which the pre-catalysts Mo(NAr)₂(NH'Bu)₂ (55) and Mo(NAr)₂Cl₂,DME (23) are employed. This suggests that EtAlCl₂ can effectively activate both molybdenum amido and chloride species generating a very similar active molybdenum initiator complex in each case.

The higher TON and activity displayed by the tungsten *bis*(imido) system (run 1) relative to the runs in which tungsten *mono*(imido) pre-catalysts were employed (runs 6 and 7) contradicts a recent DFT investigation made by Tobisch. In this theoretical study it is proposed that *mono*(imido) ethylene dimerization initiators are inherently more active than related *bis*(imido) complexes. Tobisch also states that the activity observed in systems based on a *bis*(imido) pre-catalyst must result from the evolution of *mono*(imido) active initiator complexes *in situ*. This transformation is proposed to occur via displacement of an imido ligand of a *bis*(imido) fragment by an aluminium alkyl dimer (Scheme 2.3).

**Scheme 2.3** Tobisch's proposed route to a *mono*(imido) initiator from a *bis*(imido) pre-catalysts.

If indeed *bis*(imido) pre-catalysts were converting to give *mono*(imido) initiators, then one would expect the *bis*(imido) systems never to exceed the activity and TON observed in the *mono*(imido) runs. From the data outlined in Table 2.3 this is clearly
not the case. Also of significance is the extremely limited precedent in the literature for the type of reaction outlined in Scheme 2.3. Although it has been found that displacement of an imido ligand of a bis(imido) moiety is achievable via reaction of a phosphine (Scheme 2.4) or HCl, to date there are no procedures that have been outlined in which an imido ligand is displaced from a metal centre via reaction with an aluminium alkyl halide or a similar group 13 Lewis Acid.

Scheme 2.4 Displacement of an imido ligand by PMe3

A further argument against the formation of a mono(imido) active initiator complex from a bis(imido) pre-catalyst via the pathway outlined in Scheme 2.3 can be made by comparison of the activities obtained in runs 2, 4, and 5, which employ Mo(NAr)2Cl2.DME (23), Mo(NAr)(N'Bu)Cl2.DME (11), and Mo(N'Bu)2Cl2.DME (26), respectively (Table 2.3). Although similar catalyst TONs are obtained in runs 2 and 4, a marked decrease in activity results from substitution of the pre-catalysts Mo(NAr)2Cl2.DME (23) (run 2, 63,821 mol/mol/h) for the mixed imido complex Mo(NAr)(N'Bu)Cl2.DME (11) (run 4, 44,874 mol/mol/h). This can be attributed to the influence of the electron donating 'Bu ligand, which clearly inhibits catalysis. This effect is further highlighted by reaction of the pre-catalysts Mo(N'Bu)2Cl2.DME (26), which results in the lowest TON and activity of all the bis(imido) systems (run 5; 14,028 mol/mol and 11,361 mol/mol/h). If the pre-catalysts 23, 11, and 26 were converted to mono(imido) initiators, then one would predict that the mixed complex Mo(NAr)(N'Bu)Cl2.DME (11) would give the same activity as either Mo(NAr)2Cl2.DME (23) or Mo(N'Bu)2Cl2.DME (26). Clearly this is not the case, further suggesting that formation of a mono(imido) initiator complex from bis(imido) pre-catalysts via the pathway outlined in Scheme 2.3 is not viable.

Notably, systems based on the mono(imido) complexes W(NAr)Cl4.THF (38) and W(NPh)Cl4.THF (32) (runs 6 and 7, Table 2.3) were less active than related bis(imido) systems. However, both 38 and 32 gave good selectivity for C4 products.
Furthermore, the highest selectivity for but-1-ene in all runs was obtained using complex 32 (run 6). As such, discrete mono(imido) complexes could find application as highly selective alkene dimerization initiators.

2.2.1 Activation of W(NPh)(Cl)2(PMe3)3 (34) for Ethylene Dimerization

Olivier et al. have shown that W(NPh)(Cl)2(PMe3)3 (34) can be activated by AlCl3 to give an ethylene dimerization system. To assess if it is possible to activate 34 through the use of reagents other than AlCl3, W(NPh)(Cl)2(PMe3)3 (34) was treated with EtAlCl2 or B(C6F5)3 (Table 2.3, runs 8 and 9). The boron-based Lewis acid B(C6F5)3 was selected because B(C6F5)3 is known to be an effective phosphine scavenger. For example, B(C6F5)3 can be used to activate ruthenium carbene Grubbs alkene metathesis initiators by typically displacing a PCy3 ligand, which simultaneously generates a vacant coordination site at Ru and a Cy3P.B(C6F5)3 Lewis base/Lewis acid adduct. Thus, reaction of B(C6F5)3 and W(NPh)(Cl)2(PMe3)3 (34) is anticipated to result in dissociation of PMe3 ligands giving a Wv complex potentially capable of accommodating ethylene coordination. This in turn could result in ethylene dimerization via a metallocycle (oxidative coupling) mechanism (Scheme 2.5).

**Scheme 2.5 Potential activation of W(NPh)(Cl)2(PMe3)3 (34) with B(C6F5)3**

It was found that treatment of 34 with B(C6F5)3 failed to produce an active initiator complex, with no ethylene dimerization being observed (run 9, Table 2.3). Evidently activation of 34 by displacement of a PMe3 ligand by B(C6F5)3 is not viable. Consequently, the reactivity of W(NPh)(Cl)2(PMe3)3 (34) with the Lewis acid Me3Al was examined. Following treatment of W(NPh)(Cl)2(PMe3)3 (34) with Me3Al in C6D6, the 31P NMR spectrum of the reaction mixture presented a new broad resonance at
-21.2 ppm. This is consistent with the \textit{in situ} formation of \((\text{Me}_3\text{P})_x(\text{AlMe}_3)_y\) adducts,\textsuperscript{3} suggesting that the \(\text{PMe}_3\) moieties of 34 are indeed being displaced by \(\text{Me}_3\text{Al}\). Subsequent addition of ethylene to the \(\text{Me}_3\text{Al}\) reaction mixture did not result in ethylene dimerization. This again indicates that 34 cannot be activated for ethylene dimerization by displacement of \(\text{PMe}_3\) ligands alone, with further modification of the \(\text{W(NPh)Cl}_2\) framework being necessary.

In contrast to run 9 reaction of \(\text{W(NPh)(Cl)}_2(\text{PMe}_3)_3\) (34) and \(\text{EtAlCl}_2\) (Table 2.3, run 8) generated a dimerization system with both high TON and activity (62,632 mol/mol and 55,195 mol/mol/h). Notably, run 8 has the highest TON and activity of all the dimerization systems based on \textit{mono}(imido) complexes described in Table 2.3. It can be concluded that activation of 34 by \(\text{EtAlCl}_2\) undoubtedly occurs via phosphine displacement and then modification of the \(\text{W(NPh)Cl}_2\) moiety.

\textbf{2.2.2 Dimerization Systems Based on Tantalum \textit{mono}(Imido) Complexes}

In Section 2.2 it was shown that a range of tungsten \textit{mono}(imido) chloride complexes can be used as pre-catalysts for ethylene dimerization. Of general interest is assessing if other related \textit{mono}(imido) complexes can be similarly activated for ethylene dimerization. As such, attention turned to investigating the activities of systems based on \textit{mono}(imido) tantalum complexes, which can easily be prepared from \(\text{TaCl}_5\).\textsuperscript{16} While tantalum imido complexes have been shown by Wigley \textit{et al.} to react with alkynes to form metallacycles,\textsuperscript{17} no previous investigations into the potential application of \(\text{Ta(NR)Cl}_3\) complexes as alkene dimerization pre-catalysts have been made. Hence, the complex \(\text{Ta(NAr)Cl}_3(\text{TMEDA})\) (59) was included in the ethylene dimerization study outlined in Table 2.3. It was found that moderate activity was obtained for the dimerization system based on complex 59 (run 10, 21,158 mol/mol/h). Indeed, the activity obtained from 59 is comparable to that found for \(\text{W(NPh)Cl}_4\cdot\text{THF}\) (32) (run 6, 20,807 mol/mol/h). Evidently, the production of \(\text{C}_4\) olefins in run 10 shows that a group 6 metal is not an essential prerequisite for \textit{mono}(imido) alkene dimerization pre-catalyst.

\textbf{2.2.3 Reaction of \(\text{Mo(NAr)}_2(\text{NH}^\text{Bu})_2\) (55) with \(\text{Me}_3\text{Al}\)}

In Section 2.2 it was established that \(\text{Mo(NAr)}_2(\text{NH}^\text{Bu})_2\) (55) can be activated for ethylene dimerization using \(\text{EtAlCl}_2\) (run 3, 62,876 mol/mol/h). To further assess the reactivity of \(\text{Mo(NAr)}_2(\text{NH}^\text{Bu})_2\) (55) with \(\text{R}_x\text{AlCl}_{3-x}\) reagents, complex 55 was treated with \(\text{Me}_3\text{Al}\) in \(\text{C}_6\text{D}_6\). It was found that reaction of \(\text{Me}_3\text{Al}\) resulted in the formation of the known complex \(\text{Mo(NAr)}_2\text{Me}_2\) (27).\textsuperscript{18} This demonstrates that molybdenum amido moieties can be alkylated by \(\text{R}_x\text{AlCl}_{3-x}\) reagents, indicating that reaction of \(\text{EtAlCl}_2\) and
55 in run 3 generates a molybdenum ethyl intermediate, from which the active initiator complex is then derived.

2.3 Investigating the Reactivity of EtAlCl₂ and Et₂Al₂Cl₃ with mono- and bis(imido) Complexes

It has been established in Section 1.2 that both mono and bis(imido) complexes of molybdenum and tungsten can initiate ethylene dimerization in the presence of an ethyl aluminium species. With the aim of trying to understand the mode by which EtAlCl₂ co-initiates reaction of ethylene, attention turned to investigating the stoichiometric reactions of both types of imido complexes with EtAlCl₂ or Et₂Al₂Cl₃.

2.3.1 Reaction of EtAlCl₂ and Et₂Al₂Cl₃ with bis(imido) Complexes

Addition of one equivalent of EtAlCl₂ to a hexane solution of Mo(N'Bu)₂Cl₂.DME (26) results in the formation of an unknown (EtAlCl₃)x.(DME)y Lewis base/Lewis acid adduct and the known complex Mo(N'Bu)₂Cl₂ (21). To further clarify the reactivity of complex 26 with one equivalent of EtAlCl₂, the reaction of 26 in the presence of a phosphine (PPh₃) has been examined. Thus, in a "one-pot" procedure, Mo(N'Bu)₂Cl₂.DME (26) was treated with one equivalent of EtAlCl₂ and then PPh₃, this generated the new complex Mo(N'Bu)₂Cl₂.PPh₃ (60) (Scheme 2.6).

The formation of Mo(N'Bu)₂Cl₂ (21) and complex 60 from reaction of Mo(NtBu)₂Cl₂. DME (26) and EtAlCl₂ indicates that the first action of the aluminium alkyl halide is to displace the coordinating DME moiety. Of greater interest is determining the reaction products obtained from treatment of 26 with excess EtAlCl₂, as it is through reaction of excess EtAlCl₂ that bis(imido) pre-catalysts are activated. Hence, a toluene solution of Mo(N'Bu)₂Cl₂.DME (26) was treated with three equivalents of EtAlCl₂. However, this procedure generated numerous reaction products, unidentifiable by NMR spectroscopic analysis.

Although Mo(N'Bu)₂Cl₂.DME (26) does react with excess PPh₃ to give Mo(N'Bu)₂Cl₂.PPh₃ (60) in the absence of EtAlCl₂ the reaction is slow (2 h) and only 60% conversion of 26 is obtained.
2.3.2 Reaction of $\text{W(NAr)}_2\text{Cl}_2\cdot\text{DME}$ (40) with $\text{Et}_3\text{Al}_2\text{Cl}_3$ and $\text{EtAlCl}_2$

The dimerization system based on the pre-catalyst $\text{W(NAr)}_2\text{Cl}_2\cdot\text{DME}$ (40) has been shown to be the most active system identified in the comparative ethylene dimerization study outlined in Section 2.2, Table 2.3. Consequently, attention turned to studying the reactivity of $\text{W(NAr)}_2\text{Cl}_2\cdot\text{DME}$ (40) with excess $\text{Et}_x\text{AlCl}_{3-x}$ reagents, with a view to identifying the mode by which 40 is activated. Thus, $\text{W(NAr)}_2\text{Cl}_2\cdot\text{DME}$ (40) has been reacted with both $\text{Et}_x\text{AlCl}_{3-x}$ and $\text{EtAlCl}_2$ in $\text{C}_6\text{D}_6$ in sealed NMR tubes and the reactions probed using $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy. For both aluminium reagents, numerous reaction products were observed to form. Although it was clear that complex 40 had been completely consumed in each reaction, it was not possible to identify the structure of the resulting products from reaction of $\text{W(NAr)}_2\text{Cl}_2\cdot\text{DME}$ (40) with either $\text{Et}_3\text{Al}_2\text{Cl}_3$ or $\text{EtAlCl}_2$. However, $^1\text{H}$ NMR spectroscopic analysis of each reaction mixture indicated the formation of ethane in both cases. It is proposed that this ethane originates from a tungsten diethyl precursor (formed from W-Cl/Al-Et exchange), which first undergoes $\beta$-hydride elimination and then reductive elimination, generating a $\text{W}^{IV}$ intermediate (Scheme 2.7).
Scheme 2.7 Possible mechanism for the formation of ethane upon reaction of W(NAr)2Cl2.DME (40) with EtAlCl2 or Et3Al2Cl3.

The operation of the type of reaction pathway outlined in Scheme 2.7 would be further supported by the identification of a tungsten-bound ethylene ligand or the evolution of a molecule of free ethylene. Although no ethylene moieties were observed using 1H NMR spectroscopy there is, however, strong precedent in the literature for the activation of a WII complex via the pathway summarized in Scheme 2.7. For instance, as mentioned in Chapter 1, Section 1.13, reaction of Mo(NPh)Cl2(PMe3)(o-(Me3SiN)2C6H4) (44) with PhCH2CH2MgCl has been shown by Boncella et al. to give the olefin complex Mo(NPh)(CH2CHPh)(o-(Me3SiN)2C6H4) (45) via elimination of Ph2CH2CH3 (Scheme 2.8).20

Scheme 2.8 Synthesis of Mo(NPh)(CH2CHPh)(o-(Me3SiN)2C6H4) (45)

The reaction pathway proposed in Scheme 2.7 is also supported by recent work conducted by Girolami et al. who have synthesised the d8 W(II) salt [Li(TMEDA)]3[W(H2)4] (61) via reaction of EtLi with WCl3(OMe)3 in the presence of TMEDA.21 The ethylene and hydride ligands of 61 must form via β-hydride elimination from an intermediate tungsten ethyl group as in Scheme 2.7. Furthermore, the synthesis of 61 demonstrates that WII complexes can be reduced by organometallic ethylating agents.

To further investigate the nature of dimerization systems based on W(NAr)2Cl2.DME (40), ethylene was added to the EtAlCl2/CD2 reaction mixtures. It
was found that addition of ethylene (~1 bar) to the W(NAr)_2Cl_2.DME/EtAlCl_2 and W(NAr)_2Cl_2.DME/Et_3Al_2Cl_3 reactions did not result in higher olefin formation. This is surprising since the product from the reaction of W(NAr)_2Cl_2.DME (40) with EtAlCl_2 (Section 1.2, Table 2.3, run 1) readily initiates ethylene dimerization under more forcing conditions. This is suggestive that for bis(imido) systems to produce butenes, high ethylene pressures are essential. Evidently, the activities of dimerization systems based on bis(imido) pre-catalyst W(NAr)_2Cl_2.DME (40) are highly dependent on the reaction conditions.

2.3.3 Reaction of mono(imido) Complexes with one Equivalent of EtAlCl_2

The comparative ethylene dimerization study highlighted in Section 2.2 clearly indicates that mono(imido) complexes can be activated by EtAlCl_2 for ethylene dimerization. As such, treatment of W(NR)_2Cl_4.THF complexes with EtAlCl_{3-x} reagents in the absence of alkenes could yield information regarding the mode of initiator formation. Thus, the reaction of one equivalent of EtAlCl_2 with W(NPh)_2Cl_4.THF (32), in toluene was undertaken. This gave a light brown precipitate, which was collected via filtration and analysed using NMR spectroscopy. A marked shift in the position of both the THF ^H NMR resonances was observed in the ^H NMR spectrum (compared to the related THF resonances of complex 32), consistent with the formation the adduct EtAlCl_2.(THF)_2.ii This was established by analysis of an authentic sample of EtAlCl_2.(THF)_2 which gave identical ^H NMR resonances to that obtained in the EtAlCl_2/W(NPh)_2Cl_4.THF reaction. Hence, as for Mo(N' Bu)_2Cl_2.DME (26) (Section 2.3.1), addition of one equivalent of EtAlCl_2 to W(NPh)_2Cl_4.THF (32) has been shown to result in displacement of the coordinating solvent moiety (THF), presumably generating a W(NPh)_2Cl_4 framework. It has not been possible to verify the formation of W(NPh)_2Cl_4 (31) in this system, as reaction of EtAlCl_2 generated tungsten containing products that were insoluble in polar solvents, preventing their characterization using ^H NMR spectroscopy.

2.3.4 Reaction of mono(imido) Complexes with Excess EtAlCl_2 and Et_3Al_2Cl_3

In Section 2.3.3 it was established that reaction of W(NPh)_2Cl_4.THF (32) with one equivalent of EtAlCl_2 results in displacement of the coordinated THF moiety. Of greater interest the reactivity of mono(imido) complexes with an excess of EtAlCl_2 or

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ii The adduct EtAlCl_2.(THF)_2 has been characterized by both NMR spectroscopy and mass spectrometry, m/z = 242.8 (Al(THF)_2Cl_2^-). Integration of the ^H NMR spectrum is also consistent with two THF moieties binding to an EtAlCl_2 core.
Et$_3$Al$_2$Cl$_3$, as it is through the reaction of excess EtAlCl$_2$ that mono(imido) precatalysts are activated (Section 2.2, Table 2.3). Thus, in two separate experiments W(NPh)Cl$_4$.THF (32) was dissolved in C$_6$D$_6$ and reacted with excess EtAlCl$_2$ or Et$_3$Al$_2$Cl$_3$. In both reactions ethane was observed to form. This indicates that as for the related bis(imido) systems (Section 2.3.2), addition of Et$_3$AlCl$_3$$_x$ reagents to complex 32 results in the formation of a tungsten diethyl intermediate, which undergoes β-hydride and then reductive elimination (see Section 2.3.2 Scheme 2.7).

Notably, addition of PMe$_3$ to the W(NPh)Cl$_4$.THF/EtAlCl$_2$ reaction solution resulted in the formation of but-1-ene, which was only observable using $^1$H NMR spectroscopy after PMe$_3$ addition (Scheme 2.9). The formation of but-1-ene upon treatment of W(NPh)Cl$_4$.THF (32) with EtAlCl$_2$ and then PMe$_3$ (Scheme 2.9) can be explained by PMe$_3$ destabilizing L$_n$W$^v$-Et intermediates (Scheme 2.10). However, it is unclear as to the exact pathway by which but-1-ene is formed, as at no stage have any reaction intermediates been positively identified using NMR spectroscopy.

**Scheme 2.9 But-1-ene formation via reaction of W(NPh)Cl$_4$.THF (32)**

\[
W(NPh)Cl_4\cdot THF \xrightarrow{i) \ 5EtAlCl_2} \xrightarrow{ii) \ 10 \ PMe_3} \text{Ethane}
\]

**Scheme 2.10 Proposed route of but-1-ene formation via reaction of W(NPh)Cl$_4$.THF (32) with EtAlCl$_2$ and PMe$_3$**
Upon addition of EtAlCl₂ (five equivalents) to W(NPh)Cl₄·THF (32), broad ¹H NMR resonances were observed. Such spectral features could be due to the reduction of the W⁰ centre via the pathway outlined in Scheme 2.10 to give paramagnetic species. Indeed, reduction of 32 by EtAlCl₂ could feasibly generate paramagnetic W⁰ or W⁺ complexes via reductive elimination of ethane. Similarly, broad ¹H NMR signals were found after reaction of Ta(NAr)Cl₃·TMEDA (59) with EtAlCl₂ (five equivalents) in C₆D₆, with ethane also being observed, which is suggestive of the formation of Ta¹⁻ complexes in situ.

2.4 Micro-scale Investigations into mono(lmido)-based Alkene Dimerization Systems

In Section 2.2 both mono- and bis(lmido) complexes have been used as ethylene dimerization pre-catalysts. At high ethylene partial pressures (40 bar) (Table 2.3, Section 2.2) it has been shown that both these mono- and bis(lmido) systems can initiate ethylene dimerization. However, at lower ethylene partial pressures (~1 bar) a W(NAr)₂Cl₂·DME/EtAlCl₂ reaction solution failed to initiate ethylene dimerization (Section 2.3.2). To investigate if the same difference occurs for systems based on W(NR)Cl₄·THF complexes, attention turned to evaluating the reactions of mono(lmido) systems when lower partial pressures (~1 bar) of alkenes are employed.

An initiator solution was formed by reaction of W(NAr)Cl₄·THF (32) with eight equivalents of EtAlCl₂ in C₆D₆. Addition of ethylene to this mixture, resulted in an exothermic reaction with produced C₄ (73.3%), C₆ (22.5%) and C₈ (2.1%) alkenes (established using GC). Similarly, addition of ethylene to a W(NAr)Cl₄·THF/Et₃Al₂Cl₃ C₆D₆ solution results in the production of a range of higher olefins, the relative ratios of which were determined using GC and GC-MS (Scheme 2.11). Using related procedures it was found that addition of propylene, to a mixture of W(NAr)Cl₄ (62) and Et₃Al₂Cl₃ in C₆D₆ generated exclusively 2,3-dimethylbut-1-ene.
Scheme 2.11 Using the pre-catalysts W(NAr)Cl₄·THF (38) to initiate ethylene
dimerization on a micro-scale.

Notably, significant traces of alkanes were produced using the
W(NAr)Cl₄·THF/Et₃Al₂Cl₃ system and were detected using GC-MS (Scheme 2.11). One plausible route by which these alkanes could form is via reductive elimination from a hydride complex as illustrated in Scheme 2.12.

Scheme 2.12 Mechanism of butane formation

It is clear that the selectivity of the W(NAr)Cl₄·THF/Et₃Al₂Cl₃ initiator system for ethylene dimerization is low (~35%), with a high degree of ethylene trimerization occurring (~47%). In addition to ethylene dimerization or trimerization, alkene metathesis is also being initiated in this reaction, generating "odd" C₅ hydrocarbons, presumably from reaction of "even" alkenes derived in situ from ethylene (Scheme 2.13).
Menapace et al. have shown that the selectivity of their WCl₆ dimerization system (generated from WCl₆, 2NH₂R and Et₃Al₂Cl₃) for propylene dimerization vs. olefin metathesis was highly dependent on the relative concentration of Et₃Al₂Cl₃ co-initiator.²² Thus, at relatively low Et₃Al₂Cl₃ loadings propylene metathesis occurs (W:Al molar ratio of 1:1.5). In contrast, a large excess of Et₃Al₂Cl₃ (1:10) was found to "switch" the selectivity of the initiator system to give exclusively propylene dimerization. Hence, parallels can be drawn between the selectivity of Menapace's WCl₆ system at low Et₃Al₂Cl₂ loadings and the W(NAr)Cl₄·THF/Et₃Al₂Cl₃ system highlighted in Scheme 2.11. In both systems alkene metathesis is initiated, suggesting that similar active species are formed in situ in both cases.

2.5 Dimerization of C₂D₄ and C₂H₄ using Systems Based upon mono(Imido) Precatalysts
The discovery that systems based on mono(Imido) complexes can induce ethylene dimerization on a micro-scale using small quantities of alkene feedstock, made it of interest to investigate the mechanism of ethylene dimerization via reaction of a mixture of C₂H₄ and C₂D₄. As discussed in detail in Chapter 1, Section 1.5 Bercaw et al. have examined the mechanism of their Cr³⁺ ethylene trimerization initiator through the reaction of a 1:1 mixture of C₂D₄ and C₂H₄.²³ They observed that reaction of C₂D₄/C₂H₄ was found to give C₆ alkenes containing exclusively even numbers of deuterium and hydrogen atoms. This was cited as proof of trimerization proceeding via a metallacycle mechanism, as the alternative degenerate polymerization (or hydride) cycle would inevitably give olefin products with odd
numbers of deuterium atoms.\(^V\) As alkene trimerization and dimerization are often closely related, it is feasible that using a procedure similar to that employed in Bercaw's study could yield information as to the reaction mechanism operative for a \textit{mono}(imido)-based dimerization system.

To this end, a 1:1 mixture of \(\text{C}_2\text{D}_4\) and \(\text{C}_2\text{H}_4\) was added to a \(\text{W(NAr)}\text{Cl}_4\cdot\text{THF}/\text{Et}_3\text{Al}_2\text{Cl}_3\) \(\text{CeDe}\) initiator solution. This resulted in an immediate and exothermic reaction. Following reaction analysis of the volatile components of the mixture by both GC and GC-MS confirmed that a similar distribution of \(\text{C}_4\) and \(\text{C}_6\) products was obtained to that given by the \(\text{W(NPh)}\text{Cl}_4\cdot\text{THF}/\text{Et}_3\text{Al}_2\text{Cl}_3/\text{C}_2\text{H}_4\) system discussed in the previous section (Scheme 2.4). GC-MS analysis was hampered by the fact that under the conditions used, it was found that all the \(\text{C}_4\) isotopomers co-elute. However, using ion separation the abundance of each isotopomer of but-1-ene has been determined (Table 2.4).

\begin{table}[h!]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Isotopomers & Relative abundance predicted for a hydride cycle & Relative abundance predicted for a oxidative coupling mechanism & Observed relative abundance \\
\hline
\text{C}_4\text{H}_8 & 1 & 1 & 1.08 \\
\text{C}_4\text{H}_7\text{D} & 1 & 0 & 1.71 \\
\text{C}_4\text{H}_6\text{D}_2 & 0 & 0 & 2.70 \\
\text{C}_4\text{H}_5\text{D}_3 & 1 & 0 & 3.80 \\
\text{C}_4\text{H}_4\text{D}_4 & 2 & 2 & 4.29 \\
\text{C}_4\text{H}_3\text{D}_5 & 1 & 0 & 3.68 \\
\text{C}_4\text{H}_2\text{D}_6 & 0 & 0 & 1.13 \\
\text{C}_4\text{HD}_7 & 1 & 0 & 1.00 \\
\text{C}_4\text{D}_8 & 1 & 1 & >0.2 \\
\hline
\end{tabular}
\caption{Relative abundances of but-1-ene isotopomers obtained from dimerization of a 1:1 \(\text{C}_2\text{D}_4/\text{C}_2\text{H}_4\) mixture initiated by \(\text{W(NPh)}\text{Cl}_4\cdot\text{THF} / \text{Et}_3\text{Al}_2\text{Cl}_3\).}
\end{table}

The relative abundance of a given isotopomer predicted to be produced \textit{via} a hydride or metallacycle mechanism has been determined from the number of pathways by which each isotopomer can be produced. For example, \(\text{C}_4\text{H}_8\) can only be produced by reaction of two molecules of \(\text{C}_2\text{H}_4\) and thus has a predicted relative frequency of one for both mechanisms. In contrast, \(\text{C}_4\text{H}_4\text{D}_4\), could result from reaction of \(\text{C}_2\text{H}_4\) and

\(^V\) For example, trimerization of 3 molecules of \(\text{C}_2\text{D}_4\) by a \(\text{L}_n\text{Cr}^{\text{III}}\)-H or \(\text{L}_n\text{Cr}^{\text{III}}\)-H initiator, can generate the products \(\text{C}_6\text{D}_{12}\) or \(\text{C}_6\text{D}_{11}\text{H}\).
then $\text{C}_2\text{D}_4$ or vice versa, giving two reaction pathways. Hence, $\text{C}_4\text{H}_4\text{D}_4$ is assigned a predicted relative frequency of two (Scheme 2.14).

**Scheme 2.14** Predicting the relative abundances of $\text{C}_4\text{H}_4\text{D}_4$ and $\text{C}_2\text{D}_4$ assuming an oxidative coupling mechanism

\[
\text{L}^\text{W'}\text{V}^2 - 4 \\
\text{C}_4\text{D}_4 \\
\text{C}_2\text{D}_4 \\
\text{C}_2\text{H}_4 \\
\text{C}_2\text{H}_4 \\
\text{C}_4\text{D}_4\text{H}_4
\]

It is clear that the isotopomer distribution obtained upon reaction of $\text{C}_2\text{H}_4$ and $\text{C}_2\text{D}_4$ with the $\text{W(NPh)}\text{Cl}_4\cdot\text{THF/ Et}_3\text{Al}_2\text{Cl}_3$ initiator system (Table 2.4) does not fit uniquely that for either a hydride or metallacycle cycle process. Furthermore, the formation of olefins containing both odd and even numbers of deuterium atoms could feasibly result from the operation of either mechanism. Consequently, no detailed conclusions as to the mechanism by which the $\text{W(NAr)}\text{Cl}_4\cdot\text{THF/ Et}_3\text{Al}_2\text{Cl}_3$ system dimerizes ethylene can be made.

2.6 Assessing the Abilities of Grignard Reagents to Activate *mono*(imido) Complexes for Alkene Dimerization

In Section 2.3.4 it was established that addition of $\text{EtAI}\text{Cl}_2$ or $\text{Et}_3\text{Al}_2\text{Cl}_3$ to *mono*(imido) complexes resulted in ethane evolution, indicating that catalyst activation was occurring via a diethyl intermediate undergoing first $\beta$-hydride and then reductive elimination. To evaluate the implication of $\beta$-hydride elimination on catalyst activation, the introduction of an ethyl group to the coordination sphere of a tungsten centre using $\text{EtMgCl}$ was explored. Particular emphasis was placed on assessing the capacity of $\text{EtMgCl}$ to activate the *mono*(imido) pre-catalysts $\text{W(NAr)}\text{Cl}_4$ (62).

Notably, reaction between $\text{EtMgCl}$ and $\text{W(NAr)}\text{Cl}_4$ (62) in $\text{C}_6\text{D}_6$ results in ethane evolution. Subsequent addition of ethylene to the resulting reaction mixture was found to result in the slow formation of but-1-ene (verified by $^1\text{H}$ NMR analysis) over a 2 h reaction period (Scheme 2.15).
Scheme 2.15 Activation of W(NAr)Cl₄ (62) by EtMgCl and subsequent reaction with ethylene

\[
\text{W(NAr)Cl}_4 + 4\text{EtMgCl, ethylene} \rightarrow \text{But-1-ene}
\]

To further assess the role of EtMgCl as a co-initiator, the abilities of the reagents MeMgCl and Mg to activate W(NAr)Cl₄ (62) have also been studied. It was found that in contrast to EtMgCl, neither MeMgCl nor Mg was able to co-initiate ethylene dimerisation, although \(^1\)H NMR spectroscopy confirms that reaction of 62 occurred in each case (Scheme 2.16). As Mg turnings were unable to activate complex 62 it can be concluded that the ethylene dimerization observed in the EtMgCl system is not attributable to traces of magnesium likely to be present as an impurity in the commercially purchased EtMgCl solution. It is also evident that reduction of the W⁴⁺ atom of complex 62 by Mg does not induce dimerization. Of note is that ethane was not observed upon addition of MeMgCl to W(NAr)Cl₄ (62), suggesting that MeMgCl was unable to reduce 62. Evidently alkylation of 62 to give tungsten methyl groups, which are unable to undergo \(\beta\)-hydride elimination, disbar initiator formation. This highlights the importance of \(\beta\)-hydride elimination in the formation of the active initiator complex in the W(NAr)Cl₄/EtMgCl ethylene dimerization system. Indeed, in the EtMgCl system the active initiator complex is likely to be formed via a tungsten diethyl species undergoing first \(\beta\)-hydride elimination, and then reductive elimination, generating a W⁴⁺-ethylene complex and ethane in situ (see Section 2.3.2, Scheme 2.7).

Scheme 2.16 Assessing the relative capacities of EtMgCl, MeMgCl and Mg to activate W(NAr)Cl₄ (62)

\[
\text{EtMgCl} \xrightarrow{\text{C}_6\text{D}_6} \text{W(NAr)Cl}_4 \xrightarrow{\text{4MeMgCl, C}_6\text{D}_6} \text{No Dimerization}
\]

\[
\text{No Dimerization}
\]
2.7 Attempts to Investigate the Mode of Activation of mono(imido)-based Dimerization Systems Using C₂D₄

In Section 2.3.4 it was proposed that reduction of mono(imido) complexes by Et₃Al₂Cl₃ or EtAlCl₂ generates LnW^(IV)(CH₂CH₂) intermediates, from which the active initiator complex is believed to be derived. Further evidence to support this mode of initiator activation could be provided by the detection of alkenes containing both deuterium and hydrogen atoms, resulting from the reaction of a LnW''^(IV)(CH₂CH₂) intermediate with C₂D₄ (Scheme 2.17). Hence, using procedures outlined in this Section a C₂D₄ feedstock was reacted with a range of mono(imido) based initiator systems.

**Scheme 2.17** Potential route to olefins containing both deuterium and hydrogen atoms via reaction of a LnW''^(IV)(CH₂CH₂) intermediate

Activation of complex W(NAr)Cl₄·THF (38) by Et₃Al₂Cl₃ followed by later addition of C₂D₄ resulted in C₄ (~23%), C₅ (~6%), and C₆ (~67%) products, but no alkenes containing H-atoms were detected by either GC-MS or ¹H NMR spectroscopy. Similarly, addition of EtMgCl and then C₂D₄ to a solution of W(NAr)Cl₄·THF (38) resulted in the formation of both C₄ (~90%) and C₆ (~10%) products. Notably, no olefins with both deuterium and hydrogen atoms were found using GC-MS and no alkene ¹H NMR resonances were detected. Unfortunately, the failure to detect mixed olefins such as CH₂CHCD₂CD₂H upon reaction of C₂D₄ in either the EtMgCl or Et₃Al₂Cl₃ co-initiated mono(imido) systems neither supports nor contradicts the activation of complex 38 via the pathway outlined in Scheme 2.17. This is because activation of 38 by Et₃Al₂Cl₃ or EtMgCl followed by reaction of C₂D₄ could feasibly produce alkenes such as C₄H₄D₄ in concentrations that are too low to be detected by either ¹H NMR spectroscopy or GC-MS.
2.8 Contrasting the Capacity of EtMgCl and EtAlCl₂ to Co-Initiate Propylene Dimerization

As discussed in Section 2.7, both EtMgCl and EtAlCl₂ have been shown to activate mono(imido) complexes generating species capable of initiating ethylene dimerization. Of note is that ethylene is a relatively reactive alkene, with coordination of a C₂H₄ ligand to a given metal centre being comparatively unaffected by steric constraints. In contrast, the reactivity of propylene as a neutral ligand towards organometallic reagents tends in general to be lower. For instance, Tolman has reported that the capacity of propylene to bind to Ni(P(O-o-tolyl)₃)₃ is significantly lower than that of ethylene (Scheme 2.18).

Thus, although the W(NAr)Cl₄·THF/EtMgCl and W(NAr)Cl₄·THF/EtAlCl₂ systems are both active for ethylene dimerization, the two systems may display different reactivity with less reactive propylene. Hence, assessing the abilities of EtMgCl and EtAlCl₂ to co-initiate propylene dimerization is likely to give a more descriptive, general indication as to the effectiveness of the two reagents as alkene dimerization co-initiators.

Scheme 2.18 Contrasting the coordination of ethylene and propylene to Ni(P(O-o-tolyl))₃

\[
\begin{align*}
\text{Ni(P(O-o-tolyl))₃} + \text{Olefin} & \quad \xrightarrow{K_1} \quad \text{(olefin)Ni(P(O-o-tolyl))₃}₂ + \text{P(O-o-tolyl)}₃ \\
\text{Olefin} & \\
\text{Ethylene} & \quad 2.5 \times 10^{2} \\
\text{Propylene} & \quad 5.3 \times 10^{-1}
\end{align*}
\]

With this in mind, the mono(imido) complex W(NAr)Cl₄·THF (38) was reacted with EtAlCl₂ (eight equivalents) in C₆D₆ and to this reaction solution propylene was then added. Subsequent analysis of the volatile components resulting from this reaction using GC demonstrated that propylene dimerization, trimerization, and oligomerization had indeed been initiated, with C₆, C₉, and event trace C₁₂ products being observed. This demonstrates that W(NAr)Cl₄·THF/EtAlCl₂ will readily initiate the coupling of propylene. Notably, propylene metathesis was also co-initiated by the W(NAr)Cl₄·THF/EtAlCl₂ system resulting in both C₂ and C₄ products (as detected by GC). Significantly, reaction of propylene was initiated immediately and at room temperature.
temperature. This shows that the \( \text{EtAICl}_2 \) co-initiated system is highly reactive towards propylene.

Addition of \( \text{MgEtCl} \) and then propylene to a \( \text{C}_6\text{D}_6 \) solution of \( \text{W(NAr)}\text{Cl}_4.\text{THF} \) (38) using the same conditions to that employed in the \( \text{EtAlCl}_2 \) study, repeatedly failed to result in any reaction of the propylene. The formation of higher olefins was not detected using \( ^1\text{H} \) NMR spectroscopy, even after heating of the reaction solution (60°C, 2 h). Thus, there is a clear difference between the capacity of the reagents \( \text{EtMgCl} \) and \( \text{EtAlCl}_2 \) to activate \( \text{W(NAr)}\text{Cl}_4.\text{THF} \) (38) for propylene dimerization/oligomerization (Scheme 2.19). This indicates that an aluminium-based moiety may be an intimate component of the active initiator species in the \( \text{EtAlCl}_2 \) co-initiated system.

**Scheme 2.19 Contrasting the capacity of \( \text{EtMgCl} \) and \( \text{EtAlCl}_2 \) to activate complex 38**

\[
\begin{align*}
\text{W(NAr)}\text{Cl}_4.\text{THF} \ (38) & \xrightarrow{8\text{EtAlCl}_2, \text{C}_6\text{D}_6} \text{propylene} \rightarrow \text{C}_6, \text{C}_9, \text{C}_{12} \text{ and } \text{C}_{15} \text{ olefins} \\
\Delta 8\text{EtMgCl, C}_6\text{D}_6, \text{propylene} & \rightarrow \text{No reaction}
\end{align*}
\]

2.8.1 Investigating the Impact of Lewis acidity on mono(imido) Based Dimerization Systems

The difference between the capacity of \( \text{EtMgCl} \) and \( \text{EtAlCl}_2 \) co-initiators activate \( \text{W(NAr)}\text{Cl}_4.\text{THF} \) (38) for propylene dimerization could be attributed to a number of factors. Both \( \text{EtMgCl} \) and \( \text{EtAlCl}_2 \) are likely to have different reactivity with a tungsten chloride bond due to different Mg-C and Al-C bond strengths. Furthermore, any differences between the solution structures of \( \text{EtMgCl} \) and \( \text{EtAlCl}_2 \) (i.e. dimers) could also influence their relative reactivity with a W-Cl moiety. One crucial difference between the two species is their different Lewis acidity. Indeed, aluminium-based reagents such as \( \text{EtAlCl}_2 \) or \( \text{AlCl}_3 \) are known to be strong Lewis acids. In contrast, Grignard reagents such as \( \text{EtMgCl} \) or magnesium salts such as \( \text{MgCl}_2 \) are accepted as being much weaker Lewis acids.\(^{25}\) For instance, the weak Lewis acidity of
Grignard reagents has been used to rationalise the low activity observed for ethylene polymerization systems based upon reaction of \([\text{SmCl}_2(\text{Cp}^*)_2][\text{Li(OEt)}_2]_2\) (\(\text{Cp}^* = \text{C}_8\text{Me}_8\)) with \(\text{'BuMgEt}\). Furthermore, the complex \([\text{Sm}(\text{Cp}^*)_2\text{Me(THF)}] \) (63) (Figure 2.4), which has no associating Lewis acid fragment, is used as a model for the Mg/Sm ethylene polymerization system. Although no molecular structures of bimetallic complexes of samarium and magnesium alkyls currently exist, aluminium-based reagents are known to readily bind to \((\text{Cp}^*)_2\text{Sm}\) fragments as coordinating Lewis acids. Thus, the synthesis of \([\text{Sm}(\text{Cp}^*)_2\text{AlEt}_4]\) (64) (Figure 2.4) is entirely consistent with the greater Lewis acid acidity of aluminium alkyls compared with their magnesium-based counterparts.

Figure 2.4 Molecular structures of \([\text{Sm}(\text{Cp}^*)_2\text{Me(THF)}]\) and \([\text{Sm}(\text{Cp}^*)_2\text{AlEt}_4]\)

Another relevant difference between \(\text{RMgCl}\) and \(\text{R}_x\text{AlCl}_{3-x}\) reagents concerns the reactivity of the two classes of compounds with ethylene. In contrast to \(\text{RMgX}\) reagents, it is known that simple aluminium alkyl halides can function as ethylene polymerization initiators. To investigate if alkene dimerization is occurring at an aluminium centre in the \(\text{W(NAr)Cl}_4\text{THF/EtAlCl}_2\) system rather than at the tungsten, control reactions were undertaken. Hence, a \(\text{C}_6\text{D}_6\) solution containing both \(\text{EtAlCl}_2\) and propylene was heated; no higher olefins were detected by \(^1\text{H}\) NMR spectroscopy. This indicates that the propylene dimerization and oligomerization initiated by the \(\text{W(NAr)Cl}_4\text{THF/EtAlCl}_2\) system do not result from reaction of \(\text{EtAlCl}_2\) as a chain transfer agent. Instead, the propylene dimerization initiated by the \(\text{EtAlCl}_2/\text{W(NAr)Cl}_4\text{THF}\) system, can be attributed to the formation of an active tungsten initiator complex via reaction of \(\text{EtAlCl}_2\) as a Lewis acid. However, the definitive structure of the active tungsten initiator complex derived from \(\text{W(NAr)Cl}_4\text{THF}\) (38) remains unclear.
2.9 Attempts to Identify any Imido Complexes Formed in the STUK WCl₆ Dimerization System

In Section 2.2 a range of bis- and mono(imido) complexes were employed as ethylene dimerization pre-catalysts, with a series of initiator test runs conducted at high pressure and temperatures (40 bars, 60 °C). It was consistently found that both molybdenum and tungsten bis(imido) complexes gave higher TON and activities than related mono(imido) tungsten pre-catalysts. Initially, this observation would suggest that it is a bis(imido) complex that is the active initiator in the STUK WCl₆ dimerization system. However, some results contradict this proposition, notably the fact that the reaction of W(NAr)₂Cl₂.DME (40) on a micro scale with Et₃Al₂Cl₃ in C₆D₆ gave a reaction solution that failed to initiate ethylene dimerization (Section 2.3.2).

In contrast, on a micro scale, in which significantly lower ethylene partial pressures were employed (<1 bar) systems based on mono(imido) complexes are capable of initiating ethylene dimerization or oligomerization at room temperature. For example, reaction of W(NAr)Cl₄.THF (38) with Et₃Al₂Cl₃ in C₆D₆ generates C₄ and C₆ dimerization and trimerization products as well as C₅ alkenes, produced via metathesis reactions. Evidently, the relative activities of bis- and mono(imido) systems for ethylene dimerization are highly dependent on reaction conditions, with systems based on mono(imido) complexes being more active when lower ethylene concentrations are used. Hence, the observed activities of both discrete mono- and bis(imido) complexes makes it unclear as to which type of imido complex is forming in the WCl₆ based STUK dimerization system.

To assess if it is a bis- or mono(imido) complex that is formed in situ in the STUK dimerization system (WCl₆, 2NH₂R, 4Et₃N, 10EtAl(Cl₂), WCl₆ was reacted with NH₂Ph and Et₃N in chlorobenzene and the resulting material analysed using multinuclear NMR spectroscopy. Neither the resulting ¹H nor the ¹³C NMR spectrum could be used to ascertain information as to the structure of the new tungsten-containing reaction products, as broad non-assignable resonances were observed. Similar results were obtained upon reaction of the amine NH₂Ar (Scheme 2.20). This indicates that more than one tungsten complex may be produced upon reaction of WCl₆ using the STUK conditions.
**Scheme 2.20** Reaction of $\text{WCl}_6$ using the STUK conditions

\[
\begin{align*}
\text{WCl}_6 & \quad \begin{array}{c} 2\text{NH}_2\text{R}, 4\text{Et}_3\text{N} \\ \text{C}_6\text{H}_5\text{Cl}, 60^\circ \text{C} \\ \text{R} = \text{Ph or Ar} \end{array} \rightarrow \text{Unknown reaction products} \\
\rightarrow W(\text{NR})(\text{NHR})_3\text{Cl} \\
\rightarrow W(\text{NR})_2(\text{NHR})_2
\end{align*}
\]

It is reasonable to assume that any bis(imido) complexes formed \textit{in situ} in the $\text{WCl}_6$ dimerization system must result from reaction of an intermediate mono(imido) complex with an amine. Hence, to ascertain the plausibility of bis(imido) complexes evolving in the STUK system, $W(\text{NPh})\text{Cl}_4\cdot\text{THF}$ (32) was reacted with $\text{H}_2\text{NAr}$ in $\text{C}_6\text{D}_6$ (Scheme 2.21).

**Scheme 2.21** Reaction of $W(\text{NPh})\text{Cl}_4\cdot\text{THF}$ (32) with $\text{H}_2\text{NAr}$ ($\text{Ar} = 2,6$ \text{Diisopropylphenyl})

\[
\begin{align*}
W(\text{NPh})\text{Cl}_4\cdot\text{THF} \quad \text{(32)} \quad H_2\text{NAr} \quad \text{C}_6\text{D}_6 & \rightarrow \text{Unknown reaction products}
\end{align*}
\]

Disappointingly, NMR spectroscopy could not be used to categorically determine the structure of the reaction products obtained from addition of $\text{HN}_2\text{Ar}$ to $W(\text{NPh})\text{Cl}_4\cdot\text{THF}$ (32), as analysis of the reaction solution presented multiple $^1\text{H}$ and $^{13}\text{C}$ alkyl resonances. Of note, however, is that a broad $\text{NH}_2$ resonance was identified at approximately 9.5 ppm, which indicates that coordination of the amine or an amide moiety to the tungsten atom does occur. In a separate reaction $W(\text{NAr})\text{Cl}_4\cdot\text{THF}$ (38) was dissolved in $\text{C}_6\text{D}_6$ and then mixed with $\text{Et}_3\text{N}$ and $\text{H}_2\text{NAr}$. Here, no reaction of the aniline was observed to occur, with no new bis(imido) species being identified using NMR spectroscopy. Hence, it has not been possible to determine if a bis(imido) complex could form \textit{in situ} from a mono(imido) intermediate in the STUK process.

Although it is still unclear as to whether \textit{mono} or bis(imido) complexes are forming in the STUK $\text{WCl}_6$ system, it is apparent that both types of imido complex react with $\text{Et}_3\text{AlCl}_{3-x}$ co-initiators to give systems active for ethylene dimerization.
(Table 2.3, Section 2.2). As such it is reasonable to speculate that both mono- and bis(imido) complexes could be formed in situ upon reaction of WCl₆ with Et₃N and NH₂R. Thus, the reactivity of both mono and bis imido pre-catalysts with RₓAlClₓ₋ₓ reagents is worthy of further investigation.

2.10 Conclusions

In this Chapter the reaction of EtAlCl₂ and EtₓAlₓCl₃ with W(NAr)₄Cl₂-DME (40), W(NAr)Cl₄-THF (38) or W(NPh)Cl₄-THF (32) in C₆D₆ resulted, in all cases, in the simultaneous production of multiple unidentifiable tungsten complexes and ethane. Ethane evolution upon addition of EtₓAlClₓ₋ₓ reagents to W⁶ chloride complexes strongly indicates that ethylation of tungsten chloride moieties results in reduction of the W⁶ atom giving LₐW⁶(CH₂CH₂) intermediates. Although significant to initiator formation, undoubtedly it is the instability of the tungsten ethyl moiety to β-hydride elimination that results in the formation of the observed multitude of tungsten-containing products. This, in turn, has prevented detailed examination as to how EtₓAlClₓ₋ₓ activates both mono and bis(imido) pre-catalysts for ethylene dimerization. However, comparison of the relative abilities of EtMgCl and EtAlCl₂ to activate mono(imido) pre-catalysts for propylene dimerization indicates that the greater capacity of EtAlCl₂ to react as a Lewis acid is crucial to the activation of mono(imido) systems (Section 2.8).

To gain a clearer insight into how RₓAlClₓ₋ₓ Lewis acids interact with imido complexes, attention turned to studying the reactivity of discrete imido complexes with methyl aluminium reagents, such as MeAlCl₂, Me₂AlCl or Me₃Al. Hence, in the following Chapters, the reaction of imido complexes with MeₓAlClₓ₋ₓ reagents will be examined. Here, the stability of tungsten methyl groups, for which β-hydride elimination reactions are impossible, is anticipated to facilitate the formation of stable discrete complexes. This will enable any potential interactions between MeₓAlClₓ₋ₓ Lewis acid and chloride or imido tungsten ligands to be clearly identified.

2.11 References

2 M.J. Hanton, Unpublished results.


Chapter 3: Reaction of Tungsten and Molybdenum bis(lmido) Dihalide Complexes with Aluminium Methyl Reagents

3.0 Introduction

Patents outlining alkene dimerization systems based on WCl₆ invariably specify that high loadings of Et₅AlCl₃-x co-initiators are optimal.¹ For example, in the WCl₆ dimerization system patented by Sasol Technology (UK) Ltd (STUK), the most favourable W:Al molar ratios are stated as being between 1:5 to 1:12 (W:Al).² This is directly related to the patented innovation of the STUK system, which is addition of a separate base, Et₃N, to the initiator solution after treatment of WCl₆ with H₂NR. Efficient removal of HCl, before the addition of the Et₅AlCl₃-x co-initiator, is believed to prevent reaction between Et₅AlCl₃-x reagents and HCl. As a result, in the STUK WCl₆-based dimerization system aluminium-based co-initiators (Et₅Al₂Cl₃ or EtAlCl₂) are present in higher effective concentrations than related processes in which HCl is not removed,¹ leading to higher initiator activity and selectivity. However, to date, the reasons why high Et₅AlCl₃-x co-initiator loadings are beneficial for WCl₆-based dimerization systems remain unclear.

As bis(lmido) complexes are postulated to be intermediates in WCl₆-based dimerization systems, the performance of alkene dimerization systems based on discrete bis(lmido) pre-catalysts have previously been investigated.³ Expanding on this preliminarily investigation a comparative ethylene dimerization study was undertaken, in Chapter 2, Section 2.2. This new study clearly showed that both molybdenum and tungsten bis(lmido) halide complexes can be activated for ethylene dimerization by EtAlCl₂ (Table 2.3). Furthermore, when high ethylene partial pressures were employed (40 bar) the activities of bis(lmido) systems were found to be greater than those based upon related mono(lmido) complexes. With a view to identifying the mode by which complexes such as W(NAr)₂Cl₂·DME (40) are activated, in Chapter 2, Section 2.3, complex 40 was treated with EtAlCl₂ in C₈D₈. Analysis of the resulting reaction mixtures using NMR spectroscopy revealed the formation of multiple tungsten complexes, which presented overlapping sets of CH and CH₃ 'Pr NMR resonances. However, a notable by-product from the reaction of W(NAr)₂Cl₂·DME (40) with EtAlCl₂ was found to be ethane, which is believed to result from β-hydride elimination from a tungsten ethyl ligand (Scheme 3.1). Although such reactions may be crucial to the activation of bis(lmido) pre-catalysts, the formation of numerous products from the W(NAr)₂Cl₂·DME/EtAlCl₂ reactions meant that a detailed understanding of the mode by which W(NAr)₂Cl₂·DME (40) is activated was prevented.
In order to try and circumvent the inherent instability of metal ethyl complexes, attention was shifted to the study of the reactions of $\text{M(NAr)}_2\text{Cl}_2\text{.DME}$ ($\text{M} = \text{Mo or W}$) with methyl aluminium reagents such as $\text{Me}_2\text{Al}$, $\text{Me}_2\text{AlCl}$ or $\text{MeAlCl}_2$. It was anticipated that addition of $\text{Me}_x\text{AlCl}_{3-x}$ reagents to bis(imido) complexes would give more stable tungsten (or molybdenum) methyl complexes. This in turn, would allow a clearer insight into the possible role of $\text{R}_x\text{AlCl}_{3-x}$ fragments in the activation of bis(imido) dihalide pre-catalysts, which may involve abstraction of a halide ligand by a $\text{R}_x\text{AlCl}_{3-x}$ fragment. Indeed, interaction of an $\text{R}_x\text{AlCl}_{3-x}$ group with a chloride ligand could be significant to initiator formation, something highlighted by the development of the $\text{W(NPh)}_2\text{(Cl)}_2\text{(PMe}_3)_3\text{/AlCl}_3$ ethylene dimerization system by Olivier et al.\textsuperscript{4} Here, Olivier has proposed that abstraction of a tungsten chloride ligand by $\text{AlCl}_3$, leads to an active ionic initiator species (Figure 3.1). It is plausible that a related ionic complex could be obtained upon addition of $\text{Me}_x\text{AlCl}_{3-x}$ reagents to bis(imido) complexes such as $\text{W(NAr)}_2\text{Cl}_2\text{.DME}$ (40).
3.0.1 Reactions Group 6 Imido Halide Complexes and Group 13-based co-Initiators

In this Chapter reactions between $\text{Me}_x\text{AlCl}_{3-x}$ reagents and $\text{M(NR)}\text{Cl}_2$ DME ($\text{M} = \text{Mo}$ or $\text{W}$) complexes are examined. To date no related investigations have been reported, which is surprising as isolobal tungsten oxo complexes, when bound to species such as $\text{AlBr}_3$, are known alkene metathesis initiators (Figure 3.2).\(^5\) This hints that $\text{Me}_x\text{AlCl}_{3-x}$ fragments may also be able to interact with imido ligands giving a complex capable of accommodating alkene coordination. In addition, reaction of $\text{W(NAr)}_2\text{Cl}_2$ DME (40) with $\text{Me}_x\text{AlCl}_{3-x}$ reagents is also arguably relevant to the activation of the previously reported $\text{Cr(NR)}_2\text{Cl}_2$ ethylene polymerization pre-catalysts by $\text{EtAlCl}_2$ or MAO.\(^6\) Since, in both instances, group VI bis(imido) chloride complexes are reacted with aluminium-based reagents.

Figure 3.2 AlBr$_3$-bound metathesis initiators and the isolobal relationship between the fragments $\text{W(NAr)}_2$ and $\text{WO(CHR)}$

In work conducted for this thesis, particular emphasis has been placed upon investigating the reactivity of $\text{Me}_x\text{AlCl}_{3-x}$ species with bis(imido) halide complexes containing relatively bulky 2,6-diisopropylphenyl imido ligands (NAr). The large steric bulk of the NAr ligand is generally regarded as being sufficient to prevent bridging of imido groups between two W or Mo atoms, disbarring the formation of complexes such as $\text{[W(N' Bu)Me}_2\text{]_2(μ-N' Bu)}_2$ (65),\(^7\) $\text{[Mo(N' Bu)(μ-N' Bu)Me}_2\text{]_2}$ (66),\(^8\) or even potentially a mixture of complexes. Hence, complexes with bulky imido moieties such as $\text{Mo(NAr)}_2\text{Cl}_2$ DME (23) or $\text{W(NAr)}_2\text{Cl}_2$ DME (40) are predicted as being more likely to yield discrete complexes when treated with $\text{Me}_x\text{AlCl}_{3-x}$ reagents.
3.1 Reaction of W(NAr)$_2$Cl$_2$.DME (40) and Me$_2$Al

To explore the reactivity of W(NAr)$_2$Cl$_2$.DME (40) with Me$_2$AlCl$_{3-x}$ reagents, attention turned to investigating the reactivity of Me$_3$Al with 40. A C$_6$D$_6$ solution of W(NAr)$_2$Cl$_2$.DME (40) was treated with five equivalents of Me$_3$Al (Scheme 3.2). The resulting mixture was analysed using $^1$H NMR spectroscopy. Following addition of Me$_3$Al, the $^1$H NMR spectrum of the reaction solution was found to contain signals consistent with both W-Me and Al-Me species, present in a 1:1 ratio by integration (Figure 3.3). The resonance observed at -0.15 ppm can readily be assigned to an Al-Me functionality since Al-Me groups typically appear at low frequency. Indeed, the broad low frequency signal at -0.42 ppm is attributable to the Al-Me moiety of free Me$_3$Al. Conversely the singlet at 0.56 ppm can be assigned to a W-Me resonance, as this chemical shift is typical for a W-alkyl moiety. The $^1$H NMR spectrum of this reaction mixture also exhibits three inequivalent doublets (in approximately a 1:1:2 ratio by integration) corresponding to CH$_3$'Pr resonances, and two distinct septets corresponding to two CH'Pr resonances (in a 1:1 ratio). This inequivalence of the aryl imido substituents has been attributed to the coordination a Me$_2$AlCl fragment to a NAr imido ligand on the basis of the single crystal X-ray diffraction analysis (Section 3.1.1).

Scheme 3.2 Synthesis of W(N{Ar}{AlMe$_2$}{μ-Cl})(NAr){Me$_2$}(67)

```
ArN  Cl  ArN  Cl
W   O   O   Cl
(40)  C$_6$D$_6$ or C$_6$D$_5$Cl

5Me$_3$Al

(67)
```

To further investigate the reactivity of W(NAr)$_2$Cl$_2$.DME (40) with Me$_3$Al, in a separate experiment complex 40 was reacted with a large excess (fourteen equivalents) of Me$_3$Al in C$_6$D$_6$. Identical results were obtained as to when five equivalents were employed.

Analysis of authentic samples of MeAlCl$_2$ and Me$_3$Al in C$_6$D$_6$ reveals a single $^1$H resonance at -0.42 ppm in both cases.

---

\(^1\) To further investigate the reactivity of W(NAr)$_2$Cl$_2$.DME (40) with Me$_3$Al, in a separate experiment complex 40 was reacted with a large excess (fourteen equivalents) of Me$_3$Al in C$_6$D$_6$. Identical results were obtained as to when five equivalents were employed.

\(^2\) Analysis of authentic samples of MeAlCl$_2$ and Me$_3$Al in C$_6$D$_6$ reveals a single $^1$H resonance at -0.42 ppm in both cases.
Figure 3.3 $^1H$ NMR ($C_8D_8$, 200 MHz) spectrum of mixture obtained following reaction of $W(NAr)_2Cl_2.DME$ (40) with 5 Me$_3$Al

Parallels can be drawn between this Me$_3$Al reaction, and the reactions of bis(imido) complexes with EtAlCl$_2$ outlined in Chapter 2. As discussed in detail in Chapter 2, Section 2.3.1, the complex Mo(N'Bu)$_2$Cl$_2$ (21) was synthesised via addition of one equivalent of EtAlCl$_2$ to Mo(N'Bu)$_2$Cl$_2$.DME (26). This shows that the first action of the Lewis acid EtAlCl$_2$, upon addition to 26, is to displace the coordinating DME moiety. Thus, the new DME resonances observed by $^1H$ NMR spectroscopy following reaction of complex 40 with Me$_3$Al are attributed to the formation of an AlMe$_3$.DME adduct. Again, this conclusion is supported by a single crystal X-ray diffraction study (Section 3.1.1), which confirms the displacement of the DME moiety from the tungsten core. Notably, adducts of Me$_x$AlCl$_{3-x}$ species and DME have been reported previously by Atwood, although spectroscopic or structural details are unknown.\textsuperscript{10}

The reaction of $W(NAr)_2Cl_2.DME$ (40) with five equivalents of Me$_3$Al has been repeated using C$_6$D$_5$Cl as the reaction solvent. This was undertaken as it has been established that chlorobenzene is the preferred solvent for both the Goodyear and STUK WCl$_6$-based dimerization systems, as well as being the solvent of choice when activating M(NAr)$_2$Cl$_2$.DME (M = Mo or W) complexes with EtAlCl$_2$ (Chapter 2
Section 2.2). Analysis of the resulting \( \text{C}_6\text{D}_6\text{Cl} \) reaction mixture presented a \(^1\text{H}\) NMR spectrum that was identical to that obtained when \( \text{C}_6\text{D}_6 \) was used as the reaction solvent (Figure 3.3). Evidently, reaction selectivity of the \( \text{W}\{\text{NAr}\}_2\text{Cl}_2\cdot\text{DME}/\text{Me}_3\text{Al} \) system is not altered by the use of \( \text{C}_6\text{D}_6\text{Cl} \) instead of \( \text{C}_6\text{D}_6 \), confirming the relevance of this study to "real" initiator systems.

**3.1.1 Characterization of \( \text{W}\{\text{N}\\{\text{Ar}}\text{AIMe}_2\{\\mu-\text{Cl}\}\}\{\text{NAr}\}_\text{Me}_2 \) (67) Using Single Crystal X-Ray Diffraction Analysis**

In order to clarify the precise structure of the products obtained from the reaction of \( \text{W}\{\text{NAr}\}_2\text{Cl}_2\cdot\text{DME} \) (40) with excess \( \text{Me}_3\text{Al} \), a sample of the product was prepared by addition of five equivalents of \( \text{Me}_3\text{Al} \) to \( \text{W}\{\text{NAr}\}_2\text{Cl}_2\cdot\text{DME} \) (40) in \( \text{C}_6\text{D}_6 \). This solution was then dried in vacuo giving a light brown solid, which when recrystallized in hexane, afforded light brown needles of sufficient quality for single crystal X-ray diffraction analysis (Figure 3.4 and Table 3.1). This revealed the structure of the product to be \( \text{W}\{\text{N}\\{\text{Ar}}\text{AIMe}_2\{\\mu-\text{Cl}\}\}\{\text{NAr}\}_\text{Me}_2 \) (67) in which a single \( \text{AlMe}_2\text{Cl} \) fragment bridges one of the N-imido atoms and the \( \text{W} \)-centre, forming a four-membered ring. The geometry around the tungsten atom of complex 67 is distorted trigonal bipyramidal. Notably, the aluminium and tungsten atoms of complex 67 remain in their original respective formal oxidation states of (+III) and (+VI). Thus, \( \text{Me}_3\text{Al} \) reacts with complex 40 as an alkylating agent generating both a \( \text{W}\\{\text{Me}}\text{}_2 \) moiety and \( \text{Me}_2\text{AlCl} \). A single \( \text{Me}_2\text{AlCl} \) molecule then coordinates to an imido ligand via donation of the N-atom’s lone pair to the \( \text{Me}_2\text{AlCl} \) Lewis acid. This structure of \( \text{W}\{\text{N}\\{\text{Ar}}\text{AIMe}_2\{\\mu-\text{Cl}\}\}\{\text{NAr}\}_\text{Me}_2 \) (67) is consistent with the \(^1\text{H}\) NMR spectrum obtained following treatment of \( \text{W}\{\text{NAr}\}_2\text{Cl}_2\cdot\text{DME} \) (40) with \( \text{Me}_3\text{Al} \) (Figure 3.4). The inequivalent \(^1\text{Pr} \) resonances observed presumably result from impeded free rotation around the N-C\( _\text{Cps}_s \) bond of the 2,6-diisopropylphenyl imido ligand bound to \( \text{AlMe}_2\text{Cl} \). Hence, the \(^1\text{H}\) NMR spectrum of the crude reaction mixture (displayed in Figure 3.4) is consistent with complete conversion of \( \text{W}\{\text{NAr}\}_2\text{Cl}_2\cdot\text{DME} \) (40) to \( \text{W}\{\text{N}\\{\text{Ar}}\text{AIMe}_2\{\\mu-\text{Cl}\}\}\{\text{NAr}\}_\text{Me}_2 \) (67). Furthermore, it is clear that complex 67 adopts the same structure in both the solution and the solid states.
Figure 3.4 Solid state structure of $W(N\{Ar\}AlMe_2\{\mu-Cl\})(NAr)Me_2$ (67) with the thermal ellipsoids set at the 50% level

Table 3.1 Selected bond distances (Å) and bond angles (°) for $W(N\{Ar\}AlMe_2\{\mu-Cl\})(NAr)Me_2$ (67).

<table>
<thead>
<tr>
<th></th>
<th>W-N1</th>
<th>N2-Al</th>
<th>W-N1-C11</th>
<th>N1-C21</th>
<th>N2-C11</th>
<th>W-C1</th>
<th>W-C2</th>
<th>Al-Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-N2</td>
<td>1.7402(15)</td>
<td></td>
<td></td>
<td>1.8613(15)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1-C21</td>
<td>1.439(2)</td>
<td>W-N1-C11</td>
<td>1.6590(13)</td>
<td>W-N2-C21</td>
<td>133.24(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N2-C11</td>
<td>1.399(2)</td>
<td>W-N2-Al</td>
<td>109.10(8)</td>
<td>C21-N2-Al</td>
<td>117.64(11)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W-C1</td>
<td>2.129(2)</td>
<td>C21-N2-Al</td>
<td>117.64(11)</td>
<td>Al-Cl-W</td>
<td>78.07(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W-C2</td>
<td>2.139(2)</td>
<td>Al-Cl-W</td>
<td>78.07(2)</td>
<td>C1-W-C2</td>
<td>123.63(10)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-Cl</td>
<td>2.2757(8)</td>
<td>N1-W-N2</td>
<td>108.27(7)</td>
<td>C1-W-C2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Examination of the W-N bond distances of 67 (Table 3.1) confirms that coordination of the Me$_2$AlCl fragment to the imido ligand results in a significant lengthening of the tungsten imido W-N2 bond (1.8613(15) Å), relative to the W-N contacts of the precursor complex $W(NAr)_2Cl_2\cdot$DME (40) (1.7598(17) Å) (See Chapter 2, Section 2.1). In contrast, the W-N1 bond associated with the free imido ligand of 67 at 1.7402(15) Å is shorter than the W-N contacts of the precursor complex 40. The sum of the bond angles around N2 is close to 360° and the W-N2-C21 bond angle is 133.24(12)°, indicating a 2-electron donor imido ligand (neutral formalism), with a trigonal planar geometry around the N atom. In contrast, the W-N1-C11 bond angle
of the free imido ligand is 165.90(13)°, which is within the range of that generally accepted for a 4-electron donor ligand (neutral formalism).\textsuperscript{11}

Interaction between the W\textsuperscript{VI} and Cl atoms of complex W(N{Ar}.AlMe\textsubscript{2}{\mu-Cl})(N{Ar}Me\textsubscript{2} \textsuperscript{67}) is dative in nature, with donation of a chloride lone pair to the highly electropositive W\textsuperscript{VI} centre. The chloride moiety of \textsuperscript{67} originates from the starting material W(N{Ar})\textsubscript{2}Cl\textsubscript{2}.DME (\textsuperscript{40}), with ligand metathesis of the W-Cl and Al-Me bonds giving the W-Me and Al-Cl moieties. The [W(N{Ar})\textsubscript{2}]\textsuperscript{2+} core of complex \textsuperscript{67} can be viewed as being isolobal to a [Hf(Cp)\textsubscript{2}]\textsuperscript{2+} fragment and, as such, has three frontier orbitals available for interaction with a given ligand (two of \textit{a\textsubscript{i}} and one of \textit{b\textsubscript{2}} symmetry) (\textbf{Figure 3.5}).\textsuperscript{12} Thus, coordination of the chloride ligand to the W centre generates a coordinatively-saturated W complex, with full occupancy of all available coordination sites. Due to the dative nature of the W-Cl interaction, the chloride ligand can be counted as being a 2 electron donor, making \textsuperscript{67} formally a 16-electron species.

\textbf{Figure 3.5} \textit{Isolobal relationship and frontier orbitals of the metal fragments [W(N{Ar})\textsubscript{2}]\textsuperscript{2+} and [Hf(Cp)\textsubscript{2}]\textsuperscript{2+}}

![Orbitals projected in the yz plane](image)

The W-Cl bond of \textsuperscript{67} at 2.6440(6) Å is relatively long, compared to the analogous contacts of the precursor complex W(N{Ar})\textsubscript{2}Cl\textsubscript{2}.DME (\textsuperscript{40}) at 2.3841(7) Å (\textbf{Chapter 2. Section 2.1.2}). Indeed, the W-Cl contact of \textsuperscript{67} is long, but does not exceed the longest W-Cl bond distance currently deposited in the Cambridge Structural data base.\textsuperscript{13} This is recorded for the complex [WOCl\textsubscript{3}(O{Ar})\textsubscript{2}] \textsuperscript{2+} (2.876(2) Å).\textsuperscript{14} Also of note for complex \textsuperscript{67}, is that coordination of the chloride ligand to the tungsten atom gives an acute Al-Cl-W bond angle of 78.07(2)°. Another prominent structural feature of \textsuperscript{67}
is the greater length of the N-Cipso bond of the Me₂AlCl bound imido ligand 1.439(2) Å (N1-C21) compared with that of the free imido ligand 1.399(2) Å (N2-C11). The N-Cipso bond can be viewed as having some double bond character (Figure 3.6) when the Cipso is formally sp² hybridized.¹⁵ Hence, the greater length of the N1-C21 contact can be attributed to coordination of the Me₂AlCl fragment to the nitrogen atom of the imido ligand. This makes the nitrogen lone pair less available for delocalization into the π-system of the 2,6-diisopropyl-phenyl group, and reduces the double bond character of the N-Cipso contact.

Figure 3.6 Partial double bond character of N-Cipso bond for a W phenyl imido moiety

3.2 Synthesis, Characterization and Structure of W(N(Ar)₂AlMe₂[μ-Cl])(NAr)Me₂ (67) and Comparison with Related Complexes

Interaction of an R₂AlCl₂-x fragment and an imido ligand in bonding modes analogous to that observed in complex 67 are uncommon, with only a very few related complexes having been disclosed in the literature. Notably, reaction of the related bis(oxo) complex MoO₂Cl₂, which is isolobal to a W(NAr)₂Cl₂ fragment also results in the formation of a 4-membered chelate (Scheme 3.3). However, in this system methane is evolved, via α-hydride elimination and then a reductive elimination, generating the bridging Al-CH₂ moiety. Hence, in contrast to complex 67 in this oxo-containing example it is a CH₂ fragment and not a Cl ligand that bridges between the Mo and Al atoms.¹⁵

Scheme 3.3 Reaction of MoO₂Cl₂ with Me₂Al

Although α-hydride elimination readily occurs following reaction of MoO₂Cl₂ with Me₂Al, a similar elimination reaction is clearly disfavoured for W(N{Ar}AlMe₂{μ-Cl})(NAr)Me₂ (67), which retains the WMe₂ fragment, preventing the formation of a
bridging CH$_2$ group. It has also previously been shown that aluminium-based Lewis acid fragments can coordinate to bis(imido) systems by Wilkinson et al. who prepared W[(μ-N'Bu)$_2$AlX$_2$]$_2$ (69) from reaction the lithiated bis(imido) bis(amido) complex W(N'Bu)$_2$(NLi'Bu)$_2$ (70) with Me$_3$Al (Scheme 3.4).$^{17}$

Scheme 3.4 Synthesis of W[(μ-N'Bu)$_2$AlMe$_2$]$_2$

Notably, the structure of W[(μ-N'Bu)$_2$AlMe$_2$]$_2$ (69) has parallels with that of W(N{Ar}.AlMe$_2$[μ-Cl])(NAr)Me$_2$ (67). In both 67 and 69 an imido ligand bridges between aluminium and tungsten atoms forming a four-membered chelate. Indeed, the similar N-Al contacts at 1.992(7) Å and 1.990(9) Å for W[(μ-N'Bu)$_2$AlX$_2$]$_2$ (69) and 1.9578(16) Å for 67 are typical bond distances for an Al-N dative interaction (1.86Å to 2.04Å).$^{18}$ However, in contrast to the W(N'Bu)$_2$(NLi'Bu)$_2$/Me$_3$Al reaction (Scheme 3.4), conversion of W(N{Ar})$_2$Cl$_2$.DME (40) to 67 demonstrates that in the W(N{Ar})$_2$Cl$_2$.DME/Me$_3$Al system, coordination of both imido ligands to a single aluminium centre is disfavoured. This is because in 67 the lone pair of the unbound imido ligand is strongly π-bonding to the W$^VI$ centre. Hence, the delocalization of the N2 lone pair, between the N2 and W$^VI$ atoms, significantly reduces the Lewis basicity of the imido ligand, reducing the tendency for the formation of a second Al-N contact in this system. Furthermore, for complex 67 the bulk of the NAr ligands results in little space between the two imido groups, making coordination of both imido moieties to a single R$_x$AlCl$_{3-x}$ fragment sterically highly disfavoured.

While there are clear differences between W[(μ-N'Bu)$_2$AlX$_2$]$_2$ (69) and 67, complexes have been disclosed in the literature that are directly analogous to 67, in which a R$_x$AlCl$_{3-x}$ fragment bridges between an imido N-atom and a metal centre. Such an interaction was postulated by Schrock et al. as being present in the complex W(NPh)(CCMe$_3$)(PMe$_3$_2)Cl(AlMe$_2$Cl), although this has not been confirmed by single crystal X-ray diffraction analysis. Similarly, a dative interaction between an N'Bu imido lone pair and an Me$_3$Al fragment has been considered computationally by

\[ W(N'Bu)_2(NLi'Bu)_2 \rightarrow W(N'Bu)_2(NLi'Bu)_2 \]

\[ 2Me_3Al \]

\[ W(N'Bu)_2(NLi'Bu)_2 \]

\[ \text{Me}_2\text{Al} \]
Mountford et al.\textsuperscript{15} In Mountford's study the capacity of complexes such as Ti(N'\textsuperscript{Bu})(Me\textsubscript{3}[9]aneN\textsubscript{3})\textsubscript{R\textsubscript{3}} (R = a range of alky groups including Me or CH\textsubscript{2}SiMe\textsubscript{a}) to initiate ethylene polymerization when activated by Al'\textsuperscript{Bu}\textsubscript{3} and [Ph\textsubscript{3}C][BAr\textsubscript{5}\textsuperscript{4}] was assessed. In an effort to further understand the nature of the active species, a comprehensive DFT investigation was undertaken. It was determined computationally that lone pair donation from an N'\textsuperscript{Bu} imido ligand to an Me\textsubscript{3}Al fragment, forming a four-membered chelate with connectivity analogous to 67 was a relatively stable arrangement. However, Me\textsubscript{3}Al coordination in this manner was concluded as unfavourable since the resulting complexes were believed to be less able to initiate reaction of ethylene than the analogous Me\textsubscript{3}Al-free complexes. In related studies, the cations [Ti(\mu-N'\textsuperscript{Bu})(Me\textsubscript{3}[9]aneN\textsubscript{3}(\mu-Me)\textsubscript{2}ZnMe]\textsuperscript{+} and [W(\mu-NPh)(N\textsubscript{2}Npy)Me(\mu-Me)ZnMe]\textsuperscript{+} were predicted by Mountford, again through the use of DFT, to contain four-membered chelates, resulting from a dative interaction between the N'\textsuperscript{Bu} ligand and the zinc-based Lewis acid (Figure 3.7).\textsuperscript{20,21} Hence, Mountford's investigations show that coordination of Lewis acids to imido ligands, in bonding modes similar to that of 69 is often thermodynamically favourable.

Figure 3.7 Examples computationally studied imido-bridged ZnMe\textsubscript{2} complexes

The Cambridge Structural Database was searched for complexes containing a Me\textsubscript{3}AlCl\textsubscript{3-x} fragment bridging between a transition metal and a nitrogen centre in an interaction related to that of 67. This search revealed that only three such complexes have been deposited. These structures were reported by Binger\textsuperscript{22} (Complex 72), Norton\textsuperscript{73} (Complex 73) and Duchateau\textsuperscript{\textsuperscript{24}} (Complex 74) (Figure 3.8). In addition, Mayer has prepared an osmium imido complex 75 in which an imido ligand coordinates to a Ph\textsubscript{2}BCl unit (Figure 3.9).\textsuperscript{25}
In complex 75 the phenyl imido ligand bridges between the Os and B centres. This connectivity is comparable to that determined for 67, with the imido nitrogen atom of 75 adopting the same pseudo-trigonal planar geometry found for complex 67. The similarities between the structures of 75 and 67 demonstrate that although the connectivity of 67 is unusual, a similar bonding arrangement is found in related complexes.
3.3 Reaction of M(NAr)₂Cl₂,DME (M = Mo or W) Complexes with Me₂AlCl and MeAlCl₂

In Section 3.1 it was determined that reaction of W(NAr)₂Cl₂,DME (40) with Me₃Al in C₆D₆ affords exclusively W(N{Ar}.AIMe₂{μ-Cl})(NAr)Me₂ (67). In this regard, it is also of interest to investigate the reactivity of 40 with the aluminium-based reagents Me₂AlCl and MeAlCl₂, as this could result in different reaction products to that obtained in the Me₃Al system. Indeed, the ability of Me₂AlCl and MeAlCl₂ to transfer a methyl group is considerably lower than that of Me₃Al.²⁶ Furthermore, reaction of Mo(NAr)₂Cl₂,DME (23) with Me₃AlCl₃-x reagents is also worthy of study as Mo(NR)₂Cl₂,DME complexes can also be utilized as dimerization pre-catalysts (Chapter 2, Section 2.2, Table 3.3). Thus, reaction of 23 with Me₃AlCl₃-x reagents could yield information as to the mode by which molybdenum bis(imido) pre-catalysts are activated for ethylene dimerization.

3.3.1 Synthesis of Mo(N{Ar}.AIMe₂{μ-Cl})(NAr)Me₂ (76)

With a view to exploring the reactivity of Mo(NAr)₂Cl₂,DME (23) with R₃AlCl₃-x species, attention turned to investigating the reaction of 23 with Me₃Al. On an NMR scale treatment of Mo(NAr)₂Cl₂,DME (23) with excess Me₃Al in C₆D₆ resulted in full conversion of 23 to the complex Mo(N{Ar}.AIMe₂{μ-Cl})(NAr)Me₂ (76), which presents a ¹H NMR spectrum comparable to that observed for the analogous tungsten complex 67 (Scheme 3.5). The composition of 76 has been confirmed by reaction of Mo(NAr)₂Cl₂,DME (23) with excess Me₃Al on a preparatory scale, which afforded a synthetically pure sample of 76 upon recrystallization from hexane in a 24 % yield. It is clear that the complexes Mo(NAr)₂Cl₂,DME (23) and W(NAr)₂Cl₂,DME (40) have identical reactivity with Me₃Al.

Scheme 3.5 Synthesis of Mo(N{Ar}.AIMe₂{μ-Cl})(NAr)Me₂ (76)
3.3.2 Reaction of W(NAr)$_2$Cl$_2$.DME (40) with Me$_2$AlCl

With a view to gauging if treatment of W(NAr)$_2$Cl$_2$.DME (40) with Me$_2$AlCl generates similar or different products to that of the W(NAr)$_2$Cl$_2$.DME/Me$_3$Al system, the reactivity of complex 40 with Me$_2$AlCl was investigated. Addition of Me$_2$AlCl to W(NAr)$_2$Cl$_2$.DME in C$_6$D$_6$ results in the formation of complex W(N{Ar}.AlMeCl{μ-Cl})(NAr)Me$_2$ (77) in situ. The complexes 67 and 77 are closely related, varying only in the nature of the bridging Me$_x$AlCl$_{3-x}$ fragment (Me$_2$AlCl and MeAlCl$_2$, respectively). However, in contrast to the Me$_3$Al system where 67 is obtained in 100% conversion, it is clear from $^1$H NMR spectrum presented by the Me$_2$AlCl reaction solution (Figure 3.10) that reaction of Me$_2$AlCl also generates additional as yet unidentified tungsten-containing products (Scheme 3.6).

Scheme 3.6 Contrasting the W(NAr)$_2$Cl$_2$.DME/Me$_3$Al and W(NAr)$_2$Cl$_2$.DME/Me$_2$AlCl reaction systems.
As for complex 67, coordination of an Me\textsubscript{x}AlCl\textsubscript{3-x} fragment to a NAr imido ligand in complex 77 results in inequivalent CH\textsubscript{3} \textsuperscript{1}Pr \textsuperscript{1}H NMR resonances. Although it has been possible to assign the structure of 77 using \textsuperscript{1}H NMR spectroscopy, the connectivity of the additional reaction products remains unclear. It is evident that reaction of a stronger Lewis acid (Me\textsubscript{2}AlCl) does indeed give a different reactivity to that obtained in the Me\textsubscript{2}Al system (Scheme 3.6).\textsuperscript{27} This observation is significant since Me\textsubscript{2}AlCl and MesAl have different capacities to activate W(NAr\textsubscript{2})Cl\textsubscript{2}.DME (40) towards ethylene dimerization (refer to Section 3.8.2).

### 3.3.3 Reaction of M(NAr\textsubscript{2})Cl\textsubscript{2}.DME (M = Mo or W) with MeAlCl\textsubscript{2}

To further investigate the interaction between \textit{bis}(imido) halide complexes and strong aluminium-based Lewis acids, the reactivity of both Mo(NAr\textsubscript{2})Cl\textsubscript{2}.DME (23) and W(NAr\textsubscript{2})Cl\textsubscript{2}.DME (40) with MeAlCl\textsubscript{2} was investigated. The complexes W(N{Ar}.AlCl\textsubscript{2}{μ-Cl})(NAr)Me\textsubscript{2} (78) and Mo(N{Ar}.AlCl\textsubscript{2}{μ-Cl})(NAr)Me\textsubscript{2} (79), were obtained from treatment of the appropriate \textit{bis}(imido) dihalide complex with MeAlCl\textsubscript{2}.

Of general interest is determining whether complexes such as 78 or 79 are thermally stable. To assess the thermal stability of 78, a sample of the complex was
dissolved in C₆D₆ and the resulting solution was heated. No thermal degradation of 78 was observed using ¹H NMR spectroscopy (Scheme 3.7).

**Scheme 3.7 Attempted thermolysis of W(N{Ar}.AlCl₂(μ-Cl))(NAr)Me₂ (78)**

It is clear from the NMR spectra of complexes 78 and 79 that neither undergoes facile association/dissociation in solution on an NMR timescale (~25 °C) (Scheme 3.8). However, it was found that addition of excess MeAlCl₂ to a sample of either 78 or 79 results in the formation of unknown additional products, the connectivity of which cannot be determined by multinuclear NMR spectroscopic analysis (Scheme 3.8).

**Scheme 3.8 Reaction of W(N{Ar}.AlCl₂(μ-Cl))(NAr)Me₂ (78) with MeAlCl₂**
3.3.4 Characterization of W(N{Ar}AlCl$_2${µ-Cl})(NAr)Me$_2$ (78) and Mo(N{Ar}.AlCl$_2${µ-Cl})(NAr)Me$_2$ (79) using Single Crystal X-ray Diffraction

To clarify the structures of 78 and 79, both complexes have been characterized by single crystal X-ray diffraction analysis. The molecular structures of 78 (Figure 3.11 and Table 3.2) and 79 (Figure 3.12 and Table 3.3) indicate that they are both isostructural to W(N{Ar}AlMe$_2${µ-Cl})(NAr)Me$_2$ (67).

Figure 3.11 Solid state structure of W(N{Ar}AlCl$_2${µ-Cl})(NAr)Me$_2$ (78) with the thermal ellipsoids set at the 50% level

Table 3.2 Selected bond distances (Å) and bond angles (°) for W(N{Ar}AlCl$_2${µ-Cl})(NAr)Me$_2$ (78).

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</table>

As for complex W(N{Ar}AlMe$_2${µ-Cl})(NAr)Me$_2$ (67), the W-N bond distances and angles of W(N{Ar}AlCl$_2${µ-Cl})(NAr)Me$_2$ (78) indicate that the unbound imido ligand of
78 is a 4-electron donor (neutral formalism), with a W-N1-C11 bond angle of 163.78(13)° and a short W-N1 contact (1.7290(13) Å), resulting from a high degree of π-bonding to the WV centre. Consistent with 67, the Al-bound imido ligand of complex 78 can be considered as being a 2-electron donor (neutral formalism), with a bent W-N2-C21 bond angle of 132.21(11)° and a relatively long W-N2 contact of 1.8750(15) Å. Notably, replacement of the Me2AlCl moiety in 67 for an AlCl3 fragment in complex 78 results in a shortening of the Al-N bond from 1.9578(16) (67) to 1.8873(14) Å (78). This can be attributed to the greater Lewis acidity of AlCl3 over Me2AlCl. Substitution of Me2AlCl for AlCl3 also results in a slight lengthening of the W-Cl interaction from 2.6440(6) in 67 to 2.7073(5) Å in 78. Again, the longer W-Cl bond length of 78 can be attributed to the higher Lewis acidity of the AlCl3 fragment, which makes donation of the chloride lone pair to the WV centre is less favourable.

Figure 3.12 Solid state structure of Mo(N{Ar}AlCl2{μ-Cl})(NAr)Me2 (79) with the thermal ellipsoids set at the 50% level

Table 3.3 Selected bond distances (Å) and bond angles (°) for Mo(N{Ar}AlCl2{μ-Cl})(NAr)Me2 (79).

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<thead>
<tr>
<th>Bond/Distance</th>
<th>Mo2-C22</th>
<th>N22-Mo-N21</th>
<th>C121-Mo-C22</th>
<th>Mo2-N21-C211</th>
<th>Mo-N22-C221</th>
<th>N21-C211-N22-Al2</th>
<th>N22-Al2-C221</th>
<th>Al2-C21</th>
<th>Al2-C22</th>
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<td>1.419(8)</td>
<td>1.460(9)</td>
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<td>2.196(3)</td>
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<tr>
<td>Mo2-C21</td>
<td>1.717(5)</td>
<td>1.717(5)</td>
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<td>1.460(9)</td>
<td>1.460(9)</td>
<td>1.884(6)</td>
<td>2.196(3)</td>
<td>2.196(3)</td>
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<tr>
<td>Mo-N21</td>
<td>1.854(6)</td>
<td>1.854(6)</td>
<td>1.854(6)</td>
<td>1.419(8)</td>
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<td>Mo-N22</td>
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<td>1.460(9)</td>
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<td>1.460(9)</td>
<td>1.460(9)</td>
<td>1.460(9)</td>
<td>1.884(6)</td>
<td>2.196(3)</td>
<td>2.196(3)</td>
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</table>
Direct comparison can be made between the bond lengths and angles of the tungsten complex W(N{Ar}.AlCl2{μ-Cl})(NAr)Me2 (78) and those of the molybdenum complex Mo(N{Ar}.AlCl2{μ-Cl})(NAr)Me2 (79), as both complexes have an AlCl₃ fragment bound to the imido ligand and identical coordination spheres. Of note are the almost identical N-Al bond lengths of 1.8873(14) and 1.884(6) Å respectively. Also the N-Al-Cl bond angles of complexes 78 and 79 are comparable at 93.85(5) and 94.0(2)°. It is apparent that any electronic difference between the Mo^VI and W^VI centres has little impact on the structural features of the N-Al-Cl chelate.

3.4 Reaction of the Mixed imido Complex Mo(NAr)(N'Bu)Cl₂.DME (11) with Me₃Al and MeAlCl₂

It has been shown that reaction of M(NAr)₂Cl₂.DME (M = Mo or W) with MeₓAlCl₃₋ₓ generates products of the general formula M(N{Ar}AIMeₓ₋₁Cl₃₋ₓ{μ-Cl})(NAr)Me₂ in which an MeₓAlCl₃₋ₓ fragment coordinates to a single imido ligand of the bis(imido) moiety. With this having been established, attention turned to investigating the reactivity of the mixed imido complex Mo(NAr)(N'Bu)Cl₂.DME (11). Here, with both NAr and N'Bu imido ligands being present, addition of MeₓAlCl₃₋ₓ reagents to 11 could result in aluminium-based Lewis acid fragments binding to either the NAr or N'Bu ligands, or both. Thus, it was of interest to explore the reactivity of Mo(NAr)(N'Bu)Cl₂.DME (11) to establish the preferred binding site of the Lewis acid.

3.4.1 Reaction of Mo(NAr)(N'Bu)Cl₂.DME (11) with Me₃Al

To assess which imido ligand of complex 11 a Me₃AlCl₃₋ₓ fragment would preferentially coordinate, Mo(NAr)(N'Bu)Cl₂.DME (11) was reacted with Me₃Al in C₆D₆. The reaction mixture was then analysed by ¹H NMR spectroscopy. The resulting spectrum (Figure 3.13) indicates the presence of only one Mo-Me resonance (integrating to 6H) and one N'Bu resonance, demonstrating that only one isomer is formed in solution. Furthermore, a ¹H/¹H NOESY correlation experiment revealed that the Me₃AlCl fragment binds preferentially to the NAr ligand. This is further confirmed by the observation of two inequivalent ¹Pr CH₃ resonances in the ¹H and ¹³C NMR spectrum, which has been established as being characteristic of Me₃AlCl₃₋ₓ fragments coordinating to NAr ligands (Section 3.1). Thus, together, these ¹H NMR spectral analyses are consistent with full conversion of 11 to Mo(N{Ar}.AlMe₂{μ-Cl})(N'Bu)Me₂ (80) (Scheme 3.9).
Scheme 3.9 Formation of Mo(N{Ar}.AlMe₂{μ-Cl})(N¹Bu)Me₂ (80) in situ.

Figure 3.13 **H NMR (400 MHz, C₆D₆) spectrum of the reaction of Mo(NAr)(N¹Bu)Cl₂.DME (80) with Me₃Al.

3.4.2 Synthesis and Characterisation of Mo(N{Ar}.AlCl₂{μ-Cl})(N¹Bu)Me₂ (81)

Having established that reaction of Mo(NAr)(N¹Bu)Cl₂.DME (11) with Me₃Al generates Mo(N{Ar}.AlMe₂{μ-Cl})(N¹Bu)Me₂ (80) to examine if reaction of alternative Me₃AlCl₃-x reagents would yield similar complexes, attention turned to investigating the reactivity of 11 with MeAlCl₂. Addition of MeAlCl₂ to a toluene solution of 11 has enabled, after workup, isolation of the complex Mo(N{Ar}.AlCl₂{μ-Cl})(N¹Bu)Me₂ (80) in 40% yield. The **H NMR spectrum of complex 81 comprised of a single Mo-CH₃ resonance as well as a single tBu signal. As for related complexes, inequivalent CH₃ iPr resonances were detected. A sample of 81 of sufficient quality for analysis by single
crystal X-ray diffraction was obtained upon recrystallization of 81 from toluene (Figure 3.14 and Table 3.4).

**Figure 3.14** Solid state structure of Mo(N[Ar]Me2(μ-Cl))(N'Bu)Me2 (81) with the thermal ellipsoids set at the 50% level

![Solid state structure of Mo(N[Ar]Me2(μ-Cl))(N'Bu)Me2 (81)](image)

Table 3.4 Key structural parameters, bond lengths (Å) and bond angles (°), for Mo(N'Bu)(N[Ar]AICl2(μ-Cl))Me2(81) and Mo(N'Bu)(NAr)Cl2.DME (11)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mo(N'Bu)(N[Ar]AICl2(μ-Cl))Me2</th>
<th>Mo(N'Bu)(NAr)Cl2.DME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-N1-C3 (N'Bu)</td>
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<td>157.9(2)</td>
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<td>N1-Mo-N2</td>
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<td>105.91(9)</td>
</tr>
<tr>
<td>Mo-N2-C11 (NAr)</td>
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<td>1.728(2)</td>
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<tr>
<td>N1-C3</td>
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<td>1.452(3)</td>
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<td>Mo-N2 (NAr)</td>
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<td>N2-C11</td>
<td>1.4355(19)</td>
<td>1.387(3)</td>
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The molecular structure of complex 81 confirms that the aluminium Lewis acid moiety (in this instance AlCl3) again preferentially coordinates to the NAr ligand. This is in agreement with the NMR spectra of 81. Examination of the bond angles and distances associated with complex 81 (Table 5.4) reveals that the NAr imido ligand is a 2-electron donor (neutral formalism), with a Mo-N-Cipso bond angle of 127.38(10)° and a relatively long Mo-N2 contact of 1.8870(13) Å. Indeed, coordination of the
AlCl$_3$ fragment results in a lengthening of the Mo-N contact (1.8870(13) Å) of the NAr ligand relative to the analogous contact for the starting complex Mo(NAr)(N'Bu)Cl$_2$.DME (11) (1.753(2) Å). This lengthening can be attributed to the reduction in Mo-N triple bond character resulting from the donation of the N-atom’s lone pair to the AlCl$_3$ fragment. Furthermore, AlCl$_3$ coordination in 81 also results in a lengthening of the NAr ligand’s N-C$_{ipso}$ contact relative to the starting material (1.4355(19) Å for 81 vs 1.387(3) Å for Mo(NAr)(N'Bu)Cl$_2$.DME (11)).

Of particular interest is the increased length of the Mo-Cl contact of 81 relative to that for the comparable molybdenum complex 79 (Table 3.5). Both complexes 81 and 79 adopt distorted trigonal bipyramidal geometries, but in 81 the chloride ligand lies trans to an N'Bu ligand, while in 79 it occupies a site trans to a NAr group (Figure 3.15). As the N'Bu imido ligand is a stronger π-donor, it has a greater trans influence than the NAr ligand, resulting in a relative lengthening of the Mo-Cl contact.

Table 3.5 Comparison of Mo-Cl bond lengths for complexes 79 and 81

<table>
<thead>
<tr>
<th>Complex</th>
<th>Mo-Cl Bond length (Å)</th>
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<tr>
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</tbody>
</table>

Figure 3.15 Comparison of the complexes Mo(N'Bu)(N[Ar]AlCl$_2$[μ-Cl])Me$_2$ (81) and Mo(NAr)(N[Ar]AlCl$_2$[μ-Cl])Me$_2$ (79)

For both complexes 80 and 81, the Me$_5$AlCl$_{3-x}$ fragment binds preferentially to the NAr ligand of the mixed bis(imido) moiety. Examination of the relative Mo-N bond lengths of the precursor complex Mo(NAr)(N'Bu)Cl$_2$.DME (11)$_{28}$ (Table 3.4) indicates that it is the relative π-donor capacities of the N'Bu and NAr ligands that directs the site of Me$_5$AlCl$_{3-x}$ coordination. Indeed, for complex 11 the Mo-N bond distance corresponding to the N'Bu imido ligand at 1.728(2) Å is relatively short. This reflects the greater triple bond character of this interaction, which results from a high degree
of π-donation from the N'Bu ligand to the Mo\textsuperscript{VI} atom. Conversely, the longer Mo-N interaction of the NAr ligand (1.753(2) Å) shows that this imido ligand is a less effective π-donor. As such the lone pair of the NAr ligand is not as effectively delocalized between the Mo and N atoms and is instead more centred upon the N-atom. This makes the lone pair of the NAr ligand more available for donation to the Lewis acids Me\textsubscript{2}AlCl or AlCl\textsubscript{3}.

3.5 Investigating the Reactivity of M(N{Ar}AIMe\textsubscript{x-1}Cl\textsubscript{3-x}{\mu-Cl}),(NAr)Me\textsubscript{2} (M = Mo or W) Complexes

Reaction of M(NAr\textsubscript{2}Cl\textsubscript{2}.DME (M = W or Mo) complexes with Me\textsubscript{x}AlCl\textsubscript{3-x} reagents gave a new class of compounds with the general formula M(N{Ar}AIMe\textsubscript{x-1}Cl\textsubscript{3-x}{\mu-Cl}),(NAr)Me\textsubscript{2} (M = Mo or W). As discussed previously (Section 3.2), there is little precedent for complexes such as W(N{Ar}AIMe\textsubscript{2}{\mu-Cl}),(NAr)Me\textsubscript{2} (67) in the literature. As a result the fundamental reactivity of this new group of complexes is unknown. Hence, attention turned to investigating the reactions of M(N{Ar}AIMe\textsubscript{x-1}Cl\textsubscript{3-x}{\mu-Cl}),(NAr)Me\textsubscript{2} complexes with both Lewis acids (MeAlCl\textsubscript{2}) and Lewis bases (NE\textsubscript{ts} or PMe\textsubscript{3}) as outlined in the following sections.

3.5.1 Reaction of W(N{Ar}AIMe\textsubscript{2}{\mu-Cl}),(NAr)Me\textsubscript{2} (67) with MeAlCl\textsubscript{2}

To investigate the interaction of M(N{Ar}AIMe\textsubscript{x-1}Cl\textsubscript{3-x}{\mu-Cl}),(NAr)Me\textsubscript{2} complexes with Lewis acids, the reactivity of 67 with MeAlCl\textsubscript{2} was examined. Complex 67 was first formed in situ from reaction of W(NAr\textsubscript{2}Cl\textsubscript{2}.DME (40) and MesAI in C\textsubscript{6}D\textsubscript{6}. The reaction mixture was then dried in vacuo, removing all volatile species (including any unreacted MesAI). The resulting residue was then dissolved in hexane containing MeAlCl\textsubscript{2} (3.5 molar equivalents). After 30 minutes, the hexane and any volatile species (such as MeAlCl\textsubscript{2} or Me\textsubscript{2}AlCl) were again removed in vacuo. Subsequent analysis using \textsuperscript{1}H NMR spectroscopy clearly confirmed the formation of the complex W(N{Ar}AIMeCl{\mu-Cl}),(NAr)Me\textsubscript{2} (77) (Scheme 3.10). Addition of excess MeAlCl\textsubscript{2} to 77 resulted in the formation of multiple complexes, the identity of which could not be established using \textsuperscript{1}H NMR analysis.

\textsuperscript{ii} Due a tendency of W(N{Ar}AIMe\textsubscript{2}{\mu-Cl}),(NAr)Me\textsubscript{2} (67) to degrade a batch of this starting material was not be made. Instead for each investigation 67 was prepared in situ.
The observation that complex 77 is formed \textit{in situ} from addition of MeAlCl₂ to W(N{Ar}AlMe₂{μ-Cl})(NAr)Me₂ 67 demonstrates that it is possible to exchange the Me₃AlCl₃-x fragments of species such as 67. The formation of 77 is attributable to the greater Lewis acid strength of MeAlCl₂ over Me₂AlCl.¹⁷

### 3.5.2 Reaction of M(N{Ar}AlMe₂{μ-Cl})(NAr)Me₂ (Mo or W) with Lewis Bases

To further assess the stability of the N-Al-Cl-M chelate present in the complexes W(N{Ar}AlMe₂{μ-Cl})(NAr)Me₂ (67) and Mo(N{Ar}AlMe₂{μ-Cl})(NAr)Me₂ (76), both complexes were reacted with the Lewis bases PMe₃ or NEt₃. Addition of PMe₃ to a sample of Mo(N{Ar}AlMe₂{μ-Cl})(NAr)Me₂ (76) in C₆D₆, resulted in the formation of the known complex Mo(NAr)₂(PMe₃)Me₂, previously reported by Gibson \textit{et al.}²⁹ (Scheme 3.11).
The reactivity of Mo(N(Ar)AlMe₂(μ-Cl))(NAr)Me₂ (76) with both NEt₃ and Et₃NHCl (Scheme 3.12) was also investigated. The reagent Et₃NHCl was selected to explore the interaction of 76 with a source of Cl⁻. Reaction of 76 with NEt₃ was shown by 'H NMR spectroscopic analysis to generate the known complex Mo(NAr)₂Me₂ (27) with 100% conversion. In contrast, reaction with HNEt₃Cl resulted in multiple products, the structure of which could not be identified using NMR spectroscopic analysis.

Together, the reactions of complex 76 with PMe₃ and NEt₃ have demonstrated that addition of a nucleophilic species (i.e. Lewis bases) to complexes such as
Mo(N(Ar)AlMe₂(μ-Cl))(NAr)Me₂ (76) results in displacement of the bridging Me₂AlCl fragment. The nucleophile then has the potential to coordinate to the electropositive Mo⁶⁺ centre (as was observed for PMe₃). Having established the reactivity of the molybdenum complex 76 with nucleophiles attention turned towards investigating the reactivity of the analogous tungsten complex W(N(Ar)AlMe₂(μ-Cl))(NAr)Me₂ (67) with NEt₃, in the hope of attaining a base-free W(NAr)₂Me₂ fragment. Addition of NEt₃ to a C₆D₆ solution of complex (67) was found to result in the formation of a the desired complex W(NAr)₂Me₂ in situ (Scheme 3.13).

Scheme 3.13 Reaction of W(N(Ar)AlMe₂(μ-Cl))(NAr)Me₂ (67) with Et₃N

![Scheme 3.13](image)

3.6 Reaction of Dialkyl Mo⁶⁺ bis(Imido) Complexes with MeₓAlCl₃-x

During the synthesis of Lewis acid-bound complexes such as W(NAr)(N(Ar)AlMe₂(μ-Cl))Me₂ (67), it is unclear whether the binding of the Me₂AlCl fragment to the imido ligand occurs in a separate intermolecular reaction, taking place after ligand metathesis, or whether it occurs as part of the metathesis reaction, in an intramolecular fashion. To clarify if metathesis between Al-R and M-Cl moieties is a prerequisite for chelate formation, an investigation was made into the reaction of preformed dialkyl bis(imido) Mo⁶⁺ complexes with MeₓAlCl₃-x reagents. It can be reasoned that in such systems any MeₓAlCl₃-x coordination to imido groups must occur via intermolecular reactions.

Notably, treatment of Mo(NAr)₂(CH₂C(Me)₃)₂ (82) with Me₃Al did not result in any reaction taking place (verified using ¹H NMR spectroscopy). In contrast, the reaction of Mo(NAr)₂(CH₂C(Me)₃)₂ (82) with MeAlCl₂ resulted in the formation of multiple reaction products, none of which could be unambiguously assigned by NMR spectroscopy (Scheme 3.14).
As reaction of Mo(NAr)₂(CH₂C(Me)₃)₂ (82) failed to give clear insight into the potential interactions of Me₃AlCl₅-x reagents with bis(imido) dialkyi complexes, attention turned to investigating the reactivity of Mo(NAr)₂Me₂ (27) with both MeAlCl₂ and Me₂Al (Scheme 3.15). Addition of Me₂Al to 27 failed to result in any reaction taking place, with no new species observable by ¹H NMR spectroscopic analysis. In this system neither Me₂Al nor the complex Mo(NAr)₂Me₂ (27) contains a chloride moiety. As such, the formation of a chelate similar to that found for Mo(N{Ar}AlMe₂[μ-Cl])(NAr)Me₂ (76) in which a chloride ligand bridges between the aluminium and Mo^VI atoms is impossible. The failure of Me₂Al to react with Mo(NAr)₂Me₂ (27) is of significance, as this strongly suggests that coordination of a chloride ligand to the Mo^VI atom (as in complex 76 or 79) is essential in order to enable the binding of an Me₃AlCl₅-x fragment to a bis(imido) moiety. Notably, a bridging methyl group did not evolve upon addition of Me₃Al to complex Mo(NAr)₂Me₂ (27). This demonstrates that in this system a methyl moiety does not have the capacity to bridge between the molybdenum and aluminium atoms.

Scheme 3.15 Reaction of Mo(NAr)₂Me₂ (27) with MeAlCl₂ and Me₂Al

Mo(NAr)₂Me₂ + Me₃Al, C₆D₆ → No reaction

MeAlCl₂, C₆D₆

Additional products
In contrast, reaction between Mo(NAr)₂Me₂ (27) and MeAlCl₂ does indeed occur, with the major product (~70%) as identified by ¹H NMR spectroscopy being Mo(N{Ar}AlMeCl(µ-Cl))(NAr)Me₂ (83) (Scheme 3.15). However, the reaction of MeAlCl₂ and Mo(NAr)₂Me₂ (27) also gives additional products, which cannot be separated from 83 by recrystallization and which could not be identified unambiguously by NMR spectroscopy. The formation of 83 upon reaction of 27 with MeAlCl₂, demonstrates that MeₙAlCl₃₋ₓ reagents can coordinate to bis(imido) fragments without metathesis of Mo-Cl and Al-Me ligands. Thus, the MeₙAlCl₃₋ₓ fragments observed to bind in complexes such as 67 or 76 are not restricted to exclusively coordinating to the bis(imido) moiety in an intermolecular reaction step occurring after ligand metathesis (Scheme 3.16). Instead MeₙAlCl₃₋ₓ is free to coordinate to a bis(imido) moiety in a classical Lewis base/Lewis acid intermolecular reaction, with the imido lone pair donated to the vacant LUMO orbital of the MeAlCl₂.

Scheme 3.16 MeAlCl₂ coordination to a bis(imido) fragment via an intramolecular reaction.

3.7 Synthesis, Characterization, and Reactivity of W(NAr)₂Me₂·THF (84)
The synthesis of a tungsten bis(imido) dimethyl complex with no coordinating MeₙAlCl₃₋ₓ groups is of interest for numerous reasons. Gibson et al. have found that reaction of Cr(NAr)₂Me₂ with [PhNMe₂H][B(C₆F₅)₄] generates an active ethylene polymerization initiator, believed to result from protonation of a Cr-Me moiety by
[PhNMe2H][B(C6F5)4] to give an ionic Cr complex.\(^{30}\) Similarly, it is well established that dimethyl Group 4 metalloccenes can be activated by boron-based co-initiators to give highly active ethylene polymerization systems (Scheme 3.17).\(^{31,32,33}\) As mentioned in Chapter 1, Section 1.8, Hf(Cp)2Me2 is isolobal with W(NAr)2Me2. This hints that a W(NAr)2Me2 fragment could be similarly activated by a boron-based co-initiator to give an alkene dimerization or polymerization initiator. Hence, the synthesis of a base-free W(NAr)2Me2 complex is highly desirable.

**Scheme 3.17 Activation of ZrCp'2R2 with [Ph3C][B(C6F5)4]**

3.7.1 Synthesis and Characterization of W(NAr)2Me2·THF (84)

Reaction of 67 with Et3N in C6D6 (Schemes 3.13) indicate that a "W(NAr)2Me2" complex is sufficiently stable to be isolated on a full preparatory scale. Notably, Gibson *et al.* have previously published the synthesis of both the related Cr and Mo dimethyl complexes Cr(NAr)2Me2, and Mo(NAr)2Me2 (27).\(^ {29}\) Both are generated from the reaction of the appropriate bis(imido) MCl2 fragment with MeMgBr in diethyl ether, followed by extraction. Because both the chromium and molybdenum complexes can be made in high yields via this methodology an analogous procedure was attempted using W(NAr)2Cl2·DME (40) and MeMgCl (Scheme 3.18). However, this approach repeatedly failed, giving multiple complexes that could not be identified by \(^1\)H NMR spectroscopy.

As reacting W(NAr)2Cl2·DME (40) with MeMgCl proved futile, an alternative synthesis was developed using Me3Al as an alkylating agent. In Section 3.1, the reaction between W(NAr)2Cl2·DME (40) and Me3Al was shown to give W(N{Ar}AIMe2{|JCI})(NAr)Me2 (67) with full conversion. Later, in Section 3.5.2, it
was shown that 67 reacts with nucleophiles to give a W(NAr)₂Me₂ fragment. With both of these observations in mind, it has been found that the complex W(NAr)₂Me₂.THF (84) can be synthesised on a preparatory scale via reaction of complex 67 with THF (Scheme 3.18).

Scheme 3.18 Synthesis of W(NAr)₂Me₂.THF (84)

The aluminium by-product Me₂AlCl.THF generated in this reaction can be observed by ¹H NMR spectroscopy and is readily removed following recrystallization of the crude reaction material from diethyl ether. The synthetic procedure outlined in Scheme 3.18 was repeated, but Et₂O instead of THF was used to displace the coordinating Me₂AlCl fragment of complex 67. This was undertaken with the aim of obtaining a W(NAr)₂Me₂ fragment without a bound THF moiety, which would be directly analogous to established Cr(NR)₂Me₂ ethylene polymerization precatalysts.³⁰ It was found that the Me₂AlCl fragment of 67 was readily displaced by Et₂O to give a W(NAr)₂Me₂ complex and an unknown (Me₂AlCl)ₓ(Et₂O)ᵧ adduct, which could not be removed from the product complex by recrystallization. Attempts were also made to displace the bound THF moiety of 84 by drying a sample of W(NAr)₂Me₂.THF (84) in vacuo; this did indeed lead to the removal of the bound THF group, which in turn resulted in degradation of the W(NAr)₂Me₂ fragment and the
formation of multiple W-containing complexes, as apparent by $^1$H NMR spectroscopy. Recrystallization of a crude sample of 84 gave crystals suitable for single crystal X-ray diffraction analysis (Figure 3.16 and Table 3.6).

**Figure 3.16** Solid state structure of $\text{W(NAr)}_2\text{Me}_2\text{.THF}$ (84) with the thermal ellipsoids set at the 50% level

![Solid state structure of W(NAr)$_2$Me$_2$.THF (84)](image)

**Table 3.6** Selected bond distances ($\text{Å}$) and bond angles ($) for $\text{W(NAr)}_2\text{Me}_2\text{.THF}$ (84).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance ($\text{Å}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1-N1</td>
<td>1.784(4)</td>
</tr>
<tr>
<td>W2-N2</td>
<td>1.764(4)</td>
</tr>
<tr>
<td>W1-C16</td>
<td>2.157(5)</td>
</tr>
<tr>
<td>W1-C61</td>
<td>2.159(5)</td>
</tr>
<tr>
<td>W1-O1</td>
<td>2.322(3)</td>
</tr>
<tr>
<td>C16-W1-C61</td>
<td>130.2(2)</td>
</tr>
<tr>
<td>N1-W1-N2</td>
<td>111.11(18)</td>
</tr>
<tr>
<td>W1-N2-C44</td>
<td>176.9(4)</td>
</tr>
<tr>
<td>W1-N1-C18</td>
<td>154.7(3)</td>
</tr>
</tbody>
</table>

Examinations of the structural parameters associated with complex 84 indicate that the tungsten core adopts a highly distorted pseudo trigonal bipyramidal geometry. This is consistent with the molecular structure of the closely related dimethyl molybdenum complex Mo(NAr)$_2$Me$_2$.PMe$_2$Ph. In both 84 and Mo(NAr)$_2$Me$_2$.PMe$_2$Ph the two methyl groups occupy axial sites, with the two imido ligands and the Lewis...
base moiety lying approximately in the same plane. The W-C bonds of 84 at 2.157(5) and 2.159(5) Å are within the normal range for a W-C contact (2.05 Å to 2.36 Å), and are comparable to those of W(N{Ar}AlMe2{μ-Cl})(NAr)Me2 (67) at 2.129(2) and 2.139(2) Å. The similar W-N bond lengths of 1.764(4) and 1.784(4) Å and W-N-Cipso bond angles of 154.7(3) and 176.9(4)° are suggestive of both imido ligands of 84 adopting a bonding mode intermediate between that of a 4 and 2-electron donor (neutral formalism), an arrangement that is quite common for group 6 bis(imido) fragments.

The observation that 84 adopts a distorted trigonal bipyramidal geometry can explain the apparent instability of the WMe2 moiety upon removal of THF in vacuo. As both W-Me methyl groups of 84 lie in an approximately axial orientation, the possibility of a reductive elimination reaction is reduced by the relatively large separation of the two Me groups in space. Removal of THF would force the resulting W(NAr)2Me2 species to adopt a pseudo-tetrahedral geometry in which the two methyl groups have a greater proximity and so an increased possibility of undergoing reductive elimination. The likelihood of 84 undergoing reductive elimination is also undoubtedly heightened in the solid state, by crystal packing forces. In contrast, the analogous Mo complex, Mo(NAr)2Me2.THF is stable when dried in vacuo, with no loss of the THF moiety occurring, presumably due to a stronger molybdenum-oxygen interaction resulting from a harder molybdenum centre.

Further examination of the 1H NMR spectrum of W(NAr)2Me2.THF (84) highlights a discrepancy between the structure of 84 in the solid and solution states. Notably, the 1H NMR chemical shifts for the two CH2 moieties of the bound THF in complex 84 at 3.47 and 1.40 ppm are identical to that of an authentic sample of free, unbound THF. This suggests that in solution the THF moiety of 84 dissociates readily from the tungsten centre giving the desired base-free W(NAr)2Me2 complex. The weak nature of the THF association in complex 84 has also been demonstrated by the observed ease with which the THF fragment of 84 can be removed in vacuo.

In order to study the solution interaction between what is believed to be the base-free "W(NAr)2Me2" complex and THF, a solution of 84 in C6D6Cl was analysed by 1H NMR spectroscopy at -40 °C and ambient temperature. No significant deviation in the relative positions and intensity of the spectral features were obtained upon cooling. Consequently, this neither contradicts nor supports the hypothesis that THF is dissociating from 84 in solution. However, the premise that the THF fragment of 84 dissociates is supported by the 1H NMR spectral data obtained from a study of the reaction of 84 with one equivalent of B(C6H4F)3 in C6D6. Following addition of B(C6F5)3 to 84 a pronounced shift to lower frequencies is observed for the THF
resonances (3.23 and 0.94 ppm), resulting from the formation of a THF.B(C₆F₅)₃ Lewis acid/Lewis base adduct. In contrast, the ¹H NMR resonances associated with the W(NAr)₂Me₂ fragment of 84 remain unaffected, consistent with no modification of the W(NAr)₂Me₂ moiety having taken place. Thus, the identical ¹H NMR chemical shifts of the W(NAr)₂Me₂ fragment, both before and after reaction of the THF moiety with B(C₆F₅)₃, strongly indicates that in solution 84 undergoes facile dissociation. Although the THF moiety of 84 readily dissociates, it has been found that stronger Lewis bases can more effectively bind to a W(NAr)₂Me₂ fragment. Thus, addition of PMe₃ to W(NAr)₂Me₂·THF (84) generates W(NAr)₂Me₂·PMe₃, which in contrast to 84 is stable when dried in vacuo.

3.7.2 Reaction of W(NAr)₂Me₂·THF (84) with Group 13 Compounds

As discussed in Section 3.7, it is feasible that W(NAr)₂Me₂·THF (84) may be activated by boron-based reagents to give ethylene dimerization or polymerization initiators. As such attention turned to investigating the reactivity of 84 with [PhNHR₂H][B(C₆F₅)₄], B(C₆F₅)₃, and [Ph₃C][B(C₆F₅)₄].

Addition of [Ph₃C][B(C₆F₅)₄] to a C₆D₆ solution of 84 resulted in multiple reaction products, the identity of which could not be ascertained by ¹H NMR spectroscopic analysis (Scheme 3.19). In contrast, attempts to react complex (84) with an excess of B(C₆F₅)₃ in C₆D₆ failed, with no modification of the W(NAr)₂Me₂ fragment occurring, even after the reaction solution was heated (60 °C, 2 h) (Scheme 3.19). This suggests that B(C₆F₅)₃ is not a sufficiently strong Lewis acid to abstract a W-Me moiety from of complex 84. It was also found that the W-Me bond of complex 84 in C₆D₆ is resistant to protonation by [PhNMe₂H][B(C₆F₅)₄] (Scheme 3.19).
Scheme 3.19 Attempted reactions of complex $W(NAr)_{2}Me_{2}.THF$ (84) with $[\text{Ph}_3\text{C}][\text{B}((\text{C}_6\text{F}_5)_4)]$ and $B(\text{C}_6\text{F}_5)_3$

As addition of $B(\text{C}_6\text{F}_5)_3$ to 84 did not result in tungsten methyl abstraction, attention turned to assessing the capacity of MAO to abstract a W-Me moiety of a $W(NAr)_{2}Me_{2}$ fragment. This was undertaken as the reagent MAO is used widely as a co-initiator in a broad range of catalytic systems, and is believed to activate transition metal complexes, via alkylation and methyl abstraction.\(^{37}\) In this study commercially available MAO was dried in vacuo and then reacted, in a large excess, with $W(NAr)_{2}Cl_{2}.DME$ (40) in $\text{C}_6\text{D}_5\text{Cl}$. This resulted in the in situ formation of a $W(NAr)_{2}Me_{2}$ fragment, with identical W-CH$_3$ and CH$_3$ (Pr) $^1$H NMR chemical shifts to that presented by $W(NAr)_{2}Me_{2}.THF$ (84) in $\text{C}_6\text{D}_5\text{Cl}$. The synthesis of a $W(NAr)_{2}Me_{2}$ fragment from reaction of $W(NAr)_{2}Cl_{2}.DME$ (40) and MAO can undoubtedly attributed to the Me$_3$Al component of MAO.\(^{38,39}\) Of note, is that even after heating (60 °C, 3 h) of the MAO reaction solution no tungsten methyl abstraction occurred (Scheme 3.20). Thus, it can be concluded that the tungsten methyl moieties of a $W(NAr)_{2}Me_{2}$ fragment cannot be readily abstracted by either MAO or $B(\text{C}_6\text{F}_5)_3$.

Scheme 3.20 Reaction of $W(NAr)_{2}Cl_{2}.DME$ (40) with MAO

$W(NAr)_{2}Cl_{2}.DME$ $^{150\text{MAO}}$ $W(NAr)_{2}Me_{2}$ $^{60\text{°C}, \text{3 h}}$ $\times$ No Reaction
Chapter 3

3.8 Reaction of $M(N(\text{Ar})\text{AlMe}_2\mu-\text{Cl})_2\mu-\text{Cl})(\text{NAr})\text{Me}_2 \, (M = \text{Mo or W})$ with Ethylene

Tobisch has evaluated the capacity of tungsten bis(imido) systems to initiate ethylene dimerization via an oxidative coupling mechanism using DFT.\textsuperscript{40} He concluded that the fragments $W^{\text{IV}}(\text{NPh})_2$ (85), $W^{\text{IV}}(N\{\text{Ph}\text{AlMe}_2\mu-\text{Cl}\})(\text{NPh})$ (86), and $W^{\text{IV}}(N\{\text{Ph}\text{AlMe}_2\mu-\text{Cl}\})(N\{\text{Ph}\text{AlMe}_2\mu-\text{Cl}\})$ (87) could all theoretically initiate ethylene dimerization. With the aim of experimentally evaluating Tobisch's DFT investigation, attention turned to assessing the capacity of a range of dimethyl bis(imido) complexes to react with ethylene.

3.8.1 Reaction of $W(N(\text{Ar})\text{AlMe}_2\mu-\text{Cl})_2(N\text{Ar})\text{Me}_2$ (67) and $\text{Mo}(N(\text{Ar})\text{AlMe}_2\mu-\text{Cl})_2(N\text{Ar})\text{Me}_2$ (76) with Ethylene

As it has been postulated that species such as $W(N(\text{Ph})\text{AlMe}_2\mu-\text{Cl})(\text{NPh})$ (64) can initiate ethylene dimerization, it is feasible that the related complexes 67 and 76 could also react with ethylene. To investigate if this is indeed the case, the complexes $W(N(\text{Ar})\text{AlMe}_2\mu-\text{Cl})_2(N\text{Ar})\text{Me}_2$ (67) and $\text{Mo}(N(\text{Ar})\text{AlMe}_2\mu-\text{Cl})_2(N\text{Ar})\text{Me}_2$ (76) were prepared in situ from reaction of the appropriate $M(N\text{Ar})_2\text{Cl}_2.$ DME ($M = \text{W or Mo}$) precursor with $\text{Me}_2\text{Al}$ in $\text{C}_6\text{D}_6$. The resulting solutions of both 67 and 76 were then placed under an atmosphere of ethylene. In neither case was any interaction between ethylene and either 67 or 76 observed to occur. Furthermore, even after heating the solutions (50 °C, 1 h), no reaction between complexes 67 and 76 with ethylene could be detected (Scheme 3.21). Notably, identical results were obtained when $\text{C}_6\text{D}_5\text{Cl}$ was used as the reaction solvent. It is evident that the connectivity of 67 and 76 are not altered by the addition of the Lewis base ethylene. This indicates that the intramolecularly-coordinating chloride ligands of complexes 67 and 76 are not readily displaced to accommodate ethylene coordination at the metal centres, an essential step prior to any further reaction of the alkene.
3.8.2 Assessing the Capacity of Me₃AlCl to Activate W(NAr₂Cl₂.DME (40) for Ethylene Dimerization

It is clear that Me₃Al cannot activate W(NAr₂Cl₂.DME (40) for ethylene dimerization as the product of the Me₃Al reaction, W(N{Ar}AIMe₂{μ-Cl})(NAr)Me₂ (67), is inert to reaction with ethylene. Consequently, attention turned to assessing the capacity of the stronger Lewis acid Me₂AlCl to activate complex 40. Thus, W(NAr₂Cl₂.DME (40) was reacted with Me₂AlCl (eight equivalents) in C₆D₆ and the resulting solution was treated with ethylene. In contrast to the reaction with Me₃Al, here the immediate formation of but-1-ene was observed, the identity of the organic product being verified by ¹H /¹H COSY correlation spectroscopy (Scheme 3.22).

Scheme 3.22 Ethylene dimerization, initiated by W(NAr₂Cl₂.DME and Me₂AlCl

It has been established that treatment of 40 with Me₂AlCl in the absence of alkenes gives W(N{Ar}.AlMeCl{μ-Cl})(NAr)Me₂ (77) as the principle reaction product, as well as a number of additional product complexes, the structures of which are unknown (Section 3.3.2, Figure 3.10). It is clear that one of the complexes produced in the
MeAlCl₂ system is capable of initiating ethylene dimerization. As complex 67 has been shown to be inert to reaction with ethylene, it is highly unlikely that W(N{Ar}.AlMeCl{μ-Cl})(NAr)Me₂ (77) is the active initiator complex. Indeed, it is very improbable that "replacing" the Me₂AlCl fragment of 67 with a MeAlCl₂ fragment in W(N{Ar}.AlMeCl{μ-Cl})(NAr)Me₂ (77) would generate an initiator complex. Furthermore comparison with the Me₃Al system (Scheme 3.23) in which 67 is obtained in 100% conversion, suggests that 77 can be viewed as a precursor to the initiator complex.

Scheme 3.23 Performance of Me₃Al vs Me₂AlCl as ethylene dimerization co-initiators

When considering how complex 77 could be activated for ethylene dimerization, it is possible to envisage that Me₂AlCl could react with complex 77, either as an alkylating agent or as a Lewis acid. Alkylation of the only available chloride moiety of 77 would give the inactive complex W(N{Ar}.AlMe₂{μ-Cl})(NAr)Me₂ (67). One possibility is that the enhanced Lewis acidity of Me₂AlCl compared with that of AlMe₃ enables Me₂AlCl to abstract a methyl moiety of complex 77 generating a charged species with a vacant coordination site (Scheme 3.24). Such an ionic complex could undoubtedly accommodate ethylene coordination, the pre-requisite step for alkene dimerization.

Scheme 3.24 Proposed reaction of 77 with Me₂AlCl
Activation of 77 for ethylene dimerization *via* the formation of a charged complex (Scheme 3.24) has some precedent. Discrete cationic bis(imido) chromium complexes stabilized by a B(C₆F₅)₄⁻ counter ion, have been shown to initiate ethylene polymerization without the necessity for any co-initiator. In addition, the charged complex [C₅⁺CoP(OMe)₃(Et)][BAr⁺] has been shown to initiate α-olefin dimerization, again with no additional co-initiator present. More recently, Schrock *et al.* have synthesised an ionic Mo⁶⁺ imido alkylidene complex [Mo(NAr)(CHCMe₂Ph)(py)(THF)][BAr⁺] suggesting that a M⁶⁺ charged imido complex is viable. Indeed, it has long been established for Ziegler-type polymerization initiators that charged intermediates are significant in initiating the reaction of ethylene. As such, the possible formation of ionic complexes in the Me₂AlCl co-initiated dimerization system (Scheme 3.24) is highly feasible.

### 3.9 Reaction of W(NAr)₂Me₂-THF (84) and Mo(NAr)₂R₂ (R = Me or CH₂CMe₃) with Alkenes

It is clear that the intramolecularly-coordinating chloride ligands of both W(N{Ar}(µ-Cl))(NAr)Me₂ (67) and Mo(N{Ar}(µ-Cl))(NAr)Me₂ (76) are not readily displaced, with both 67 and 76 being inert to reaction with ethylene (*Section 3.8.1*), undoubtedly because neither 67 nor 76 has a vacant orbital available for coordination of an α-donor ligand. In contrast to the complexes 67 or 76, the base-free W(NAr)₂Me₂ fragment, (formed in solution *via* facile dissociation of W(NAr)₂Me₂-THF (84)), does have a vacant metal-based orbital available for ethylene coordination. Thus, 84 and related molybdenum complexes are anticipated to have a higher affinity than either 67 or 76 for reaction with alkenes. To assess if this is indeed the case, the reactivity of 84 and Mo(NAr)₂R₂ (R = Me or CH₂CMe₃) complexes with alkenes (ethylene or propylene) was investigated.

#### 3.9.1 Reaction of W(NAr)₂Me₂-THF (84) with Ethylene

Initially, the reactivity of W(NAr)₂Me₂-THF (84) with alkenes was examined. It was found that direct addition of ethylene (approximately five equivalents) to a C₆D₆ solution of complex 84 resulted in an immediate reaction to give multiple unknown reaction products (verified using ¹H NMR spectroscopy). Re-analysis of the reaction solution after a 48 h period, again by NMR spectroscopy, indicated that the formation of both but-1-ene and methane (in a 4:1 molar ratio) had occurred slowly, resulting in complete consumption of ethylene (Scheme 3.25). The presence of the but-1-ene was confirmed by GC analysis of the volatile components of the reaction solution.
Scheme 3.25 *Ethylene dimerization initiated by complex 84*

\[
\begin{align*}
\text{W(NAr)}_2\text{Me}_2\cdot\text{THF} & \quad \text{Ethylene} \quad \text{Multiple reaction products} \\
(84) & \quad \text{at } t=0 \\
\downarrow & \quad 48\text{hrs} \\
\text{But-1-ene} & + \\
\text{Methane} &
\end{align*}
\]

To assess the thermal stability of 84, a sample of W(NAr)_2Me_2·THF (84) was dissolved in C_6D_6 and the solution was heated (60 °C, 2 h). Notably no hydrolysis or thermal degradation of 84 occurred. Evidently complex 84 is stable to reductive elimination of ethane (Scheme 3.26).

**Scheme 3.26 Assessing the thermal stability of W(NAr)_2Me_2·THF (84)**

\[
\begin{align*}
\text{W(NAr)}_2\text{Me}_2\cdot\text{THF} & \quad 60^\circ\text{C}, 2\text{ h} \quad \text{C}_6\text{D}_6 \quad \times \quad \text{No Reaction}
\end{align*}
\]

It may be concluded, from the thermal stability of 84, that activation of 84 by reductive elimination of ethane alone is not viable; instead activation of 84 is more likely to occur via elimination of methane (Scheme 3.27). As complex 84 has been shown to dissociate in solution, the first reaction step on interaction with C_2H_4 is proposed to be coordination of the alkene to give the intermediate A. Next, a migratory insertion reaction could take place to give a tungsten propyl complex B, which has the capacity to undergo β-hydride elimination to give intermediate C. Reductive elimination of methane from intermediate C would then afford the W^V intermediate D. Both the intermediates C or D of Scheme 3.27 have the capacity to dimerize ethylene via a hydride cycle or cross coupling mechanism, respectively (Chapter 1, Section 1.2).
Scheme 3.27 Proposed mechanism for methane formation from reaction of complex 84 and ethylene

There is literature precedent for some of the steps involved in the reaction pathway outlined in Scheme 3.27. Macgregor et al. have examined the degradation of the iridium complex \( \text{Ir}(C_6F_5)(\text{Et})(\text{Me})(\text{PEt}_2\text{F})(\text{PEt}_3)_2 \) (88) using DFT. They established that degradation of complex 88 is initiated when a Ir-Et moiety undergoes β-hydride elimination, to give an Ir-H intermediate, from which methane is eliminated (Scheme 3.28). This is the same sequence of reactions to that proposed to generate methane upon reaction of 84 with ethylene (Scheme 3.27).
Clearly, the formation of an active initiator species via β-hydride elimination from a W propyl group as outlined in Scheme 3.27 would necessitate the formation of propylene. However, despite extensive investigation, propylene could not be detected by either 1H NMR spectroscopic or GC analysis. It is possible that any propylene generated in situ reacted with ethylene to give a range of C₅ products, each in too low a concentration to be detected upon analysis of the reaction solution.

3.9.2 Reaction of W(NAr)₂Me₂·THF (84) with Propylene

It has now been established that complex 84 can initiate the dimerization of ethylene. Thus, it was of interest to assess whether complex 84 would be capable of initiating dimerization of higher α-olefins. To this end, a C₆D₆ solution of 84 was treated with propylene which resulted in the formation of multiple unknown W-containing complexes (Scheme 3.29). In contrast to the ethylene system, no dimerization of propylene, occurred (as verified using 1H NMR spectroscopy) (Scheme 3.29). However, the by-product methane was observed, indicating that similar reactions to those outlined in Scheme 3.27, Section 3.9.1 did occur, namely migratory insertion of propylene followed by β-hydride elimination and then reductive elimination. It is unclear as to why reaction of 84 and propylene did not generate a complex in situ capable of initiating propylene dimerization.
3.9.3 Reaction of Mo(NAr)_2Me_2 (27) with Ethylene

To assess if Mo(NAr)_2Me_2 (27) would display similar reactivity with alkenes to that of the closely related tungsten complex W(NAr)_2Me_2·THF (84), the reaction of 27 with ethylene was investigated. Addition of ethylene to a C_6D_6 solution of Mo(NAr)_2Me_2 (27) (approximately 3 equivalents) resulted in the immediate formation of multiple products the structures of which could not be determined using NMR spectroscopy. It was clear from ^1H NMR analysis of the reaction solution that all of complex 27 reacted upon addition of ethylene. However, no ethylene dimerization occurred, the excess ethylene added to the reaction solution was not consumed, and no butenes were detected (^1H NMR spectroscopy).

3.9.4 Rationalizing the Different Reactivity of W(NAr)_2Me_2·THF (84) and Mo(NAr)_2Me_2 (27) with Ethylene

It has now been established that although Mo(NAr)_2Me_2 (27) reacts with ethylene, this reaction does not generate higher olefins. In contrast, but-1-ene is generated from reaction of the closely related complex W(NAr)_2Me_2·THF (84) with ethylene. This difference in reactivity between the 27 and 84 systems is unlikely to be a steric effect, as both complexes have very similar coordination spheres. Indeed, it is unlikely that the dimethyl moiety in either complex 27 or 84 would hinder ethylene coordination. Instead the discrepancy between the Mo- and W-systems has to be attributed to electronic factors.

As represented in Section 3.9.1, Scheme 3.27 the activation of a W(NAr)_2Me_2 fragment is proposed to occur via coordination of ethylene to the tungsten centre, followed by insertion of an ethylene ligand into a W-Me bond. It is likely that the thermodynamic penalty associated with ethylene inserting into an M-Me bond will be similar in both the molybdenum and tungsten systems. Although this feature has not been studied in detail for group 6 complexes, a DFT study has been...
reported that quantifies the thermodynamic parameters associated with ethylene inserting into the M-Me bonds of a series of Ti\textsuperscript{VI}, Zr\textsuperscript{IV} and Hf\textsuperscript{VI} complexes.\textsuperscript{45} This computational study found that the barrier to ethylene insertion for all three systems was similar. Thus, the observed difference in reactivity of complexes W(NAr\textsubscript{2})Me\textsubscript{2}.THF (84) and Mo(NAr\textsubscript{2})Me\textsubscript{2} (27) with ethylene is more likely to originate from the different strengths of the Mo(\texteta\textsuperscript{2}-CH\textsubscript{2}CH\textsubscript{2}) and W(\texteta\textsuperscript{2}-CH\textsubscript{2}CH\textsubscript{2}) interactions.

The relative strengths of M(\texteta\textsuperscript{2}-CH\textsubscript{2}CH\textsubscript{2}) (M = Mo, W) interactions have previously been examined using energy partitioning analysis.\textsuperscript{46} It has been reported that the enthalpy of dissociation of Mo(CO)\textsubscript{5}(\texteta\textsuperscript{2}-CH\textsubscript{2}CH\textsubscript{2}) is -20.6 kcal/mol. In contrast, for the analogous tungsten complex, W(CO)\textsubscript{5}(\texteta\textsuperscript{2}-CH\textsubscript{2}CH\textsubscript{2}), is reported as being thermodynamically more stable, having a more negative enthalpy of dissociation, -27.9 kcal/mol. Similarly, the tungsten complex WCl\textsubscript{4}(\texteta\textsuperscript{2}-CH\textsubscript{2}CH\textsubscript{2}) is thermodynamically more stable than the analogous complexes MoCl\textsubscript{4}(\texteta\textsuperscript{2}-CH\textsubscript{2}CH\textsubscript{2}), with respective bond dissociation energies calculated as being -12.9 kcal/mol and +7.8 kcal/mol. Thus, it can be concluded that MoCl\textsubscript{4}(\texteta\textsuperscript{2}-CH\textsubscript{2}CH\textsubscript{2}) is only kinetically not thermodynamically stable. Together, these observations suggest that molybdenum complexes seemingly have a lower affinity for ethylene than their comparable tungsten counterparts. Hence, Mo(\texteta\textsuperscript{2}-CH\textsubscript{2}CH\textsubscript{2}) species may not be thermodynamically sufficiently stable to act as catalytic intermediates, potentially hampering ethylene dimerization in the Mo(NAr\textsubscript{2})Me\textsubscript{2} (27) reaction.

3.9.5 Addition of Ethylene to Mo(NAr\textsubscript{2})(CH\textsubscript{2}CMe\textsubscript{3})\textsubscript{2} (82)

Although it is unlikely that the dimethyl moieties of W(NAr)Me\textsubscript{2}.THF (84) and Mo(NAr\textsubscript{2})Me\textsubscript{2} (27) will inhibit ethylene coordination in either case, the same may not be true if different alkyl groups are employed. To assess the influence of steric factors upon reaction of Mo(NAr)\textsubscript{2}R\textsubscript{2} with olefins, ethylene was added to a C\textsubscript{6}D\textsubscript{6} solution of the dialkyl complex Mo(NAr)\textsubscript{2}(CH\textsubscript{2}C(CH\textsubscript{3})\textsubscript{3})\textsubscript{2} (82). Upon addition of ethylene no reaction of 82 occurred, with the \textsuperscript{1}H NMR spectrum of the reaction solution comprised exclusively of resonances assignable to free ethylene and unreacted 82 (Scheme 3.30). This demonstrates that even ethylene, a relatively small molecule, can be physically blocked by the bulk of the CH\textsubscript{2}C(CH\textsubscript{3})\textsubscript{3} alkyl groups from binding to the vacant coordination site of a Mo\textsuperscript{VI} atom. Clearly reaction of ethylene with both Mo(NAr)\textsubscript{2}Me\textsubscript{2} (27) and W(NAr)\textsubscript{2}Me\textsubscript{2}.THF (84) is facilitated by the relatively low steric influence of the Mo-Me or W-Me groups.
3.10 Reaction of W(NAr)$_2$Me$_2$.THF (84) with a 1:1 Mixture of C$_2$D$_4$ and C$_2$H$_4$

As discussed in detail in Chapter 1, Section 1.4, Bercaw et al. have examined the mechanism of their chromium-initiated ethylene trimerization reaction through reaction of a 1:1 mixture of C$_2$D$_4$ and C$_2$H$_4$.

The resulting C$_6$ products were found to contain exclusively even numbers of D and H atoms, which was cited as being proof of a metallacycle mechanism. With the aim of building upon the investigation of Bercaw, in this thesis work a C$_2$D$_4$:C$_2$H$_4$ mixture was reacted with a dimerization system generated in situ from the reaction of W(NPh)Cl$_4$.THF (32) with Et$_3$Al$_2$Cl$_3$ (Chapter 2 Section 2.5). Treatment of the W(NPh)Cl$_4$.THF/Et$_3$Al$_2$Cl$_3$ solution with equimolar quantities of C$_2$D$_4$ and C$_2$H$_4$ (approximately 3 equivalents of each), resulted in the formation of a mixture of C$_4$ alkene products, many of which (such as C$_8$H$_7$D or C$_9$H$_8$D$_5$) contained odd numbers of deuterium atoms. Furthermore, the relative abundances of the C$_4$ isotopomers did not fit that predicted for either a hydride or a metallacycle pathway. Thus, no information as to the mechanism of the W(NPh)Cl$_4$.THF/Et$_3$Al$_2$Cl$_3$ based dimerization system could be ascertained.

It has now been established that W(NAr)$_2$Me$_2$.THF (84) can be utilized as a pre-catalyst for ethylene dimerization, generating exclusively but-1-ene (Section 3.9.1). Indeed, this high selectivity for but-1-ene makes the W(NAr)$_2$Me$_2$.THF (84) reaction system ideally suited for mechanistic investigations. With the aim of identifying the reaction mechanism of the 84 system (hydride vs metallacycle) attention turned to examining the reactivity of 84 with a 1:1 C$_2$H$_4$:C$_2$D$_4$ feedstock.

Addition of C$_2$H$_4$ and then C$_2$D$_4$ to a C$_6$D$_6$ solution of W(NAr)$_2$Me$_2$.THF (84) resulted in the slow formation of C$_4$ alkenes over a 48 h period. Analysis of the reaction solution using GC-MS determined that a multitude of C$_4$ products had been generated, which contained both odd and even numbers of D or H atoms (Scheme 3.31).

---

*iv* Ion recognition software was used to detect the presence of the products C$_4$H$_8$, C$_4$H$_7$D, C$_4$H$_6$D$_2$, C$_4$H$_5$D$_3$, C$_4$H$_4$D$_4$, C$_4$H$_3$D$_5$, C$_4$H$_2$D$_6$ and C$_4$HD$_7$. 

---
Scheme 3.31  
**Dimerization of C$_2$D$_4$ and C$_2$H$_4$ initiated by W(NAr)$_2$Me$_2$.THF (84)**

![Scheme 3.31](attachment:image.png)

Disappointingly, because C$_4$ olefins containing both odd and even numbers of deuterium atoms were obtained, detailed insights into the mechanism of ethylene dimerization for the 84-based system cannot be ascertained. However, it is clear that “odd” products, such as the observed C$_4$H$_7$D, can only result from transfer of a D atom of a W-D moiety, to a C$_n$H$_{2+n}$ molecule. Thus, this generation of “odd” products can be attributed to the in situ formation of W-H or W-D moieties. However, both the chain growth and metallocycle mechanisms of olefin dimerization have W-H (or W-D) intermediates (Scheme 3.32) (see Chapter 1, Section 1.2), which have the capacity to react with C$_2$D$_4$ or C$_2$H$_4$, and exchange H and D atoms.

Scheme 3.32  
**Formation of W-H complexes in both metallocycle and hydride mechanisms**

![Scheme 3.32](attachment:image.png)
3.11 Attempts to Synthesise Tungsten and Molybdenum Hydrides From Reaction of Discrete Imido Complexes

The complex \( \text{Cp}_2\text{TiH(dmpe)}_2 \) (89) has been reported by Girolami et al. to initiate ethylene dimerization/trimerization.\(^{48}\) These researchers have also shown, using \(^1\text{H}\) NMR spectroscopy, that insertion of ethylene into the Ti-H bond is surprisingly unfavourable, with no depletion in the \(^1\text{H}\) NMR resonance associated with the Ti-H moiety being apparent upon ethylene dimerization. Thus, in the reaction of \( \text{Cp}_2\text{TiH(dmpe)}_2 \) (89) with ethylene the hydride is viewed as being a 'spectator ligand', with dimerization of ethylene in this system being preferentially initiated via a metallacycle mechanism. The investigation made by Girolami and co-workers clearly demonstrates that characterization of a discrete hydride complex can ultimately lead to experimental observations that can assist in determining the mechanism of an ethylene dimerization initiator. Consequently, attention was turned to the synthesis of discrete tungsten and molybdenum imido hydride complexes.

3.11.1 Treatment of Discrete Imido Complexes with \text{HSiMe}_2^{1\text{Bu}}

It has long been established that metathesis of a Group 14 hydrides can be utilized to synthesis a transition metal hydride moiety.\(^{49}\) Thus, a range of discrete Mo and W imido complexes were treated with \text{HSiMe}_2^{1\text{Bu}} with the aim of synthesising an imido hydride complex via metathesis. Disappointingly, it was found that following addition of stoichiometric amounts of \text{HSiMe}_2^{1\text{Bu}} to \( \text{CeDe} \) solutions of \( \text{W(NAr}_2\text{Cl}_2)\text{DME} \) (40), \( \text{W(NAr)_Cl}_4\text{THF} \) (38), and \( \text{W(NPh)(Cl}_2)\text{(PMe}_3)_3 \) (34), no reaction was observed to occur in either case (Scheme 3.33).

**Scheme 3.33** Attempts to synthesise a \( M-H \) complex with \text{HSiMe}_2^{1\text{Bu}}

\[
\begin{align*}
\text{W(NAr}_2\text{Cl}_2)\text{DME} & \nwarrow \text{Me} \\
\text{W(NAr)_Cl}_4\text{THF} & \nwarrow \text{Me} \\
\text{W(NPh)(Cl}_2)\text{(PMe}_3)_3 & \nwarrow \text{Me} \\
\text{Mo(NAr}_2\text{Me}_2) & \nwarrow \text{Me} \\
\end{align*}
\]

Of note is that neither of these three complexes formally has a vacant coordination site; this could block the formation of the four membered \( W-\text{Cl-Si-H} \) transitional chelate required for ligand metathesis. As such attention turned to investigating the reactivity of the complex \( \text{Mo(NAr}_2\text{Me}_2) \) (27) with \text{HSiMe}_2^{1\text{Bu}}, as 27 is coordinatively...
unsaturated. However, disappointingly 27 proved to be equally inert to reaction with HSiMe₂Bu (Scheme 3.33).

3.11.2 Reaction of Discrete Imido Complexes with NaBH₄

With HSiMe₂Bu seemingly incapable of generating an imido M-H moiety (Mo or W), efforts were made to synthesise an imido hydride complex, using alternative procedures. It has been reported that the bis(imido) complex Mo(NAr)₂(PMe₃)₂(η²-BH₄) can be synthesised via reaction of Mo(NAr)₂Cl₂·DME (23) and NaBH₄ in the presence of PMe₃.⁵⁰ This indicates that stable tungsten hydride complexes could be produced via reaction of NaBH₄.

Addition of NaBH₄ to a C₆D₆ solution of W(NAr)Cl₄·THF (38) or W(NPh)(Cl)₂(PMe₃)₃ (34) did not result in reaction of either complex 38 or 33 (Scheme 3.34).⁶ In contrast to the 33 and 38 systems, addition of NaBH₄ to a C₆D₆ solution of W(NAr)₂Cl₂·DME (40) did result in the partial reaction of 40, giving unknown complexes that presented new, broad resonances at 1.40 and 3.52 ppm assignment of which has not been possible. However, no W-H moieties could be identified upon analysis of the reaction solution using NMR spectroscopy.

Scheme 3.34 Addition of NaBH₄ to the complexes 33 and 38

3.12 Summary and Conclusions

The reaction of W(NAr)₂Cl₂·DME (40) with Me₃Al has been shown to generate the dimethyl complex W(N{Ar}AlMe₂{μ-Cl})(NAr)Me₂ (67), in which a AlMe₂Cl fragment bridges the nitrogen and tungsten centres. Coordination of the Me₂AlCl Lewis acid fragment to the bis(imido) moiety results in a bonding motif for 67 in which one imido adopts a linear configuration and the second a bent geometry. Identical results are obtained upon reaction of the Mo complex Mo(NAr)₂Cl₂·DME (23) with Me₃Al to give Mo(N{Ar}AlMe₂{μ-Cl})(NAr)Me₂ (76). Notably, complexes 67 and 70 are obtained with full conversion (verified using ¹H NMR spectroscopy). Conversely, reaction of Me₂AlCl with W(NAr)₂Cl₂·DME (40) gives both W(N{Ar}AlMeC{l{μ-Cl}})(NAr)Me₂ (77), as well as multiple unknown complexes. The different reactivity of Me₂AlCl and

¹ NaBH₄ shows an appreciable solubility in C₆D₆, with a quartet being observed by ¹H NMR spectroscopy at 0.85 ppm (400 MHz, C₆D₆).
Me₂Al with W(NAr)₂Cl₂.DME (40) has been attributed to the greater Lewis acidity of Me₂AlCl.²⁷

Addition of MeAlCl₂ to W(NAr)₂Cl₂.DME (40) and Mo(NAr)₂Cl₂.DME (23) gives the complexes W(N{Ar}AlCl₂{μ-Cl})(NAr)Me₂ (78) and Mo(N{Ar}AlCl₂{μ-Cl})(NAr)Me₂ (79), respectively, which were shown by single crystal X-ray diffraction analysis to be isostructural with 67. Hence, the synthesis of complexes 67, 78, and 79 demonstrates that upon reaction of W(NAr)₂Cl₂.DME (40) with either Me₂Al or MeAlCl₂, the MeₓAlClₓ-x species reacts both as an alkylating agent and as a Lewis acid. A study of 78 and 79 by multinuclear NMR spectroscopy demonstrates that this new class of complex does not undergo facile dissociation. The complexes 67 and 78 are both thermally stable. However, all the M(N{Ar}AIMe(x-i)Cl(3-x){M-Cl})(NAr)Me₂ complexes identified in this study were found to be highly air and moisture sensitive.

It has been shown by comparison of the molecular structures of W(N{Ar}AIMe₂{M-Cl})(NAr)Me₂ (67) and W(N{Ar}AlCl₂{M-Cl})(NAr)Me₂ (78) that the different Lewis acidities of the coordinating Me₂AlCl and AlCl₃ moieties can influence the relative lengths of the N-Al and Cl-W contacts. Substitution of Me₂AlCl (67) for AlCl₃ (78) results in both a lengthening of the W-Cl bond and a shortening of the N-Al contact. In contrast, variation of the group 6 metal from molybdenum (79), to tungsten (78), has no discernable effect upon the bond lengths or angles of the 4-membered chelate.

Upon reaction of the mixed imido complex Mo(NAr)(N'Bu)Cl₂.DME (11) with Me₂Al and MeAlCl₂, the difference in π-donor ability of the two imido ligands directs coordination of the MeₓAlClₓ-x fragments to the NAr ligand exclusively. Hence, reaction of Mo(NAr)(N'Bu)Cl₂.DME (11) with Me₂Al and MeAlCl₂ gives the respective complexes Mo(N{Ar}AIMe₂{μ-Cl})(N'Bu)Me₂ (80) and Mo(N{Ar}AlCl₂{μ-Cl})(N'Bu)Me₂ (81). Notably, the greater trans influence of the strongly π-donor N'Bu ligand results in a lengthening of the Mo-Cl interaction in Mo(N{Ar}AlCl₂{μ-Cl})(N'Bu)Me₂ (80) relative to the complex Mo(N{Ar}AlCl₂{μ-Cl})(N'Bu)Me₂ (81).

The reactivity of W(N{Ar}AIMe₂{μ-Cl})(NAr)Me₂ (67) with ethylene has been investigated. When generated in situ from reaction of W(NAr)₂Cl₂.DME and Me₂Al, complex 67 has been shown to be inert towards reaction with ethylene. This demonstrates that complexes such as 67 are unlikely to react as ethylene dimerization initiators, requiring further modification in order to fulfill this role. This observation is directly relevant to the ethylene dimerization system formed upon reaction of W(NAr)₂Cl₂.DME (40) with Me₂AlCl. It can be concluded that ethylene dimerization co-initiated by Me₂AlCl cannot be attributed to the complex.
W(N{Ar}AIMeCl{μ-Cl})(NAr)Me₂ (77), but is instead initiated by an unknown complex formed from reaction 77 and the Lewis acid Me₂AlCl.

Further investigation into the reactivity of this new class of M(N{Ar}AIMeCl₂,₂{μ-Cl})(NAr)Me₂ complex has revealed that exchange of the coordinating Me₂AlClₓ moieties is possible via intramolecular reactions. Hence, addition of one equivalent of MeAlCl₂ to complex 67 gives W(N{Ar}AIMeCl{μ-Cl})(NAr)Me₂ (77). It has also been found that both W(N{Ar}AIMe₂{μ-Cl})(NAr)Me₂ (67) and Mo(N{Ar}AIMe₂{μ-Cl})(NAr)Me₂ (76) readily react with Lewis bases, resulting in displacement of the coordinating Me₂AlClₓ moiety. For instance, reaction of Mo(N{Ar}AIMe₂{μ-Cl})(NAr)Me₂ (76) with NEt₃ and PMe₃, generates the known complexes Mo(NAr)₂Me₂ (27) and Mo(NAr)₂Me₂PMe₃, respectively. Similarly addition of the Lewis bases THF and Et₃N to W(N{Ar}AIMe₂{μ-Cl})(NAr)Me₂ (67) has been shown to give a base-free "W(NAr)₂Me₂" species. Hence, the reactivity of complex 67 with Lewis bases has been used to synthesise the complex W(NAr)₂Me₂·THF (84).

In the solid state the complex W(NAr)₂Me₂·THF (84) has been shown by single crystal X-ray diffraction to adopt a highly distorted trigonal bipyramidal structure with a bound THF moiety. However, in solution (84) is believed to dissociate, giving free THF and a W(NAr)₂Me₂ species. Attempts to remove the coordinating THF fragment of 84 by drying a sample of 84 in vacuo resulted in degradation of the compound. This demonstrates that in the solid state THF stabilizes the WMe₂ fragment forcing the methyl groups to adopt an axial geometry and hence enhancing its stability, presumably by blocking reductive elimination. In solution the W(NAr)₂Me₂ fragment of 84 readily binds to the strong Lewis base PMe₃ to give W(NAr)₂Me₂·PMe₃, which in contrast to complex 84, is stable in vacuo.

With a vacant coordination site the "W(NAr)₂Me₂" species formed in situ through displacement of the extremely weakly-bound THF molecule, in contrast to the saturated complex W(N{Ar}AIMe₂{μ-Cl})(NAr)Me₂ (67), can readily react with olefins such as propylene and ethylene. Indeed, reaction of W(NAr)₂Me₂·THF (84) with ethylene initiates the selective formation of but-1-ene via dimerization over a 48 hour period. Notably reaction of 84 and ethylene has been found to generate the by-product methane. It has been observed that complex 84 is thermally stable and, upon heating is not susceptible to reductive elimination. Thus, activation of 84 is unlikely to occur via reductive elimination of ethane.²

² Reductive elimination of ethane could feasibly give a W⁴ complex capable of initiating ethylene dimerization via oxidative coupling.
Simultaneous reaction of **84** with equimolar quantities of **C₂D₄** and **C₂H₄** gives “odd” products (such as **C₂H₇D**) and “even” products (such as **C₂H₆**), according to GC-MS analysis. Hence, no detailed mechanistic information into how **84** initiates ethylene dimerization can be made. What has been established, however, is that upon reaction of **84** with ethylene, both W-H or W-D moieties are formed *in situ*, and that migratory insertion of alkenes into W-H bonds does occur in this system. Initial attempts to synthesise relevant discrete hydride complexes have been made. However, reactions of discrete molybdenum and tungsten complexes with both HSiMe₂Bu and NaBH₄ have failed to produce a complex with a hydride moiety.

### 3.13 References

1. US Patents, 3,784,6(31), 30, 29 and (3,903,193), (3,897,512) to The Goodyear Tire and Rubber Company (1974-75), H.R. Menapace, G.S. Benner and N.A. Maly.
13. A search of the Cambridge Structural data base indicates that typical W-Cl bond distances are between 2.30 and 2.55 Å.
A search of the Cambridge Structural Database for all relevant N-Al contacts (the Al was specified as having four contacts) indicates distances of between 1.86 and 2.04 Å are typical for an N-Al dative bond.


Molecular structures containing W-C bond lengths of between 2.05 and 2.36 Å are currently deposited in the Cambridge Structural Database.

36 An authentic sample of THF.B(C₆F₅)₃ was obtained from dissolution of B(C₆F₅)₃ in THF. The 'H NMR spectrum of THF.B(C₆F₅)₃ (CDₑ₆, 400 MHz) was found to consist of two THF resonances at 3.23 and 0.94 ppm.


Chapter 4: Reaction of Tungsten mono(Imido) Chloride Complexes with Methyl Aluminium Reagents

4.0 Introduction

In Chapter 2, Section 2.8, the relative capacities of the reagents EtMgCl and EtAlCl₂ to activate W(NAr)Cl₄·THF (38) for propylene dimerization were assessed. This revealed that the greater ability of EtAlCl₂ to react as a Lewis acid was crucial to the formation of an active propylene dimerization initiator. With a view to further clarifying the mode by which R₃AlCl₃-x reagents interact with imido chloride pre-initiators, attention turned to investigating the reactivity of discrete mono(Imido) chloride complexes and methyl aluminium reagents such as Me₂Al or MeAlCl₂.

Previous investigations into the reactivity of mono(Imido) complexes and Group 13 Lewis acids have been reported in the literature. For example, Osborn et al. have studied the reactivity of the complexes W(NR)(X)(CH₂Bu)₃ (X = F, Cl, Br), with GaCl₃, AlCl₃ and AlBr₃.¹ It was found that addition of AlCl₃ to a solution of W(NMe)(Cl)(CH₂Bu)₃ (90) gave the single 1:1 adduct 91, which was characterized using ¹⁴N NMR spectroscopy (Scheme 4.1).

Scheme 4.1 Reaction of W(NMe)(Cl)(CH₂Bu)₃ (90) with AlCl₃ affording adduct 91

Comparison of the ¹⁴N NMR spectra of the parent complex 90 and the adduct 91, shows that an increase in the magnitude of the ¹JWN coupling is observed following AlCl₃ coordination (83 to 105 Hz). This strongly suggests that AlCl₃ binding to complex 90 actually decreases the W-N bond distance, presumably as a consequence of enhanced lone pair donation from the N-atom to the tungsten core. Significantly, a decrease in the length of the W-N contact is inconsistent with AlCl₃ binding to the imido ligand of 90 (as observed for complex 67 in Chapter 3, Section 3.1.1), since this would reduce the extent of π-donation from the nitrogen to the tungsten atom, which in turn would lengthen the W-N bond. Furthermore, the AlCl₃ adduct of complex 91 presented a sharp ¹⁴N resonance with a line width of 11 Hz,
which is incompatible with a quadrupolar $^{27}\text{Al}$ nuclei lying adjacent to a $^{14}\text{N}$ atom. Instead, coordination of the Lewis acid is proposed to occur preferentially to the W-Cl ligand, giving exclusively W(NR)(CH$_2$Bu)$_3$($\mu_2$-ClAlCl$_4$) (91) (Scheme 4.1). A similar bonding mode is observed in the molecular structure of the carbene complex WBr(CH(CH$_2$)$_4$)(OCH$_2$C(CH$_3$)$_3$)$_2$( $\mu_2$-GaBr$_4$) (92) in which a GaBr$_3$ fragment bridges between the tungsten and bromine ligands (Figure 4.1).

**Figure 4.1 Molecular structure adopted by complex 92**

More recently, Tobisch examined the interaction of Me$_2$AlCl with the complex W(NPh)Cl$_2$((CH$_2$)$_4$) (93) using DFT.$^3$ He concluded that coordination of the Lewis acid (Me$_2$AlCl) occurs preferentially via a bridging chloride ligand giving the adduct W(NPh)(Cl)((CH$_2$)$_4$)( $\mu_2$-Cl$_2$AlMe$_2$) (Figure 4.2, complex 94), which has a low $\Delta G$ of association (3.4 kcal/mol). In contrast, an unfavourably high $\Delta G$ of association of 17.4 kcal/mol was found to result from Me$_2$AlCl binding to the mono(imido) ligand of complex 93 giving the adduct W(N{Ph}AlMe$_2$($\mu$-Cl))(Cl)((CH$_2$)$_4$) (Figure 4.2, complex 95). Formation of adduct 95 is postulated to be disfavoured as the lone pair of the imido N-atom is believed to be preferentially donated to the W$^\text{VI}$ core, and is thus less available for donation to a MeAlCl$_2$ fragment.

**Figure 4.2 Comparison of the structure of adducts 94 and 95**

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Significantly, Tobisch also showed that coordination of Me₂AlCl to W(NPh)Cl₂((CH₂)₄) through a bridging chloride ligand (as in structure 94, Figure 4.2) considerably reduced the energetic barrier associated with W(NPh)Cl₂((CH₂)₄) initiating ethylene dimerization via a metallacycle mechanism. In the metallacycle mechanism examined, two molecules of ethylene oxidatively couple to a W⁷⁺ atom giving a W⁷⁺ metallacycle, which decomposes first by β-hydride and then by reductive elimination to simultaneously give but-1-ene and a regenerated W⁷⁺ intermediate. Coordination of Me₂AlCl to 93 via a bridging chloride ligand, as in 94 (Figure 4.2), was found to lower the energetic penalty associated with reductive elimination of but-1-ene, without affecting the thermodynamics of the rate determining β-hydride elimination step.¹ Hence, the information from Tobisch’s theoretical study strongly suggests that the capacity of Me₂AlCl₃-x to react as a Lewis acid by accepting a chloride lone pair is important for the activation of mono(imido) pre-initiators. Similar conclusions have been made by Olivier et al. who found that reaction of the Lewis acid AlCl₃ with W(NPh)(Cl)₂(PMe₃)₃ (34) generates, in situ, an active ethylene dimerization initiator that is postulated to be the ionic complex [W(NPh)(Cl)((CH₂)₄(PMe₃)₂][AlCl₄].⁴

Together, the investigations made by both Olivier and Tobisch indicate that mono(imido) halide pre-catalysts are activated for ethylene dimerization via the reaction of R₆AlCl₃-x species as Lewis acids. To further clarify the mode by which mono(imido) halide complexes are activated by R₆AlCl₃-x co-initiators, a series of model reactions using Me₆AlCl₃-x reagents have been investigated in this thesis. Thus, in this Chapter the capacity of Me₆AlCl₃-x groups to coordinate to and/or react with mono(imido) halide complexes will be discussed.

4.1 Reaction of W(NR)Cl₄·THF (R = Ph or Ar) with Me₆Al in C₆D₆

A number of model reactivity studies using Me₆AlCl₃-x reagents were undertaken and analyzed using NMR spectroscopy. In order to evaluate the reactivity of mono(imido) tetrahalide complexes with Me₆Al, a C₆D₆ solution of W(NPh)Cl₄·THF (32) was treated with six equivalents of Me₆Al (Scheme 4.2). This was followed by immediate analysis using ¹H NMR spectroscopy, which identified complete loss of the starting material 32 and the clean formation of W(NPh)(Cl)Me₆ (96) (Figure 4.3). Identical results are obtained from addition of Me₆Al to complex 32 in CD₂Cl₂.

¹ See Chapter 1, Section 1.1 for in-depth discussion of the metallacycle mechanism
Scheme 4.2 Reaction of $W(N\text{Ph})\text{Cl}_4\cdot\text{THF}$ (32) with $\text{Me}_3\text{Al}$

$$W(N\text{Ph})\text{Cl}_4\cdot\text{THF} \quad \xrightarrow{\text{Me}_3\text{Al}} \quad W(N\text{Ph})(\text{Cl})\text{Me}_3$$

Figure 4.3 $^1\text{H}$ NMR (200 MHz, C$_6$D$_6$) spectrum of the reaction mixture following treatment of $W(N\text{Ph})\text{Cl}_4\cdot\text{THF}$ (32) with $\text{Me}_3\text{Al}$

The $^1\text{H}$ NMR resonances of the two THF $\text{CH}_2$ moieties observed at 3.31 and 0.91 ppm (Figure 4.3) can be attributed to an unknown THF/$\text{Me}_3\text{Al}$ adduct. Although it has not been possible to ascertain the actual structure of the THF adduct despite repeated attempts, the most plausible complex is $\text{Me}_3\text{Al}\cdot\text{THF}$, which has been previously characterized by X-ray diffraction.\(^5\)

The most notable spectral feature, resulting from reaction of $W(N\text{Ph})\text{Cl}_4\cdot\text{THF}$ (32) with $\text{Me}_3\text{Al}$, is the singlet at 1.27 ppm (integrated to 9H). This resonance has tungsten satellites ($^2J_{\text{WH}} = 7.2$ Hz) and so can readily be assigned to a W-Me moiety ($^2J_{\text{WH}}$ values of between 4 to 11 Hz are typical for $\alpha$-H atoms of W-alkyl complexes) (Figure 4.3).\(^6\) Moreover, a comparison of the $^1\text{H}$ and $^{13}\text{C}$ chemical shifts for the new product confirms it to be the known complex $W(N\text{Ph})(\text{Cl})\text{Me}_3$ (96), previously reported by Schrock et al.\(^7\) It is evident that upon reaction of complex 32 with $\text{Me}_3\text{Al}$ no binding of $\text{Me}_3\text{AlCl}_{3-x}$ fragments generated in situ to the mono(imido) ligand occurs;
with the Me₃Al in this reaction acting only as an alkylating agent. It was also found that heating (1 h, 60°C) a mixture of W(NPh)(Cl)Me₃ (96) and Me₃Al in C₆D₆ did not induce any additional reaction of 96 (Scheme 4.3).

Scheme 4.3 Attempted reaction of 96 with Me₃Al at 60°C

\[
\begin{align*}
\text{W(NPh)(Cl)Me₃} & \xrightarrow{\text{Me₃Al, C₆D₆, 60°C, 1 h}} \text{No reaction} \\
(96) & \\
\end{align*}
\]

Using closely related procedures to that employed for the reaction of W(NPh)Cl₄·THF (32) and Me₃Al, it was found that the complexes W(NAr)Cl₄ (31) and W(NAr)Cl₄·THF (38) when treated with Me₃Al in C₆D₆ both gave W(NAr)(Cl)Me₃ (97) with full conversion.¹

4.2 Synthesis and Characterization of W(NR)(Cl)Me₃ (96)

Schrock et al. have previously reported the synthesis of 96, via reaction of the salt [Et₄N][W(NPh)Cl₅] with Me₂Zn. However, in work conducted for this thesis it has been found convenient to synthesise 96 directly from the reaction of W(NPh)Cl₄·THF (32) and Me₃Al (Scheme 4.4). Similarly, W(NAr)(Cl)Me₃ (97) can be readily synthesised on a preparatory scale from reaction of Me₃Al with either W(NAr)Cl₄ (31) or W(NAr)Cl₄·THF (38) also in CH₂Cl₂. Recrystalization of complex 96 from diethyl ether (~15°C) gave light yellow crystals of sufficient quality for single crystal X-ray diffraction analysis (Figure 4.4 and Table 1.1).

¹ In contrast, reaction of the related mono(imido) complex Ta(NAr)Cl₃·(TMEDA) with Me₃Al in C₆D₆, failed to produce discrete complexes, with ¹H NMR spectroscopic analysis indicating that no alkylation of the Ta(NAr)Cl₃ core occurs.
Scheme 4.4 Alternative routes for the synthesis of $W$(NPh)(Cl)Me$_3$ (96)

$$[\text{Et}_4\text{N}][W$(NPh$)\text{Cl}_5]$$

Et$_4$NCl, CH$_2$Cl$_2$

(100%)

Me$_2$Zn, CH$_2$Cl$_2$

(77%)

W(NPh)Cl$_4$.THF

$\xrightarrow{\text{Me}_3\text{Al, CH}_2\text{Cl}_2}$

(55%)

W(NPh)(Cl)Me$_3$

Figure 4.4 Solid state structure of W(NPh)(Cl)Me$_3$ (96) with the thermal ellipsoids set at the 50% level (rotational disorder associated with the phenyl ring is shown).

Table 4.1 Selected bond distances (\AA) and bond angles (°) for W(NPh)(Cl)Me$_3$ (96)

<table>
<thead>
<tr>
<th></th>
<th>Bond Distance (\AA)</th>
<th>Bond Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-N</td>
<td>1.738(3)</td>
<td>C1-W-C2 122.90(15)</td>
</tr>
<tr>
<td>W-C1</td>
<td>2.101(4)</td>
<td>N-W-C1 92.96(8)</td>
</tr>
<tr>
<td>W-C2</td>
<td>2.106(3)</td>
<td>Cl-W-C2 87.99(12)</td>
</tr>
<tr>
<td>W-Cl</td>
<td>2.4198(9)</td>
<td>N-W-Cl 176.87(10)</td>
</tr>
<tr>
<td>N-C3</td>
<td>1.396(4)</td>
<td>N-W-Cl 176.87(10)</td>
</tr>
</tbody>
</table>

A notable feature of the molecular structure of 96 is the disorder associated with the imido phenyl ring substituent. This is manifested as two possible orientations of this ring relative to a Cl-N-W mirror plane, giving two inequivalent rotamers. Despite this disorder, it is clear that complex 96 adopts pseudo trigonal bipyramidal geometry about the W atom, with the electronegative Cl atom lying preferentially trans to the
strongly π-donating imido ligand. Indeed, the high trans influence of the phenyl imido ligand results in a lengthening of the W-Cl bond of 96 (2.4198(9) Å), relative to the W-Cl contacts of the related pseudo octahedral complex W(NC₆H₄(p-Me))Cl₄.THF (98) (2.338(4) Å), in which the imido and chloride ligands are cis (Figure 4.5).

Figure 4.5 Molecular structure adopted by W(NC₆H₄(p-Me))Cl₄.THF (98) in the solid state

![Molecular structure](image)

Another significant feature of complex 96 is the W-N-C₃ bond angle, which at 174.9(4)° is close to the ideal 180° angle associated with an LX₂ donor imido ligand. Indeed, the short W-N bond distance of 96 at 1.738(3) Å is typical of a 4-electron donor imido ligand (neutral formalism) bound to tungsten. The observation that the mono(imido) ligand of W(NPh)(Cl)Me₃ (96) is a 4-electron donor, can be used to rationalize the formation of Lewis acid-free complex 96 from reaction of W(NPh)Cl₄.THF (32) with Me₃Al (see Section 4.3). It can be reasoned that the formation of 96 via reaction of 32 and Me₃Al must also generate MeₓAlCl₃₋ₓ fragments in situ. These MeₓAlCl₃₋ₓ fragments are unable to coordinate to the imido moiety of complex 96 as in the bis(imido) M(N{Ar}AIMe₂Clₓ{µ-Cl})(NAr)Me₂ complexes investigated in Chapter 3, since the phenyl imido N-lone pair of 96 is preferentially donated to the electropositive W⁺ centre.

4.3 Reaction of W(NPh)(Cl)Me₃ (96) with LiMe
As is evident from the molecular structure of complex 96, the W-Cl bond is seemingly weakened by the strong trans influence of the phenyl imido moiety; consequently it would be expected that the chloride ligand of 96 would be relatively labile. With a view to assessing if the tungsten chloride ligand of complex 96 can indeed readily be substituted, attention turned to the reactivity of W(NPh)(Cl)Me₃ (96) with alkylating...
agents. In this regard, Schrock et al. have reacted W(NPh)(Cl)Me₃ (96) with LiMe, reporting that this gives the complex W(NPh)Me₄ (99), although no characterization of 99 was made due to the complex's reported instability. In work conducted during the preparation of this thesis, it has been observed that even after heating 96 in the presence of excess Me₅Al, no methylation of the W-Cl moiety of 96 occurs, indicating that formation of complex 99 is unfavourable presumably as a result of locating a strongly trans-influencing methyl group trans to the imido moiety.

However, to further clarify if alkylation of 96 is indeed viable, W(NPh)(Cl)Me₃ (96) was reacted with LiMe in C₆D₆. This reaction was observed to result in a shift of the W-Me ¹H NMR resonance (1.27 to 1.34 ppm), with integration of the ¹H NMR spectrum confirming the formation of W(NPh)Me₄ (99) in situ (Scheme 4.5). Notably, only one broad ¹H NMR resonance was presented for 99, which is suggestive of the fact that the two W-(CH₃) environments of 99 resonate with similar frequencies, generating a single broad peak (or overlapping resonances). Alternatively complex 99 may have a fluxional structure; this again would be consistent with the broad nature of the resonance observed.

In solution, degradation of W(NPh)Me₄ (99) was found to occur over a 16 h period, generating an insoluble material that could not be characterized using NMR analysis. Of note, is that decomposition of 99 did not produce ethane, demonstrating that the decay of 99 does not result from the reductive elimination of two cis W-Me ligands.

Scheme 4.5 Reaction of W(NPh)(Cl)Me₃ (96) with LiMe

4.3.1 Reaction of W(NPh)(Cl)Me₃ (96) with Me₃SiOSO₂CF₃

The strong trans influence exerted by the imido ligand in complex 96 should also correspond to the trans chloride atom being particularly susceptible to abstraction by a Lewis acid. Furthermore, reaction of 96 with Lewis acids is of particular interest

ⁿ The Reaction of W(NPh)(Cl)Me₃ (96) with LiMe, generating 99 was carried out in a sealed NMR tube.
here, as this could generate a cationic tungsten core with a vacant coordination site capable of accommodating alkene coordination. Hence, in the first instance, attention turned to investigating the reactivity of 96 with strong Lewis acids such as Me₃SiOSO₂CF₃.

Addition of Me₃SiOSO₂CF₃ to a C₆D₆ solution of W(NPh)(Cl)Me₃ (96) led to the formation of the complex W(NPh)Me₃(OSO₂(CF₃)) (100) and the by-product CISO₃Me in the expected 1:1 molar ratio (verified by ¹H NMR) over a 4 h period. Complex 100 has been characterized by NMR spectroscopy and displays a single tungsten methyl resonance, indicating that 100 adopts the same pseudo trigonal bipyramidal geometry as the parent complex W(NPh)(Cl)Me₃ (96). It is presumed that the triflate moiety of 100 will coordinate to the tungsten core, as triflate counterions are known to be moderately coordinating. Indeed, numerous complexes containing M-OTf bonds have been isolated and characterized. Thus, the conversion of complex (96) to W(NPh)Me₃(OSO₂(CF₃)) (100) reveals that the chloride ligand of 96 can readily be abstracted by an appropriate Lewis acid (Scheme 4.6). This conclusion is of consequence when evaluating the solution structure of W(NR)(Cl)Me₃.AlCl₃ (R = Ph or Ar) adducts, which will be discussed later in Section 4.7.

**Scheme 4.6 Reaction of W(NPh)(Cl)Me₃ (96) with Me₃SiOSO₂CF₃**

![Scheme 4.6](image)

**4.3.2 Reaction of W(NPh)Me₃(OSO₂(CF₃)) (100) with Ethylene**

A rationalization of the impact and effect of Lewis acid coordination upon the reactivity of mono(imido) pre-catalysts with alkenes is of general interest. In the context of this work, the way in which such coordination can modify a complexes reaction with alkenes (such as ethylene) is of particular significance. Thus, attention was turned to investigating the reactivity of 100 with ethylene.

Ethylene was added to a C₆D₆ solution of W(NPh)Me₃(OSO₂(CF₃)) (100) (Scheme 4.7). Neither reaction of complex 100 nor the formation of higher olefins...
were observed to occur by \(^1\)H NMR spectroscopy. The inability of \(\text{100}\) to interact with ethylene is presumed to be attributed to the strongly coordinating triflate moiety, which blocks ethylene coordination to the \(W^\text{III}\) centre.

**Scheme 4.7** Reaction of \(W(\text{NPh})\text{Me}_3(\text{OSO}_2\text{(CF}_3)\rangle\) (\(\text{100}\)) and ethylene

[Diagram of Scheme 4.7]

4.4 Reaction of \(W(\text{NR})\text{Cl} \text{Me}_3\) (\(R = \text{Ph, Ar}\)) with \([\text{Li(OEt)}_2][\text{B(C}_6\text{F}_5)_4]\) and \([\text{Na}][\text{B}(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_4]\)

Olivier and co-workers have proposed that activation of the ethylene dimerization pre-catalyst \(W(\text{NPh})\text{Cl}_2(\text{PMe}_3)_3\) (\(\text{34}\)) by the Lewis acid \(\text{AlCl}_3\) generates, *in situ*, the active ionic initiator complex \([W(\text{NPh})\text{Cl}(\text{CH}_2)_4(\text{PMe}_3)_2][\text{AlCl}_4]\) (Scheme 4.8).\(^4\)

Consequently, abstraction of tungsten chloride ligands by a Lewis acid to give a charged complex may be a viable general route to initiator formation. To evaluate if mono(imido) complexes can indeed react with Lewis acids to give stable salts, the complexes \(W(\text{NPh})\text{Cl}\text{Me}_3\) (\(\text{96}\)) and \(W(\text{NAr})\text{Cl}\text{Me}_3\) (\(\text{97}\)) have been reacted with both \([\text{Li(OEt)}_2][\text{B(C}_6\text{F}_5)_4]\) and \([\text{Na}][\text{B}(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_4]\) These Lewis acids were selected because the corresponding anions \([\text{B}(\text{C}_6\text{F}_5)_4]^\text{−}\) and \([\text{B}(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_4]^\text{−}\) are known to be weakly-coordinating.\(^14\)

**Scheme 4.8** Olivier’s proposed route of \(W(\text{NPh})\text{Cl}_2(\text{PMe}_3)_3\) (\(\text{34}\)) activation.

\[
\text{W(Ph)}\text{Cl}_2(\text{PMe}_3)_3 + \text{AlCl}_3, \text{ethylene} \rightarrow [\text{W(Ph)}\text{Cl}(\text{C}_2\text{H}_4)]\text{[AlCl}_4] + (\text{Me}_3\text{P})_2(\text{AlCl}_3)_y
\]

In the first instance, an MeCN solution of \(W(\text{NPh})\text{Cl}\text{Me}_3\) (\(\text{96}\)) was treated with an equimolar quantity of \([\text{Na}][\text{B}(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_4]\). This resulted in the rapid formation of a yellow precipitate. Disappointingly, characterization of this material by NMR spectroscopy was hampered by its lack of solubility even in polar solvents such
as CD₂Cl₂ or CD₃CN. Consequently, attention turned to the reaction of the more soluble complex W(NAr)(Cl)Me₃ (97), which can readily be synthesised via reaction of W(NAr)Cl₄·THF (38) and Me₃Al (Section 4.2).

Using a similar procedure to that described above, a CD₂Cl₂ solution of W(NAr)Me₃Cl (97) was treated with [Na][B(3,5-(CF₃)₂C₆H₃)₄], which resulted in the immediate formation of a bright purple solution. Monitoring the reaction by ¹H NMR spectroscopy revealed the slow conversion of 97 to what is believed to be [W(NAr)Me₃][B(3,5-(CF₃)₂C₆H₃)₄] (101); after a period of 5 h 101 was present in approximately 30% (by integration) as the only new product. It was found that complex 101 presented a new ¹H NMR singlet resonance at 1.86 ppm (W-CH₃) and a doublet at 1.24 ppm (CH₃, 'Pr) in a 9:12 ratio by integration. All attempts to induce further conversion of 97 to 101 by heating (2 h, 60 °C) failed.

In order to try and obtain an ionic mono(imido) complex in higher yield, a different salt of a weakly-coordinating anion was explored. Thus, W(NAr)(Cl)Me₃ (97) was dissolved in CeD₅Cl and mixed with [Li(OEt)₂][B(C₆F₅)₄]. Here, no reaction of 97 was observed to occur at ambient temperature. However, subsequent heating of the same sample (60°C, 16 h) was found to induce the formation of a new product, formulated as [W(NAr)Me₃][B(C₆F₅)₄] (102), with approximately 30% conversion by integration (Scheme 4.9), as verified by ¹H NMR analysis (Figure 4.6). Attempts to induce further conversion of 97 to 102 by additional heating (60°C, 48 h) resulted in a decomposition of both 97 and 102.

**Scheme 4.9** Reaction of W(NAr)(Cl)Me₃ (97) with [Li(OEt)₂][B(C₆F₅)₄]
Figure 4.6 $^1$H NMR (C$_6$D$_5$Cl, 400 MHz) spectrum obtained in situ from reaction of W(NAr)(Cl)Me$_3$ (97) and [Li(OEt)$_2$][B(C$_6$F$_5$)$_4$], (aromatic region omitted)

In the $^1$H NMR spectrum of the crude reaction mixture (Figure 4.6), a somewhat broadened resonance was observed at 1.23 ppm ($\beta V_{1/2}$ = 6 Hz), which corresponds to the W-CH$_3$ signal of the precursor complex W(NAr)(Cl)Me$_3$ (97), with a second less intense resonance at 1.04 ppm being attributable to the W-CH$_3$ unit of the product [W(NAr)Me$_3$][B(C$_6$F$_5$)$_4$] (102). The CH$_3$ $^3$Pr groups of the complexes 97 and 102 resonate with similar chemical shifts, giving two overlapping doublets at 0.99 and 0.98 ppm.

Although investigations into the reactivity of the phenyl mono(imido) complex W(NPh)(Cl)Me$_3$ (96) with [Na][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] were hampered by the insolubility of the resulting product complexes, it was found that C$_6$D$_5$Cl was a sufficiently polar to permit examination of the reaction of 96 with [Na][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]. Addition of [Na][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] to a C$_6$D$_5$Cl solution of W(NPh)(Cl)Me$_3$ (96) resulted in the formation of a new, $^1$H NMR, W-CH$_3$ resonance at 1.16 ppm (c.f. the W-Me resonance of 96 is detected at 1.28 ppm). This observation is consistent with the in situ formation of [W(NPh)Me$_3$][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] (103) with approximately 40% conversion (by integration). The structure of 103 can be assigned as W(NPh)Me$_3$(OSO$_2$(CF$_3$)) (100) as it also displays a W-CH$_3$ resonance at 1.16 ppm.
(albeit in C₆D₆) which indicates that a similar [W(NPh)Me₃] core is present in each case.

Complex 103 was observed (over a 2 h period) to convert to an unknown product, with two new resonances being observed at 1.70 and 1.20 ppm in an approximately 1:2 ratio. Of note, is the influence of the imido subsistent, with W(NPh)(Cl)Me₃ (96) reacting with [Na][B(3,5-(CF₃)₂C₆H₃)₄] at room temperature in contrast to the analogous W(NAr)(Cl)Me₃ (97) system, which required heating (60°C, 16 h) to induce any formation of [W(NAr)Me₃][B(3,5-(CF₃)₂C₆H₃)₄] (101).

While reaction of W(NAr)(Cl)Me₃ (97) with [Li(OEt)₂][B(C₆F₅)₄] and [Na][B(3,5-(CF₃)₂C₆H₃)₄] did generate in situ the complexes [W(NAr)Me₃][B(C₆F₅)₄] (102) and [W(NAr)Me₃][B(3,5-(CF₃)₂C₆H₃)₄] (103), respectively, neither 102 nor 103 were obtained in full conversion despite a lengthy period of heating. It remains unclear as to why incomplete reaction of 97 with either [Li(OEt)₂][B(C₆F₅)₄] or [Na][B(3,5-(CF₃)₂C₆H₃)₄] was observed. However, one possibility is that the reactions between the W-Cl bond of 97 and the Lewis acid reagents are slow. This is potentially further complicated by the poor solubility of these lithium and sodium salts in the reaction solvents employed (i.e. C₆D₆, CD₂Cl₂ and C₆D₅Cl).

Despite the lack of complete conversion, the limited formation of [W(NAr)Me₃][B(C₆F₅)₄] (102) and [W(NAr)Me₃][B(3,5-(CF₃)₂C₆H₃)₄] (101) from W(NAr)(Cl)Me₃ (97) is significant as this demonstrates that abstraction of a tungsten chloride by a Lewis acid to give a stable ionic complex is indeed a viable reaction pathway. This supports Olivier's hypothesis that the active initiator complex in her W(NPh)(Cl)₂(PMe₃)₃/AICl₃ ethylene dimerization system is an ionic complex, which results from abstraction of a tungsten chloride ligand by the Lewis acid AlCl₃, generating a weakly-coordinating AlCl₄⁻ anion.

4.5 Investigation of the Reactivity of W(NR)(Cl)Me₃ (R = Ph or Ar) with the Lewis Acid MeAlCl₂

As illustrated in the preceding section, the reaction of compounds such as [Li(OEt)₂][B(C₆F₅)₄] with the complexes 96 and 97 has shown that the W-Cl bond of 96 or 97 can be cleaved via abstraction of the chloride atom by a Lewis acid. This indicates that a similar reaction pathway, resulting from reaction of RₙAlCl₃₋ₓ as a Lewis acid, is viable and may be significant in the activation of mono(imido) halide complexes by RₙAlCl₃₋ₓ co-initiators (see Chapter 2.2, Table 2.3). To evaluate if abstraction of a tungsten chloride ligand by RₙAlCl₃₋ₓ species is indeed feasible, attention turned to investigating a series of model reactions between MeAlCl₂ and the complexes W(NR)(Cl)Me₃ (R = Ph or Ar).
To this end, the complexes W(NPh)(Cl)Me₃ (96) and W(NAr)(Cl)Me₃ (97) were treated with five equivalents of MeAlCl₂ in CH₂Cl₂ solution. After a period of 20 mins, all volatile components of the reaction solutions were removed in vacuo, giving residues that were analysed using ¹H NMR spectroscopy (CD₂Cl₂ or C₆D₆). Both the residues from the reactions of 96 and 97 with MeAlCl₂ gave a single W-CH₃ resonance by ¹H NMR spectroscopy (integrated as 9 H) at a different chemical shift to that presented by the starting complex (Table 4.2A and 4.2B). The observed change in the ¹H NMR spectral data is suggestive that the coordination spheres of both 96 and 97 have been perturbed following the addition of MeAlCl₂.

**Table 4.2A** Comparison of selected ¹H NMR spectroscopic data for W(NPh)(Cl)Me₃ (96) and W(NAr)(Cl)Me₃ (97) in C₆D₆ and CD₂Cl₂

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Complex</th>
<th>δ ¹H W(CH₃)₃ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆D₆</td>
<td>96</td>
<td>1.28</td>
</tr>
<tr>
<td>CD₂Cl₂</td>
<td>96</td>
<td>1.36</td>
</tr>
<tr>
<td>C₆D₆</td>
<td>97</td>
<td>1.40</td>
</tr>
<tr>
<td>CD₂Cl₂</td>
<td>97</td>
<td>1.43</td>
</tr>
</tbody>
</table>

**Table 4.2B** Products from the reaction of MeAlCl₂ with 96 and 97

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Reaction</th>
<th>δ ¹H W(CH₃)₃ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆D₆</td>
<td>96 + 5MeAlCl₂</td>
<td>1.35</td>
</tr>
<tr>
<td>CD₂Cl₂</td>
<td>96 + 5MeAlCl₂</td>
<td>1.89</td>
</tr>
<tr>
<td>C₆D₆</td>
<td>97 + 5MeAlCl₂</td>
<td>1.47</td>
</tr>
<tr>
<td>CD₂Cl₂</td>
<td>97 + 5MeAlCl₂</td>
<td>1.96</td>
</tr>
</tbody>
</table>

Significantly, no resonances for an Al-CH₃ moiety were observed in either the ¹H or ¹³C NMR spectra presented by the residues resulting from reaction of 96 and 97 with MeAlCl₂. One possible explanation as to why no such resonances were detected, is that an AlCl₃ fragment coordinates to the W(NR)(Cl)Me₃ (R = Ph or Ar) framework to give the adducts of empirical formula W(NPh)(Cl)Me₃.AICl₃ (104) and W(NAr)(Cl)Me₃.AICl₃ (105) (Scheme 4.10).

**Scheme 4.10** Possible Synthesis of W(NR)(Cl)Me₃.AICl₃ adducts

\[
\begin{align*}
\text{W(NR)(Cl)Me₃} & \quad \xrightarrow{\text{CH₂Cl₂, 5MeAlCl₂}} \quad \text{W(NR)(Cl)Me₃.AICl₃} \\
\text{R = Ph (96)} & \quad \text{R = Ph (104)} \\
\text{Ar (97)} & \quad \text{Ar (105)}
\end{align*}
\]
Notably, Osborn et al. determined that addition of Lewis acids (such as AlCl₃) to W(NMe)(Cl)(CH₂Bu)₃ (90) resulted in coordination of the AlCl₃ fragment to the tungsten halide giving W(NMe)(CH₂Bu)₃(μ²-AlCl₄) (91) (Scheme 4.1). These results strongly suggest that reaction of W(NR)(Cl)Me₃ (R = Ph or Ar) with MeAlCl₂ could also lead to an MeₓAlCl₃₋ₓ fragment interacting with the tungsten chloride ligand. Less clear is the mode of MeₓAlCl₃₋ₓ association; with the aluminium-based Lewis acid fragment capable of interacting with the W(NR)(Cl)Me₃ (R = Ph or Ar) framework as a coordinating or non-coordinating Lewis acid (Figure 4.7).

**Figure 4.7** Possible bonding modes of AlCl₃ in the adduct [W(NPh)(Cl)Me₃-AlCl₃] (104)

![Diagram showing possible bonding modes of AlCl₃ in the adduct [W(NPh)(Cl)Me₃-AlCl₃].]

In order to explore the structures of the adducts 104 and 105, ²⁷Al NMR spectroscopy was employed (Figure 4.8). This technique is uniquely suited to analysis of the solution structures of 104 (and 105), since δ ²⁷Al has been shown to be extremely sensitive to the coordination number of the aluminium centre in a given complex.¹⁵
The $^{27}\text{Al}$ NMR spectrum (CD$_2$Cl$_2$) of the proposed adduct [W(NPh)(Cl)Me$_3$.AlCl$_3$] (104) presents three broad resonances at $\delta$ 102, 99, and 93 ppm (Figure 4.8). The same three resonances were detected upon analysis of the proposed adduct [W(NAr)(Cl)Me$_3$.AlCl$_3$] (105), although for 105 the resonance at 102 ppm was less intense. Assignment of the resonance at 102 ppm to an $\text{AlCl}_4^-$ ion can be made. This assignment is possible as a comparable $^{27}\text{Al}$ NMR spectrum of an authentic sample of the ionic complex $[\text{AlCl}_4][\text{P(N'Pr}_2)_2]$ (107), was found to comprise a single sharp resonance at 102 ppm.

Assignment can also be made to the resonances detected at 99 and 93 ppm in the $^{27}\text{Al}$ NMR of both 104 and 105. It has previously been reported that AlCl$_3$ presents two $^{27}\text{Al}$ NMR resonances at $\delta$ 99 and 91 ppm in C$_6$D$_6$. Although it is unclear as to why AlCl$_3$ presents two resonances, it is apparent from the similarity in the $^{27}\text{Al}$ NMR chemical shifts that an AlCl$_3$ moiety is formed from treatment of both W(NPh)(Cl)Me$_3$ (96) and W(NAr)(Cl)Me$_3$ (97) with MeAlCl$_2$. One potential explanation

---

Figure 4.8 $^{27}\text{Al}$ NMR (CD$_2$Cl$_2$, 130 MHz) spectrum of [W(NPh)(Cl)Me$_3$.AlCl$_3$] (104)
as to the origin of the AlCl₃ fragment is given in Scheme 4.11. It is proposed that 96 reacts initially with MeAlCl₂ to form an adduct such as 106. Then, subsequent reaction of intermediate 106 with the excess MeAlCl₂ present in the reaction solution, initiates a methyl exchange process, which eliminates Me₂AlCl and gives the product complex 104.

**Scheme 4.11** Proposed mechanism for the formation of the AlCl₃ adduct 104 from reaction of W(NPh)(Cl)Me₃ (96) with MeAlCl₂

![Scheme 4.11](image)

The change in the chemical shift of the W-CH₃ resonances, observed by ²H NMR spectroscopy, following reaction of MeAlCl₂ with W(NR)(Cl)Me₃ (R = Ph or Ar) (Tables 4.2), indicate that the ensuing AlCl₃ moiety binds to the W(NR)(Cl)Me₃ (R = Ar or Ph) fragment. This conclusion is corroborated by the theoretical work of Tobisch, which showed that coordination of a Me₅AlCl₃ₓ fragment to the tungsten chloride ligand of a related mono(imido) complex is highly favourable. The notion that AlCl₃ is coordinating to a W(NR)(Cl)Me₃ core has also been investigated here experimentally. It was found that addition of THF to a solution of W(NPh)(Cl)Me₃·AlCl₃ (104) resulted in the formation of free W(NPh)(Cl)Me₃ (96) and an unknown (AlCl₃)ₓ(THF)ₓ adduct. However, the set of ¹H NMR spectra obtained, before and after THF addition, clearly showed that displacement of the bound AlCl₃ fragment of 104 by THF resulted in a shift in the W-CH₃ resonance from 1.35 to 1.28 ppm (the ¹H NMR chemical shift associated with free 96). This indicates that prior to THF addition, AlCl₃ was indeed interacting with a tungsten chloride ligand.

The formation of an AlCl₄⁻ anion upon reaction of 96 and 97 with MeAlCl₂ is also of significance. This is suggestive of an AlCl₃ fragment abstracting a W-Cl...
chloride ligand to give a "non-coordinating" AlCl₄⁻ counter ion. Notably the AlCl₄⁻ resonances detected upon analysis of 104 and 105 using ²⁷Al NMR were somewhat broader than the related signal presented by the ionic complex [AlCl₄][P(N¹Pr₂)₂] (107) (Figure 4.8). Similarly the W-CH₃ resonances of 104 and 105 observed by ¹H NMR were broadened to the extent that no ²J_WH satellites were observed in either case. One possible explanation for the broadening of both the ²⁷Al and ¹H NMR spectra is that an exchange process is occurring in solution between a 1:1 adduct and a charge separated salt. Notably, Osborn and co-workers determined that W(NMe)(CH₂Bu)₃Cl (90) forms a 1:1 adduct with a range of Lewis acids, including AlCl₃. As such, it is plausible that both W(NPh)(Cl)Me₃ (96) and W(NAr)(Cl)Me₃ (97) similarly form a 1:1 adduct with AlCl₃ in solution. The dissociation of these AlCl₃ adducts could then generate the observed AlCl₄⁻ anion in situ (Scheme 4.12).

Scheme 4.12 Proposed equilibrium between the limiting structures of the complexes [W(NR)(Cl)Me₃AlCl₃] (R = Ph or Ar)

With a view to assessing whether complexes 104 and 105 were in fact labile, both 104 and 105 were analysed by ¹H and ²⁷Al NMR spectroscopy at -80°C (CD₂Cl₂). At -80°C the ¹H NMR spectra for both 104 and 105 were consistent with those obtained at ambient temperature (25°C), although a broadening of the W-CH₃ resonance was observed in both cases (B_V1/2 = ~25 Hz). The ²⁷Al NMR spectra of both 104 and 105 at -80°C consisted of a single broad resonance centred at 95 ppm. As such, the low temperature ²⁷Al NMR spectra do not provide nor disprove the notion that either 104 or 105 dissociate in solution to give an AlCl₄⁻ counter ion.

---

viii The complete abstraction of the tungsten chloride ligand of W(NPh)Me₃Cl (96) by a strong Lewis acid has previously been shown to be viable as reaction of 96 with TMS-triflate generated W(NPh)Me₃(OSO₂(CF₃)) (100) (see Section 4.3.1).
4.6 Investigating the Interaction Between MeAlCl₂ and W(NPh)(Cl)Me₃ (96) in Solution

In Section 4.5 the adduct [W(NPh)(Cl)Me₃AlCl₃] (104) was examined using ²⁷Al NMR (at ~25°C) spectroscopy. The presence of a broad AlCl₄⁻ resonance in the ensuing spectrum suggests that 104 partially dissociates in solution to give [W(NPh)Me₃][AlCl₄]. With the aim of gaining further insight into the interaction of mono(imido) complex and Me₃AlCl₂ Lewis acids, W(NPh)(Cl)Me₃ (96) was reacted with varying numbers of equivalents of MeAlCl₂ in C₆D₆. This allowed direct observation of the reaction products using ¹H NMR spectroscopy (Figure 4.9 and Table 4.3).
Figure 4.9 $^1H$ NMR (400 MHz, $C_6D_6$) spectra obtained from reaction of $W(NPh)(Cl)Me_3$ (96) with $MeAlCl_2$ (aromatic and tungsten-alkyl regions omitted).

Table 4.3 $^1H$ NMR (400 MHz, $C_6D_6$) $Al-CH_3$ resonances presented after reaction of $W(NPh)(Cl)Me_3$ (96) with $MeAlCl_2$.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equivalents of $MeAlCl_2$</th>
<th>$\delta$ $^1H$ (ppm) $Al-CH_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.23</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>$-0.05$ and $-0.42$</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>$-0.30$ and $-0.43$</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>$-0.38$</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>$-0.39$</td>
</tr>
</tbody>
</table>

A sample of $MeAlCl_2$ in $C_6D_6$ presented a single $^1H$ NMR resonance at 0.42 ppm.

The established $^1H$ NMR resonance of the $W-CH_3$ moieties of $W(NPh)(Cl)Me_3$ (96) is 1.28 ppm in $C_6D_6$. Addition of $MeAlCl_2$ to complex 96 in Reactions 1-5 resulted in the formation of a single new $^1H$ NMR $W-CH_3$ resonance at 1.32 ppm, which was the only tungsten methyl signal presented by each reaction solution, even when excess $MeAlCl_2$ was utilized. In contrast, it is clear that that the chemical shifts of the $Al-CH_3$
\textsuperscript{1}H NMR resonances are highly dependent on the amount of MeAlCl\textsubscript{2} employed (Table 4.3, Figure 4.9). When one equivalent of MeAlCl\textsubscript{2} is utilized (Reaction 1) the resulting Al-CH\textsubscript{3} resonance at 0.23 ppm, is at considerably higher frequency than that measured for an authentic sample of MeAlCl\textsubscript{2} ($-0.42$ ppm, C\textsubscript{6}D\textsubscript{6}, 400 MHz). This suggests that in this instance a MeAlCl\textsubscript{2} fragment closely associates to the W centre, most likely giving a 1:1 adduct of the formula \([\text{W(NPh})(\text{Cl})\text{Me}_3,\text{AlMeCl}_2]\) (106).\textsuperscript{ix}

In contrast, treatment of \(\text{W(NPh)}(\text{Cl})\text{Me}_3\) (96) with a slight excess of MeAlCl\textsubscript{2} (two equivalents) as in Reaction 2, gives two broad Al-CH\textsubscript{3} resonances by \textsuperscript{1}H NMR at $-0.05$ and $-0.42$ ppm in a 1:1 ratio. This indicates that a slow exchange is occurring in solution between the MeAlCl\textsubscript{2} fragment of 106 and free non-associated MeAlCl\textsubscript{2}. A similar equilibrium is believed to be established in Reaction 3 in which five equivalents of MeAlCl\textsubscript{2} are used, with two Al-CH\textsubscript{3} resonances again being detected by \textsuperscript{1}H NMR. However, for Reaction 3 the two signals are further broadened and are beginning to converge (Figure 4.9), possibly indicating a more rapid exchange between coordinated and non-coordinating MeAlCl\textsubscript{2}, resulting from the presence of MeAlCl\textsubscript{2} in higher concentrations. Indeed, the rate of this equilibrium is seemingly heightened further still when larger excesses of MeAlCl\textsubscript{2} are used. As a result, both reactions 4 and 5 present a single converged Al-CH\textsubscript{3} resonance with a chemical shift ($-0.39$ ppm) approaching that of free MeAlCl\textsubscript{2} ($-0.42$ ppm). Together all these observations are suggestive that a rapid exchange between free MeAlCl\textsubscript{2} and MeAlCl\textsubscript{2} groups bound to \(\text{W(NPh)}(\text{Cl})\text{Me}_3\) (96) occurs in solution.

4.6.1 Investigating the Interaction of \(\text{W(NPh)}(\text{Cl})\text{Me}_3\) (96) with MeAlCl\textsubscript{2} at Low Concentrations

In the previous sub-section 4.6.0 it was established that \(\text{W(NPh)}(\text{Cl})\text{Me}_3\) (96) reacts with MeAlCl\textsubscript{2} to give the 1:1 adduct \([\text{W(NPh)}(\text{Cl})\text{Me}_3,\text{AlMeCl}_2]\) (106). Furthermore, rapid exchange occurs between the MeAlCl\textsubscript{2} fragment of 106 and any non-coordinated MeAlCl\textsubscript{2} present in solution. The rate of this exchange is clearly dictated by the concentration of MeAlCl\textsubscript{2}. As such, attention turned to investigating the

\textsuperscript{ix} \textsuperscript{1}H NMR spectroscopic evidence is consistent with the formation of the adduct \(\text{W(NPh)}(\text{Cl})\text{Me}_3,\text{AlMeCl}_2\) (106) in reactions 1-5. Evaporation of volatile components from Reaction 3 gave a brown residue, which was analysed by \textsuperscript{1}H NMR spectroscopy and was found to be the adduct \([\text{W(NPh)}(\text{Cl})\text{Me}_3,\text{AlCl}_3]\) (104). This reinforces the hypothesis that 104 forms via 106 through exchange of aluminium groups, as illustrated in Section 4.5, Scheme 4.11.
interaction between complex \( 96 \) and MeAlCl₂ at relatively low concentrations, with the aim of establishing if interaction of \( 96 \) and MeAlCl₂ can occur in dilute solutions.

To this end, a Ce₆D₆ solution of \( \text{W(NPh)(Cl)Me₃} (96) \) with a molarity of approximately 0.015 M was reacted with five equivalents of MeAlCl₂ and analysed using \(^1\text{H} \) NMR spectroscopy. No interaction between \( 96 \) and MeAlCl₂ was found to occur. This contrasts with Reaction 5 (see Table 4.3, Section 4.6.0) in which treatment of an approximately 0.75 M Ce₆D₆ solution of \( 96 \) with five equivalents of MeAlCl₂ gave the adduct \([\text{W(NPh)(Cl)Me₃,AlMeCl₂}] (106)\). Evidently, formation of the adduct \( 106 \) is disfavoured at low concentrations. Indeed, dilution of the solution from Reaction 3, from 0.75 M to 0.013 M, resulted in dissociation of the adduct \([\text{W(NPh)(Cl)Me₃,AlMeCl₂}] (106)\) to give free MeAlCl₂ and \( \text{W(NPh)(Cl)Me₃} (96) \). This establishes that formation of the adduct \( 106 \) is a reversible process (Scheme 4.13).

\[\text{Scheme 4.13 Reversible formation of } [\text{W(NPh)(Cl)Me₃,AlMeCl₂}] (106)\]

\[\text{W(NPh)(Cl)Me₃ + MeAlCl₂} \rightleftharpoons \text{W(NPh)(Cl)Me₃,AlMeCl₂} \]

(96) (106)

The tendency of the adduct \([\text{W(NPh)(Cl)Me₃,AlMeCl₂}] (106)\) to dissociate when diluted is important. This suggests that the capacity of \( R_x\text{AlCl}_{3-x} \) co-initiators to bind to tungsten chloride ligands as Lewis acids can be affected by co-initiator or pre-catalyst concentration. In turn, this could rationalize the fact that the selectivity (alkene metathesis vs dimerization) of WCl₆ based initiators (WCl₆, 2NH₂R) is heavily dependent on the W:Al molar ratio as illustrated in Scheme 4.14 (see Chapter 2, Section 2.4).

\[\text{Scheme 4.14 Alternative selectivity of WCl₆-based initiator solutions}\]

As it has now been established that the adduct \([\text{W(NPh)(Cl)Me₃,AlMeCl₂}] (106)\) undergoes facile dissociation in a dilute solutions, it can be proposed that at low \( \text{Et₃Al₂Cl₃} \) concentrations coordination of aluminium-based Lewis acid fragments to tungsten chloride complexes will be unfavourable. In contrast, at high \( \text{Et₃Al₂Cl₃} \) concentrations adduct formation via interaction of \( \text{Et₃AlCl₃-x} \) Lewis acid fragments to
tungsten chloride ligands (in an interaction similar to that of 106) is likely to be more feasible. Thus, it can be postulated that it is the favourability of adduct formation at high concentrations that may direct WCl₆-based systems (WCl₆, 2NH₂R) to olefin dimerization.

4.7 Activation of mono(Imido) Tetrahalide pre-Catalysts Using Me₃AlCl₃-x co-Initiators
In this Chapter the reaction of discrete W(NR)Cl₄·THF (R = Ph, Ar) complexes with methyl aluminium reagents has been examined. It has been shown that the mono(imido) ligands of both W(NPh)(Cl)Me₃ (96) and W(NAr)(Cl)Me₃ (97) do not readily coordinate to Lewis acids. In contrast, it has been demonstrated that Lewis acids will readily interact with the W-Cl moieties of both 96 and 97. Coordination of Me₃AlCl₃-x groups to complex 96 has been achieved via reaction of the strong Lewis acid Me₃AlCl₂, generating the adducts [W(NPh)(Cl)Me₃·AlCl₃] (104) or [W(NPh)(Cl)Me₃·AlMeCl₂] (106), depending on the reaction procedure. Furthermore, the detection of an AlCl₄⁻ anion in the ²⁷Al NMR spectrum of 104, suggests that the adduct partly dissociates in solution to potentially give [W(NPh)Me₃][AlCl₄]. It has also been established via an examination of 106 at various concentrations that adduct formation is a reversible process. Hence, the interaction of mono(imido) complexes and Me₃AlCl₃-x Lewis acids in solution is now well understood. As such, attention turned to investigating the capacity of Me₃Al, Me₂AlCl and MeAlCl₂ to activate mono(imido) pre-catalysts for ethylene dimerization.

4.8 Activation of mono(Imido) Tetrahalide pre-Catalysts with Me₃Al
Treatment of a CD₂Cl₂ solution of W(NPh)Cl₄·THF (32) with Me₃Al (five equivalents) generated complex W(NPh)(Cl)Me₃ (96) in situ with 100% conversion (by NMR). Subsequently, this solution was placed under an atmosphere of ethylene (ten equivalents) and was then heated (60°C, 1 h). This resulted in full conversion of ethylene to but-1-ene (as verified by ¹H NMR spectroscopy and GC) (Scheme 4.15). Similarly, an ethylene dimerization system can be formed via reaction of W(NAr)Cl₄·THF (38) using comparable conditions. Addition of Me₃Al to 38 in CD₂Cl₂ resulted in the formation of W(NAr)(Cl)Me₃ (47) in situ. When the reaction solution was placed under an atmosphere of ethylene, but-1-ene was again formed after the mixture was heated (60°C, 1 h). Notably, both systems produced the by-product methane (which presented a singlet at δ 0.3 ppm), which was obtained in a 1:1 ratio with but-1-ene in both cases.
Scheme 4.15 Activation of W(NR)Cl₄.THF by Me₃Al

\[
\begin{align*}
W(NR)Cl_4.THF & \quad \text{(R = Ph or Ar)} \\
5Me_3Al & \quad \text{W(NR)(Cl)Me}_3 \quad 60^\circ C, 1 \text{ h, CD}_2Cl_2 \\
& \quad \text{(R = Ph or Ar)}
\end{align*}
\]

To determine the role of each component in the W(NPh)Cl₄.THF/Me₃Al ethylene dimerization system a series of control reactions was undertaken. To this end, a CD₂Cl₂ solution of Me₃Al was heated (60°C, 1 h) in the presence of ethylene (ten equivalents). No reaction occurred and no methane was observed to evolve (according to ¹H NMR spectroscopy). This shows that the methane observed in the initiator systems outlined in Scheme 4.15 is not due to any inadvertent hydrolysis of Me₃Al. Furthermore, heating a solution of W(NPh)(Cl)Me₃ (96) in the presence of either ethylene or Me₃Al alone did not induce any reaction (Scheme 4.16). Consequently, as no ethylene dimerization occurred in the absence of Me₃Al, it is clear that for the W(NR)Cl₄.THF/Me₃Al dimerization system the presence of all three components are required for the conversion of ethylene to higher olefins.

Scheme 4.16 Treatment of W(NPh)(Cl)Me₃ (96) with Me₃Al and ethylene

\[
\begin{align*}
W(NR)(Cl)Me_3 & \quad 60^\circ C, 1 \text{ h} \quad \text{No reaction} \\
5Me_3Al, 60^\circ C, 1 \text{ h} & \quad \text{No reaction}
\end{align*}
\]
4.8.1 Examining the Route of Methane Formation in the W(NR)Cl₄·THF/Me₃Al Dimerization Systems

It has been established that the W(NR)Cl₄·THF/Me₃Al (R = Ph, Ar) ethylene dimerization systems produce methane upon initiator formation. To simultaneously assess the mode by which methane and the active initiator complex are formed, a W(NAr)Cl₄·THF/Me₃Al reaction solution was used to dimerize C₂D₄ (ten equivalents) in CD₂Cl₂. Analysis of the resulting reaction mixture using ¹H NMR spectroscopy both before and after dimerization had taken place, did not identify the active initiator complex. Instead broad alkyl resonances were detected, which were unassignable using ¹H and ¹³C NMR spectroscopy. Of note, is that dimerization of C₂D₄ produced both CH₄ and CH₃D, the later presenting a resonance at 0.21 ppm by ¹H NMR spectroscopy (CD₂Cl₂, 500 MHz, ²J̃HD = 1.5 Hz). Together, these observations indicate that methane formation must occur via β-hydride elimination with transfer of a deuterium atom from a C₂D₄ molecule giving a W-D intermediate, which can then undergo reductive elimination (Scheme 4.17).

Scheme 4.17 Rationalizing the formation of both CH₄ and CH₃D upon dimerization of C₂D₄ by a W(NAr)Cl₄·THF/Me₃Al initiator solution.
The reaction pathways outlined in Scheme 4.17 are supported by GC-MS analysis of the volatile components obtained from the W(NAr)Cl₄·THF/Me₃Al/C₂D₄ reaction solution. These analyses determined that trace C₅D₁₀ is produced by this system, indicating that the propylene moiety formed via reductive elimination of CH₄, couples with a molecule of C₂D₄ to give C₅ products. It is conceivable that olefin dimerization by the W(NAr)Cl₄·THF/Me₃Al system is induced by either W⁺⁺ or W-H intermediates (Scheme 4.17) via an oxidative coupling or hydride cycle, respectively. A similar activation pathway to that outlined in Scheme 4.17 is believed to be occurring in the W(NAr₂)₂Me₂·THF/C₂H₄ dimerization system outlined in Chapter 3, Section 3.9.1, from which methane is also observed to evolve.

**4.8.2 Contrasting the Abilities of the Lewis Acids MeAICl₂, Me₂AlCl, Me₃Al to co-Initiate Ethylene Dimerization**

In Section 4.8.1 an ethylene dimerization initiator solution was formed via reaction of W(NPh)Cl₄·THF (32) with Me₃Al. However, it has been established that reaction of 32 with Me₃Al in the absence of olefins gives W(NPh)(Cl)Me₃ (96) as the only tungsten-containing reaction product. With both of these observations in mind, attention turned to investigating the capacity of a discrete sample of 96 to initiate ethylene dimerization when treated with Me₃Al, Me₂AlCl and MeAlCl₂. All of the reactions were conducted using comparable conditions, with the aim of establishing the different capacities of the MeₙAlClₓ,ₓ reagents to co-initiate ethylene dimerization. It was found that Me₃Al, Me₂AlCl and MeAlCl₂ can all indeed activate W(NPh)(Cl)Me₃ (96) for ethylene dimerization (Table 4.4).

<table>
<thead>
<tr>
<th>Co-initiator (four equivalents)</th>
<th>Olefin observed (¹H NMR spectroscopy)</th>
<th>Conditions (nine equivalents of C₂H₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeAICl₂</td>
<td>But-1-ene</td>
<td>C₆D₆, 25°C</td>
</tr>
<tr>
<td>Me₂AlCl</td>
<td>But-1-ene</td>
<td>C₆D₆, 25°C</td>
</tr>
<tr>
<td>Me₃Al</td>
<td>No reaction of ethylene</td>
<td>C₆D₆, 25°C</td>
</tr>
<tr>
<td>Me₃Al</td>
<td>But-1-ene</td>
<td>CD₂Cl₂, (60°C, 1 h)</td>
</tr>
</tbody>
</table>

Evidently the Lewis acid strength of the MeₙAlClₓ,ₓ co-initiator can influence the reactivity of a given dimerization system. For instance, when MeAICl₂ or MeAlCl₂ are
used to activate W(NPh)(Cl)Me₃ (96) ethylene dimerization can be achieved in a non-polar solvent (e.g. C₆D₆) and without the requirement of heating. In contrast, when the weaker Lewis acid Me₃Al is used, ethylene dimerization only occurs at elevated temperatures (ca. 60°C). Furthermore, it has been found that Me₃Al can only activate 96 in polar solvents (such as CD₂Cl₂) with no dimerization being observed when C₆D₆ is utilized. As ethylene dimerization is co-initiated by both MeAlCl₂ and Me₂AlCl in C₆D₆, this indicates that the inability of Me₃Al to co-initiate dimerization in C₆D₆ is not due to the insolubility of an initiator complex in C₆D₆.

Before addition of ethylene to the MeAlCl₂/W(NPh)(Cl)Me₃ initiator solution, the mixture was analyzed using ¹H NMR spectroscopy. This confirmed the formation of the adduct [W(NPh)(Cl)Me₃.AiMeCl₂] (106), which was identified using ¹H NMR spectroscopy (as in Section 4.6). Indeed, ¹H NMR analysis showed that in the W(NPh)(Cl)Me₃/MeAlCl₂ system, 96 was fully converted to 106 before addition of ethylene. As such it can be concluded that in this MeAlCl₂-based ethylene dimerization system, the active initiator complex is formed via modification of 106.

4.8.3 Evaluating the Role of Adduct Formation in Me₂AlCl₃-x co-Initiated Dimerization Systems

In the W(NPh)(Cl)Me₃/MeAlCl₂ ethylene dimerization system, the adduct [W(NPh)(Cl)Me₃.AiMeCl₂] (106) has been observed to form in situ. The co-initiator MeAlCl₂ has also been found to activate W(NPh)Cl₄·THF (32) for ethylene dimerization (Scheme 4.18). Notably, reaction of MeAlCl₂ and 32 in C₆D₆ in the absence of ethylene is found to generate the adduct [W(NPh)(Cl)Me₃.AlCl₃] (104) (verified by ¹H NMR spectroscopy). This tendency of adducts such as 106 or 104 to form upon reaction of MeAlCl₂ with mono(imido) tungsten chloride complexes, indicates that adduct formation is crucial to the generation of the active initiator complex in the Me₂AlCl₃-x co-initiated ethylene dimerization systems.

—

Heating a CD₂Cl₂ solution of Me₃Al did not result in any reaction. This indicates that in the Me₃Al dimerization system, the active initiator complex is not formed via reaction of Me₃Al with CD₂Cl₂.
In Section 4.5 it was shown that a Lewis base (THF) can displace the coordinating AlCl₃ moiety of 104. This suggests that ethylene as a Lewis base could displace the Me₃AlClₓ fragment of [W(NPh)(Cl)Me₃AlCl₃] (104) or [W(NPh)(Cl)Me₃AlMeCl₂] (106). However, such a reaction is unlikely to generate an initiator complex, as removal of the MeAlCl₂ or AlCl₃ groups of 104 and 106 would generate the inactive complex 96. Instead, it is highly probable that the ethylene dimerization observed in the MeAlCl₂/W(NPh)Cl₄·THF (32) system is initiated upon coordination of ethylene to the tungsten core of [W(NPh)(Cl)Me₃AlCl₃] (104) via the pathway outlined in Scheme 4.19.

Scheme 4.18 Ethylene dimerization systems based on the activation of mono(imido) complexes by MeAlCl₂

Scheme 4.19 Proposed route by which ethylene coordinates to 104
The computational investigation carried out by Tobisch indicates that ethylene coordination to 104 can occur when the AlCl₃ fragment is closely bound to the tungsten core as a coordinating Lewis acid. However, association of ethylene to the dissociated form of 104, [W(NPh)Me₃][AlCl₄], as outlined in Scheme 4.19 is arguably more viable. This is because introduction of ethylene into the coordination sphere of a [W(NPh)Me₃]⁺ fragment will be more favourable since there will be no steric constraints imposed by the bound Lewis acid fragment. Furthermore, coordination of a strong σ-donor (ethylene) to a positively charged tungsten centre (stabilized by an AlCl₄⁻ anion) will also be highly favourable electronically and electrostatically. Thus, it is hereby proposed that initiator formation in the W(NPh)(Cl)Me₃/Me₃AlCl₃ dimerization systems outlined in 4.9.3 occurs via the intermediate [W(NPh)Me₃(η²-C₂H₄)][Me₃AlCl₄-x] (Scheme 4.19). This sequence can be used to rationalize the observation that Me₃Al can only activate W(NPh)(Cl)Me₃ (96) in polar solvents such as CD₂Cl₂.

As Me₃Al is a weaker Lewis acid (relative to MeAlCl₂), it is reasonable to postulate that Me₃Al will be less able to abstract the chloride atom of 96 to give the corresponding ionic complex [W(NPh)Me₃][Me₃AlCl] (108). Indeed, formation of the adduct 108 via reaction of Me₃Al would be hampered further still by a non-polar environment such as C₆D₆. If indeed 108 was the precursor to the active initiator complex, then this would explain why Me₃Al cannot co-initiate ethylene dimerization in C₆D₆. Conversely, the ionic intermediate 108 would feasibly be stabilized by a polar solvation environment such as that of CD₂Cl₂. Thus, the use of CD₂Cl₂ would feasibly allow for greater conversion of 96 to 108, which could explain why using CD₂Cl₂ is essential for the Me₃Al co-initiated dimerization systems identified in this study.

4.9 Summary and Conclusions

In this Chapter the association of Me₃AlCl₃-x Lewis acids to mono(imido) systems has been investigated. This was undertaken with a view to clarifying the effect of aluminium coordination on the reactivity of mono(imido) systems with ethylene. Generation of W(NPh)(Cl)Me₃ (96) by treatment of W(NPh)Cl₄·THF with Me₃Al has shown that coordination of Me₃AlCl₃-x groups to mono(imido) ligands is not favourable. In contrast, it has been found that Me₃AlCl₃-x fragments will readily coordinate to tungsten chloride ligands to give adducts such as [W(NPh)(Cl)Me₃AlCl₃] (104) or [W(NPh)(Cl)Me₃AlMeCl₂] (106). Indeed, adduct formation has been shown to be crucial in the activation of mono(imido) systems. Furthermore, the adduct 104 has been observed to dissociate in solution giving an
AlCl₄⁻ cation (identified by ²⁷Al NMR spectroscopy). Consequently, it is proposed that for MeₓAlCl₃₋ₓ co-initiated systems, active initiator complexes are formed via [W(NPh)Me₃(η²-C₂H₄)][MeₓAlCl₄₋ₓ] intermediates as illustrated in Scheme 4.19.

4.10 References

Chapter 4


Chapter 5: Experimental

5.0 Introduction
All operations were conducted under an atmosphere of dry nitrogen using standard Schlenk and cannula techniques, or in a nitrogen-filled glove box, unless stated otherwise. NMR-scale reactions were conducted using NMR tubes fitted with Young's tap valves. Bulk solvents were purified using an Innovative Technologies SPS facility and degassed prior to use. NMR solvents (C₆D₆, C₆D₅Cl, CD₂CN and CDCl₃) were dried over P₂O₅, distilled and degassed before use. DME was distilled under nitrogen from sodium/benzophenone. When appropriate, liquid reagents were dried, distilled and deoxygenated. Nitrogen gas was passed through a drying column (silica/CaCO₃/P₂O₅) and ethylene was dried using a column of activated alumina.

The known complexes and compounds Mo(NR)₂Cl₂.DME (R = 'Bu (26), Ar (23),¹ Mo(NAr)₂(CH₂C(Me)₃)₂ (82),² Mo(NAr)(N'Bu)Cl₂.DME (11),³ Mo(NAr)₂Me₂ (27),⁴ W(NR)Cl₄, THF (R = Ph (32), Ar (38)),⁵ W(NAr)Cl₄ (62),⁶ W(NPh)(Cl)₂(PMe₃)₃ (34)⁷, Ta(NAr)Cl₃(TMEDA) (59),⁸ and [AlCl₄][P(NPr₂)₂] (107)⁹ were prepared using standard literature procedures. Aluminium reagents were purchased from Albermarle R and D centre and Aldrich either neat (Me₃Al, EtAlCl₂ and Et₂AlCl₃) or as solutions in hexane (Me₂AlCl, MeAlCl₂, MAO and EtAlCl₂). Neat MeAlCl₂, Me₂AlCl and MAO were obtained by evaporation of hexane from the appropriate commercial solution. Similarly, neat samples of EtMgCl, MeMgCl and LiMe were obtained by the drying the commercially available solutions in vacuo. All other chemicals were obtained commercially and used as received.

Mass spectra (ES) were obtained using a Micromass Autospec instrument. GC analysis was performed on an Agilent Technologies 6890N GC system equipped with PONA (50m×0.020mm×0.50μm) and MDN12 (60m×0.025mm×0.25μm) columns. GC-MS analysis was performed on an Agilent Technologies 6890N GC system equipped with a MDN12 (60m×0.025mm×0.25μm) column, coupled to an Agilent Technologies 5973N MSD Mass Spectrometric instrument. Elemental analyses were performed by the Analytical Services Department of the Chemistry Department, Durham University. Full crystallographic experimental details are presented in Appendix 1.

Routine NMR spectra were collected on a Varian Unity 300 or 200, a Varian Mercury 400, Avance 400 MHz Bruker, Varian Inova 500, or a Varian 700 MHz spectrometers. Chemical shifts were referenced to residual protio impurities in the deuterated solvent (¹H) or the ¹³C shift of the solvent (¹³C). Solvent proton shifts (ppm): CDCl₃, 7.26; C₆D₆, 7.15; CD₂Cl₂, 5.34; C₆D₅Cl, 7.13, 6.98, 6.95. Solvent carbon shifts (ppm): CDCl₃, 77.2; C₆D₆, 128.3; CD₂Cl₂, 54.0. ³¹P NMR chemical
shifts were referenced against an external standard of 85% phosphoric acid, while \(^{27}\)Al NMR chemical shifts were referenced against a saturated aqueous solution of aluminium nitrate. \(^{13}\)C NMR spectra were assigned with the aid of DEPT 135 and gHMOC \(^1\)H/\(^{13}\)C correlation experiments. Chemical shifts are reported in ppm and coupling constants in Hz unless otherwise stated.

5.1 General Procedure for the Testing of Ethylene Dimerization Systems Based on the Reaction of Imido Complexes

A stainless steel autoclave (250 mL) was charged with \(\text{C}_6\text{H}_5\text{Cl}\) (78 mL) and the required pre-catalyst (20 \(\mu\)mol). The vessel was then heated (60°C), pressurized with ethylene (5 bars), and stirred (1800 rpm). Next, the autoclave was vented, which enabled addition of the desired co-initiator, \(\text{EtAlCl}_2\) (300 \(\mu\)mol) or \(\text{B(C}_6\text{F}_5)_3\) (80 \(\mu\)mol). After co-initiator addition, the vessel was pressurized with ethylene (40 bars). A constant pressure of 40 bars was maintained throughout the reaction period, with a gas-flow meter providing a measure of ethylene consumption. After gas uptake was observed to decrease, the autoclave was isolated from the ethylene supply, and was then cooled (\(-5^\circ\text{C}\)) and slowly vented. Addition of an external standard, nonane (1 mL, 5.60 mmols), to the spent initiator solutions allowed for the calculation of a given initiator’s activity and selectivity using GC analysis.

5.2 Synthesis of \(\text{W(NAr)}_2\text{Cl}_2\text{DME (40)}\)

In work conducted for this thesis, the complex \(\text{W(NAr)}_2\text{Cl}_2\text{DME (40)}\) was prepared using a slight modification of the procedure developed by Schrock et al. Initially, \(\text{WO}_2\text{Cl}_2\) (3.00 g, 0.010 mols) was suspended in DME (5 mL). To this suspension was added sequentially \(\text{CISiMe}_3\) (15.82 mL, 0.124 mols) followed by 2,6-lutidine (7.51 mL, 0.064 mols) and then \(\text{H}_2\text{NAr}\) (4.14 mL, 0.022 mols). This mixture was heated (60°C, 24 h), which generated a bright red solution that was filtered and allowed to stand for 20 minutes. During this time dark red single crystals of 40 precipitated from solution and were then collected via filtration; yield 2.10 g, 28 %. The \(^1\)H and \(^{13}\)C NMR chemical shifts, displayed by a sample of 40 prepared by this methodology, were found to be consistent with the values previously reported by Schrock et al.

\(^1\)H NMR (CDCl₃, 200 MHz): \(\delta 7.09\) (4H, d, \(\text{H}_\text{meta}, \^3\text{J}_{\text{HH}} = 6.8\text{ Hz}\)), 6.89 (2H, t, \(^3\text{J}_{\text{HH}} = 6.8\text{ Hz}\)), 3.96 (6H, broad, \(\text{CH}_2\text{OCH}_2\)), 3.86 (12H, broad, \(\text{CH}_3\text{OCH}_2\) and \(\text{CH}_3\text{CH}_2\)), 1.06 (24H, d, \(\text{CH}_3\)), \(^3\text{J}_{\text{HH}} = 6.8\text{ Hz}\).
\(^{13}\text{C} \{(^1\text{H})\} \text{NMR (CDCl}_3, 125.6 \text{ MHz)}: \delta \text{ 150.1 (C}_\text{ipso}, \text{ 144.6 (C}_\text{ortho}, \text{ 125.5 (C}_\text{meta}, \text{ 122.2 (C}_\text{para}, \text{ 71.5 (CH}_3\text{OCH}_2, \text{ 63.6 (CH}_3\text{OCH}_2, \text{ 27.2 (CH}_3\text{CH}, \text{ 24.6 (CH}_3\text{CH).}

5.3 Synthesis of \text{Mo(NAr)}_2(\text{NH}_3^\text{Bu})_2(55)

\text{Mo(NAr)}_2\text{Cl}_2\text{.DME (23) (2.0 g, 3.38 mmols) was dissolved in Et}_2\text{O (30 mL) and the solution was cooled to \(-78^\circ\text{C). A separate solution was formed via the dissolution of LiNH}_3^\text{Bu} (0.52 g, 6.57 mmols) also in Et}_2\text{O (100 mL). The two solutions were combined slowly at \(-78^\circ\text{C). The resulting mixture was then allowed to warm to room temperature, before being stirred for an additional 4 h period. The reaction solution was then dried in vacuo, enabling \text{Mo(NAr)}_2(\text{NH}_3^\text{Bu})_2 (55) to be extracted from LiCl using hexane (3 \times 30 mL). Concentration of the hexane solution and recrystallization (\(-35^\circ\text{C}) gave orange cube-shaped crystals of sufficient quality for solid state analysis; Yield 0.36g (20%).}

\text{^1H NMR (CDCl}_3, 200 \text{ MHz): } \delta \text{ 6.96 (6H, broad, } H_\text{meta} \text{ and } H_\text{para}, \text{ 6.29 (2H, broad, NH),} \\
\text{3.57 (4H, septet, CH}_3\text{CHCH}_3, \text{ } \gamma J_\text{HH} = 6.8 \text{ Hz),} \text{ 1.29 (18H, s, CH}_3, \text{ 1.11 (24H, d, CH}_3\text{CH, } \gamma J_\text{HH} = 6.8 \text{ Hz).}

\text{^13C \{(^1\text{H})\} NMR (CDCl}_3, 125.6 \text{ MHz): } \delta \text{ 153.5 (C}_\text{ipso}, \text{ 140.5 (C}_\text{ortho}, \text{ 123.3 (C}_\text{meta}, \text{ 122.1 (C}_\text{para}, \text{ 55.2 (CCH}_3, \text{ 33.1 (CCH}_3 \text{ 28.3 (CH}_2\text{CH}_2, \text{ 23.1 (CH}_2\text{CH}_3.}

\text{Anal. Calcd for C}_{35}\text{H}_{54}\text{MoN}_{4}: C; 65.06, H; 9.21, N; 9.48, found C; 65.00, H; 9.34 and N; 9.58.}

\text{Mass Spectrometry (ES): } m/z = 592.2.

5.4 Reaction of \text{Mo(NAr)}_2(\text{NH}_3^\text{Bu})_2 (55) with Me}_3\text{Al}

\text{Mo(NAr)}_2(\text{NH}_3^\text{Bu}_2 (55) (50 mg, 0.08 mmols) was dissolved in C}_6\text{D}_6 (0.8 mL). \text{ To this solution was added Me}_3\text{Al (12.0 mg, 0.16 mmols). The reaction mixture was then analysed using } ^1\text{H NMR spectroscopy. This revealed resonances assignable to the known complex Mo(NAr)}_2\text{Me}_2 (27).}

5.5 Reaction of \text{W(NPh)}(\text{Cl})_2(\text{PMe}_3)_2 (34) with Me}_3\text{Al}

\text{W(NPh)}(\text{Cl})_2(\text{PMe}_3)_2 (34) (20 mg, 0.03 mmols) was dissolved in C}_6\text{D}_6 (0.8 mL). \text{ To this solution was added Me}_3\text{Al (15 mg, 0.20 mmols) and the reaction mixture was analysed using } ^3\text{P NMR spectroscopy. The established } ^3\text{P NMR shifts of 34 were not detected. Instead, a broad resonance at \(-21.16 \text{ ppm and two sharper signals at}

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-29.8 and -33.5 ppm were obtained. Ethylene (0.17 mmols) was added to the reaction mixture. No consumption of ethylene was observed to occur, even after heating the reaction solution (1 h, 60°C).

5.6 Reaction of Mo(N^Bu)_2Cl_2.DME (26) with One Equivalent of EtAlCl_2

Mo(N^Bu)_2Cl_2.DME (1.0 g, 2.30 mmols) was dissolved in toluene (20 mL) and to this solution was added EtAlCl_2 (1.3 mL, 1.8 M in toluene, 2.30 mmols). The reaction solution was then dried in vacuo generating a dark red solid, which was extracted with hexane (3 x 30 mL). The hexane washings were collected, concentrated in vacuo and then cooled (-30°C). This induced the precipitation of a light red solid, which was collected via filtration. The ^1H and ^13C NMR spectroscopic data presented by this material are consistent with previously reported data for the known complex Mo(N^Bu)_2Cl_2 (21).^10 Yield; 0.46 g (65%).

^-1H (C_6D_6, 400 MHz): δ 1.28 (s, CCH_3).

^-13C {^1H} (C_6D_6, 125.5 MHz): δ 30.06 (CCH_3) and 74.11 (CCH_3).

5.7 Synthesis of Mo(N^Bu)_2Cl_2PPh_3 (60)

Mo(N^Bu)_2Cl_2.DME (1.0 g, 2.3 mmols) was dissolved in toluene (20 mL). The solution was cooled to -78°C before addition of a solution of EtAlCl_2 (1.3 mL, 1.8 M in toluene, 2.3 mmols). Next, PPh_3 (0.8 g, 3.05 mmols) was added to the reaction mixture, also as a solution in toluene (20 mL). The reaction mixture was then allowed to warm to room temperature, and on warming, a light yellow solid precipitated from solution. This material was collected via filtration and recrystallized from acetonitrile (-35°C); yield 0.4 g (28%).

^-1H (CDCl_3, 200 MHz): δ 7.89 (15H, b, P(C_6H_5)_3), 1.26 (18H, s, CCH_3).
13C \{^1 H\} (CDCl$_3$ 125.6 MHz): δ 134.8 (C$_{ortho}$), 131.3 (C$_{meta}$), 129.0 (C$_{para}$), 74.6 (CCH$_3$), 30.3 (CCH$_3$). The C$_{ipso}$ resonance was not detected.

31P \{^1 H\} (CDCl$_3$, 81 MHz): δ 33.8.

Anal. Calcd for C$_{26}$H$_{33}$Cl$_2$MoN$_2$P: C; 54.65, H; 5.82, N; 4.90. Found: C; 54.52, H; 5.74, N; 4.80%.

5.8 Reaction of Mo(N$^\text{iBu}$)$_2$Cl$_2$.DME (26) with PPh$_3$

Mo(N$^\text{iBu}$)$_2$Cl$_2$.DME (26) (30 mg, 0.07 mmols) was dissolved in CDCl$_3$ (0.8 mL) and to this solution was added PPh$_3$ (20 mg, 0.07 mmols). The mixture was then analysed using $^1$H NMR spectroscopy. After a 2 h period the $^1$Bu $^1$H NMR resonance of Mo(N$^\text{iBu}$)$_2$Cl$_2$.PPh$_3$ (60) was observed at 1.26 ppm (see Section 5.8). Furthermore, the known $^1$Bu resonance of the starting complex 26 was also detected at 1.48 ppm. Integration of the $^1$H NMR spectra showed that 60% of complex 26 had converted to 60.

5.9 Reaction of Mo(N$^\text{iBu}$)$_2$Cl$_2$(26) and Excess EtAlCl$_2$

\[
\text{Mo(N}^\text{iBu})_2\text{Cl}_2\text{.DME (26)} \rightarrow \text{3EtAlCl}_2
\]

Mo(N$^\text{iBu}$)$_2$Cl$_2$.DME (26) (1.0 g, 2.40 mmols) was dissolved in toluene (20 mL) before addition of a solution of EtAlCl$_2$ (3.9 mL, 1.8 M in toluene, 7.02 mmols). The reaction mixture was then dried in vacuo producing a dark red oil, which was analysed using $^1$H and $^{13}$C NMR spectroscopy. This revealed that reaction of 26 and EtAlCl$_2$ gave multiple products, unassignable by $^1$H and $^{13}$C NMR spectroscopy.

5.10 Reaction of W(NAr)$_2$Cl$_2$.DME (40) with EtAlCl$_2$

W(NAr)$_2$Cl$_2$.DME (40) (50 mg, 0.07 mmols) was dissolved in C$_6$D$_6$ (0.8 mL). To this solution was added EtAlCl$_2$ (53 mg, 0.42 mmols) and the reaction mixture was analysed immediately using $^1$H NMR spectroscopy. This showed that the reaction gave multiple products unassignable by $^1$H NMR spectroscopy, although ethane was detected at δ 0.79 ppm. Next, ethylene (0.17 mmols) was added to this C$_6$D$_6$
solution. No reaction of ethylene occurred and no higher olefins were detected by $^1$H NMR spectroscopy.

5.11 Reaction of W(NAr)$_2$Cl$_2$DME (40) with Et$_3$Al$_2$Cl$_3$

The procedure outlined in Section 5.11 was repeated, but with replacement of EtAlCl$_2$ with Et$_3$Al$_2$Cl$_3$ (27 mg, 0.10 mmols). Ethane was again observed in the $^1$H NMR spectrum presented by the reaction mixture. However, the reaction also gave multiple products unassignable by $^1$H NMR spectroscopy. After addition of ethylene (0.17 mmols) to the Et$_3$Al$_2$Cl$_3$ reaction solution, the mixture was again analysed using $^1$H NMR spectroscopy. It was clear from the resulting spectrum that no consumption of ethylene occurred and no higher olefins were detected.

5.12 Synthesis of EtAlCl$_2$(THF)$_2$

A toluene solution of EtAlCl$_2$ (1 mL, 1.8 M in toluene, 1.8 mmols) was dissolved in excess THF (5 mL). The resulting mixture was stirred for 30 minutes, before being dried in vacuo. This generated EtAlCl$_2$(THF)$_2$, which was found to be a highly air sensitive, clear and colourless liquid.

$^1$H (C$_6$D$_6$, 300 MHz): δ 3.46 (8H, m, OCH$_2$CH$_2$), 1.25 (3H, CH$_2$CH$_3$, t, $^3$J$_{HH}$ = 8.1 Hz), 0.80 (8H, m, OCH$_2$CH$_3$), 0.25 (2H, q, $^3$J$_{HH}$= 8.1 CH$_2$CH$_3$).

$^{13}$C ($^1$H) (C$_6$D$_6$, 125.6 MHz): δ 73.76 (OCH$_2$CH$_2$), 25.65 (OCH$_2$CH$_2$), 9.17 (CH$_2$CH$_3$).

The CH$_2$ (ethyl) resonance was not detected.

Mass Spectroscopy (ES): $m/z = 242.8$ (Al(THF)$_2$Cl$_2$$^+$).

5.13 Reaction of W(NPh)Cl$_4$,THF (32) with One Equivalent of EtAlCl$_2$

W(NPh)Cl$_4$.THF (32) (64 mg, 0.13 mmols) was dissolved in toluene (5 mL) before addition of a solution of EtAlCl$_2$ (0.07 mL, 1.8 M in toluene, 0.13 mmols). The resulting solution was allowed to stir for 5 minutes during which time a light brown precipitate developed. This material was collected via filtration and was analysed using $^1$H NMR spectroscopy. This analysis detected two $^1$H NMR resonances at δ 3.46 and 0.80 ppm, consistent with the formation of the adduct EtAlCl$_2$(THF)$_2$ in situ (Section 5.14).
5.14 Reaction of W(NPh)Cl₄.THF (32) with Et₃Al₂Cl₃

W(NPh)Cl₄.THF (32) (30 mg, 0.06 mmols) was dissolved in C₆D₆ (0.8 mL). To this solution was added Et₃Al₂Cl₃ (38 mg, 0.15 mmols); the reaction mixture was then analysed using ¹H NMR spectroscopy. This showed that 32 reacted with Et₃Al₂Cl₃ to give multiple unassignable products as well as the by-product ethane.¹²

5.15 Reaction of W(NPh)Cl₄.THF (32) with EtAlCl₂

W(NPh)Cl₄.THF (32) (30 mg, 0.06 mmols) was dissolved in C₆D₆ (0.8 mL). To this solution was added EtAlCl₂ (39 mg, 0.30 mmols) and the reaction mixture was analysed using ¹H NMR spectroscopy. This confirmed the formation of ethane, as well as multiple, unassignable products. Next, to the reaction solution was added excess PMe₃ (0.06 mL, 0.61 mmols) and the solution was re-analysed using ¹H NMR spectroscopy. This confirmed the formation of but-1-ene.¹³

5.15.1 Reaction of Ta(NAr)C₅(tmeda) (59) with EtAlCl₂

Ta(NAr)Cl₃(tmeda) (59) (50 mg, 0.10 mmols) was dissolved in C₆D₆ (0.8 mL). To this solution was added EtAlCl₂ (55 mg, 0.43 mmols) and the mixture was analyzed using ¹H NMR spectroscopy. This confirmed the formation of ethane as well as multiple unassignable reaction products.¹²

5.16 Activation of W(NAr)Cl₄ (62) using Et₃Al₂Cl₃ and Subsequent Propylene Dimerization

W(NAr)Cl₄ (62) (20 mg, 0.04 mmols) was dissolved in C₆D₆ (0.8 mL). To this solution was added Et₃Al₂Cl₃ (20 mg, 0.08 mmols) and the mixture then charged into a Young's NMR tube, which was then placed under an atmosphere of propylene (0.17 mmols). After propylene addition, a spontaneous and exothermic reaction occurred. Next, the reaction solution was analysed by GC-MS. The GC-MS trace contained a peak with a retention time of 2.65 mins (m/z = 83, C₆H₁₁⁻), consistent with the formation of 2,3-dimethylbut-1-ene.¹⁴ No other alkenes were detected using GC-MS.

5.17 Activation of W(NAr)Cl₄.THF (38) using Et₃Al₂Cl₃ and EtAlCl₂ and Subsequent Ethylene Dimerization/Oligomerization

W(NAr)Cl₄.THF (38) (30 mg, 0.05 mmols) was dissolved in C₆D₆ (0.8 mL). To this solution was added Et₃Al₂Cl₃ (32 mg, 0.13 mmols) and the reaction mixture charged to a Young's NMR tube, which was placed under an atmosphere of ethylene (0.17 mmols). The solution was analysed by both ¹H NMR spectroscopy and GC-MS.
These analyses confirmed the formation of a range of C₄, C₅, and C₆ olefins (see Chapter 2, Section 2.4).

The above procedure was repeated but Et₃Al₂Cl₃ was replaced with EtAlCl₂ (53 mg, 0.40 mmols). After addition of ethylene, the reaction mixture was analysed using GC. This analysis confirmed the formation of C₄, C₆ and C₈ alkenes (see Chapter 2, Section 2.4).

5.18 Dimerization of C₂D₄ and C₂H₄ (1:1) using W(NAr)CU.THF (38)
W(NAr)CU.THF (38) (30 mg, 0.05 mmols) was dissolved in C₆D₆. To this solution was added Et₃Al₂Cl₃ (32 mg, 0.25 mmols) and the reaction mixture charged into a Young’s NMR tube. The reaction solution was then frozen (−78°C), allowing for the addition of first C₂H₄ (0.17 mmols) and then C₂D₄ (0.17 mmols). Next, the solution was allowed to warm to room temperature, which induced an exothermic reaction. After this reaction had ceased, the solution was sampled by GC and GC-MS (see Chapter 2, Section 2.6 for C₄ product isotopmer distributions which were determined using Agilent ion recognition software).

5.19 Activation of W(NAr)Cl₄ (62) using EtMgCl and Subsequent Ethylene Dimerization
W(NAr)Cl₄ (62) (20 mg, 0.04 mmols) was dissolved in C₆D₆ (0.8 mL) and the solution then mixed with solid EtMgCl (25 mg, 0.28 mmols) and charged into a Young’s NMR tube. The solution was then placed under an atmosphere of ethylene (0.15 mmols) and analysed using ¹H NMR spectroscopy. This ¹H NMR analysis indicated that full conversion of ethylene to but-1-ene had occurred in a 2 h reaction period. The formation of but-1-ene was verified by analysis of the reaction solution using GC.

5.20 Attempts to Activate W(NAr)Cl₄ (62) for Ethylene Dimerization using MeMgCl and Mg
W(NAr)Cl₄ (62) (40 mg, 0.08 mmols) was dissolved in C₆D₆ (0.8 mL). To this solution was added solid MeMgCl (39 mg, 0.32 mmols) and the mixture charged into a Young’s NMR tube. Next, the solution was placed under an atmosphere of ethylene (0.15 mmols) and then analysed using ¹H NMR spectroscopy. No higher olefins were detected using ¹H NMR spectroscopy.
This procedure was repeated as above, but replacing of MeMgCl with Mg turnings (8 mg, 0.33 mmols). Again, no higher olefins were formed after addition of ethylene to the reaction solution.

5.21 Activation of W(NAr)Cl₄·THF (38) with Et₃Al₂Cl₃ and Subsequent C₂D₄ Dimerization

W(NAr)Cl₄·THF (38) (30 mg, 0.05 mmols) was dissolved in C₆D₆ (0.8 mL). To this solution was added Et₃Al₂Cl₃ (33 mg, 0.13 mmols) and the mixture charged into a Young's NMR tube. The solution was then placed under an atmosphere of C₂D₄ (0.15 mmols) and allowed to react for a 1 h period. The reaction was then analysed using ¹H NMR spectroscopy; no alkene ¹H NMR resonances were detected. The initiator solution was also analysed using GC-MS, which showed that reaction of C₂D₄ had generated C₄ (~23%), C₅ (~6%) and C₆ (~67%) products, which contained exclusively deuterium atoms (verified by the mass spectrum obtained from each fraction).

The procedure outlined above was repeated, but replacing Et₃Al₂Cl₃ by EtMgCl (28 mg, 0.31 mmols). The ensuing reaction was analysed using GC-MS, which identified both C₄ (~90%) and C₆ (~10%) products. Again the mass spectrum of each fraction confirmed that alkenes containing deuterium atoms were formed exclusively in each case.

5.22 Activation of W(NAr)Cl₄·THF (38) for Propylene Dimerization

W(NAr)Cl₄·THF (38) (30 mg, 0.05 mmols) was dissolved in C₆D₆ (0.8 mL). To this solution was added EtAlCl₂ (53 mg, 0.42 mmols). The reaction was then placed under an atmosphere of propylene (0.15 mmols). This resulted in an exothermic reaction converting all of the propylene present to C₆, C₉ and C₁₂ alkenes (verified using GC).¹⁷

The procedure outlined above was repeated, but EtAlCl₂ was replaced with EtMgCl (38 mg, 0.43 mmols). No higher olefins were detected upon analysis of the EtMgCl reaction solution using ¹H NMR, even after the mixture was heated (60°C, 2 h).

5.23 Addition of Ethylene and Propylene to EtAlCl₂

EtAlCl₂ (53 mg, 0.42 mmols) was dissolved in C₆D₆. To this solution was added ethylene (0.15 mmols). The ensuing mixture was analysed using ¹H NMR
spectroscopy, which indicated no reaction had taken place. Identical results were obtained when ethylene was replaced with propylene (0.15 mmols).

5.24 Reaction of WCl₆ with Et₃N and H₂NR (R = Ph or Ar)
WCl₆ (40 mg, 0.10 mmols) was dissolved in chlorobenzene (5.0 mL). To this solution was added Et₃N (41 mg, 40.1 μL, 0.40 mmols) and then H₂NAr (42.7 μL, 0.22 mmols). This mixture was then heated at 60°C for 1 hour. Next, the reaction solution was dried in vacuo, which gave a residue that was analysed using ¹H NMR spectroscopy. The resulting spectra presented multiple resonances, the assignment of which has not been possible. Identical results were obtained when this procedure was repeated replacing H₂NAr for H₂NPh (18.2 μL, 0.19 mmols).

5.25 Reaction of W(NPh)Cl₄·THF (32) with H₂NAr
W(NPh)Cl₄·THF (32) (50 mg, 0.10 mmols) was dissolved in C₆D₆ (0.8 mL) and mixed with H₂NPh (12 mg, 0.12 mg). This solution was analysed using ¹H NMR spectroscopy, which presented multiple broad resonances, the assignment of which has not been possible.

5.26 Reaction of W(NAr)Cl₄·THF (38) with Et₃N and H₂NAr
W(NAr)Cl₄·THF (38) (50 mg, 0.08 mmols) was dissolved in C₆D₆ (0.8 mL) and to this solution was added first NEt₃ (17.7 mg, 0.17 mmols), and then H₂NAr (16 mg, 0.09 mmols). The reaction mixture was then analysed using ¹H NMR spectroscopy, which presented multiple broad resonance, the assignment of which cannot be made.
5.27 Reaction of W(NAr)2Cl2,DME with Me3Al in C6D6: Generation of W(N(Ar)AIMe2(µ-Cl))(NAr)Me2 (67) in situ

\[
\begin{align*}
\text{W(NAr)2Cl2,DME} & \quad \xrightarrow{\text{Me3Al}} \quad \text{Me3Al} \\
(40) & \quad \xrightarrow{\text{Me3Al}} \quad \text{W(N(Ar)AIMe2(µ-Cl))(NAr)Me2 (67)}
\end{align*}
\]

To a solution of W(NAr)2Cl2,DME (40) (50 mg, 0.07 mmol) in C6D6 (0.8 mL) was added Me3Al (64 mg, 0.88 mmol), which resulted in an immediate color change. This solution was analyzed using multinuclear NMR spectroscopy, after which the mixture was heated (60°C, 1 h); this did not result in any additional reaction between 40 and Me3Al. Repetition of this procedure using lower Me3Al loadings (25 mg, 0.34 mmol) gave an identical ¹H NMR spectrum.

Removal of volatile components from the C6D6 solution in vacuo gave a small quantity of a tan brown solid. This material was recrystallized from the minimal amount of hexane (−5°C) to give single crystals of W(N(Ar)AIMe2(µ-Cl))(NAr)Me2 (67) of sufficient quality for X-ray diffraction analysis.

¹H (C6D6, 200 MHz): δ 6.96 (6H, b, Hmeta and Hpara), 3.50 (2H, septet, CH3CH, 3JHH = 6.8 Hz), 2.65 (2H, septet, CH3CH, 3JHH = 6.6 Hz), 1.56 (6H, s, W(CH3)2), 1.17 (6H, d, CH3CH, 3JHH = 6.8 Hz), 1.03 (6H, d, CH3CH, 3JHH = 6.8 Hz), 0.89 (12H, d, CH3CH, 3JHH = 6.6 Hz), 0.15 (6H, s, Al(CH3)2Cl).

¹³C (¹H) (C6D6, 125.6 MHz): δ 151.3 (Cipso), 149.2 (Cortho), 140.8 (Cmeta), 124.8 (Cpara), 71.1 (CH3OCH2), 61.3 (CH3OCH2), 50.9 (W(CH3)2), 29.4 (CH2CH), 28.6 (CH2CH), 26.3 (CH2CH), 24.2 (CH2CH), −6.80 (Al(CH3)3).

Satisfactory elemental analyses of 67 could not be obtained, despite repeated attempts, presumably due to the complex's high sensitivity to air and moisture.

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¹ Large Me3Al loadings were used in this procedure in order to assess if at high Me3Al concentrations any additional reaction between W(N(Ar)AIMe2(µ-Cl))(NAr)Me2 (67) and Me3Al occurs.
5.28 Addition of Ethylene to W(N{Ar}AlMe₂{μ-Cl})(NAr)Me₂ (67)

In a variation to the procedure for the preparation of 67, W(NAr)₂Cl₂.DME (40) (50 mg, 0.07 mmol) was dissolved in C₆D₆ (0.8 mL). Following addition of Me₃Al (25 mg, 0.34 mmols), ¹H NMR spectroscopic analysis confirmed the formation of 67 in situ. The reaction mixture was then placed under an atmosphere of ethylene (0.15 mmols). The presence of ethylene in solution was confirmed by ¹H NMR spectroscopy, and the sample heated (60°C, 1 h). No reaction between ethylene and 67 was observed to occur.

ii) Reaction of W(NAr)₂Cl₂.DME (40) (50 mg, 0.07 mmol) and Me₃Al (25 mg, 0.34 mmols) in C₆D₅Cl (0.8 mL) generated 67 in situ. Addition of ethylene (0.15 mmols) followed by heating (60°C, 1 h), did not result in the occurrence of any observable interaction or reaction between 67 and ethylene (verified using ¹H NMR spectroscopy).

5.29 Synthesis of Mo(N{Ar}AlMe₂{μ-Cl})(NAr)Me₂ (76)

Mo(NAr)₂Cl₂.DME (23) (1.0 g, 1.64 mmols) was dissolved in hexane (30 mL) and a solution of Me₃Al (0.80 g, 11.11 mmols) in hexane (30 mL) was added. This resulted in the immediate formation of a dark brown solution. The reaction was allowed to proceed for 16 hours, after which time the solution was filtered to remove insoluble Me₃Al/DME adducts. The resulting solution was then cooled (-35°C), which led to the formation of a small quantity of brown precipitate (Me₃Al/DME by-product), which was again removed via filtration. Further concentration of the hexane solution
resulted in precipitation of 76 as a yellow solid, which was collected by filtration and recrystallized from hexane; Yield 230 mg (24%):

$^1$H NMR (C$_6$D$_6$, 200 MHz): $\delta$ 6.93 (6H, s, H$_{meta}$ and H$_{para}$), 3.53 (2H, CH$_3$CH, septet $^3$J$_{HH}$ = 6.8 Hz), 2.59 (2H, CH$_3$CH, septet $^3$J$_{HH}$ = 6.6 Hz), 1.64 (6H, s, Mo(CH$_3$)$_2$), 1.17 (6H, d, CH$_3$CH, $^3$J$_{HH}$ = 6.8 Hz), 1.02 (6H, d, CH$_3$CH, $^3$J$_{HH}$ = 6.8 Hz), 0.87 (12H, d, CH$_3$CH, $^3$J$_{HH}$ = 6.6 Hz), −0.09 (6H, s, Al(CH$_3$)$_2$Cl).

$^{13}$C {$^1$H} NMR (C$_6$D$_6$, 125.6 MHz): $\delta$ 154.0 (C$_{ipso}$), 150.0 (C$_{ortho}$), 140.6 (C$_{meta}$), 125.0 (C$_{para}$), 124.9 (C$_o$), 41.5 (Mo(CH$_3$)$_2$), 30.1 (CH$_3$CH), 28.7 (CH$_3$CH), 26.2 (CH$_3$CH), 24.2 (CH$_3$CH), −7.0 (Al(CH$_3$)$_3$).

Anal. Calcd for C$_{28}$H$_{46}$AlClMoN$_2$: C; 59.10, H; 8.15, N; 4.92 Found C; 59.28, H; 8.14, N; 5.10.

5.30 Attempted Reaction of Mo(N(AR)AlMe$_2$($\mu$-Cl))(NAR)Me$_2$(76) with Ethylene

Mo(NAR)$_2$Cl$_2$-DME (50 mg, 0.08 mmols) was dissolved in C$_6$D$_6$ (0.8 mL) and Me$_2$Al (40 mg, 0.55 mmols) was added giving a dark brown solution. $^1$H NMR analysis was consistent with the formation of 76 in situ. The reaction mixture was then placed under an atmosphere of ethylene (0.15 mmols) and then heated (60°C, 1 h). No reaction of ethylene or 76 was observed to take place by $^1$H NMR spectroscopy.

5.31 Reaction of W(N(AR)AlMeCl($\mu$-Cl))(NAR)Me$_2$(77) and Additional Products in situ

W(N(AR)AlMeCl($\mu$-Cl))(NAR)Me$_2$ (77) and Additional Products in situ

W(NAR)$_2$Cl$_2$-DME (40) (30 mg, 0.04 mmols) was dissolved in C$_6$D$_6$ (0.8 mL) and Me$_2$AlCl (31 mg, 0.33 mmols) added. $^1$H NMR spectroscopic analysis indicated the formation of multiple reaction products, the identity of which could not be established. However, it has been possible to assign the $^1$H NMR resonances presented by W(N(AR)AlMeCl($\mu$-Cl))(NAR)Me$_2$ (77) (see below), which was present in the reaction mixture.

$^1$H NMR (C$_6$D$_6$, 400MHz): $\delta$ 6.95 (6H, b, H$_{meta}$ and H$_{para}$), 3.58 (2H, CH$_3$CH, septet $^3$J$_{HH}$ = 6.8 Hz), 2.59 (2H, CH$_3$CH, septet $^3$J$_{HH}$ = 6.8 Hz), 1.60 (6H, s, W(CH$_3$)$_2$), 1.26 (6H, d, CH$_3$CH, $^3$J$_{HH}$ = 6.4 Hz), 1.01 (6H, d, CH$_3$CH, $^3$J$_{HH}$ = 6.8 Hz), 0.87 (12H, d, CH$_3$CH, $^3$J$_{HH}$ = 6.8 Hz), 0.14 and 0.13 (6H, s, Al(CH$_3$)$_2$Cl).
5.32 Activation of $\text{W(NAr)}_2\text{Cl}_2\cdot\text{DME}$ (40) by $\text{MeAlCl}_2$ for Ethylene Dimerization

Addition of ethylene (0.15 mmols) to a solution of $\text{W(NAr)}_2\text{Cl}_2\cdot\text{DME}$ (30 mg, 0.04 mmols) and $\text{Me}_2\text{AlCl}$ (31 mg, 0.33 mmols) resulted in ethylene dimerization, over a 1 h period at room temperature. The identity of the olefin product but-1-ene was confirmed by a COSY $^1\text{H}/^1\text{H}$ correlation experiment. After dimerization, volatile components were removed in vacuo and the sample reanalysed using $^1\text{H}$ NMR spectroscopy. No information as to the connectivity of the active initiator complex could be ascertained from this NMR analysis.

5.33 Reaction of $\text{W(NAr)}_2\text{Cl}_2\cdot\text{DME}$ (40) with $\text{MeAlCl}_2$ in $\text{C}_6\text{D}_6$: Generation of $\text{W(N(Ar)<AlCl}_3\mu-\text{Cl}}\rangle\rangle(\text{NAr})\text{Me}_2$ (78) in situ

$\text{W(NAr)}_2\text{Cl}_2\cdot\text{DME}$ (40) (40 mg 0.05 mmols) was dissolved in $\text{C}_6\text{D}_6$ (0.8 mL). To this solution was added $\text{MeAlCl}_2$ (52 mg, 0.46 mmols) giving a light brown reaction mixture, which was then charged to a recrystallization tube. Over a 16 h period, single crystals of sufficient quality for X-ray diffraction analysis formed. These crystals were then collected, washed with hexane (3×2 mL), and allowed to dry over a 24 h period.

Satisfactory elemental analyses were not obtained due to the high sensitivity of complex 78 to air and moisture. To assess the thermal stability of 78, a $\text{C}_6\text{D}_6$ solution of 78 was heated (1 h, 60°C); no change in the $^1\text{H}$ NMR spectrum was observed.

$^1\text{H}$ NMR ($\text{C}_6\text{D}_6$, 500 MHz): δ 6.95 (6H, b, H$_{meta}$ and H$_{para}$), 3.67 (2H, septet, CH$_3$CH, $^3$J$_{HH}$ = 6.5 Hz), 2.47 (2H, septet, CH$_3$CH, $^3$J$_{HH}$ = 6.5 Hz), 1.57 (6H, s, W(CH$_3$)$_2$), 1.33 (6H, d, CH$_3$CH, 6.5 Hz), 0.98 (6H, d, CH$_3$CH, $^3$J$_{HH}$ = 6.5 Hz), 0.83 (12H, d, CH$_3$CH, $^3$J$_{HH}$ = 6.5 Hz).
\(^{13}\text{C}\) \(^{(1\text{H})}\) NMR \((\text{C}_6\text{D}_6, 125.6 \text{ Hz})\): \(\delta\) 149.0 (C\(_{\text{ppp}}\)), 141.2 (C\(_{\text{ortho}}\)), 129.8 (C\(_{\text{meta}}\)), 125.2 and 124.8 (C\(_{\text{para}}\)), 56.8 (W(CH\(_3\)_2)), 29.6 and 29.2 (CH\(_3\)CH), 26.1 and 24.5 (CH\(_3\)CH).

Repetition of the above procedure, but with the use of a higher MeAlCl\(_2\) (91 mg, 0.81 mmols) loadings, resulted in the formation of multiple complexes, assignment of which was not possible using \(^{1}\text{H}\) NMR spectroscopy.

5.34 Synthesis of Mo(N(Ar)Cl\(_2\)(\(\mu\)-Cl))(NAr)Me\(_2\) (79) from Reaction of MeAlCl\(_2\) and Mo(NAr)_2Cl\(_2\).DME

\[
\text{Mo(NAr)}_2\text{Cl}_2.\text{DME} \xrightarrow{\text{MeAlCl}_2} \text{Mo(NAr)}_2\text{Cl}_2.\text{DME} - \text{Me} \quad \text{(23)}
\]

\(\text{i})\) Mo(NAr)_2Cl_2.DME (23) (400 mg, 0.65 mmols) was dissolved in a minimal amount of toluene (20 mL), before addition of a solution of MeAlCl\(_2\) (1.9 mL, 1.0 M in hexanes, 1.90 mmols). The reaction mixture was allowed to stir (16 h) before being filtered and the volatile components removed \textit{in vacuo}. Recrystallization from CH\(_2\)Cl\(_2\) gave brown micro crystals of complex 79 of sufficient quality for single crystal X-ray diffraction analysis. However, \(^{1}\text{H}\) NMR spectroscopy of the bulk reaction material consistently indicated the formation of multiple reaction products. Furthermore, all attempts to purify the bulk of the material by recrystallization repeatedly failed. Repetition of this procedure using a larger amount of Mo(NAr)_2Cl_2.DME (3.0 g, 4.93 mmols) also failed to produce material of sufficient purity for full micro analysis.

\(\text{ii})\) Addition of solid MeAlCl\(_2\) (30 mg, 0.26 mmols) to a toluene solution (0.8 mL) of Mo(NAr)_2Cl_2.DME (23) (50 mg, 0.08 mmols) resulted in an immediate color change to give a dark brown solution; this solution was then charged to a recrystallization tube. Over a 24 h period several large red crystals of 79 evolved in the tube and were collected \textit{via} filtration and then washed with hexane (3x2 mL). Dissolution of a sample of these crystals in C\(_6\)D\(_6\) allowed 79 to be characterized using \(^{1}\text{H}\) NMR spectroscopy.

\(^{1}\text{H}\) NMR \((\text{C}_6\text{D}_6, 200 \text{ MHz})\): \(\delta\) 6.90 and 6.79 (6H, aromatic), 3.70 (2H, septet, CH\(_3\)CH, \(^3\text{J} = 6.8 \text{ Hz}\)), 2.37 (2H, septet, CH\(_3\)CH, \(^3\text{J} = 6.8 \text{ Hz}\)), 1.67 (6H, s, Mo(CH\(_3\)_2)), 1.33 (6H, d, CH\(_3\)CH, \(^3\text{J} = 6.8 \text{ Hz}\)), 0.98 (6H, d, CH\(_2\)CH, \(^3\text{J} = 7 \text{ Hz}\)), 0.82 (12H, d, CH\(_2\)CH, \(^3\text{J} = 6.6 \text{ Hz}\)).
Heating (1 h, 60°C) a C₆D₆ solution of complex 79 did not alter its ¹H NMR spectrum. However, complex 79 was not sufficiently stable in solution to enable characterization using ¹³C NMR spectroscopy. Attempts to obtain elemental analysis of 79 have also proven unsuccessful on repeated occasions due to the sensitivity of complex 79 to air and moisture.

5.35 Reaction of Mo(NAr)(N^Bu)Cl₂,DME (11) with Me₃Al: Generation of MoN(Ar)AlMe₂(μ-Cl)(N^Bu)Me₂ (80) in situ

Mo(NAr)(N^Bu)Cl₂,DME (11) (75 mg, 0.14 mmols) was dissolved in C₆D₆ (0.8 mL) and to this solution was added Me₃Al (64 mg, 0.88 mmols). The C₆D₆ solution was then analyzed using multinuclear NMR spectroscopy.

¹H (C₆D₆, 500 MHz): δ 6.92 (3H, s, aromatic), 3.45 (2H, septet, CH₃CH₂, ³J_HH = 6.5 Hz), 3.19 (4H, s, CH₃OCH₂), 1.39 (6H, s, Mo(CH₃)₂), 1.19 (12H, b, CH₃CH₂), 0.84 (6H, s, Al(CH₃)₂Cl), −0.42 (45H, s, Al(CH₃)₃).

In a ¹H/¹H NOESY spectrum of the reaction solution revealed a correlation between the CH₃CH₂ resonances and Al(CH₃)₂Cl resonances. This verifies, that in solution, the Me₃AlCl fragment of 80 coordinates at the site of the 2,6-diisopropyl phenyl imido (NAr) ligand.

¹³C {¹H} NMR (C₆D₆, 125.6 MHz): δ 156.0 (Cₚₚₚ), 140.4 (Cₚₚₚₚ), 127.2 (Cₚₚₚₚ), 124.5 (Cₚₚₚₚ), 74.2 (Cₚₚₚₚ), 71.2 (CH₃OCH₂), 61.4 (CH₃OCH₂), 39.3 (Mo(CH₃)₂), 28.6 (C(CH₃)₃), 28.2 (CH₃CH₂), 25.8 (CH₃CH), 25.0 (CH₃CH), 25.0 (CH₃CH), −6.74 (Al(CH₃)₃) and Al(CH₃)₂Cl.)
5.36 Synthesis of MoN{Ar}AlCl₂(μ-Cl)(N'Bu)Me₂ (81)

Mo(NAr)(N'Bu)Cl₂.DME (800 mg, 1.58 mmols) was dissolved toluene (30 mL) and a hexane solution of MeAlCl₂ (4.76 mL, 1M in hexanes, 4.76 mmols) was added. The reaction was allowed to stir for 16 h, after which time the solution was filtered. Concentration of the toluene solution followed by cooling (−5°C) gave an initial crop of yellow micro crystals of complex 81 that were of sufficient quality for X-ray diffraction. After collection of the micro crystals the toluene washings were concentrated in vacuo resulting in further precipitation of complex 81, which was collected via filtration and washed with hexane (3 × 5 mL). This material was then recrystallized from CH₂Cl₂ to give a yellow powder; Yield 330 mg (40%).

¹H NMR (C₆D₆, 500 MHz): δ 6.90 (3H, s, H_meta and H_para), 3.63 (2H, septet, CH₃CH, JHH = 7.0 Hz), 1.38 (6H, s, Mo(CH₃)₂), 1.32 (6H, d, CH₃CH, JHH = 7.0 Hz), 1.11 (6H, d, CH₅CH, J = 7.0 Hz), 0.68 (9H, s, C(CH₃)₃).

¹³C {¹H} NMR (C₆D₆, 125.6 MHz): δ 154.5 (C ipso), 140.9 (C ortho), 128.1 (C meta), 124.9 (C para), 76.3 (C(CH₃)₃), 45.1 (Mo(CH₃)₂), 28.6 (CH₃CH), 28.1 (C(CH₃)₃), 25.7 (CH₃CH), 25.3 (CH₃CH).

Anal. Calcd for C₁₈H₃₅AlCl₃MoN₂: C; 42.66, H; 6.56, N; 5.53. Found: C; 42.87, H; 6.47, N; 5.56.
5.37 Reaction of W(N(Ar)AlMe₂(μ-Cl))(N²Bu)Me₂ (67) with MeAlCl₂: Generation of W(N(Ar)AlMeCl(μ-Cl))(N²Bu)Me₂ (77) in situ

As in Section 5.27, W(NAr)₂Cl₂.DME (40) (30 mg, 0.04 mmols) was reacted with Me₃Al (18 mg, 0.25 mmols) in C₆D₆. Analysis by ¹H NMR spectroscopy confirmed the formation of complex 67 in situ. The C₆D₆ solution was then transferred to a Schlenk before addition of a solution of MeAlCl₂ (0.14 mmols, 1 M in hexanes, 0.14 mL). After a period of 30 minutes volatile components were removed in vacuo giving a light brown solid. This material was analyzed using ¹H NMR spectroscopy; the resulting spectrum presented signals assignable to complex 77 (Section 5.31). The ¹H NMR spectrum also contained resonances attributable to an unknown Me₃AlCl₃.x.DME adduct, a by-product of the reaction of W(NAr)₂Cl₂.DME (40) and Me₃Al. Further reaction of 77 with an additional portion of MeAlCl₂ (0.14 mmols, 1 M in hexanes, 0.14 mL) resulted in the formation of multiple reaction products, the connectivity of which cannot be established by NMR spectroscopic analysis.

5.38 Reaction of Mo(NAr)₂(CH₂C(CH₃)₃)₂ (82) with MeAlCl₂
Mo(NAr)₂(CH₂C(CH₃)₃)₂ (82) (400 mg, 0.67 mmols) was dissolved in hexane (40 mL) and MeAlCl₂ (1.43 mL, 1 M in hexanes, 1.43 mmols) was added, resulting in the immediate formation of a small amount of precipitate. This material was separated by filtration. Concentration of the hexane solution and cooling to (-35°C), gave a dark brown precipitate that was isolated by filtration and analysed using ¹H NMR spectroscopy. The resulting spectra contained multiple, overlapping alkyl resonances, the assignment of which was not possible. Further attempts at separation and purification were unsuccessful.

5.39 Addition of Me₂Al to Mo(NAr)₂(CH₂C(CH₃)₃)₂ (82)
Mo(NAr)₂(CH₂C(CH₃)₃)₂ (82) (400 mg, 0.67 mmols) was dissolved in hexane (40 mL) and a solution of Me₂Al (103 mg, 1.43 mmols) in hexane (20 mL) was added. After 30 mins the mixture was filtered to remove trace precipitates. The filtrate was then concentrated, which resulted in the development of a precipitate that was analysed
using $^1$H NMR spectroscopy. The resulting spectrum was consistent with that of the starting material, complex 82.²

5.40 Attempted Reaction of Mo(NAr)$_2$Me$_2$ (27) with Me$_2$Al

Mo(NAr)$_2$Me$_2$ (27) (47 mg, 0.12 mmols) was dissolved in C$_6$D$_6$ (0.8 mL) and to this solution was added Me$_2$Al (14 mg, 0.19 mmols). Subsequent $^1$H NMR spectroscopic analysis revealed that no reaction had occurred, with only resonances corresponding to each of the starting materials being present.

5.41 Reaction of Mo(NAr)$_2$Me$_2$ (27) with MeAlCl$_2$: Formation of Mo(N(Ar)AlMeCl(μ-Cl))(NAr)Me$_2$ (83) in situ

Mo(NAr)$_2$Me$_2$ (27) (350 mg, 0.71 mmols) was dissolved in the minimal amount of hexane before addition of MeAlCl$_2$ (0.73 mL, 1M in hexanes, 0.73 mmols), which immediately caused an orange precipitate to develop. This solid was collected via filtration and recrystallized from the minimal amount of toluene. It was shown by $^1$H NMR spectroscopy that the desired product Mo(N(Ar)AlMeCl(μ-Cl))(NAr)Me$_2$ (83) was formed, but in conjunction with significant quantities of various impurities. Repeated attempts to remove these impurities by recrystallization proved unsuccessful.

$^1$H (C$_6$D$_6$, 300 MHz): δ 6.92 (6H, b, H$_{meta}$ and H$_{para}$), 3.61 (4H, septet, CH$_3$CH, $^3$J$_{HH}$ = 6.6 Hz), 2.51 (4H, septet, CH$_3$CH, $^3$J$_{HH}$ = 6.6 Hz), 1.69 (6H, s, Mo(CH$_3$)$_2$), 1.24 (6H, d, CH$_2$CH, $^3$J$_{HH}$ = 6.6 Hz), 0.99 (6H, d, CH$_2$CH, $^3$J$_{HH}$ = 6.6 Hz), 0.84 (12H, d, CH$_2$CH, $^3$J$_{HH}$ = 6.6 Hz) -0.017 (3H, s, Al(CH$_3$)$_2$).
5.42 Reaction of Mo(N{Ar}AlMe₂(μ-Cl))(NAr)Me₂ (76) with PMe₃, NEt₃, and HNEt₃Cl

Mo(NAr)₂Cl₂·DME (1 g, 1.64 mmols) was dissolved in CH₂Cl₂ (40 mL) and then Me₃Al (800 mg, 11.10 mmols) diluted in CH₂Cl₂ (20 mL) was added. Next the solution was dried in vacuo, to give a light brown solid. Subsequent ¹H NMR spectroscopic analysis showed that this crude reaction mixture comprised a 1:1 mixture of Mo(N{Ar}AlMe₂(μ-Cl))(NAr)Me₂ (76) and a Me₂AlCl·DME adduct. This 1:1 mixture was then reacted with PMe₃, NEt₃, and HNEt₃Cl in C₆D₆ without further purification, as outlined below.

Reaction of Mo(N{Ar}AlMe₂(μ-Cl))(NAr)Me₂ (76) with PMe₃: A crude sample of 76 (50 mg, 0.06 mmols) was dissolved in C₆D₆ and the solution degassed via freeze-pump-thaw, before the addition of an excess of PMe₃ (0.034 mL, 0.32 mmols) by vac-transfer. The subsequent ¹H and ³¹P NMR spectra were consistent with the data previously reported for the known complex Mo(NAr)₂Me₂·PMe₃.⁴

Reaction of Mo(N{Ar}AlMe₂(μ-Cl))(NAr)Me₂ (76) with NEt₃: A crude sample of 76 (50 mg, 0.06 mmols) was dissolved in C₆D₆. Next, to this solution was added Et₃N (13 mg, 0.12 mmols). Subsequent ¹H NMR spectroscopic analysis was consistent with the formation of the known complex Mo(NAr)₂Me₂ in situ.

Reaction of Mo(N{Ar}AlMe₂(μ-Cl))(NAr)Me₂ (76) with HNEt₃Cl: A crude sample of 76 (50 mg, 0.06 mmols) was dissolved in C₆D₆. Next, to this solution was added HNEt₃Cl (9 mg, 0.06 mmols). Ensuing ¹H NMR spectroscopic analysis indicated the formation of multiple products, assignment of which could not be made.

5.43 Reaction of W(N{Ar}AlMe₂(μ-Cl))(NAr)Me₂ (67) with NEt₃
Complex 67 was formed in situ from reaction of W(NAr)2Cl2.DME (40) (50 mg, 0.07 mmols) with Me2Al (25 mg, 0.34 mmols) in C6D6 (0.8 mL). Next, the reaction mixture was dried in vacuo, giving a tan brown solid. This material was then redissolved in C6D6 (0.8 mL) containing NEt3 (8 mg, 0.08 mmols) and the reaction re-analysed using 1H NMR spectroscopy. The resulting spectrum was consistent with the formation of a W(NAr)2Me2 fragment in situ. The 1H NMR spectrum also contained resonances attributable to aluminium adducts of both DME and Et3N, formed as reaction by-products in this procedure. Only the 1H NMR data for the W(NAr)2Me2 fragment are reported:

1H (C6D6, 400 MHz): δ 7.08 (6H, b, Hpara and Hmeta), 3.62 (4H, septet, CH3CH, 3JHH = 6.8 Hz), 1.24 (6H, s, W(CH3)2), 1.16 (24H, d, CH2CH, 3JHH = 6.8 Hz).

5.44 Reaction of W(NAr)2Cl2.DME (40) with MeMgBr
W(NAr)2Cl2.DME (40) (1.0 g, 1.44 mmols) was dissolved in diethyl ether (40 mL) and the solution then cooled (-35°C) before the drop-wise addition of an MeMgCl solution (1.05 mL, 3M in hexanes, 3.15 mmols) in diethyl ether (20 mL). After 16 h the solution was dried in vacuo giving a light brown precipitate, which was extracted with pentane (3 x 20 mL). Concentration of the pentane solution followed by cooling (-15 °C) gave a crystalline yellow solid, which was collected via filtration. 1H NMR spectroscopic analysis revealed the presence of multiple tungsten-containing complexes, the connectivity of which could not be ascertained.
5.45 Synthesis of W(NAr)₂Me₂·THF (84)

\[ \text{W(NAr)₂Cl₂·DME (40)} \text{ (0.80 g, 1.15 mmols) was dissolved in CH₂Cl₂ (30 mL) and Me₃Al (414 mg, 5.75 mmols) dissolved in CH₂Cl₂ (10 mL) was added. The solution was allowed to stir for approximately five minutes before the volatile components were then removed in vacuo to give a dark brown solid, which was then re-dissolved in hexane (40 mL). To this hexane solution was added THF (0.41 mL, 5.76 mmols) and, after 5 minutes, the mixture was concentrated in vacuo. This resulted in the immediate formation of a yellow precipitate that was collected via filtration and recrystallized from diethyl ether (−15°C), giving light brown crystals of sufficient quality for X-ray diffraction analysis; yield 200 mg (27%).} \]

\[ ^1\text{H (C₆D₆, 400 MHz): } \delta 7.07 (6H, b, H_{meta} and H_{para}), 3.62 (4H, septet, CH₂CH₂, \text{ }^3\text{J}_{HH} = 7.2 \text{ Hz}), 3.57 (4H, m, OCH₂CH₂), 1.39 (4H, m, OCH₂CH₂), 1.25 (6H, s, W(CH₃)₂, \text{ }^2\text{J}_{WH} = 7.6 \text{ Hz}), 1.17 (24H, d, CH₃CH₂, \text{ }^3\text{J}_{HH} = 7.2 \text{ Hz}). \]

\[ ^{13}\text{C} \{^1\text{H} \} (\text{C₆D₆, 175.9 MHz}): \delta 152.8 (C_{ipso}), 143.1 (C_{ortho}), 126.0 (C_{meta}), 123.0 (C_{para}), 68.6 (OCH₂CH₂), 48.6 (W(CH₃)₂), 29.3 (CH₃CH₂), 26.3 (OCH₂CH₂), 23.9 (CH₃CH₂). \]

**Anal. Calcd for C₃₀H₄₈N₂OW:** C; 56.60, H; 7.60, N; 4.40. Found: C; 55.80, H; 7.52 N; 4.70.

W(NAr)₂Me₂·THF (84) has also been analysed by \(^1\text{H NMR spectroscopy (C₆D₆Cl)} at both room temperature (~20°C) and at −40°C. No difference between the two \(^1\text{H NMR spectra are apparent.} \]

On subjecting a solid sample of W(NAr)₂Me₂·THF (84) (20mg, 0.03 mmols) to vacuum for a period of 1 h, removal of the THF moiety of 84 took place (as shown by \(^1\text{H NMR spectroscopy}). This leads to the decomposition of 84, again verified using \(^1\text{H NMR spectroscopy. In contrast, heating a C₆D₆ solution of 84 for 1 h (60°C) did not result in any apparent changes to the \(^1\text{H NMR spectra presented by complex 84.} \]
5.46 Synthesis of W(NAr)$_2$Me$_2$PMe$_3$ from reaction of W(NAr)$_2$Me$_2$.THF (84) and PMe$_3$

A solution of W(NAr)$_2$Me$_2$.THF (40 mg, 0.06 mmols) in C$_6$D$_6$ was degassed via freeze-pump-thaw in a Young's NMR tube, followed by the addition of PMe$_3$ (0.19 mmols) by vacuum transfer. After 20 min, the volatile components were removed in vacuo, giving a light brown solid. Dissolution of this solid in C$_6$D$_6$ (0.8 mL) enabled the product complex W(NAr)$_2$Me$_2$.PMe$_3$ to be characterized using NMR spectroscopy.

$^1$H (C$_6$D$_6$, 700 MHz): $\delta$ 7.12 (4H, d, $H_{\text{eta}}$, $^3J_{HH} = 7.7$ Hz), 7.02 (2H, t, $H_{\text{para}}$, $^3J_{HH} = 7.7$ Hz), 3.88 (4H, septet, CH$_3$CH, $^3J_{HH} = 7.7$ Hz), 1.25 (24H, d, CH$_3$CH, 7.7 Hz), 1.08 (6H, s, W(CH$_3$)$_2$, $^2J_{WH} = 5.2$ Hz), 0.93 (9H, d, P(CH$_3$)$_3$, $^2J_{PH} = 7.7$ Hz).

$^{13}$C $^1$H (C$_6$D$_6$, 175.9 MHz): $\delta$ 154.1 (C$_{\text{ipso}}$), 144.2 (C$_{\text{ortho}}$), 125.1 (C$_{\text{meta}}$), 123.0 (C$_{\text{para}}$), 28.8 (CH$_3$CH), 24.4 (CH$_3$CH), 21.9 (W(CH$_3$)$_2$), 13.4 (P(CH$_3$)$_3$, $^1J_{WP} = 18$ Hz).

$^{31}$P $^1$H (C$_6$D$_6$, 283.2 MHz): $\delta$ -25.03 ppm.

5.47 Reaction of B(C$_6$F$_5$)$_3$ with W(NAr)$_2$Me$_2$.THF (84)

i) W(NAr)$_2$Me$_2$.THF (84) (20 mg, 0.03 mmols) was dissolved in C$_6$D$_6$ (0.8 mL) and B(C$_6$F$_5$)$_3$ (18 mg, 0.03 mmols) added. Later $^1$H NMR (400 MHz, C$_6$D$_6$) analysis of the reaction solution indicated no modification of the signals assigned to the W(NAr)$_2$Me$_2$ fragment. However, a downfield shift of both CH$_2$ resonances of the THF moiety was observed (from 3.57 and 1.39 ppm to 3.21 and 0.91 ppm), suggesting the formation of the adduct THF.B(C$_6$F$_5$)$_3$.\textsuperscript{a}

This procedure was repeated using excess B(C$_6$F$_5$)$_3$ (54 mg, 0.10 mmols). Ensuing $^1$H NMR spectroscopic did not indicate any change in the resonances of the W(NAr)$_2$Me$_2$ fragment within a 16 h period.

\textsuperscript{a} To verify this a sample of B(C$_6$F$_5$)$_3$ (20 mg, 0.039 mmols) was dissolved in THF (5 mL). The mixture was then dried in vacuo to give a solid which was then analyzed using $^1$H NMR spectroscopy (C$_6$D$_6$, 400 MHz). The resulting spectrum consisted of two THF resonances at 3.20 and 0.92 ppm, consistent with the formation of a B(C$_6$F$_5$)$_3$/THF adduct observed to form upon reaction of W(NAr)$_2$Me$_2$.THF (84).
5.48 Reaction of [Ph₃C][B(C₆F₅)₄] with W(NAr)₂Me₂.THF (84)

W(NAr)₂Me₂.THF (84) (20 mg, 0.03 mmols) was dissolved in C₆D₅ (0.8 mL) and to this solution was added [Ph₃C][B(C₆F₅)₄] (29 mg, 0.04 mmols). ¹H NMR spectroscopy revealed that multiple products had formed, unassignable by ¹H NMR.

5.49 Addition of [PhNMe₂H][B(C₆F₅)₄] to W(NAr)₂Me₂.THF (84)

W(NAr)₂Me₂.THF (84) (20 mg, 0.03 mmols) was dissolved in C₆D₅Cl (0.8 mL) and [PhNMe₂H][B(C₆F₅)₄] (127 mg, 0.16 mmols) added. Later ¹H NMR spectroscopic analysis (in a sealed Young’s NMR tube) indicated that no methane formation occurred. In addition, no depletion in the ¹H NMR resonances assigned to the W(NAr)₂Me₂ fragment of 84 was observable, even after heating (1 h, 60°C) the C₆D₅Cl solution.

5.50 Reaction of W(NAr)₂Cl₂.DME (40) with MAO

W(NAr)₂Cl₂.DME (40) (15 mg, 0.02 mmols) was dissolved in C₆D₅Cl (0.8 mL) and solid MAO (267 mg, 3.24 mmols) added. The mixture was then analysed using ¹H NMR spectroscopy, which confirmed the formation of a W(NAr)₂Me₂ fragment in situ. Heating (2 h, 60°C) of the reaction mixture did not result in any apparent changes to the W(NAr)₂Me₂ fragment.

¹H (C₆D₅Cl, 400 MHz): δ 7.07 (6H, b, H₆ meta and H₆ para), 3.21 (4H, b, CH₃CH₂, ¹JHH = 6.8 Hz), 1.16 (6H, s, W-CH₃), 1.07 (24H, d, CH₃CH₂, ¹JHH = 6.8 Hz).

5.51 Reaction of W(NAr)₂Me₂.THF (84) with Ethylene and Propylene

A solution of W(NAr)₂Me₂.THF (84) (20 mg, 0.03 mmols) was prepared in C₆D₆ (0.8 mL), which was then charged into a Young’s NMR tube and placed under an atmosphere of ethylene (0.17 mmols). The reaction solution was immediately then analysed using ¹H NMR spectroscopy, which demonstrated methane evolution had taken place. After a 48 h reaction period but-1-ene (confirmed by a ¹H/¹H NMR COESY correlation) was observable in the ¹H NMR spectrum. This was verified by analysis of the volatile component of the reaction solution using GC.

The same procedure was repeated using propylene (0.17 mmols) instead of ethylene. Addition of propylene to 84 generated multiple and unassignable products (verified using ¹H NMR spectroscopy) and methane. However, re-analysis of the reaction solution after a 48 h period indicated that the excess propylene was not
consumed. Furthermore, no higher olefins were detected using $^1$H NMR spectroscopy.

5.52 Reaction of Mo(NAr)$_2$Me$_2$ (27) and Mo(NAr)$_2$(CH$_2$C(CH$_3$)$_3$)$_2$ (82) with Ethylene

Mo(NAr)$_2$Me$_2$ (27) (20 mg, 0.04 mmols) was dissolved in C$_6$D$_6$ (0.8 mL) and this solution charged into a Young's NMR tube. The sample was then placed under an atmosphere of ethylene (0.11 mmols) and the reaction mixture analysed by $^1$H NMR spectroscopy. The resulting spectrum contained multiple, overlapping and unassignable resonances. After a 48 h period the sample was re-analyzed using $^1$H NMR; no resonances assignable to higher olefins were detected.

This procedure was repeated with ethylene (0.17 mmols) added to a C$_6$D$_6$ solution of Mo(NAr)$_2$(CH$_2$C(CH$_3$)$_3$)$_2$ (82) (20 mg, 0.03 mmols). $^1$H NMR spectroscopy showed that no reaction of Mo(NAr)$_2$(CH$_2$C(CH$_3$)$_3$)$_2$ (82) occurred.

5.53 Reaction of W(NAr)$_2$Me$_2$.THF (84) with C$_2$D$_4$ and C$_2$H$_4$

A C$_6$D$_6$ solution of W(NAr)$_2$Me$_2$.THF (84) (20 mg, 0.03 mmols) was charged to a Young’s NMR tube. The solution was then frozen (liquid N$_2$) and to the sample was added equal quantities of C$_2$D$_4$ and then C$_2$H$_4$ (0.17 mmols). Next, the solution was warmed to room temperature and left for 48 h. At this point higher olefins were detected using $^1$H NMR spectroscopy. This was verified by analysis of the volatile components of the reaction solution by GC and GC-MS, which highlighted the presence of C$_4$ olefin products. Ion recognition software, supplied by Agilent Technologies was used to identify isotopomers, C$_4$H$_8$, C$_4$H$_7$D, C$_4$H$_6$D$_2$, C$_4$H$_5$D$_3$, C$_4$H$_4$D$_4$, C$_4$H$_3$D$_5$, C$_4$H$_2$D$_6$ and C$_4$HD$_7$, the ions of which were present in the mass-spectrum of the but-1-ene fraction.

5.54 Addition of HSiMe$_2$Bu to Discrete Imido Complexes

HSiMe$_2$Bu (14 mg, 0.12 mmols) was mixed with a solution of W(NAr)$_2$Cl$_2$.DME (40) (40 mg, 0.06 mmols) in C$_6$D$_6$. This mixture was then analyzed using $^1$H NMR spectroscopy. No reaction was observed, even after heating (1 h, 60°C).

A variation of this experimental procedure was used to study the reactivity of HSiMe$_2$Bu with the complexes Mo(NAr)$_2$Cl$_2$.DME (23), W(NPh)Cl$_4$.THF (32), W(NAr)Cl$_4$.THF (38), W(NPh)(Cl)$_2$(PMe$_3$)$_3$ (34), Mo(NAr)$_2$(NH$_2$Bu)$_2$ (55), and Mo(N' Bu)$_2$Cl$_2$.PPh$_3$ (60). In no case was reaction observed to have taken place ($^1$H NMR spectroscopy), even after heating (1 h, 60°C).
5.55 Reaction of W(NAr)_2Cl_2.DME (40) with NaBH_4

To a solution of W(NAr)_2Cl_2.DME (40) (60 mg, 0.08 mmols) in C_6D_6 (0.8 mL) was added NaBH_4 (7 mg, 0.19 mmols). Subsequent ^1H NMR spectroscopic analysis did indicate reaction of W(NAr)_2Cl_2.DME (40) occurred. However, the nature of the reaction products could not be ascertained and no resonances were detected that could be assigned to a W-H moiety.iii

5.56 Addition of NaBH_4 to W(NAr)Cl_4.THF (38) and W(NPh)(Cl)_2(PMe_3)_3 (34)

i) NaBH_4 (11 mg, 0.29 mmols) was added to a solution of W(NAr)Cl_4.THF (38) (40 mg, 0.07 mmols) in C_6D_6. Ensuing ^1H NMR spectroscopic analysis indicated no reaction occurred, even after both sonication and heating (1 h, 60°C).

This procedure was repeated to study the reactivity of W(NPh)(Cl)_2(PMe_3)_3 (34) (40 mg, 0.07 mmols) and NaBH_4 (24 mg, 0.65 mmols). No reaction of 32 was detected.

ii) To a solution of W(NAr)Cl_4.THF (38) (40 mg, 0.070 mmols) in THF (15 mL) was added NaBH_4 (11 mg, 0.30 mmols). The solution was stirred for 30 min, before being dried in vacuo giving a green solid, which was found to be unreacted W(NAr)Cl_4.THF (38) according to ^1H NMR spectroscopy. This procedure was repeated using W(NPh)(Cl)_2(PMe_3)_3 (34) (40 mg, 0.07 mmols) and NaBH_4 (24 mg, 0.648 mmols). No reaction of 34 occurred (verified using ^1H NMR spectroscopy).

5.57 Reaction of W(NPh)Cl_4.THF (38) with Me_3Al

\[
\text{W(NPh)Cl}_4\text{.THF (38)} \xrightarrow{\text{Me}_3\text{Al}} \text{W(NPh)(Cl)Me}_3\text{.THF (96)}
\]

W(NPh)Cl_4.THF (30 mg, 0.06 mmols) was dissolved in C_6D_6 (0.8 mL) and Me_3Al (27 mg, 0.37 mmols) was added; the reaction mixture was then analysed using both ^1H and ^13C NMR spectroscopy. These analyses showed that 96 was fully converted to the known complex W(NPh)(Cl)Me_3 (96).¹⁹ Next, the reaction solution was heated (60°C, 1 h); this did not result in any change to 96 (verified by ^1H NMR spectroscopy).

NaBH_4 shows an appreciable solubility in C_6D_6, with a quartet being observed by ^1H NMR spectroscopy at 0.85 ppm (400 MHz, C_6D_6).
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The procedure outlined above was repeated using CD₂Cl₂ (0.8 mL) as a reaction solvent. Later ¹H NMR spectroscopic analysis was again consistent with the formation of W(NPh)(Cl)Me₃ (96) in full conversion.

5.58 Reactions of W(NAr)Cl₄ (62) and W(NAr)Cl₄·THF (38) with Me₃Al in C₆D₆

\[
\begin{align*}
\text{W(NAr)Cl₄} & \quad \text{Me₃Al} \quad \text{C₆D₆} \quad \text{W(NAr)(Cl)Me₃} \\
(62) & \quad (97)
\end{align*}
\]

W(NAr)Cl₄ (62) (25 mg, 0.05 mmols) was dissolved in C₆D₆ (0.8 mL) and mixed with Me₃Al (21 mg, 0.29 mmols). Analysis of the resulting solution by both ¹H and ¹³C NMR spectroscopy was consistent with full conversion of 62 to W(NAr)(Cl)Me₃ (97).

¹H (C₆D₆, 500 MHz): δ 7.03 (2H, d, H₉₆, ³J₉₆ = 8.0 Hz), 6.95 (1H, t, H₉₈ = 8.0 Hz), 3.38 (2H, septet, CH₃CH, ³J₉₆ = 6.8 Hz), 1.38 (6H, s, WCH₉ = 6.4 Hz), 1.04 (12H, d, CH₃CH, ³J₉₆ = 6.8 Hz).

¹³C {¹H} (C₆D₆, 125.6 MHz): δ 150.9 (C₉₆), 147.6 (C₉₈), 123.7 (C₉₈), 57.1 (W(CH₃)₂ ³J₉₆ = 309 Hz), 29.3 (CH₃CH), 24.8 (CH₃CH). No resonance assignable to the C₉₈ were detected.

The procedure outlined above was repeated replacing W(NAr)Cl₄ (62) with W(NAr)Cl₄·THF (38) (28 mg, 0.05 mmols). Complex 97 was again obtained in full conversion, presenting identical ¹H and ¹³C NMR chemical shifts to that reported above.

5.59 Synthesis of W(NPh)(Cl)Me₃ (96) via Reaction of Me₃Al

W(NPh)Cl₄·THF (38) (260 mg, 0.53 mmols) was dissolved in CH₂Cl₂ (20 mL) and Me₃Al (80mg, 1.11 mmols) dissolved in CH₂Cl₂ (15 mL) was added. The reaction was allowed to stir for 20 minutes and then the volatile components were removed in vacuo, giving a light brown solid. This material was then extracted with ether (3 x 20 mL) and the ether washings were collected and concentrated. This gave a solution that yielded, upon cooling (~5°C), golden needle-shaped crystals of complex 96 of sufficient quality for single crystal X-ray diffraction analysis; Yield 150 mg (65%).

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A sample of 96 prepared by the above methodology was dissolved in C₆D₆; both the ¹H and ¹³C NMR spectroscopic data were consistent with those reported previously by Schrock et al.

¹H (C₆D₆, 200 MHz): δ 6.96 (5H, multiplet, Hₘ₀₆, H₀₉₀, H₀₄₀), 1.28 (9H, s, W(CH₃)₃, ²Jₙₜ = 7.2 Hz).

¹³C {¹H} (C₆D₆, 400 MHz): δ 156.3 (Cₚ₃₉₀), 128.5 (C₀₉₀), 126.9 (Cₚ₃₀), 124.7 (C₀₉₀), 56.9 (W(CH₃)₃).

5.60 Synthesis of W(NAr)(Cl)Me₃ (97) via Reaction of Me₃Al with W(NAr)Cl₄ (62)

W(NAr)Cl₄ (62) (400 mg, 0.80 mmols) was dissolved in CH₂Cl₂ (30 mL) and a solution of Me₃Al (69 mg, 0.96 mmols) in CH₂Cl₂ (10 mL) added. After 15 mins the solution was filtered and the volatile components removed in vacuo giving W(NAr)(Cl)Me₃ (97), which was isolated as a red-orange solid; yield 262 mg, (75 %). The ¹H and ¹³C NMR chemical shifts presented by a sample of 97 prepared by this methodology were identical to those reported for 97 in Section 5.58.

Anal. Calcd for C₁₅H₂₆ClNW: C; 40.98, H; 5.96, N; 3.19. Found: C; 40.70, H; 5.80, N; 3.25.

5.61 Synthesis of Complex (97) via Reaction of W(NAr)Cl₄·THF (38) and Me₃Al

W(NAr)Cl₄·THF (38) (400 mg, 0.70 mmols) was dissolved in CH₂Cl₂ (20 mL) and a solution of Me₃Al (101 mg, 1.40 mmols) dissolved in CH₂Cl₂ (10 mL) added. After 15 minutes the volatile components of the reaction were removed in vacuo, affording a dark brown solid, which was extracted with hexane (3 x 20 mL). The hexane washings were then collected and dried in vacuo giving a sample of W(NAr)(Cl)Me₃ (97) of sufficient purity for further reaction; yield (214 mg, 70%). The ¹H and ¹³C NMR chemical shifts presented by a sample of 97 prepared by this methodology were identical to those reported for 97 in Section 5.58.

5.62 Reaction of Ta(NAr)Cl₃(TMEDA) (59) with Me₃Al

Ta(NAr)Cl₃(TMEDA) (59) (50mg, 0.11 mmols) was dissolved in C₆D₆ (0.8 mL) and then mixed with Me₃Al (12 mg, 0.17 mmols). Multiple, unassignable signals were observed by ¹H NMR spectroscopy; no resonance could clearly be assigned as being that of a Ta-(CH₃) moiety.
5.63 Reaction of W(NPh)(Cl)Me$_3$ (96) with LiMe

Complex (96) (50 mg, 0.14 mmols) was dissolved in C$_6$D$_6$ and then mixed with solid LiMe (8 mg, 0.36 mmols). Subsequent $^1$H NMR spectroscopic analysis revealed the quantitative formation of W(NPh)Me$_4$ (99). Furthermore, complex 99 was observed to decay over a 16 h period (verified by $^1$H NMR spectroscopy). However, it has been possible to assign the $^1$H NMR chemical shifts of W(NPh)(Cl)Me$_3$ (96):

$^1$H (C$_6$D$_6$, 200 MHz): $\delta$ 7.02 (5H, b, H$_{ortho}$, H$_{meta}$ and H$_{para}$), 1.33 (12H, s, W(CH$_3$)$_4$).

5.64 Reaction of W(NPh)(Cl)Me$_3$ (96) with Me$_3$SiOS(O)$_2$CF$_3$: Generation of W(NPh)Me$_3$(OSO$_2$CF$_3$) (100)

W(NPh)(Cl)Me$_3$ (100) (30 mg, 0.08 mmols) was dissolved in C$_6$D$_6$ and mixed with Me$_3$SiOS(O)$_2$CF$_3$ (30 mg, 0.13 mmols). After 4 h, the solution was analysed by $^1$H and $^{13}$C NMR spectroscopy, which revealed complete conversion of 96 to complex 100. The new complex 100 was characterised spectroscopically:

$^1$H (C$_6$D$_6$, 500 MHz): $\delta$ 6.97 (2H, t, H$_{meta}$, $^3$J$_{HH}$ = 8.0 Hz), 6.88 (1H, t, H$_{para}$, $^3$J$_{HH}$ = 8.0 Hz), 6.83 (2H, d, H$_{ortho}$, $^3$J$_{HH}$ = 8.0 Hz), 1.17 (9H, s, W(CH$_3$)$_3$, $^2$J$_{HH}$ = 6.8 Hz).

$^{13}$C {$^1$H} (C$_6$D$_6$, 125.5 Hz): $\delta$ 129.5 (C$_{ipso}$), 129.4 (C$_{ortho}$), 127.4 (C$_{para}$), 57.2 (W(CH$_3$)$_3$, $^{1}$J$_{WC}$ = 87.8 Hz), 54.0 (CF$_3$).

Next, the reaction solution was placed under an atmosphere of ethylene (0.11 mmols). No reaction of 100 occurred and no higher olefins were detected using $^1$H NMR spectroscopy.

5.65 Reaction of W(NPh)(Cl)Me$_3$ (96) with [Na][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] in MeCN

W(NPh)(Cl)Me$_3$ (75mg, 0.21 mmols) (96) was dissolved in MeCN (20 mL) and [Na][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (188 mg, 0.21 mmols) added; the resulting mixture was stirred for 2 h. During this period a yellow precipitate developed which was collected via filtration and dried in vacuo. The insolubility of this solid in D$_3$CCN, CD$_2$Cl$_2$, and C$_6$D$_3$Cl precluded characterization using NMR spectroscopy.
5.66 Reaction of W(NAr)(Cl)Me$_3$ (97) with [Li(OEt)$_2$][B(C$_6$F$_5$)$_4$]

W(NAr)(Cl)Me$_3$ (97) (30 mg, 0.07 mmols) was dissolved in C$_6$D$_5$Cl (0.8 mL) and to this solution was added [Li(OEt)$_2$][B(C$_6$F$_5$)$_4$] (72 mg, 0.08 mmols). The reaction was then heated (16 h, 60°C) and the solution re-analyzed using $^1$H NMR spectroscopy (400 MHz). The resulting spectra contained a new singlet at 1.04 ppm with $^2$J$_{WH}$ satellites ($^2$J$_{WH} = 6.8$ Hz) and a new doublet at 0.99 ppm ($^4$J$_{HH} = 6.8$ Hz). These resonances have been assigned to the W(CH$_3$)$_3$ and 'Pr moieties of [W(NAr)Me$_3$][B(C$_6$F$_5$)$_4$] (102) which was formed in 30% conversion.

$^1$H NMR (C$_6$D$_5$Cl, 400 MHz): δ 3.17 (2H, septet, CH$_3$CH, $^3$J$_{HH} = 7.0$ Hz), 1.04 (6H, s, W-CH$_3$), 0.99 (12H, d, CH$_3$CH, $^3$J$_{HH} = 7.0$ Hz).

$^{13}$C ($^1$H) NMR (C$_6$D$_5$Cl, 125.5 MHz): δ 62.7 Hz (W-CH$_3$), 29.6 (CH$_3$CH), 24.5 (CH$_3$CH).

The $^{13}$C and $^1$H NMR resonances of the phenyl ring of complex 102 could not be assigned, as these were obscured by the related resonances of the starting material. Similarly the $^{13}$C resonances of the B(C$_6$F$_5$)$_4^-$ anion of 102 were also obscured.

5.67 Reaction of W(NAr)(Cl)Me$_3$ (97) with [Na][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]

W(NAr)(Cl)Me$_3$ (97) (30 mg, 0.07 mmols) was dissolved in CD$_2$Cl$_2$ (0.8 mL) and to this solution was added [Na][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (146 mg, 0.16 mmols). After 5 h the mixture was analysed using $^1$H NMR spectroscopy (400 MHz). The resulting spectra contained a new singlet at 1.86 ppm with $^2$J$_{WH}$ satellites ($^2$J$_{WH} = 6.8$ Hz) and a new doublet at 1.24 ppm ($^4$J$_{HH} = 6.8$ Hz). These resonances have been assigned to the W(CH$_3$)$_3$ and 'Pr moieties of [W(NAr)Me$_3$][B(C$_6$H$_3$-m-(CF$_3$)$_2$)$_4$] (103) which was formed in 30% conversion after 5 h. Heating of the reaction solution (2h, 60°C) did not induce further formation of 103.

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): δ 1.89 (6H, s, W-CH$_3$, $^2$J$_{WH} = 6.8$ Hz), 1.24 (12H, CH$_3$CH, d, $^3$J$_{HH} = 6.8$ Hz). The H$_{meta}$, H$_{para}$ and CH$_3$CH ('Pr) resonances of 103 were obscured by those of the starting complex 97.

Attempts to obtain meaningful $^{13}$C NMR data for complex 103 failed. This was hampered by the low concentration of 103 in solution.
5.68 Reaction of W(NPh)(Cl)Me₃ (96) with [Na][B(3,5-(CF₃)₂-C₆H₃)₄]

W(NPh)(Cl)Me₃ (96) (20 mg, 0.05 mmols) was dissolved in C₆D₅Cl (0.8 mL) and to this solution was added [Na][B(3,5-(CF₃)₂-C₆H₃)₄] (49 mg, 0.05 mmols). The mixture was analyzed using ¹H NMR spectroscopy (400 MHz), with the resulting spectrum containing a new singlet at 1.16 ppm. This has been assigned to the W-Me moieties of the product [W(NAr)Me₃][B(3,5-(CF₃)₂-C₆H₃)₄] (103). Integration of the spectrum is consistent with 40% of 96 converting to 103. The 3:2 reaction mixture of 96 and 103 was re-analyzed after a 2 h reaction period, at which point it was apparent that 103 had decomposed.

¹H NMR (C₆D₅Cl, 400 MHz): 1.16 (6H, s, W-CH₃, ²J_WH = 6.8 Hz). The Hortho, Hmeta and Hpara resonances of 103 were obscured by those of the starting complex.

5.69 Synthesis and Characterization of [W(NPh)(Cl)Me₃,AlC₃] (104)

W(NPh)(Cl)Me₃ (96) (75 mg, 0.21 mmols) was dissolved in CH₂Cl₂ (10 mL) and MeAlCl₂ (1.05 mL, 1M in hexanes, 1.05 mmols) added. After 15 minutes, the volatile components were removed in vacuo, generating a brown residue, which was dissolved in C₆D₆ (0.8 mL). Subsequent analysis of this solution by ¹H and ¹³C NMR spectroscopy are consistent with the formation of the product [W(NPh)(Cl)Me₃,AlCl₃] (104).

¹H NMR (C₆D₆, 500 MHz): 7.03 (2H, m, Hortho), 6.98 (1H, m, Hpara), 6.84 (2H, m, Hmeta). 1.35 (9H, s, W(CH₃)₃).

¹³C (¹H) (C₆D₆, 125.6 MHz): 152.9 (Cipso), 131.1 (Cortho), 129.7 (Cmeta), 127.2 (Cpara), 65.0 (W(CH₃)₃, ¹J_WC = 87.8 Hz).

The procedure outlined above was repeated replacing C₆D₆ with CD₂Cl₂ (0.8 mL). This has enabled the ²⁷Al and ¹H NMR spectrum of 104 to be measured in CD₂Cl₂.

²⁷Al (CD₂Cl₂, 130.2 MHz, ~ 20°C): 102.6, 99.5 and 93.6.
²⁷Al (CD₂Cl₂, 130.2 MHz, ~ 80°C): 94.3 (γ₁/₂ = 6.5 MHz).

iv An identical ¹H NMR chemical shift is found for the W-(CH₃) moieties of W(NPh)Me₃(OSO₂(CF₃)) (100).
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The $^1$H NMR spectrum of 104 acquired at $-80^\circ$C was consistent with that obtained at ambient temperature.


W(NAr)(Cl)Me$_3$ (97) (75 mg, 0.17 mmols) was dissolved in CH$_2$Cl$_2$ (10 mL) and to this solution was added MeAlCl$_2$ (0.85 mL, 1 M in hexanes, 0.85 mmols). After 15 minutes volatile components were removed in vacuo giving a dark brown residue, which was dissolved in C$_6$D$_6$ (0.8 mL). Subsequent analysis of this solution by $^1$H and $^{13}$C NMR spectroscopy revealed the product to be [W(NAr)(Cl)Me$_3$.AlCl$_3$] (105).

$^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta$ 6.91 (3H, s, $H_{meta}$ and $H_{para}$), 3.16 (2H, septet, CH$_3$CH, $^3J_{HH} = 6.5$ Hz), 1.46 (6H, s, W(CH$_3$)$_3$), 0.97 (12H, d, CH$_3$CH, $^3J_{HH} = 6.5$ Hz).

$^{13}$C ($^1$H) NMR (C$_6$D$_6$, 125.5 MHz): $\delta$ 150.4 (C$_{ipso}$), 131.1 (C$_{ortho}$), 124.1 (C$_{para}$), 67.0 (W(CH$_3$)$_3$), 29.6 (CH$_3$CH), 24.5 (CH$_3$CH). No resonances assignable to the C$_{mota}$ were detected.

The procedure outlined above was repeated replacing C$_6$D$_6$ with CD$_2$Cl$_2$ (0.8 mL), enabling the $^{27}$Al NMR spectrum of 105 to be determined in CD$_2$Cl$_2$.

$^{27}$Al (CD$_2$Cl$_2$, 130.2 MHz): $\delta$ 102.8, 99.9 and 93.5.

$^{27}$Al (CD$_2$Cl$_2$, 130.2 MHz, $-80^\circ$C): $\delta$ 95.0 ($^\gamma_{1/2} = 6.5$ MHz).

The $^1$H NMR spectrum of 105 acquired at $-80^\circ$C was consistent with that obtained at ambient temperature.

5.71 Characterization of [AlCl$_4$][P(N$\text{Pr}^2$)$_2$] (107) using $^{27}$Al NMR Spectroscopy

The known salt [AlCl$_4$][P(N$\text{Pr}^2$)$_2$] (107) (50 mg, 0.12 mmols) was dissolved in CD$_2$Cl$_2$ (0.8 mL) and analysed by $^{27}$Al NMR spectroscopy.

$^{27}$Al (CD$_2$Cl$_2$, 130.2 MHz): $\delta$ 102.0 ($^\gamma_{1/2} = 455$ Hz)

5.72 Reaction of W(NPh)(Cl)Me$_3$ (96) with MeAlCl$_2$ in C$_6$D$_6$

W(NPh)(Cl)Me$_3$ (96) (20 mg, 0.05 mmols) was dissolved in C$_6$D$_6$ (0.8 mL) and to this solution was added MeAlCl$_2$ (7 mg, 0.06 mmols). The mixture was then analyzed using $^1$H NMR spectroscopy. This procedure was repeated using varying amounts of
The amount of MeAlCl₂ used in a given reaction and the resulting Al-CH₃ ¹H NMR chemical shifts are reported in Table 5.1.

<table>
<thead>
<tr>
<th>Amount of MeAlCl₂</th>
<th>δ ¹H (ppm) Al-CH₃</th>
</tr>
</thead>
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<tr>
<td>7 mg, 0.06 mmols</td>
<td>0.23</td>
</tr>
<tr>
<td>26 mg, 0.23 mmols</td>
<td>-0.05 and -0.42</td>
</tr>
<tr>
<td>51 mg, 0.45 mmols</td>
<td>-0.30 and -0.43</td>
</tr>
<tr>
<td>102 mg, 0.91 mmols</td>
<td>-0.38</td>
</tr>
</tbody>
</table>

a) For all solutions a single W-CH₃ ¹H NMR resonance was detected at 1.32 ppm. b) All ¹H NMR spectra were acquired using a 400 MHz instrument. c) All solutions were prepared using C₆D₆ (0.8 mL).

To establish the ¹H NMR spectrum of MeAlCl₂ in C₆D₆, MeAlCl₂ (102 mg, 0.91 mmols) was dissolved in C₆D₆ (0.8 mL). This solution presented a single ¹H NMR resonance at 0.42 ppm.

5.7.2.1 Reaction of W(NPh)(Cl)Me₃ (96) with MeAlCl₂ in C₆D₆ at Low Dilutions

W(NPh)(Cl)Me₃ (96) (4 mg, 0.01 mmols) was dissolved in C₆D₆ (0.8 mL) and MeAlCl₂ (6 mg, 0.05 mmols) was added. The resulting mixture was analysed using ¹H NMR spectroscopy (400 MHz), with the ensuing ¹H NMR chemical shifts consistent with only the presence of unreacted 96 and MeAlCl₂.

5.7.2.2 Dilution of a W(NPh)(Cl)Me₃/MeAlCl₂ Reaction Solution

W(NPh)(Cl)Me₃ (96) (20 mg, 0.05 mmols) was dissolved in C₆D₆ (0.8 mL) and to this solution was added MeAlCl₂ (26 mg, 0.23 mmols). The resulting mixture was analysed using ¹H NMR spectroscopy. A single W-CH₃ ¹H resonance was detected at 1.32 ppm along with two Al-Me resonances, which were detected at -0.05 and -0.42 ppm. Next, a 0.1 mL aliquot of the reaction solution was diluted in C₆D₆ (5.2 mL). A sample of this newly diluted solution was then charged to a Young’s NMR tube and the mixture was again analyzed using ¹H NMR spectroscopy. The resulting spectra contained exclusively resonances assignable to 96 and free MeAlCl₂.
5.73 Catalytic Ethylene Dimerization Testing using W(NR)Cl₄·THF (R = Ph, Ar) and Me₃Al

W(NPh)Cl₄·THF (32) (75 mg, 0.15 mmols) was dissolved in CD₂Cl₂ (0.8 mL) and mixed with Me₃Al (55 mg, 0.76 mmols). Analysis of the reaction mixture using ¹H NMR spectroscopy was consistent with W(NPh)(Cl)Me₃ (96) having been formed in situ with full conversion. The reaction solution was then placed under an atmosphere of ethylene (0.15 mmols) and the mixture heated (60°C, 1 h) prior to analysis by ¹H NMR spectroscopy. The resulting spectra presented signals assignable to both methane and but-1-ene in a 1:1 ratio. Addition of a second portion of ethylene (0.15 mmols), followed by additional heating (60°C, 2 h), resulted in further but-1-ene formation.

This procedure outlined above was repeated replacing complex 38 by W(NAr)Cl₄·THF (38) (50 mg, 0.09 mmols). After heating, both but-1-ene and methane were observed using ¹H NMR spectroscopy in a 1:1 ratio. Reaction of either 32 or 38 with Me₃Al and then ethylene in C₆D₆ (0.8 mL) did not result in the production of any higher olefins.

5.73.1 Addition of Ethylene to Me₃Al

Me₃Al (55 mg, 0.76 mmols) was dissolved in CD₂Cl₂ (0.8 mL) in a Young’s NMR tube and placed under an atmosphere of ethylene (0.15 mmols). The solution was heated (2 h, 60°C) and then analysed using ¹H NMR spectroscopy; no reaction between ethylene and Me₃Al was observed to have occurred.

5.73.2 Addition of Ethylene to W(NPh)(Cl)Me₃ (96)

W(NPh)(Cl)Me₃ (96) (25 mg, 0.07 mmols) was diluted in CD₂Cl₂ (0.8 mL). This solution was charged into a young’s NMR tube and placed under an atmosphere of ethylene (0.15 mmols). The sample was then heated (2 h, 60°C) and then analyzed using ¹H NMR spectroscopy; no reaction between complex 96 and ethylene had occurred.

5.73.3 Analysis of Me₃Al in CD₂Cl₂

Me₃Al (55 mg, 0.76 mmols) was dissolved in CD₂Cl₂ (0.8 mL) and the solution heated (2 h, 60°C). Subsequent analysis using ¹H NMR spectroscopy showed that no reaction of Me₃Al had occurred, with a single resonance detected at 0.42 ppm, which is assignable to free Me₃Al.
5.74 Reaction of W(NAr)Cl₄·THF (38), Me₃Al and C₂D₄

W(NAr)Cl₄·THF (38) (30 mg, 0.05 mmols) was dissolved in CD₂Cl₂ (0.8 mL) and Me₃Al (20 mg, 0.27 mmols) was added. The mixture was then charged to a Young’s NMR tube, placed under an atmosphere of C₂D₄ (0.15 mmols) and heated (2 h, 60°C). Subsequent analysis using ¹H NMR spectroscopy (500 MHz) revealed a singlet at 0.23 ppm resulting from methane formation and a triplet at 0.21 ppm, which can be assigned to CH₃D (2J_DH = 2.0 Hz).

The C₂D₄ reaction solution was analyzed using GC-MS. Peaks were detected with retention times of 3.62, 3.91 and 4.48. The MS of these fractions contained signals with an m/z of 62 (C₄D₇⁺). Furthermore a peak was detected at 5.49 mins, the MS of this fraction had an m/z of 79 (C₅D₉⁺). The relative GC counts of each peak indicate that the C₄ and C₅ products were produced in the molar ratio of 16:1.

5.75 Activation of W(NPh)(Cl)Me₃ (96) for Ethylene Dimerization using Me₃Al

W(NPh)(Cl)Me₃ (96) (20 mg, 0.05 mmols) was dissolved in CD₂Cl₂ (0.8 mL) and to this solution was added Me₃Al (17 mg, 0.24 mmols). The mixture was placed under an atmosphere of ethylene (0.15 mmols) and then heated (2 h, 60°C). Subsequent ¹H NMR spectroscopic and GC analysis of this reaction solution confirmed the formation of but-1-ene.¹³,¹⁶

The above procedure was repeated, but CD₂Cl₂ was replaced with C₆D₆ (0.8 mL). No higher olefins were detected using ¹H NMR spectroscopy and the ethylene added was not consumed.

5.76 Activation of W(NPh)(Cl)Me₃ (96) for Ethylene Dimerization using Me₂AlCl or MeAlCl₂

W(NPh)(Cl)Me₃ (96) (20 mg, 0.05 mmols) was dissolved in C₆D₆ (0.8 mL) and to this solution was added Me₂AlCl (26 mg, 0.23 mmols). The mixture was placed under an atmosphere of ethylene (0.15 mmols) and analyzed using ¹H NMR spectroscopy. This analysis indicated that complete conversion of ethylene to but-1-ene occurred over a 2 h period.¹³

The above procedure was repeated but MeAlCl₂ was replaced with Me₂AlCl (21 mg, 0.23 mmols). Again ethylene dimerization had occurred at room temperature giving but-1-ene.
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5.77 Using MeAlCl₂ to activate W(NPh)Cl₄·THF (32) for Ethylene Dimerization

W(NPh)Cl₄·THF (32) (30 mg, 0.05 mmols) was dissolved in C₆D₆ and to this solution was added MeAlCl₂ (24 mg, 0.21 mmols). The mixture was then analyzed using ¹H NMR spectroscopy (200 MHz). A single W-CH₃ resonance was detected at 1.34 ppm consistent with the formation of [W(NPh)(Cl)Me₃·AlCl₃] (104). Ethylene (0.15 mmols) was added to the solution, which was converted to but-1-ene over a 2 h period.

5.78 References

12. An authentic sample of ethane in C₆D₆ presented a single ¹H NMR resonance at 0.79 ppm.
13. An authentic sample of but-1-ene was analyzed using ¹H NMR spectroscopy. ¹H NMR (CD₂Cl₂, 500 MHz): δ 5.88 (1H, multiplet, CH₂CH), 5.02 (1H, d, cisCH₂, ³JHH = 13 Hz), 4.93 (1H, doublet, transCH₂, ³JHH = 10 Hz), 2.07 (2H, quartet,
CH$_2$CHCH$_2$CH$_3$, $^3$J$_{HH} = 7.0$ Hz), 1.01 (2H, t, CH$_2$CHCH$_2$CH$_3$, $^3$J$_{HH} = 7.0$ Hz).

Similar $^1$H NMR resonances were detected when but-1-ene was analyzed in C$_6$D$_6$.

The fragmentation pattern obtained here experimentally was identical to that found for an authentic sample of 2,3-dimethyl but-1-ene.

GC analysis of a range of authentic samples of C$_4$-, C$_6$-, C$_8$- alkenes established the retention times associated with each type of alkene. It was found that C$_4$ alkenes had a retention time of between 2.96 and 3.03 mins. Conversely the retention times associated with C$_6$-alkenes were between 4.08 and 5.37 mins and C$_8$-alkenes were detected between 10.38 and 10.33 mins. This knowledge was used to established the product distribution obtained in the EtAlCl$_2$/W(NAr)Cl$_4$.THF (38) ethylene dimerization/oligomerization system outlined in Section 5.18.

Identification of but-1-ene was possible using GC as a peak was detected with a retention time of 2.96 minutes. This is the same retention time found for an authentic sample of but-1-ene analyzed using the same conditions.

This assignment was enabled by the knowledge that authentic samples of hex-1-ene, Non-1-ene and Dodec-1-ene have established retention times of 5.59, 13.52 and 18.86 mins.

A $^1$H NMR spectrum of an authentic sample of methane gives rise to a singlet resonance at 0.30 ppm.

Chapter 6: Further Work

6.1 Hex-1-ene Dimerization

Notably, there has been a recent interest in using WCl₆-based systems for the dimerization of higher olefins such as hex-1-ene. As such, repeating the comparative ethylene dimerization study outlined in Chapter 2, Section 2.2 using hex-1-ene instead of ethylene is of interest. Furthermore, the use of hex-1-ene for dimerization studies has the advantage of not requiring high pressure reaction vessels. Ideally a range of bis and mono(imido) pre-catalysts would be activated using EtAlCl₂ and subsequently screened (Scheme 6.1).

Scheme 6.1 Potential hex-1-ene dimerization investigation

\[
\begin{align*}
W(\text{NAr})_2\text{Cl}_2, \text{DME} & \quad (40) \\
W(\text{NAr})\text{Cl}_4, \text{THF} & \quad (38)
\end{align*}
\]

The complexes Mo(\text{NAr})_2\text{Cl}_2, \text{DME} (23), Mo(\text{NAr})_2(\text{NH'Bu})_2 (56), W(\text{NPh})(\text{Cl})\text{Me}_3 (96) and W(\text{NPh})\text{Cl}_4, \text{THF} (32) could also be used as pre-catalysts, with emphasis placed on comparing the different TOF and selectivity obtained from each pre-catalyst. This would establish whether or not similar active initiator complexes were forming in each system.

6.2 Further Ethylene Dimerization Studies

In Chapter 4, Section 4.8.2, a range of ethylene dimerization systems were described based upon the reaction of W(\text{NPh})(\text{Cl})\text{Me}_3 (96) with MeAlCl₂, Me₂AlCl and Me₃Al. Notably, these studies were conducted at low ethylene pressures (~1 bar) in C₆D₆. It would be of interest to conduct similar investigations using higher ethylene pressures (40 bars) and the same reaction conditions to those employed in the comparative ethylene dimerization system outlined in Chapter 2, Section 2. Furthermore, the relative capacities of MeAlCl₂ or EtAlCl₂ to activate complex 96 for ethylene dimerization could be examined. This could provide further clarification as to the role of β-hydride elimination reactions in initiator formation.
6.3 Potential DFT Calculations

6.3.1 Examining the Reaction of $\text{M(NAr)}_2\text{Me}_2$ ($\text{M} = \text{Mo or W}$) Complexes With Ethylene

This thesis has revealed a number of cases in which theoretical studies could enhance understanding of a given reaction pathway. For instance, it is unclear as to why reaction of $\text{W(NAr)}_2\text{Me}_2.\text{THF}$ (84) with ethylene results in but-1-ene formation, while reaction of $\text{Mo(NAr)}_2\text{Me}_2$ (27) using similar procedures does not. This discrepancy could potentially be rationalized by a DFT investigation. Of particular interest is determining the relative capacity of ethylene to coordinate to a $\text{M(NAr)}_2\text{Me}_2$ ($\text{M} = \text{Mo or W}$) fragment. Also of curiosity would be the relative energy penalties associated with ethylene inserting into the $\text{M-Me}$ ($\text{M} = \text{W or Mo}$) bonds. It is hoped that quantifying these key parameters could give an indication as to the relative favourability of initiator formation in each system.

6.3.2 Examining the $\text{W(NAr)}_2\text{Me}_2.\text{THF}$ (84) $\text{C}_2\text{D}_4/\text{C}_2\text{H}_4$ Reaction

Another situation in which DFT calculations could be helpful lies in the reaction of $\text{W(NAr)}_2\text{Me}_2.\text{THF}$ (84) with $\text{C}_2\text{D}_4$ and $\text{C}_2\text{H}_4$ (Chapter 3, Section 3.10). Following reaction of complex 84, olefins containing odd numbers of deuterium atoms, such as $\text{C}_4\text{H}_7\text{D}$ were produced. Such products can only result from transfer of a deuterium atom to a molecule of $\text{C}_2\text{H}_4$ or $\text{C}_4\text{H}_8$ via insertion of the alkene into the $\text{W-D}$ bond. As $\text{W-D}$ or $\text{W-H}$ intermediates could be present in either a hydride or a metallacycle mechanism, disappointingly this reaction could not be used to draw firm conclusions regarding the mechanism of the $\text{W(NAr)}_2\text{Me}_2.\text{THF}$ (84) ethylene dimerization system.

Of interest would be assessing the viability of an ethylene moiety inserting into the $\text{W-H}$ bond of an intermediate originating from a tungsten metallacycle, using a theoretical approach. It may be that such a species preferentially undergoes rapid reductive elimination, to give but-1-ene (Scheme 6.2). If this was indeed the case, then a metallacycle mechanism would not be compatible with the formation of products such as $\text{C}_4\text{H}_7\text{D}$, as the hydride moiety would not be “available” for ethylene insertion. Alternatively, the hydride intermediate may be sufficiently stable to allow insertion of ethylene into the $\text{W-H}$ bond (Scheme 6.2). If such insertions were possible, then a metallacycle mechanism would be compatible with the observed transfer of $\text{W-D}$ or $\text{W-H}$ atoms in the $\text{C}_2\text{D}_4/\text{C}_2\text{H}_4$ reaction. Thus, calculating the kinetic and thermodynamic parameters associated with the migratory insertion and/or reductive elimination pathways outlined in Scheme 6.2, could allow assessment as
to the viability of a metallacycle mechanism operating in the \( \text{W(NAr)}_2\text{Me}_2\text{.THF} \) (84) ethylene dimerization system.

Scheme 6.2 Possible reactions of a tungsten hydride species with ethylene

![Scheme 6.2](image)

6.3.3 Examining the Solution Structure of \([\text{W(NR)}(\text{Cl})\text{Me}_3\text{.AlCl}_3]\) \(R = \text{Ph or Ar}\) Adducts

In Chapter 4, Section 4.7 the adducts \([\text{W(NPh)}(\text{Cl})\text{Me}_3\text{.AlCl}_3]\) (104) and \([\text{W(NAr)}(\text{Cl})\text{Me}_3\text{.AlCl}_3]\) (105) were characterized using \(^{27}\text{Al}\) NMR spectroscopy. This strongly indicated that both 105 and 104 partly dissociated in solution to give an \(\text{AlCl}_4^-\) anion. Of interest would be to use theoretical calculations to determine the thermodynamic parameters associated with this dissociation. This would provide further clarification as to the stability of a \([\text{W(NPh)}\text{Me}_3]^+\) cation. This is of particular interest as it is believed that coordination of ethylene to a \([\text{W(NPh)}\text{Me}_3]^+\) fragment is the prerequisite step for the formation of the active initiator complexes in the \(\text{W(NPh)}(\text{Cl})\text{Me}_3/\text{Me}_x\text{.AlCl}_{3-x}\) ethylene dimerization systems outlined in Chapter 4, Section 4.8.2.

6.4 References

Appendix 1 – Crystallographic data

All collections were conducted using graphite-monochromated Mo-Kα radiation (\(\lambda = 0.71073\) Å) on a Bruker Smart 1K or a 6K CCD area diffractometer at 120K. Cell parameters were determined and refined using SMART\(^1\) software and raw frame data were integrated using SAINT\(^2\) programs. Structures were refined using SHELXL-97.\(^3\)

Parameters from X-Ray Diffraction Experiments

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<th>Complex</th>
<th>Mo(NAr)(_2)(NH(_3)Bu)(_2) (55)</th>
<th>W(NAr)(_2)Cl(_2).DME (40)</th>
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<td>C(<em>{56})H(</em>{88})N(_4)W(_2)Cl(_4)O(_4)</td>
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<td>Volume/Å(^3)</td>
<td>6724(1)</td>
<td>3049.5(7)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>(\rho_{\text{calc}})/mg/mm(^3)</td>
<td>1.167</td>
<td>1.515</td>
</tr>
<tr>
<td>m/mm(^3)</td>
<td>0.414</td>
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<tr>
<td>F(000)</td>
<td>2528</td>
<td>1400</td>
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<tr>
<td>Crystal size</td>
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<td>0.35 × 0.30 × 0.20</td>
</tr>
<tr>
<td>Theta range for data collection</td>
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<td>1.59 to 30.00°</td>
</tr>
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<td>Index ranges</td>
<td>-14 ≤ h ≤ 14, -14 ≤ s ≤ 14</td>
<td>-14 ≤ h ≤ 14, -22 ≤ k ≤ 22</td>
</tr>
<tr>
<td>Reflections collected</td>
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<td>43557</td>
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<td>Independent reflections</td>
<td>8928</td>
<td>17064</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>8928/0/370</td>
<td>17064/0/671</td>
</tr>
<tr>
<td>Goodness-of-fit on F(^2)</td>
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<td>1.056</td>
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<tr>
<td>Final R indexes [I&gt;2σ (I)]</td>
<td>R(<em>1) = 0.0334, R(</em>{all}) = 0.0197</td>
<td>wR(<em>2) = 0.0750, wR(</em>{2}) = 0.0432</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
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<tr>
<td>Largest diff. peak/hole</td>
<td>0.456/-0.768</td>
<td>0.990/-0.478</td>
</tr>
</tbody>
</table>


\(^3\) SHELX – G.M. Sheldrick, Acta Crysta., 2008, A64, 112.
<table>
<thead>
<tr>
<th>Complex</th>
<th>W(N{Ar}.AlMe$_2${µ-Cl})(NAr)Me$_2$</th>
<th>W(N{Ar}.AlCl$_2${µ-Cl})(NAr)Me$_2$</th>
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<tbody>
<tr>
<td>(67)</td>
<td>C$<em>{28}$H$</em>{46}$N$_2$WCIA</td>
<td>C$<em>{44}$H$</em>{40}$D$_18$N$_2$WAICl$_3$</td>
</tr>
<tr>
<td>(78)</td>
<td></td>
<td></td>
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<tr>
<td>Empirical formula</td>
<td>C$<em>{28}$H$</em>{46}$N$_2$WCIA</td>
<td>C$<em>{44}$H$</em>{40}$D$_18$N$_2$WAICl$_3$</td>
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<td>120(2)</td>
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<td>Crystal system</td>
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<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2$_1$/n</td>
<td>P-1</td>
</tr>
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<td>11.691(2)</td>
<td>11.534(1)</td>
</tr>
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<td>b/Å</td>
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<td>14.342(2)</td>
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<tr>
<td>β/°</td>
<td>92.64(1)</td>
<td>92.80(1)</td>
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<td>γ/°</td>
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<td>1956.4(3)</td>
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<td>$\rho_{calc}$/g/mm$^3$</td>
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<td>-15 ≤ h ≤ 15</td>
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</tr>
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<td></td>
<td>-24 ≤ k ≤ 23</td>
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<td></td>
<td>-19 ≤ l ≤ 18</td>
<td>-21 ≤ l ≤ 21</td>
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<td>Reflections collected</td>
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<td>27232</td>
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<td>Independent reflections</td>
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<td>11397</td>
</tr>
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<td>[R(int) = 0.0282]</td>
<td></td>
<td>[R(int) = 0.0462]</td>
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<td>Data/restraints/parameters</td>
<td>8025/0/362</td>
<td>11397/28/432</td>
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<td>Goodness-of-fit on $F^2$</td>
<td>1.055</td>
<td>1.030</td>
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<td>Final R indexes</td>
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<td>$[I&gt;2\sigma(I)]$</td>
<td>$wR_2 = 0.0363$</td>
<td>$wR_2 = 0.0451$</td>
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<td>$R_1 = 0.0228$</td>
<td>$R_1 = 0.0232$</td>
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<td>$wR_2 = 0.0380$</td>
<td>$wR_2 = 0.0461$</td>
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<td>Largest diff. peak/hole</td>
<td>0.934/-0.464</td>
<td>1.455/-0.568</td>
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205
<table>
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<th>Complex</th>
<th>Mo(N(Ar).AlCl$_2$(μ-Cl))(NAr)Me$_2$ (79)</th>
<th>Mo(N(Ar)AlMe$_2$(μ-Cl))(N'Bu)Me$_2$ (81)</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{108}$H$</em>{165}$N$_8$Mo$<em>4$Cl$</em>{20}$Al$_4$</td>
<td>C$<em>{18}$H$</em>{32}$N$_2$MoCl$_3$Al</td>
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<td>Formula weight</td>
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<td>505.73</td>
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<td>125(2)</td>
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<td>Crystal system</td>
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<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P$_2_1$/n</td>
<td>P$_2_1$/c</td>
</tr>
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<td>a/Å</td>
<td>16.424(2)</td>
<td>9.046(1)</td>
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<td>b/Å</td>
<td>19.713(2)</td>
<td>16.393(18)</td>
</tr>
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<td>c/Å</td>
<td>39.485(4)</td>
<td>16.6047(19)</td>
</tr>
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<td>α/°</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>β/°</td>
<td>97.22(1)</td>
<td>101.757(10)</td>
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<td>γ/°</td>
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<td>90.00</td>
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<td>2410.8(5)</td>
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<td>4</td>
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<td>1.04 to 25.01°</td>
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<tr>
<td>Index ranges</td>
<td>-18 ≤ h ≤ 19</td>
<td>-12 ≤ h ≤ 12</td>
</tr>
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<td></td>
<td>-16 ≤ k ≤ 23</td>
<td>-22 ≤ k ≤ 22</td>
</tr>
<tr>
<td></td>
<td>-46 ≤ l ≤ 44</td>
<td>-22 ≤ l ≤ 22</td>
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<td>Reflections collected</td>
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<td>28594</td>
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<td>Independent reflections</td>
<td>22279[R(int) = 0.1405]</td>
<td>6418 [R(int) = 0.0351]</td>
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<td>Data/restraints/parameters</td>
<td>22279/0/1255</td>
<td>6418/0/244</td>
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<td>Goodness-of-fit on $F^2$</td>
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<td>$wR_2 = 0.0612$</td>
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<td>Final R indexes [all data]</td>
<td>$R_1 = 0.1634$</td>
<td>$R_1 = 0.0337$</td>
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<td>$wR_2 = 0.1313$</td>
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<td>0.733/-0.679</td>
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<td>Complex</td>
<td>W(NAr)$_2$Me$_2$.THF (84)</td>
<td>W(NPh)(Cl)Me$_3$ (96)</td>
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<tr>
<td>---------</td>
<td>--------------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C$<em>{90}$H$</em>{144}$N$_6$W$_3$O$_3$</td>
<td>C$<em>{90}$H$</em>{108}$NWCl</td>
</tr>
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<td>Formula weight</td>
<td>636.55</td>
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<td>Temperature</td>
<td>120(2)</td>
<td>120(2)</td>
</tr>
<tr>
<td>Crystal system</td>
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<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2$_1$/c</td>
<td>P2$_{1}$/m</td>
</tr>
<tr>
<td>a/Å</td>
<td>19.506(2)</td>
<td>6.3483(10)</td>
</tr>
<tr>
<td>b/Å</td>
<td>16.994(2)</td>
<td>7.2804(11)</td>
</tr>
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<td>c/Å</td>
<td>26.404(3)</td>
<td>11.9671(18)</td>
</tr>
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<td>α/°</td>
<td>90.00</td>
<td>90.00</td>
</tr>
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<td>β/°</td>
<td>95.20(2)</td>
<td>93.60(18)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>Volume/Å$^3$</td>
<td>8716.4(18)</td>
<td>552.00(15)</td>
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<td>Z</td>
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<td>$\rho_{calc}$mg/mm$^3$</td>
<td>1.455</td>
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<td>m/mm$^3$</td>
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<td>10.656</td>
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<tr>
<td>F(000)</td>
<td>3888</td>
<td>332</td>
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<td>Crystal size</td>
<td>0.26 x 0.23 x 0.15</td>
<td>0.28 x 0.27 x 0.14</td>
</tr>
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<td>Theta range for data collection</td>
<td>1.05 to 30.03°</td>
<td>1.71 to 29.01°</td>
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<td>Index ranges</td>
<td>-27 ≤ h ≤ 27</td>
<td>-8 ≤ h ≤ 8</td>
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<td>-23 ≤ k ≤ 23</td>
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<tr>
<td></td>
<td>-36 ≤ l ≤ 37</td>
<td>-16 ≤ l ≤ 16</td>
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<td>Reflections collected</td>
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</tr>
<tr>
<td>Independent reflections</td>
<td>25037</td>
<td>1561</td>
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<td>[R(int) = 0.0456]</td>
<td>[R(int) = 0.0236]</td>
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</tr>
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<td>Data/restraints/parameters</td>
<td>25037/0/979</td>
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<td>Final R indexes</td>
<td>$R_l = 0.0447$</td>
<td>$R_l = 0.0141$</td>
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<td>[I &gt; 2σ (I)]</td>
<td>$wR_2 = 0.1032$</td>
<td>$wR_2 = 0.0339$</td>
</tr>
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<td>Final R indexes [all data]</td>
<td>$R_l = 0.0721$</td>
<td>$R_l = 0.0145$</td>
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<td>$wR_2 = 0.1189$</td>
<td>$wR_2 = 0.0341$</td>
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<tr>
<td>Largest diff. peak/hole</td>
<td>3.876/-3.908</td>
<td>0.739/-0.883</td>
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</table>

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Appendix 2 – Postgraduate First Year Modules

All first year postgraduates are required to pass a compulsory module in their first year.

Functional Materials – 56% (pass).

Appendix 3 – Chemistry Colloquia Attended at Durham University Chemistry

Prof. RH Grubbs, Caltech, Tuesday 20 June 2006.
"The Design and Synthesis of new Selective Olefin Metathesis Catalysts"

Dr. Simon Aldridge, Dept of Chem, Cardiff University, Monday 17 July 2006.
"Transition Metal - Group 13 Element Multiple Bonds"

Dr Patrick Toy, University of Hong Kong, Monday 4 September 2006.
"Multipolymer Reactions and Organocatalytic Mitsunobu Reactions"

Prof. Odile Eisenstein, University of Montpellier, Wednesday 15 November 2006. "Simple Ideas for d(0) Olefin Metathesis Catalyst Design from a DFT Perspective"

Dr Michael Whittlesey, Department of Chemistry, University of Bath, Wednesday 14 February 2007. "N-Heterocyclic Carbenes: Far From Inert Ligands"

Prof. Keith Pannell, University of Texas at El Paso, USA, Tuesday 24 April 2007. "Recent Advances in the Transition Metal Organometallic Chemistry of Tin, Germanium and Silicon"

Prof. Guy Bertrand, Joint Research Laboratory, University of California, Riverside, USA, Wednesday 30 May 2007. "New Families of Stable Cyclic Carbenes for the Preparation of Low Ligated Transition Metals, and Highly Active Catalysts. Can a Carbene do the Job of a Metal?"

Ian Manners, School of Chemistry, University of Bristol, Wednesday 30 May 2007. "Functional Metallized Supramolecular Materials via Block Copolymer Self-assembly and Living Supramolecular Polymerisations"
Prof. CNR Rao, Friday 22 June 2007. "Materials at the Liquid-liquid Interface"

Prof. Régis Réau, Université de Rennes 1, France, Friday 3 August 2007. "Organophosphorus pi-Conjugated Systems: From Model Molecules to Functional Materials"

Prof. Malcolm Chisholm, Ohio State University, USA, Wednesday 31 October 2007. "Linking MM Quadruple Bonds (M = Mo or W) with Organic p-Systems: Studies of Mixed Valency and M2d-p Conjugation"

Dr. Richard Layfield, University of Manchester, Wednesday 14 November 2007. "Organometallic Chemistry with Manganese(II): a Transition Metal Masquerading as a Main Group Element"

Prof. Kalman Szabo, Stockholm University, Sweden, Wednesday 5 December 2007. "One-Pot Transformations Involving Catalytic Generation of Allyl Boronates"

Prof. T. Don Tilley, University of California, Berkeley, USA, Friday 9 May 2008. "New Bond Activations at Transition Metal Centres: Fundamental Studies and Applications to Catalysis"

Prof. Penny Brothers, University of Auckland, New Zealand, Friday 9 May 2008. "Diboron Porphyrins and Corroles: Unexpected Chemistry for Both Boron and the Ligands"

Appendix 4 – External Inorganic Conferences Attended and Presentations Given

- **September 2007** – Catalysis Summer School, Liverpool University, poster presentation.
- **May 2008** – Postgraduate Symposium, University of Durham, oral presentation (25 minutes).
- **July 2008** – Final Year Postgraduate Symposium on "Catalysis enabled synthetic methodology for pharmaceuticals and fine chemicals," oral presentation (20 minutes).
- **July 2008** – International Conference on Organometallic Chemistry, poster presentation.
- **September 2008** – Universities of Scotland Inorganic Chemistry Conference, oral presentation (20 minutes).
Appendix 5 – Numbering Scheme for Key Complexes Referred to in the Text

**Key pre-cursor complexes**

<table>
<thead>
<tr>
<th>Mo(NAr)(N'Bu)Cl₂.DME (11)</th>
<th>Mo(NAr)₂Cl₂.DME (23)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(N'Bu)₂Cl₂.DME (26)</td>
<td>Mo(NAr)₂Me₂ (27)</td>
</tr>
<tr>
<td>W(NPh)Cl₄.THФ (32)</td>
<td>W(NPh)(Cl)₂(PMe₃)₃ (34)</td>
</tr>
<tr>
<td>W(NAr)Cl₄.THФ (38)</td>
<td>W(NAr)₂Cl₂.DME (40)</td>
</tr>
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**Synthesised bis(imido) complexes**

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<th>(76)</th>
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<td>(84)</td>
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### Synthesised *mono*(imido) complexes

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<th>$\text{W(NPh)(Cl)Me}_3$ (96)</th>
<th>$\text{W(NAr)(Cl)Me}_3$ (97)</th>
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<tr>
<td>$[\text{W(NAr)Me}_3][\text{B(3,5-}(\text{CF}_3)_2\text{C}_6\text{H}_3)]$ (101)</td>
<td>$[\text{W(NAr)Me}_3][\text{B(}\text{C}_6\text{F}_5)]$ (102)</td>
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<tr>
<td>$[\text{W(NPh)(Cl)Me}_3\text{AlCl}_3]$ (104)</td>
<td>$[\text{W(NAr)Cl}3\text{AlCl}_3]$ (105)</td>
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<tr>
<td>$[\text{W(NPh)(Cl)Me}_3\text{AlMeCl}_2]$ (106)</td>
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