Half-Sandwich Imido into related complexes of niobium and tantulum - relative of the zirconocene family

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Half-Sandwich Imido and Related Complexes of Niobium and Tantalum - Relatives of the Zirconocene Family.

by

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A thesis submitted in part fulfillment of the requirements for the degree of

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October 1992.

Statement of Copyright

Declaration

The work described in this thesis was carried out in the Department of Chemistry at the University of Durham between October 1989 and September 1992. All the work is my own, unless stated to the contrary, and it has not been submitted previously for a degree at this or any other University.

For Elizabeth.

Acknowledgements

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Abstract

Half-Sandwich Imido and Related Complexes of Niobium and Tantalum - Relatives of the Zirconocene Family.

This thesis describes studies directed towards the preparation of half-sandwich niobium and tantalum compounds containing imido and phosphino-carbene ligands, with particular emphasis on the relationship of such species with bent metallocene complexes of the Group 4 triad.

Chapter 1 highlights areas of transition metal chemistry of relevance to the general theme of this thesis, including reviews of metal imido and zirconocene chemistry.

Chapter 2 describes the use of silylated anilines for convenient solution syntheses of half-sandwich imido complexes of niobium and tantalum of the type $Cp'M(N\text{-}2,6\text{-}{}^{i}Pr_2\text{-}C_6H_3)Cl_2$ ($Cp' = Cp, Cp^*$). In addition, the syntheses and reactivities of mono- and bis-alkyl derivatives (methyl, neopentyl, and benzyl) are presented. The bis-neopentyl complexes $CpNb(NR)(CH_2CMe_3)_2$ ($R = CMe_3$; $2,6\text{-}{}^{i}Pr_2\text{-}C_6H_3$), reveal multiple α-agostic interactions which have been primarily studied *via* an X-ray crystal structure determination and NMR spectroscopy. Thermolysis of $Cp^*Nb(N\text{-}2,6\text{-}{}^{i}Pr_2\text{-}C_6H_3)(CH_2Ph)_2$ in the presence of PMe_3 affords the benzylidene complex $Cp^*Nb(N\text{-}2,6\text{-}{}^{i}Pr_2\text{-}C_6H_3)(\eta^1\text{-}CHPh)(PMe_3)$ whose X-ray crystal structure has been determined.

Chapter 3 describes the preparation of the niobium and tantalum imido complexes $Cp'M(N\text{-}2,6\text{-}{}^{i}Pr_2\text{-}C_6H_3)(L)(PMe_3)$ ($M = Nb$, $L = C_2H_4$, C_3H_6, CO, Me_2C_2, Ph_2C_2, C_6H_4, PMe_3; $M = Ta$, $L = C_2H_4$, C_3H_6, CO). Single crystal structure determinations on $CpNb(N\text{-}2,6\text{-}{}^{i}Pr_2\text{-}C_6H_3)(\eta^2\text{-}C_3H_6)(PMe_3)$ and $CpNb(N\text{-}2,6\text{-}{}^{i}Pr_2\text{-}C_6H_3)(\eta^2\text{-}C_6H_4)(PMe_3)$ have been undertaken and their relationship to Group 4 metallocenes noted. Treatment of $Cp^*Ta(N\text{-}2,6\text{-}{}^{i}Pr_2\text{-}C_6H_3)(L)(PMe_3)$ ($L = C_2H_4$, C_3H_6) with α-olefins was found to lead to displacement of PMe_3 and the generation of tantallacycle containing species.

Chapter 4 compares the reactivity of tantalum imido and phosphino-carbene derivatives of the form $Cp^*Ta(E)(H)(X)(PMe_3)$ ($E = N\text{-}2,6\text{-}{}^{i}Pr_2\text{-}C_6H_3$, $\eta^2\text{-}CHPMe_2$; $X = H, I$) with a number of α-olefins. Investigations into the mechanism of catalytic oligomerisation of α-olefins by $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)$ reveal that pathways involving metallacycle intermediates are most probable, whereas $Cp^*Ta(N\text{-}2,6\text{-}{}^{i}Pr_2\text{-}C_6H_3)(H)_2(PMe_3)$ reacts with α-olefins to afford stable tantallacycle complexes. The reactivity of the dihydrido species has been moderated by the preparation of mono-iodide derivatives and their reactivity towards α-olefins studied. $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)(I)(PMe_3)$ dimerises ethylene selectively to but-1-ene, while $Cp^*Ta(N\text{-}2,6\text{-}{}^{i}Pr_2\text{-}C_6H_3)(H)(I)(PMe_3)$ reacts with ethylene to form the stable ethyl species $Cp^*Ta(N\text{-}2,6\text{-}{}^{i}Pr_2\text{-}C_6H_3)(Et)(I)$. Furthermore, studies investigating a variety of niobium and tantalum imido species as possible catalysts for the oligomerisation and polymerisation of α-olefins under industrially relevant conditions have been undertaken in collaboration with B.P. Chemicals Ltd..

Chapter 5 gives experimental details for chapter 2-4.

Andrew David Poole (October 1992)

Abbreviations

L	General 2-electron donor ligand
X	General 1-electron donor ligand
R	General alkyl ligand
Cp	Cyclopentadienyl (C_5H_5)
Cp*	Pentamethylcyclopentadienyl (C_5Me_5)
Cp'	Generalised (C_5R_5) ligand
DEPT	Distortionless Enhancement by Polarisation Transfer
DMAP	4-Dimethylaminopyridine
G. C.	Gas Chromatography
HETCOR	Heteronuclear Correlation
IR	Infrared
LUMO	Lowest Unoccupied Molecular Orbital
NAr	2,6-diisopropylphenylimido
NBS	N-Bromo-succinimide
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect
py	Pyridine
THF	Tetrahydrofuran

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CHAPTER ONE

Transition Metal-Imido Bonds: the Relationship Between Group 5 Half-Sandwich Imido and Group 4 Metallocene Complexes.

1.1 Introduction.

This thesis is concerned primarily with the chemistry of mononuclear complexes in which nitrogen is multiply bonded to transition metals of the Group 5 triad, specifically those containing a cyclopentadienyl ligand.

In general, transition metal-nitrogen multiply bonded species play a crucial role in many chemical processes, acting as homogeneous and heterogeneous catalysts for a variety of important industrial and biochemical reactions.

Recent years have witnessed much renewed interest in the chemistry of cyclopentadienyl metal oxo and imido species due to the stabilizing and solubilizing properties of the cyclopentadienyl ligand. There is also considerable interest presently in the isolobal relationship between cyclopentadienyl (Cp) and imido (NR) moeities. This allows the possible development of half-sandwich imido complexes of Group 5 which should exhibit zirconocene-like reactivity.

Thus, in chapters 2 and 3, a convenient synthetic entry into a range of half-sandwich imido derivatives of the heavier Group 5 metals is exploited. Alkyl and olefin derivatives have been prepared and characterised and strategies for the development of synthetically useful species based on the well-established chemistry of Group 4 metallocenes have been investigated.

Chapter 4 describes the synthesis and characterisation of a number of hydrido half-sandwich tantalum imido compounds. A comparison between these and compounds of the type $Cp^{*}Ta(\eta^{2}\text{-}CHPMe_2)(PMe_3)HX$ (X = H, I), containing the unusual phosphino-carbene ligand (η^{2}-$CHPMe_2$), especially with regard to their reactivity towards α-olefins is addressed. Furthermore, this chapter describes the investigation of a number of half-sandwich imido species of niobium and tantalum as possible catalysts for the oligomerisation and polymerisation of α-olefins under industrially relevant conditions.

The remainder of this chapter is devoted to a review of metal imido chemistry and its possible relationship to the reactivity of zirconocene complexes.

The first section (1.2 - 1.6) discusses the general occurrence, structure and uses of transition metal imido compounds particularly those containing cyclopentadienyl and/or Group 5 metals. Since most of the imido compounds discussed in this thesis are of low nuclearity, the following review is primarily restricted to mononuclear species. The middle section (1.7) outlines the isolobal relationship between η^5-cyclopentadienyl and imido moeities, while the final section (1.8 - 1.9) details several important aspects of zirconocene chemistry which provide possible target areas for the development of the derivative chemistry of the half-sandwich imido system.

1.2 Imido Complexes.

1.2.1 Bonding Modes.

Five different bonding modes for the imido moiety have been established[1]. These are shown in Figure 1.1, but this discussion will be restricted to terminally bonded arrangements (1 and 2) since these are the bonding modes relevant to the compounds described within this thesis.

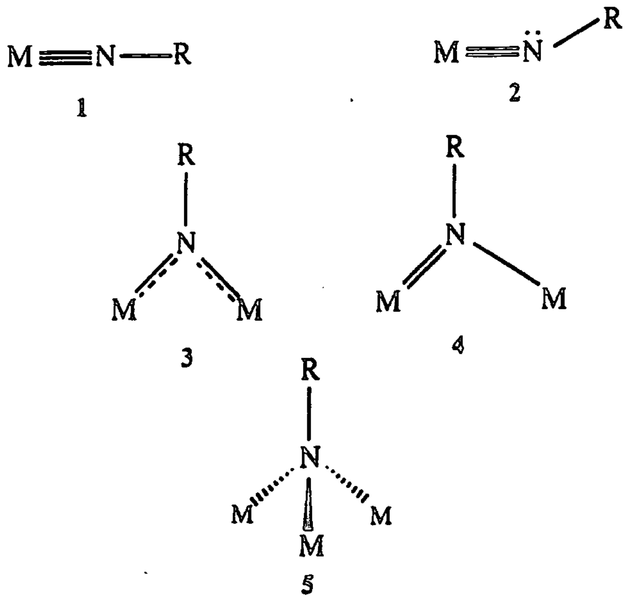


Figure 1.1 *Bonding modes of imido ligands.*

The terminal linear arrangement (1) is the most commonly observed structure. A linear M-N-R arrangement implies that the nitrogen is *sp* -hybridised and there is a metal nitrogen triple bond consisting of a σ-bond and two π-bonds. The bent terminal imido structure (2) is believed to indicate a reduced bond order with a lone pair of electrons on the nitrogen[1]. The bent imido configuration is expected when the nitrogen lone pair cannot be donated to the metal, for example when a triply bonded ligand would cause the electron count of the complex to exceed 18 electrons (the effective atomic number rule)[1,2]. In orbital terms, bent imido ligands are observed when only one metal orbital of π-symmetry is available for bonding to the nitrogen, either because of competition with another π-bonding ligand or because all metal d orbitals are already filled.

More recently however the validity of the argument that linear or near linear species are indicative of electron pair donation from the nitrogen to the metal has been questioned. Schrock *et al* [3] have prepared the 'apparently 20 electron' terminal osmium imido species $Os(N\text{-}2,6\text{-}^iPr_2C_6H_3)_3$ which has been shown to contain linear imido ligands. Preparation also of the related bis phosphine species $Os(N\text{-}2,6\text{-}^iPr_2C_6H_3)_2(PMe_2Ph)_2$[3] with an Os-N-C bond angle of 177.9(5)°, led to the proposal that these complexes have an electron pair in a nitrogen centered non-bonding orbital made up of a combination of 2 in-plane p-orbitals on the nitrogen atoms. Bergman's '20 electron' imido complex $Cp_2Zr(N^tBu)(THF)$[4] with a Zr-N-C bond angle of 174.4(3)° and Bercaw's $Cp^*_2Ta(NPh)H$[5] (see 1.5.1) provide further evidence that a linear imido group is not necessarily a 4 electron donor.

To date there is only one example of a structurally characterised bent imido ligand. The bis imido species $Mo(NPh)_2(S_2CNEt_2)_2$ (Figure 1.2) exhibits a near linear imido group with a Mo-N-C bond angle of 169.4(4)° and also a bent imido group with a Mo-N-C bond angle of 139.4(4)°. This molecule is described as having one metal-nitrogen double bond (Mo-N = 1.789Å) and one triple bond (Mo-N = 1.754Å), using the three d-orbitals of π-symmetry on the metal centre[6].

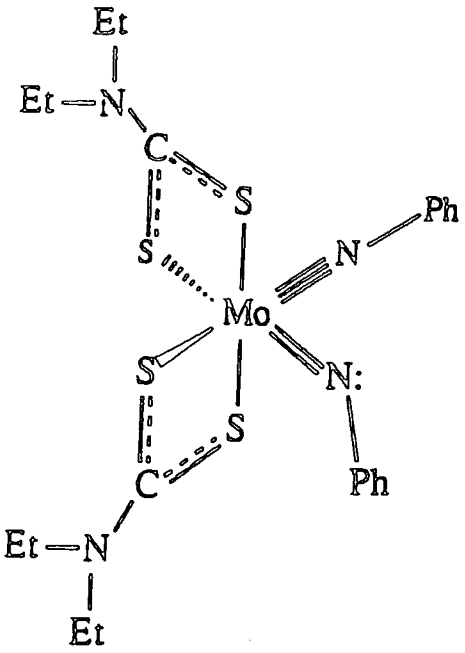


Figure 1.2 *Molecular structure of* $Mo(NPh)_2(S_2CNEt_2)_2$.

1.3 Spectroscopic Properties of Imido Complexes.

1.3.1 ^1H NMR Spectroscopy

In d^0 alkylimido complexes there is a significant deshielding of the α-protons. In fact the α-proton resonance of the imido group occurs 1 - 4 ppm downfield of the α-resonance of trialkyl amines, which are typically in the range 2.2 - 2.6 ppm[7]. In d^2 imido compounds the situation is more complex; the α- proton resonances being located upfield of the α-proton in amines. The origin of this effect is as yet unknown. The α-proton resonances of some alkylimido species are shown in Table 1.1.

1.3.2 ^{13}C NMR Spectroscopy.

^{13}C chemical shift data have been reported for a number of ^{t}butylimido complexes of d^0 transition metals[9,10,20,21]. It has been shown by Nugent *et al* that decreasing the electron density on the imido nitrogen causes a downfield shift of the α-carbon resonance and an upfield shift of the β-carbon resonance. Thus, the amount of electron density on the imido nitrogen can be probed by measuring the difference between the chemical shifts of the α and β carbon atoms These values can therefore give an indication of the reactivity of the imido complex, for example predicting the nucleophilic character of the imido nitrogen atom.

Complex	d electrons	δ (ppm)	Ref.
CpNb(NMe)Cl$_2$	0	3.21	8
CpNb(NMe)(O-2,6-Me$_2$C$_6$H$_3$)$_2$	0	3.30	9
CpNb(NMe)(O^{t}Bu)$_2$	0	3.43	9
CpNb(NMe)Cl$_2$(PMe$_3$)	0	3.85	9
Cp*Ta(NMe)Me$_2$	0	3.97	10
Ta(NEt)(NEt$_2$)$_3$	0	4.04	11
[W(NMe)F$_5$]$^-$	0	5.50	12
W(NMe)F$_4$(MeCN)	0	5.53	13
W(NEt)$_2$(NEt$_2$)$_2$	0	4.22	13
[W(NEt)F$_5$]$^-$	0	5.80	12
W(NEt)(O)Cl(NHEt)	0	7.3	14
Re(NMe)Cl$_3$(PEtPh$_2$)$_2$	2	0.2	15
Re(NMe)Cl$_3$(AsMe$_2$Ph)$_2$	2	0.7	16
[Re(NMe)(dtc)$_2$(PMe$_2$Ph)]BF$_4$	2	1.77	16
Cp*Re(NMe)Cl$_2$	2	2.17	17
Re(NMe)(dtc)$_3$	2	2.20	18
Re(NMe)(dtc)$_2$Cl	2	2.21	18
Os(NMe)Me$_4$	2	0.27	19
Os(NMe)(CH$_2$SiMe$_3$)$_4$	2	1.59	20

Table 1.1 *α-Proton chemical shifts of some mononuclear alkylimido complexes.*

1.3.3 Infrared Spectra of Organoimido Complexes.

The assignment of metal ligand stretching frequencies in organoimido complexes has proven problematic. The coupling of M-N with N-R stretching modes and/or vibrations of the R group give rise to significant complications. Dehnicke has suggested that the M-N stretch will occur at a higher frequency than the C-N stretch due, in part , to the vibrational coupling[22]. This view though is opposed by Osborn and Trogler[23] who assign υ(C-N) and υ(M-N) as 1330cm^{-1}and 934cm^{-1} respectively in the IR spectrum of $Cp^*_2V(NPh)$. This conflict of views awaits resolution through further investigation.

1.4 Uses of Imido Complexes

1.4.1 Heterogeneous Catalysis

In the heterogeneous ‘ammoxidation’ of propylene to acrylonitrile Grasselli at SOHIO proposed allylimido species as key intermediates in the catalytic process[24]. The reaction (Equation 1.1) is typically carried out at temperatures of *ca.* 450 °C with a catalyst of composition ($Bi_2O_3.nMoO_3$).

$$2CH_2{=}CHCMe \ + \ 3O_2 \ + \ 2NH_3 \xrightarrow[\text{catalyst}]{450^{\circ}C} 2CH_2{=}CHC{\equiv}N \ + \ 6H_2O \quad (1.1)$$

Several studies strongly suggest that the sites responsible for the initial C-H cleavage occurs at the [Bi-O] component whereas subsequent C-N bond formation involves interaction of the allyl fragment with a molybdenum imido site.

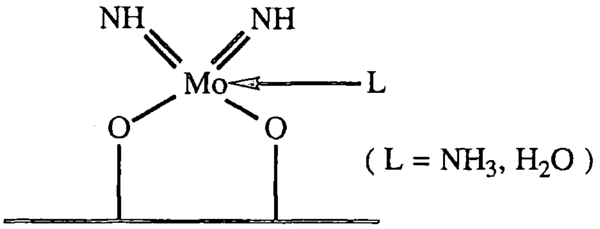
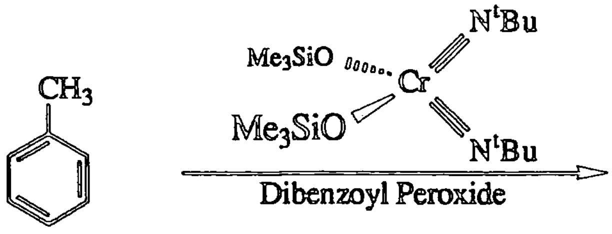


Figure 1.3 *Proposed active site in propylene ammoxidation.*

Recently the investigation of tungsten imido and molybdenum allylimido complexes have been undertaken in order to serve as an entry point for homogeneous modelling studies[25-27]. The C-N bond forming steps from the proposed reaction mechanism have been reproduced under mild conditions employing soluble imido species[28].

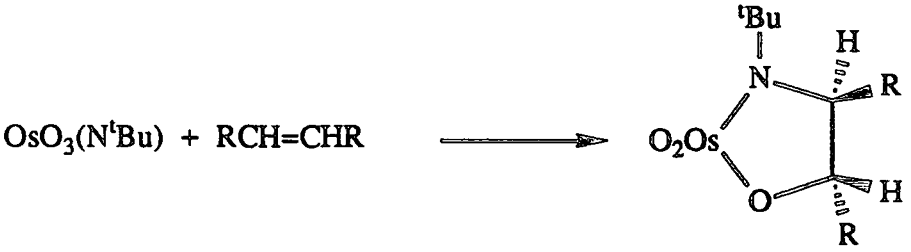


(1.2)

Furthermore imido species are believed to be involved in the metabolism of certain hydrazines and nitrogen fixation by enzymes[29,30].

1.4.2 Organic Synthesis and Homogeneous Catalysis

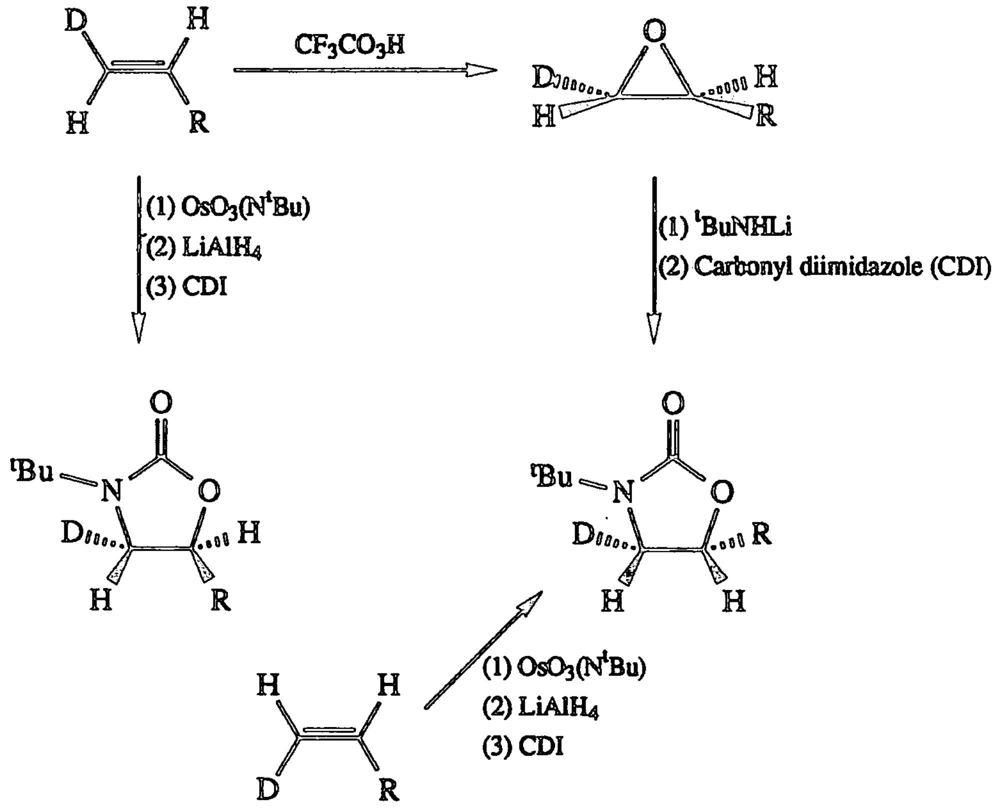
The importance of the observation that the osmium imido complex $Os(N^tBu)O_3$ reacts with olefins (Equation 1.3) was first commented on by Sharpless[31].



(1.3)

Through the exploitation of deuterated decenes Sharpless was able to show that the osmium imido derivative would effect cis vicinal oxyamination of olefins, as shown in Scheme 1.1.

Subsequent to this, the Sharpless group was able to prepare di, tri, and tetraimido osmium species that would promote the corresponding vicinal diamination[32] (Figure 1.4).



Scheme 1.1 *Stereoselective cis vicinal oxyamidation of olefins using $OsO_3(N^tBu)$.*

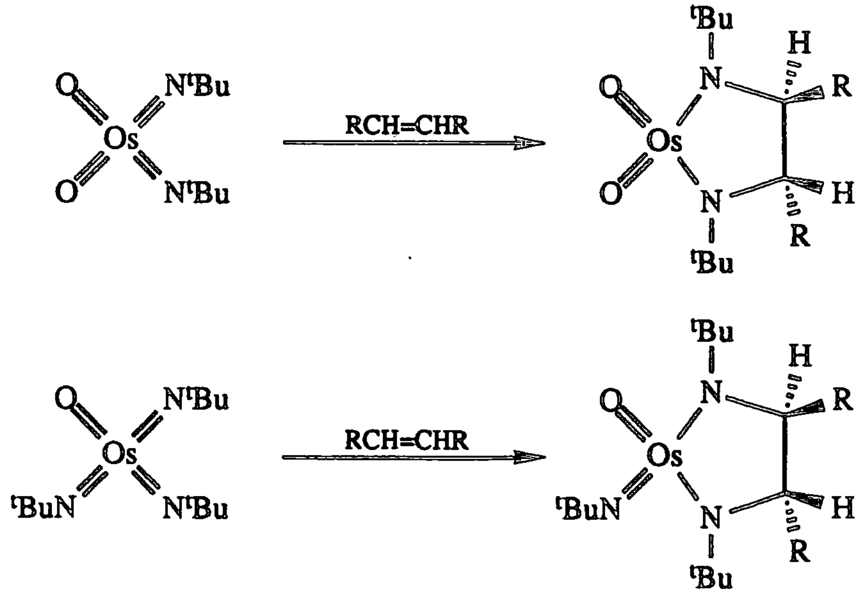
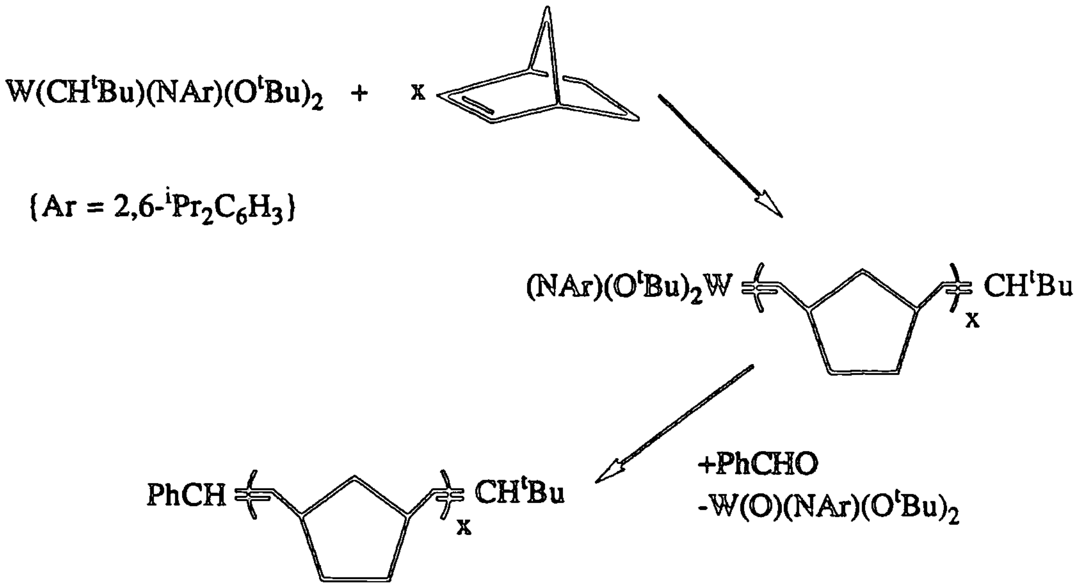


Figure 1.4

The well-characterised imido compounds of the type $M(NAr)(CHR)(OR')_2$ (M=W[33], Mo[34]) have received considerable interest of late as they have been shown to effect the ring-opening metathesis polymerisation (ROMP) of mono- and polycyclic olefins[35-38]. This in many cases allows access to highly stereoregular functionalized polymers[39]. Recently it has been shown that the cis/trans content of these polymers can be controlled using such initiators[40].



Scheme 1.2 *The polymerisation of norbornene using* $W(CH^tBu)(NAr)(O^tBu)_2$.

1.5 Group 5 Organoimido Complexes.

In the last two decades there has been a growth in the number of Group 5 imido species characterised and studied. Various strategies for the synthesis of such species have been employed, a number of which are highlighted below:

1.5.1 Monoimido Complexes.

Early work by Bradley and co-workers found that treatment of $NbCl_5$, or $TaCl_5$ with lithium dialkylamides afforded a mixture containing the unusual alkylimido species $(R_2N)_3M(NR')$, (M = Nb, Ta)[41]. The mechanism for the formation of this imido species is unclear, simple thermolysis of $M(NR)_5$ being ruled out as these species can be isolated and are thermally stable.

Nugent[42] later synthesised $(Me_2N)_3M(N^tBu)$, (M = Nb, Ta) selectively by the treatment of $NbCl_5$, or $TaCl_5$ with lithium dimethylamide and lithium t-butylamide. The crystal structure of the tantalum derivative was obtained and showed a linear Ta-N-C unit. Reactivity studies subsequently showed that electrophiles (ROH, R_2CO, CO, CO_2, CS_2, and RI) underwent typical insertion reactions with the dialkylamides, reaction at the imido group only being observed with benzaldehyde which resulted in oxygen for imido ligand exchange with the generation of $RCH{=}N^tBu$.

Cotton[43] found that the reaction of the dimer $Ta_2Cl_6(SC_4H_8)_3$ with a variety of alkyl cyanides resulted in coupling and the formation of the unusual tantalum(V) imido species below (Figure 1.5).

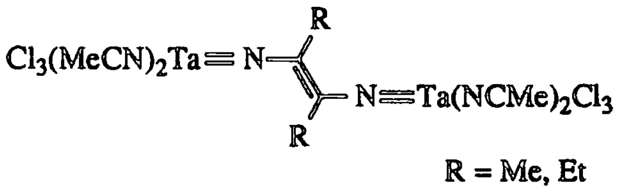


Figure 1.5

These tantalum imido species were shown to undergo an oxygen for imido group exchange reactions. Though relatively resistant to protic acids, no reaction being observed in HCl / Et_2O even after several hours, treatment of the tantalum imido with acetone readily yielded $Ta(O)Cl_3(MeCN)_2$.

Schrock has shown that imido units can be generated through the metathesis of alkylidenes with alkyl or aryl cyanides[44]. Tris(neopentyl)neopentylidene tantalum was found to react vigorously with either acetonitrile or benzonitrile to afford organoimido compounds. (Equation 1.4).

$$Np_3Ta{=}CHCMe_3 \quad + \quad RC{\equiv}N \longrightarrow Np_3Ta(N\overset{\overset{R}{\|}}{C}{\equiv}CHCMe_3) \quad (1.4)$$

In each case the pure Z isomer can be isolated from the Z and E mixture by recrystallisation and sublimation. Similarly chlorotetrakis(neopentyl) tantalum was found to react with acetonitrile, which led in this case to the isolation of the E isomer[44]. (Equation 1.5).

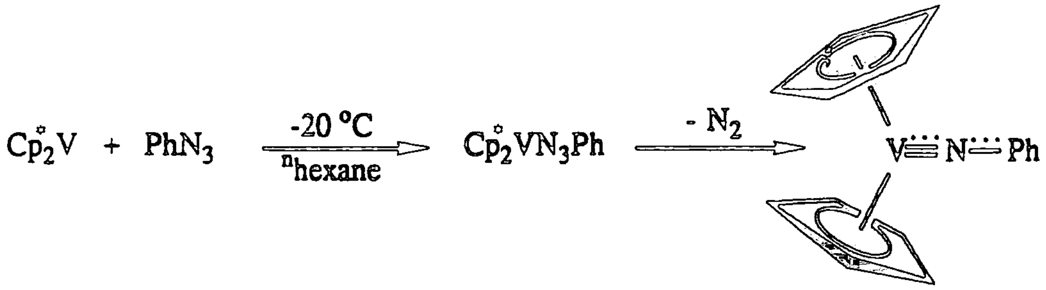
$$Np_4TaCl \;+\; MeC{\equiv}N \longrightarrow Np_2Ta(N\overset{\overset{Me}{|}}{C}{\equiv}CHCMe_3) \qquad (1.5)$$

Although many vanadium(V) organoimido complexes are now known, it was not until the preparation of the (arylimido)vanadium trichloride species $V(NC_6H_4X)Cl_3$, (X = Me, CF_3, OMe, F, Cl, Br) that any attempt at systematic derivative chemistry was undertaken[45,46]. Maatta and co-workers reacted $VOCl_3$ with a variety of para-substituted arylisocyanates *p*-XC_6H_4NCO (X = as above) to afford the corresponding imido complexes.

Reaction of these imido complexes with Lewis bases afforded monoaddition products such as $V(Ntol)Cl_3(THF)$, and $V(Ntol)Cl_3(PPh_3)$. The chloride ligands were found to readily participate in nucleophilic substitution reactions to afford $CpV(Ntol)Cl_2$ (see 1.6) and a range of alkoxide and aryloxide derivatives ($V(Ntol)Cl_{3-n}(OR)_n$) : n=1, 2, 3; (R = ^tBu, 2,6-$^iPr_2$-C_6H_3).

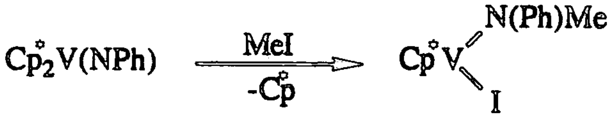
Azides have been shown to act as useful reagents in the synthesis of stable imido derivatives, the first vanadocene mononuclear imido being obtained by the use of such reagents[47]. Gambarotta, Rheingold and Trogler[48,49] have exploited this technique to synthesise and structurally characterise a number of arylimidos species of the form $Cp^*_2V(NAr)$.

Gambarotta found that low temperature reaction of decamethylvanadocene with phenylazide gave a dark brown insoluble azide adduct which lost nitrogen on warming to room temperature and afforded green crystals of the phenylimido $Cp^*_2V(NPh)$ on subsequent cooling, (Scheme 1.3)[48]. Structural analysis showed that the V-N-C bond was nearly linear (178.2(6)°) and had a N-C bond length of 1.345(9)Å, which is intermediate between a single and a double bond. This was taken to imply *sp* - hybridisation of the nitrogen with delocalisation of the nitrogen lone pair onto both the vanadium atom and into the phenyl ring.



Scheme 1.3 *Formation of Cp*$^*_2$*V(NPh).*

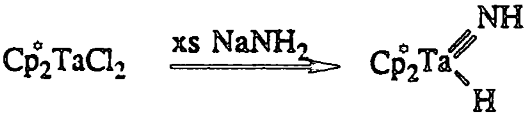
The V=N bond was also shown to be quite stable except with regard to hydrolysis or electrophilic addition, for example of methyl iodide (Equation 1.6).



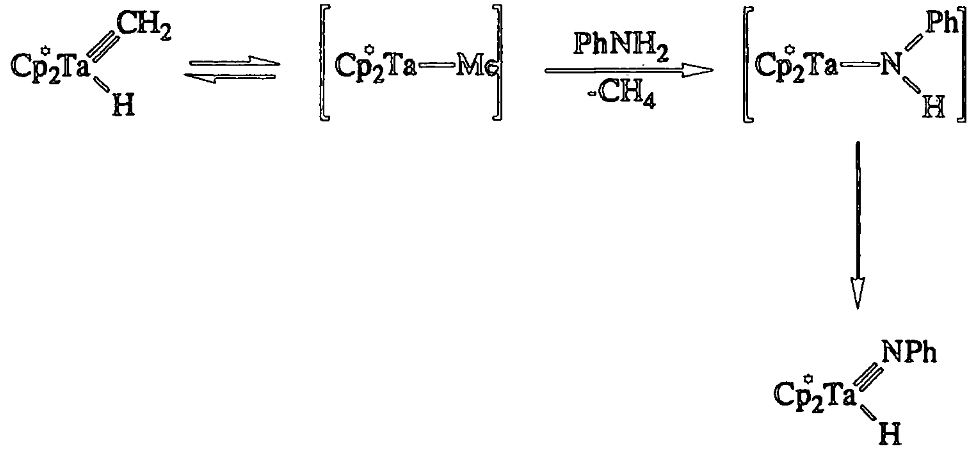
$$Cp^*_2V(NPh) \xrightarrow[-Cp^*]{MeI} Cp^*V(N(Ph)Me)(I) \qquad (1.6)$$

A further route to Group 5 imido species has recently been described by Bercaw. The imido-hydrido derivative of permethyltantalocene, Cp$^*_2$Ta(NPh)H was prepared by the treatment of Cp$^*_2$Ta(=CH$_2$)H with aniline, (Scheme 1.4)^5. The reaction sequence involves initial tautomerisation of Cp$^*_2$Ta(=CH$_2$)H to [Cp$^*_2$TaMe], oxidative addition of amine followed by reductive elimination of methane, and subsequent 1,2 α-hydrogen shift from the amide to yield the imido-hydrido species.

The parent imido-hydrido derivative, Cp$^*_2$Ta(NH)H, could only be generated in poor yield by the reaction of Cp$^*_2$Ta(=CH$_2$)H with NH$_3$. The preferred method of preparation was *via* the reaction of Cp$^*_2$TaCl$_2$ with NaNH$_2$ (Equation 1.7). The mechanism of this unusual reaction is as yet unclear.



$$Cp^*_2TaCl_2 \xrightarrow{xs\ NaNH_2} Cp^*_2Ta(=NH)(H) \qquad (1.7)$$



Scheme 1.4 *Preparation of Cp*$^*{}_2$*Ta(NPh)H*

On the basis of its electron count $Cp^*{}_2Ta(NPh)H$ may be expected to have a structure with sp^2 -hybridised nitrogen and consequently a bent Ta-N-C arrangement. The X-ray crystal structure determination unexpectedly found a near linear (177.8(9)^o) Ta-N-C arrangement implying that the nitrogen is *sp* -hybridised, and if the lone pair is donated to the metal, this complex would be a 20 electron species since the Cp^* ring possessed a η^5 bonding mode. The Ta-N bond length suggests a bond order of between 2 and 3, challenging the notion that the linearity of an imido ligand implies donation of the electron pair on the nitrogen to the metal, (see 1.2.1).

1.5.2 Polyimido Complexes.

Although various monoimido complexes of the Group 5 triad are now known, single sites co-ordinating by more than one imido ligand are mainly restricted to Group 6-8 metals[1,2]. Recently, Wigley and co-workers have reported that bis(arylimido) complexes of niobium and tantalum may be prepared through α-hydrogen abstraction reactions of Group 5 bis(dialkylamides)[50].

Treatment of $Ta(NEt_2)_2Cl_3(OEt_2)$ with the lithium arylamide, LiNHAr (Ar = 2,6-${}^iPr_2$-C_6H_3) afforded a tantalum bis(imido) complex which could be stabilised as the bis(pyridine) adduct $Ta(NAr)_2Cl(py)_2$. The analogous niobium bis(imido) species was synthesised from $Nb(NEt_2)_2Cl_3(OEt_2)$ employing the same procedure.

The X-ray analysis of the tantalum species showed the two Ta-N distances to be equivalent with Ta-N =1.812(6) and 1.809(6)Å, with Ta-N-C angles corresponding to near linear 4 electron imido ligands.

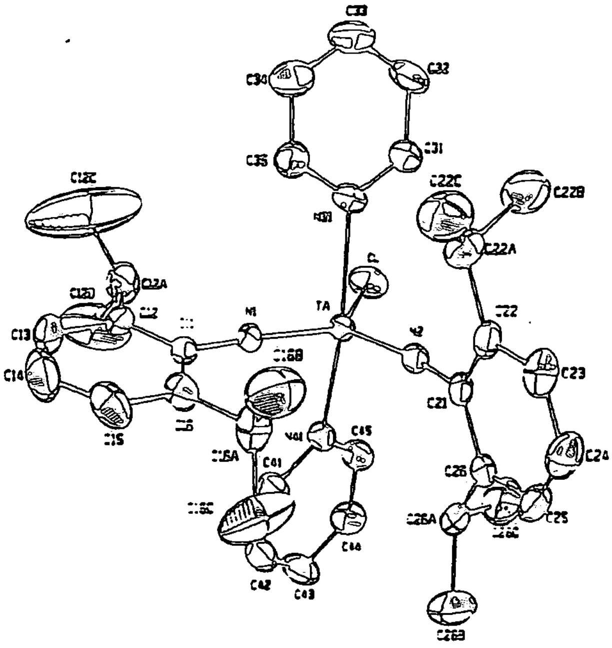


Figure 1.6 *Molecular structure of* $Ta(NAr)_2Cl(py)_2$.

Subsequent to this, Wigley[51] has shown that although treatment of $[Nb(NEt_2)_2Cl_3]_2$ with 2 equivalents of LiNHAr afforded the bis(imido) complex described above, the employment of a large excess (>6 equivalents) of LiNHAr afforded a yellow crystalline material which has been reported as the tris(imido) complex $[Li(THF)_2]_2[Nb(NAr)_3(NHAr)]$. The tris(imido) tantalum species was prepared by an analogous procedure using $[Ta(NEt_2)_2Cl_3]_2$. Both of these complexes are believed to be derived from an intermolecular deprotonation of $[M(NAr)_2(NHAr)_2]^-$.

Subsequent attempts to deprotonate these tris(imido) species failed to afford tetrakis(imido) metalates, $[Nb(NR)_4]^{3-}$. However, the reaction of $[Li(THF)_2]_2[Nb(Nmes)_3(NHmes)]$ (mes = 2,4,6-Me_3-C_6H_2), with ^nBuLi did yield $[Li(THF)_2]_2[Nb(=Nmes)_3(^nBu)]$, subsequent structural characterisation of this complex revealed three Nb-N bonds bridged by lithium atoms and hence the complex cannot be regarded as possessing true terminal imido ligands.

1.6 Half-Sandwich Organoimido Complexes.

There have been very few attempts to develop the chemistry of half-sandwich imido transition metal complexes. The first examples were complexes of formulae $Cp^*Ta(NR)Me_2$ (R = Me, ^tBu, $CH_2{}^tBu$), prepared by Bercaw *et al.* [10], *via* the reaction of monoalkylamides (LiNHR) with Cp^*TaMe_3Cl. Hydrogenation of these imido compounds in the presence of phosphine ligands yielded the imido-hydrido complexes $Cp^*Ta(NR)H_2(L)$, (L = PMe_3, PMe_2Ph), through loss of methane. (Scheme 1.5).

$$Cp^*TaMe_3Cl \xrightarrow[-CH_4]{LiNHR} Cp^*Ta(NR)Me_2 \xrightarrow[-CH_4]{H_2\,/\,L} Cp^*Ta(NR)(H)_2L$$

Scheme 1.5

Work by Maatta[46] demonstrated that the reaction of the vanadium complex $V(Ntol)Cl_3$ with either CpNa or Me_3SiCp afforded the first half-sandwich Group 5 imido halide species $CpV(Ntol)Cl_2$ (Equation 1.8 - 1.9).

$$CpV(Ntol)Cl_3 + Me_3SiCp \longrightarrow CpV(Ntol)Cl_2 + Me_3SiCl \quad (1.8)$$

$$CpV(Ntol)Cl_3 + NaCp \longrightarrow CpV(Ntol)Cl_2 + NaCl \quad (1.9)$$

Syntheses of what is believed to be the first niobium half-sandwich imido halide species were undertaken by Gibson *et al* exploiting a variety of silylated amines[8,9]. Room temperature treatment of $CpNbCl_4$ with a stoichiometric amount of $(Me_3Si)_2NMe$ in acetonitrile, gave $CpNb(NMe)Cl_2$ in high yield. (Equation 1.10).

$$CpNbCl_4 + (Me_3Si)_2NMe \xrightarrow{MeC\equiv N} CpNb(NMe)Cl_2 + 2Me_3SiCl \quad (1.10)$$

The X-ray structure was determined and showed a Nb-N distance of 1.752(2)Å. This lies within the range expected for a metal-nitrogen triple bond (typically 1.73-1.79Å for niobium imido compounds[52-54]). The Nb-N-C angle of 163.4(3)° is at the low end of the range (161-180°)[2] typically observed for a terminal imido ligand containing an *sp* -hybridized nitrogen.

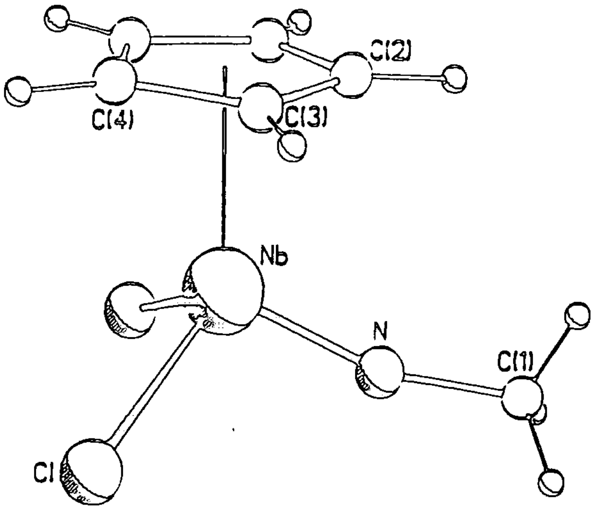


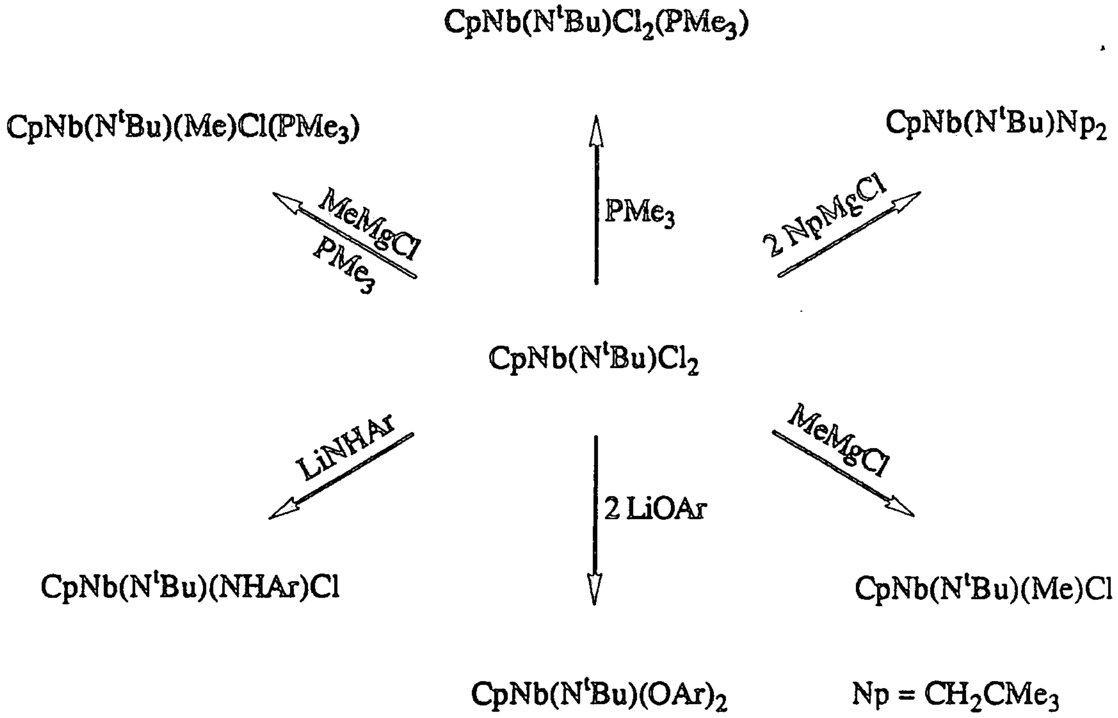
Figure 1.7 *Crystal Structure of CpNb(NMe)Cl$_2$.*

Although CpNb(NMe)Cl$_2$ is formally a 16 electron species, it is found not to bind acetonitrile, the reaction solvent. However, it readily reacts with the highly basic PMe$_3$ to give the adduct CpNb(NMe)Cl$_2$(PMe$_3$).

Sterically demanding imido derivatives were accessed through the reaction of mono silylamines, (Me$_3$SiNHR), (R = ^{t}Bu, 2,6-^{i}Pr$_2$-C$_6$H$_3$) with CpNbCl$_4$[9]. (Equation 1.11).

$$\mathrm{CpNbCl_4} + \mathrm{(Me_3Si)NHR} \longrightarrow \mathrm{CpNb(NR)Cl_2} + \mathrm{2Me_3SiCl} + \mathrm{RNH_2} \qquad (1.11)$$

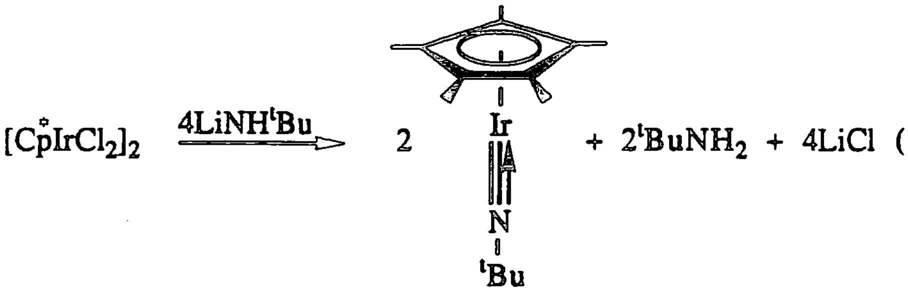
A number of derivatives of CpNb(N^{t}Bu)Cl$_2$ have been prepared and characterised which suggest that a rich and diverse chemistry may be anticipated for these systems[55]. (Scheme 1.6).



Scheme 1.6

Wigley has described the preparation of a half-sandwich bis(imido) derivative of niobium, CpNb(NAr)$_2$(py), (Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$) by treatment of Nb(NAr)$_2$Cl(py)$_2$ with NaCp[50].

Through the treatment of [Cp*IrCl$_2$]$_2$ with 4 equivalents of LiNH^{t}Bu Bergman and co-workers[56] have synthesised the unusual monomeric complex Cp*Ir(N^{t}Bu). (Equation 1.12).



(1.12)

An X-ray diffraction study performed on $Cp^*Ir(N^tBu)$ showed the complex to adopt a 'one-legged piano stool', or 'pogo-stick' geometry. The near linear Ir-N-C angle (177.2(5)°) and short Ir-N bond (1.712(7)Å) suggest that the imido ligand functions as a four-electron donor, making $Cp^*Ir(N^tBu)$ an 18 electron complex. The imido moeity has shown remarkable reactivity undergoing [2+2] cycloadditions with unsaturated substrates such as CO_2 and exhibiting nucleophilic character at the nitrogen, reacting with methyl iodide, for example (Figure 1.8).

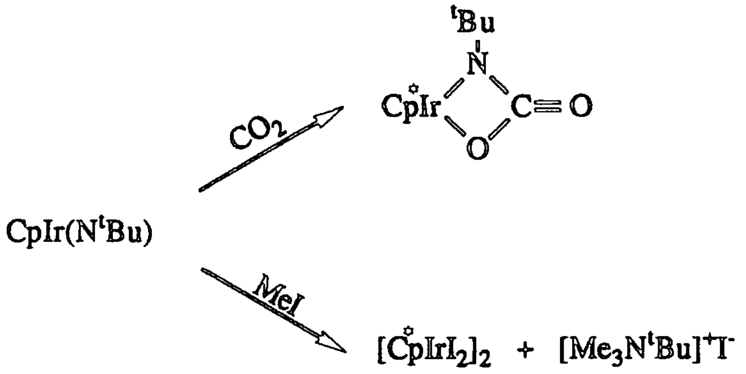


Figure 1.8

The d^2 rhenium complex $Cp^*Re(NR)Cl_2$, (R = Me, ^tBu), may be prepared *via* the aminolysis of the tetrachloro precursor compound according to Equation 1.13[17]. The triply bonded nature of the imido ligand can be seen in the structure of $Cp^*Re(N^tBu)Cl_2$ as a near linear Re-N-C unit (170.5(2)°) and short Re-N distance (1.709(3)Å) are observed.

$$\overset{*}{Cp}ReCl_4 \xrightarrow[-\,2[RNH_3]Cl]{+\,3RNH_2} \overset{*}{Cp}Re(NR)Cl_2 \quad (1.13)$$

Green has recently demonstrated that aminolysis of the tetrachlorides $(C_5H_4R)MCl_4$ (M = Mo, W; R = H, Me) with 3 equivalents of $R'NH_2$ (R' = ^tBu, ^nPr, Ph) in toluene affords the corresponding cyclopentadienylimidodichloro compounds $(C_5H_4R)M(NR')Cl_2$[57].

Reduction of $CpMo(N^tBu)Cl_2$ with potassium in the presence of ethylene or alkyne affords the compounds $[CpMo(N^tBu)(\eta^2\text{-}C_2H_4)Cl]$ and $[CpMo(N^tBu)(\eta^2\text{-}C_2R_2)Cl]$, (R = Me, Ph) respectively. Oxidation of $CpMo(N^tBu)Cl_2$ with chlorine gas is found to afford the d^0 imidotrichloro compound $CpMo(N^tBu)Cl_3$.

Recently Sundermeyer has demonstrated a convenient route to d^0 Group 6 complexes of the form $CpM(N^tBu)_2Cl$, (M = Mo, W)[58]. Treatment of the bis(imido) dihalide species $Mo(N^tBu)_2Cl_2$ and $W(N^tBu)_2Cl_2(py)_2$ with LiCp, and NaCp respectively affords the corresponding half-sandwich bis(imido) complexes $CpM(N^tBu)_2Cl$. (Equation 1.14 - 1.15).

$$Mo(N^tBu)_2Cl_2 + LiCp \longrightarrow CpMo(N^tBu)_2Cl + LiCl \quad (1.14)$$

$$WCl_2(py)_2(NBu)_2 + NaCp \longrightarrow CpW(N^tBu)_2Cl + NaCp + 2py \quad (1.15)$$

1.7 The Isolobal Relationship Between Imido and η^5-Cyclopentadienyl Ligands.

From simple MO considerations of the π-molecular orbitals of the cyclopentadienyl ligand (Cp), it can be shown that the ligand has one orbital of σ-symmetry and two orbitals of π-symmetry available for possible interaction with metal orbitals[59] (Figure 1.9). It must be noted though a Cp ligand possesses two empty antibonding orbitals which could participate in δ-bonding with appropriate metal d-orbitals.

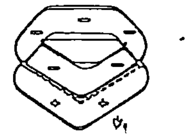
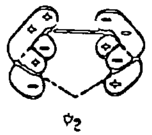
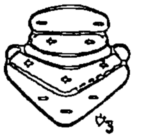
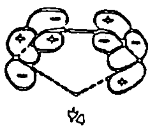
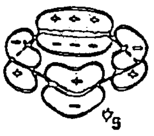
Classified as σ-symmetry	Classified as π-symmetry	Classified as δ-symmetry
	 	 

Figure 1.9 *Representation of the π-molecular orbitals of the cyclopentadienyl ligand.*

This information has been utilised to investigate the bonding in the bent metallocenes of general formulation Cp_2ML_n, (n = 1-3). Work by Lauher and Hoffmann involving Extended Hückel Molecular Orbital (EHMO) Calculations has shown that three new highly directional bonding orbitals are obtained as the Cp rings in ferrocene are tilted back to give a bent metallocene configuration[60]. It is these three new orbitals, shown in Figure 1.10 that may be used to bind additional ligands to the metal centre[61]. The orbitals are essentially orientated in the yz plane (as illustrated below), the b_2 orbital being mainly of d_{yz} character, while the two a_1 orbitals are formed from the metal's s, p_z, d_{z^2} and $d_{x^2-y^2}$ atomic orbitals. This suggests that when further ligands are added to this bent metallocene fragment, they will lie in a plane which bisects the $Cp_{(centroid)}$-M-$Cp_{(centroid)}$ angle.

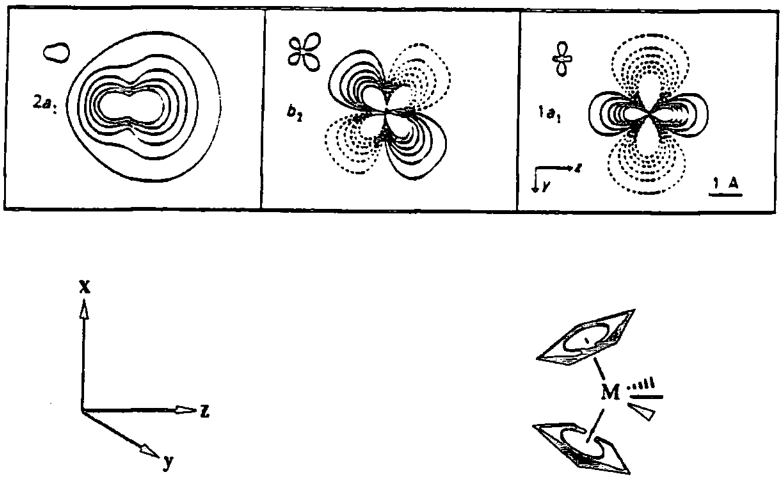


Figure 1.10 *Contour diagrams of the three bonding orbitals in the bent metallocene fragment [Cp'$_2$M].*

The terminal linear arrangement of an imido ligand implies that the nitrogen is *sp* - hybridised and that there is a metal nitrogen triple bond consisting of a σ-bond and two π-bonds. Following on from this, Gibson *et al*[9] applied Fenske-Hall Calculations to both Cp and imido containing fragments, and concluded that there are close similarities between their frontier orbital symmetry properties.

Since the linear imido unit formally contributes one electron fewer than the Cp ligand to the metal electron count, Gibson went on to suggest that half-sandwich imido complexes of the Group 5 triad may be regarded as being isolobal and valence isoelectronic with Group 4 metallocene complexes. This relationship can be extended further to allow a direct comparison with the seemingly unconnected non-cyclopenadienyl bis(imido) compounds of the Group 6 metals[62,63]. (Figure 1.11).

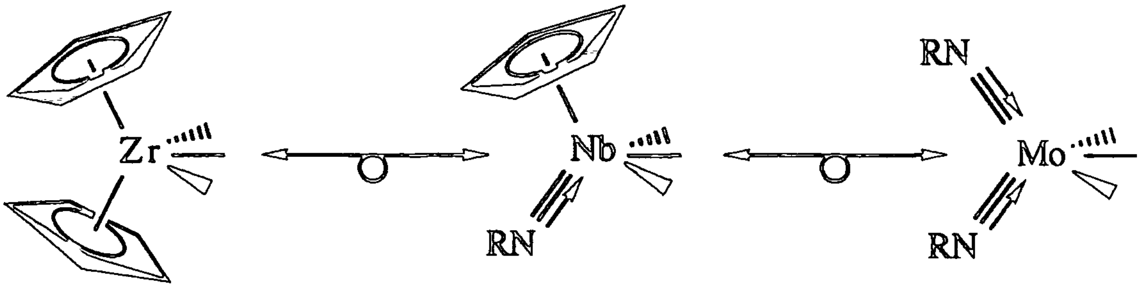


Figure 1.11

This analogy has also been pointed out by Schrock for the reactions of some tungsten(IV) bis(imido) complexes[64]. Reaction of $W(NAr)_2(PMe_2Ph)_2$, (Ar = 2,6-${}^iPr_2$-C_6H_3) with acetone readily affords the oxametallacyclopropane complex $W(NAr)_2(PMe_2Ph)(\eta^2\text{-}OCMe_2)$. (Equation 1.16).

$$W(NAr)_2(PMe_2Ph) \xrightarrow[-\,PMe_2Ph]{+\,Me_2CO} W(NAr)_2(PMe_2Ph)(\eta^2\text{-}OCMe_2) \quad (1.16)$$

An X-ray study of this complex showed that the W, P, O, and C atoms lie close to aplane that bisects the N-W-N angle. (Figure 1.12). By regarding the $[W(NAr)_2]$

fragment as isolobal and isoelectronic with the [Cp_2M] fragment, (M = Ti, Zr, Hf), the orientation of the acetone ligand can be rationalised. Furthermore, $W(NAr)_2(PMe_2Ph)_2$ was shown to undergo a number of reactions with olefins and acetylenes to give complexes containing π-bound ligands. The isolobal and isoelectronic relationship was further reinforced as the orientation of these π-bound ligands could again be rationalised by comparison with the analogous complexes of $Cp_2Ti(PMe_3)_2$[65].

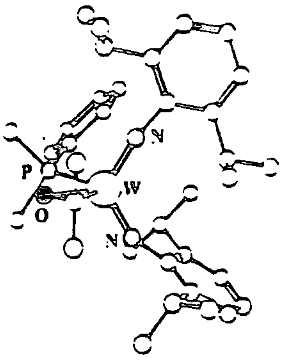


Figure 1.12 *Molecular structure of* $W(NAr)(PMe_2Ph)(\eta^2\text{-}OCMe_2)$.

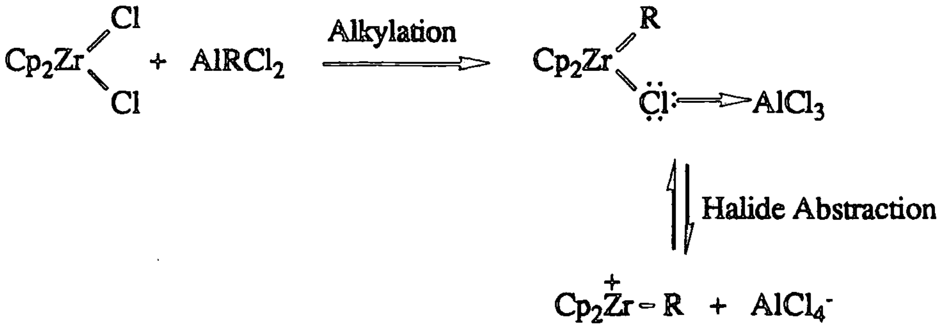
1.8 Reactivity of Group 4 Metallocenes.

In recent years, the complexes of titanocene and zirconocene have proven to be important both as stoichiometric and catalytic reagents for a variety of organic transformations. A review of some aspects of this extensive chemistry is given below:

1.8.1 Ziegler-Natta Polymerisation.

Bis(cyclopentadienyl) metal complexes such as Cp_2MCl_2 (M = Ti, Zr) in the presence of aluminium alkyl reagents have long been an important class of soluble catalysts for Ziegler-Natta olefin polymerisation[66-69]. Although early efforts by Shilov and co-workers[70] to identify the catalytically active species were unsuccessful, they suggested that the polymerisation process involved the participation of a highly electrophilic, cationic metallocene alkyl complex Cp_2MR^+. Evidence for this was later provided by Eisch and co-workers[71] who trapped and characterised the cationic alkenyl species $[Cp_2TiC(SiMe_3)=C(Ph)Me][AlCl_4]$ following the addition of $PhC\equiv CSiMe_3$ to an active catalyst mixture containing titanocene dichloride and $AlMeCl_2$.

These highly coordinatively and electronically unsaturated cationic d^0 alkyl complexes are postulated to form on alkylation of Cp_2MCl_2 by the aluminium alkyl co-catalyst, followed by halide abstraction. (Scheme 1.7).



Scheme 1.7

Although the isolation of these species remains to be accomplished, several synthetic strategies have been employed to prepare their base adducts. Taube and Krukowka[72] have reported that $[Cp_2TiMe(THF)][BPh_4]$ can be obtained by partial protonolysis of Cp_2TiMe_2 with $[NPhMe_2H][BPh_4]$ in a CH_2Cl_2/THF mixture. Bochmann and co-workers[73] have prepared $[Cp^*_2TiMe(THF)][BPh_4]$ by the oxidation of $Cp^*_2TiMe_2$ with $AgBPh_4$ in THF. Jordan[74-75] has relied on the one-electron oxidation of a neutral zirconocene dialkyl complex with either $AgBPh_4$ in CH_3CN or $[Cp_2Fe][BPh_4]$ in THF to prepare a series of zirconocene alkyl cations, $[Cp_2ZrR(L)]^+$ (R = Me, Ph, CH_2Ph; L = CH_3CN, THF). Reactivity studies have shown that $[Cp_2ZrR(THF)]^+$ catalyses the polymerisation of ethylene in the absence of aluminium co-catalyst or oxide support[76]. However, the activity of this system is hindered by the presence of the coordinating solvent, (THF), which is only partially displaced in dichloromethane, the polymerisation solvent.

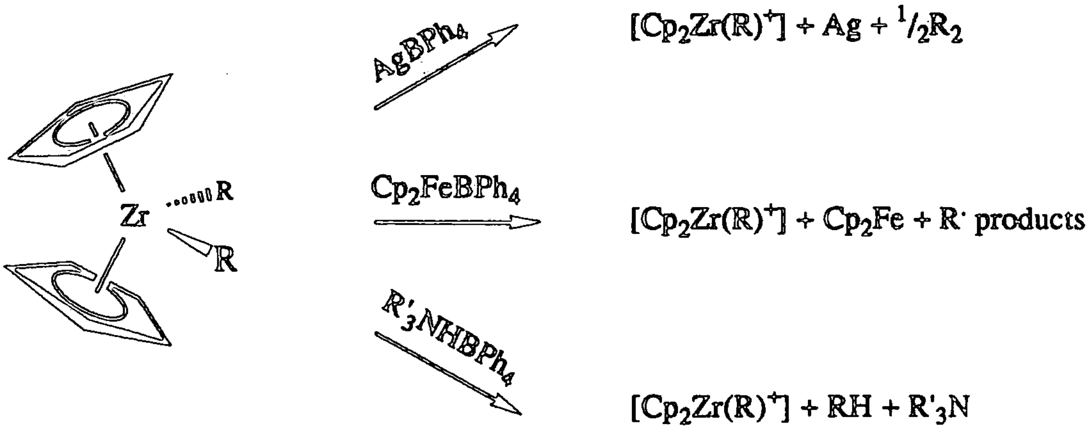


Figure 1.13 *Possible strategies for the generation of zirconocene alkyl cations.*

Kaminsky has shown that the higher olefins propene and butene may be polymerised by chiral linked-bis(indenyl)zirconium derivatives in the presence of an aluminoxane co-catalyst[77]. Furthermore, Ewen using prochiral metallocene complexes of zirconium and hafnium with methylaluminoxane co-catalyst has shown that syndiospecific control of propylene polymerisations can be achieved[78]. Turner and Hlatky[79] at Exxon have prepared highly active, Lewis acid-free catalysts, (Figure 1.14) which polymerise ethylene and propylene under mild conditions.

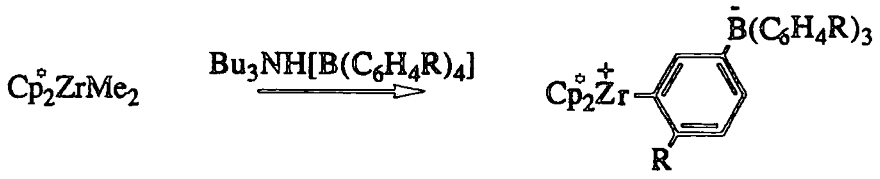
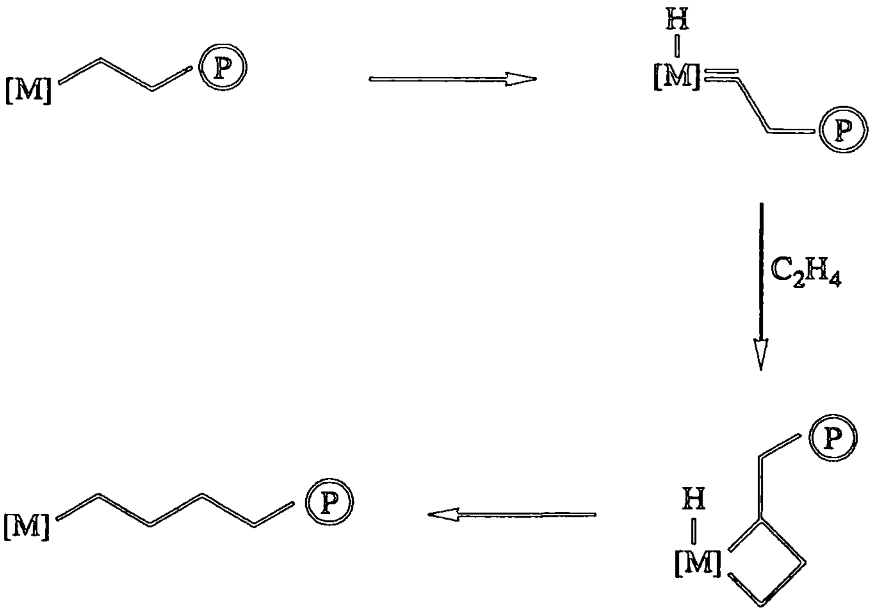


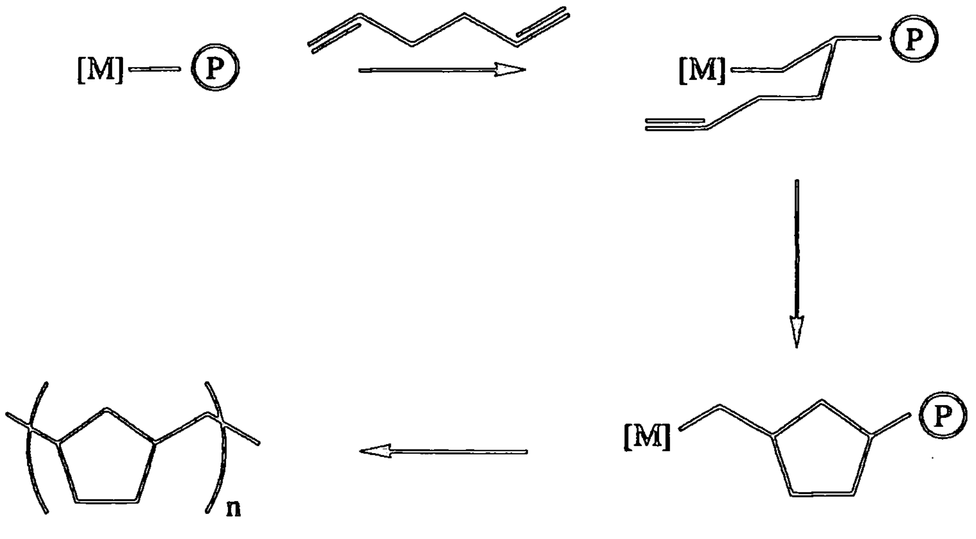
Figure 1.14

From the measurement of the kinetic isotope effect in the polymerisation of ethylene, Grubbs[80] suggested that the mechanism of olefin insertion into these cationic metal alkyl species proceeds *via* the Cossee direct insertion mechanism[81] rather than a Green and Rooney metathesis-type mechanism[82], (Scheme 1.8), since no kinetic isotope effect was observed for the latter.



Scheme 1.8 *Green-Rooney mechanism of olefin insertion into metal-carbon bonds.*

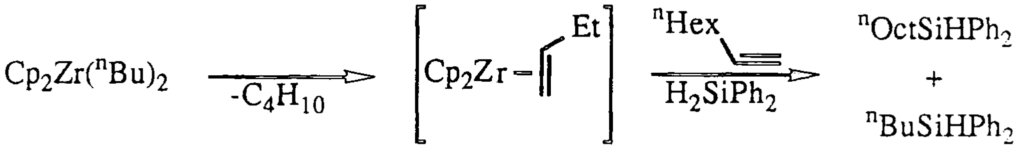
Waymouth[83] has demonstrated that homogeneous Cp'_2ZrX_2 / aluminoxane systems, (Cp' = Cp, Cp^*; X = Cl, Me), are efficient for the cyclopolymerisation of nonconjugated diolefins, (Scheme 1.9). The microstructure of the resulting polymers can be varied by the choice of different catalyst precursors, Cp_2ZrX_2 and $Cp^*_2ZrX_2$ having been shown to lead to high trans and cis polymer content respectively. Subsequent work showed that optically active poly(methylene-1,3-cyclopentene) could be formed if chiral metallocenes were employed for the cyclodimerisation of 1,5-hexadiene[84].



Scheme 1.9 *The cyclopolymerisation of 1,5-hexadiene.*

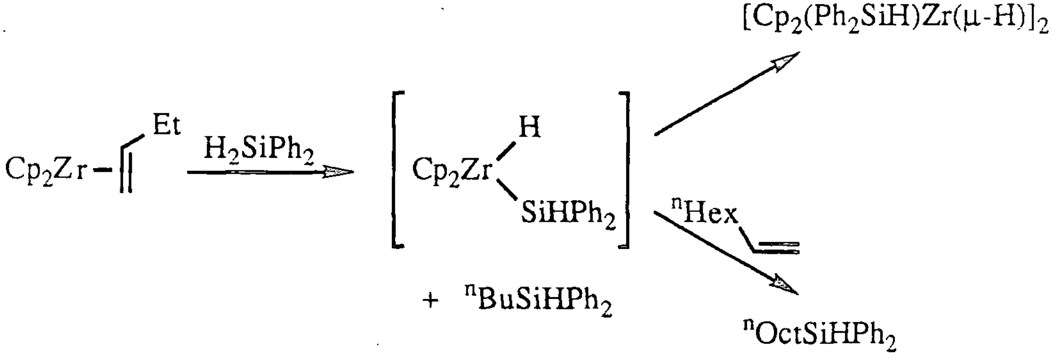
1.8.2 Hydrosilation Reactions.

Takahashi and Negishi[85] have shown that $Cp_2Zr(^nBu)_2$ will undertake the highly regiospecific hydrosilation of 1-alkenes, in the presence of H_2SiPh_2 according to Scheme 1.10.



Scheme 1.10

Isolation of the silyl(hydrido)-zirconocene species $Cp_2Zr(H)(PMe_3)(SiHPh_2)$ and the catalytically inactive hydrido-bridged dimer $Cp_2Zr(SiHPh_2)(\mu\text{-}H)_2(Ph_2HSi)ZrCp_2$ from reaction mixtures suggest that the monomer $Cp_2Zr(H)(SiHPh_2)$ is generated *in situ* and reacts with alkenes to give hydrosilated products before dimerization to an inactive species. (Scheme 1.11).

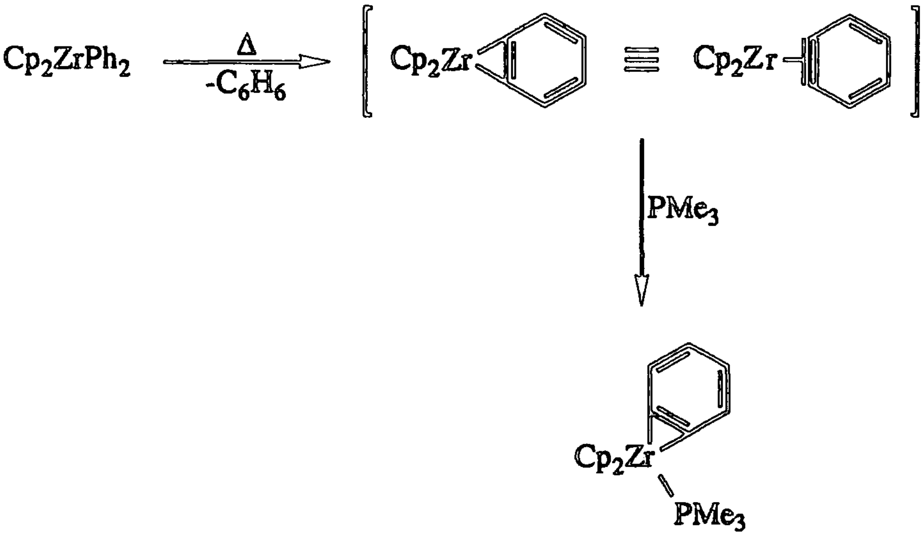


Scheme 1.11

Recently Corey[86] has demonstrated that Cp_2MCl_2 / ^nBuLi (M = Ti, Zr, Hf) catalysed reactions of $PhMeSiH_2$ in the presence of near-stoichiometric quantities of cyclic and acyclic olefins lead to a range of reactions. Zirconocene was shown to promote hydrosilation of terminal acyclic olefins and isomerisation of internal olefins, whereas with a titanocene-catalysed reaction cyclic olefins promoted the formation of silicon oligomers.

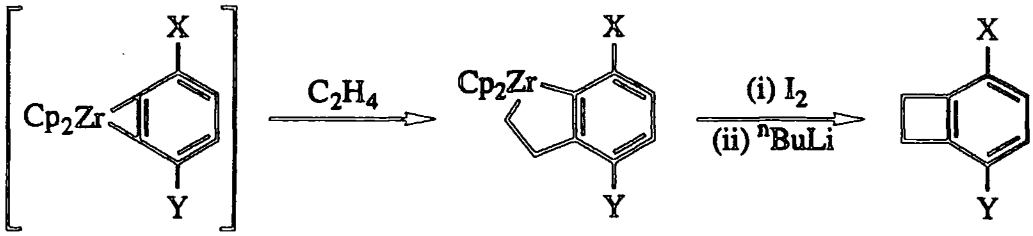
1.8.3 Benzyne Complexes.

Although several η^2-benzyne complexes of transition metals have been reported[87], the thermolysis of diphenylzirconocene in benzene to generate the benzyne species $Cp_2Zr(\eta^2\text{-}C_6H_4)$, which may be trapped as the phosphine adduct, has proven to be of synthetic use. (Scheme 1.12).



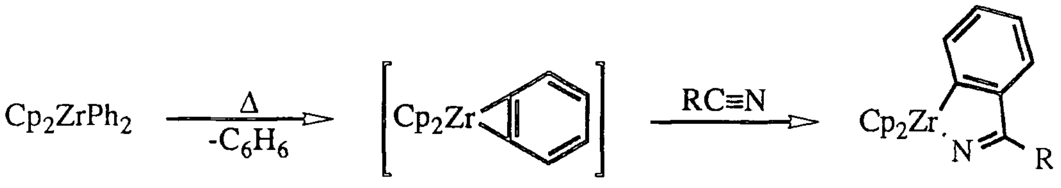
Scheme 1.12 *Preparation of (benzyne)zirconocene species.*

Buchwald has demonstrated that this 'nascent benzyne' may be used for efficient carbon-carbon bond forming reactions in organic synthesis[88]. If a substituted benzyne complex is generated under an atmosphere of ethylene, coupling of the ethylene with the benzyne occurs. Treatment of this metallacycle, without isolation, with excess iodine followed by exposure to ^nBuLi at -78°C cleanly yields substituted benzocyclobutenes. (Scheme 1.13).



Scheme 1.13

Thermolysis of Cp_2ZrPh_2 in the presence of one equivalent of a wide variety of nitriles led to a series of novel azazirconacyclopentenes, (Scheme 1.14). These can be readily converted to simple aromatic ketones upon hydrolysis.



Scheme 1.14

In addition to providing novel routes for the preparation of carbocyclic and substituted aromatic compounds, benzyne-derived metallacycles can be used as precursors to sulphur-containing heterocycles. Benzisothiazoles may be prepared from nitrile coupling of azametallacycles with S_2Cl_2. (Figure 1.15). This is of general interest as these heterocycles have not been studied in detail, due to the lack of a convenient method of synthesis. The coupling of 'nascent benzyne' with a non-terminal alkyne followed by treatment with SCl_2 provides excellent yields of benzothiophenes (Figure 1.15). In most of the examples studied Buchwald reported almost complete regioselectivity , both with respect to the substituents of the benzyne and to those of the alkyne.

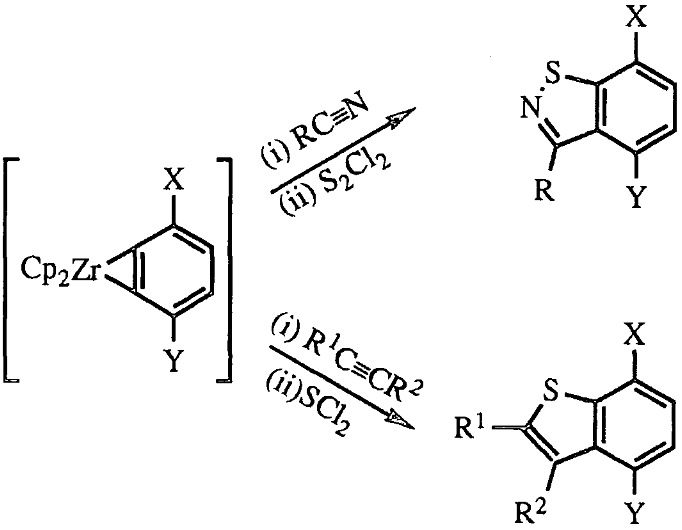


Figure 1.15 *Preparation of heterocycles via (benzyne)zirconocene species.*

1.8.4 Hydrozirconation.

The synthesis of $Cp_2Zr(H)Cl$ (Schwartz reagent) led to the development of procedures for functionalization of alkenes, alkynes, and 1.3-dienes *via* organozirconium(IV) intermediates[89]. These intermediates have been found to react with a variety of electrophilic regents to give organic products in high yields. The zirconium hydride $Cp_2Zr(H)Cl$ was first prepared by Wailes and co-workers[90] from Cp_2ZrCl_2 and $LiAlH_4$, although $NaAlH_2(OR)_2$ can be employed as an alternative source of hydride[91].

The hydrozirconation of alkenes takes place at the sterically least hindered position of the olefin chain. Formation of this product involves either addition of Zr-H to a terminal double bond or Zr-H addition to an internal double bond followed by rapid rearrangement to place the metal at the least hindered position of the alkyl chain[91]. (Figure 1.16).This is in contrast to other transition metal hydrides where conversion of the α-olefin into the thermodynamically more favoured internal olefin is observed[92].

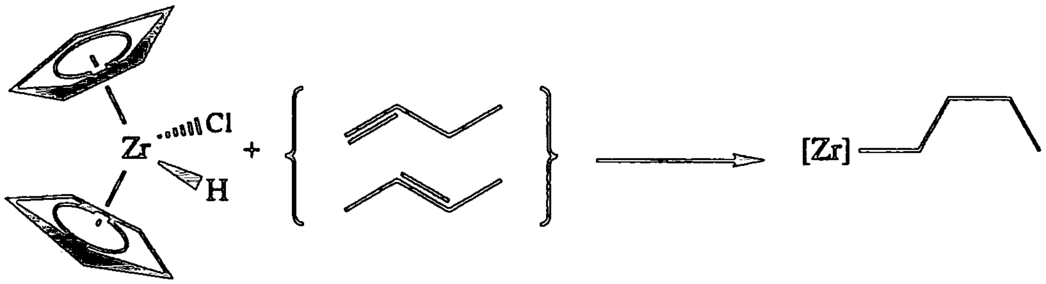


Figure 1.16 *Hydrozirconation of alkenes.*

The reaction of $Cp_2Zr(H)Cl$ with terminal alkynes leads to cis stereochemistry[93]. Hydrozirconation of unsymmetrical disubstituted acetylenes readily gives mixtures of (alkenyl)zirconium complexes which are dictated by the steric bulk of the alkyne substituents[94]. In contrast to boron[95], which often doubly metalates 1,3-dienes or gives a mixture of products, $Cp_2Zr(H)Cl$ reacts with 1,3-dienes at the sterically less hindered double bond to give γ,δ-unsaturated alkyl compounds[96]. (Figure 1.17).

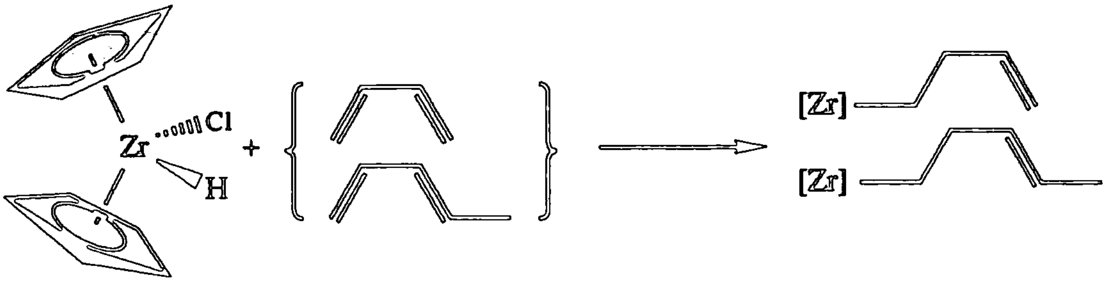


Figure 1.17 *Hydrozirconation of 1,3-dienes.*

Cleavage of the Zr-C bond in (alkyl)- and (alkenyl)zirconium complexes by electrophilic halogenation reagents, Br_2 or I_2 for example, yield the corresponding organic halides[91,94,96], (Figure 1.18). It is also noteworthy that the isomeric composition of the vinyl halide products closely duplicates that of its (alkenyl)zirconium precursors.

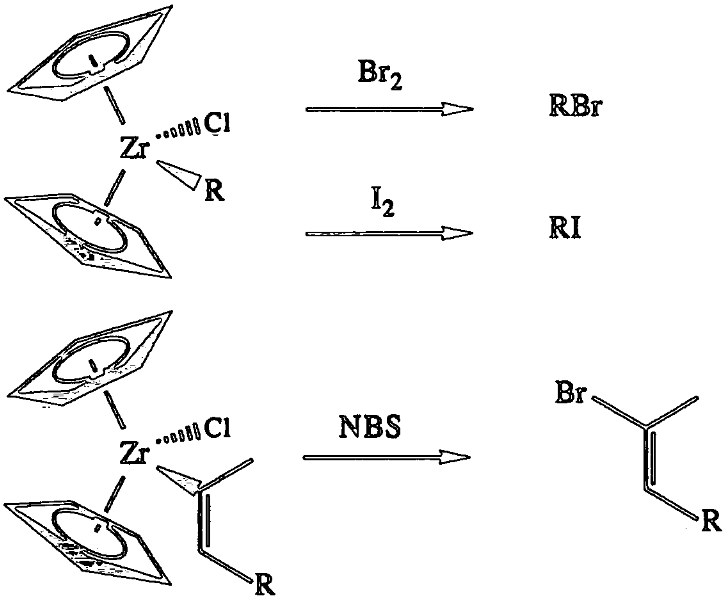


Figure 1.18

Oxidation of the alkyl Zr-C bond by dioxygen or various electrophilic oxidising reagents such as hydrogen peroxide or chromyl chloride gives the corresponding alcohol[97]. (Figure 1.19).

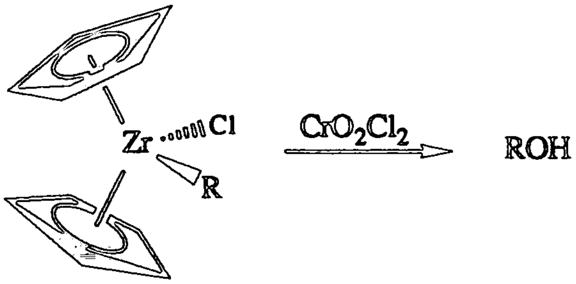
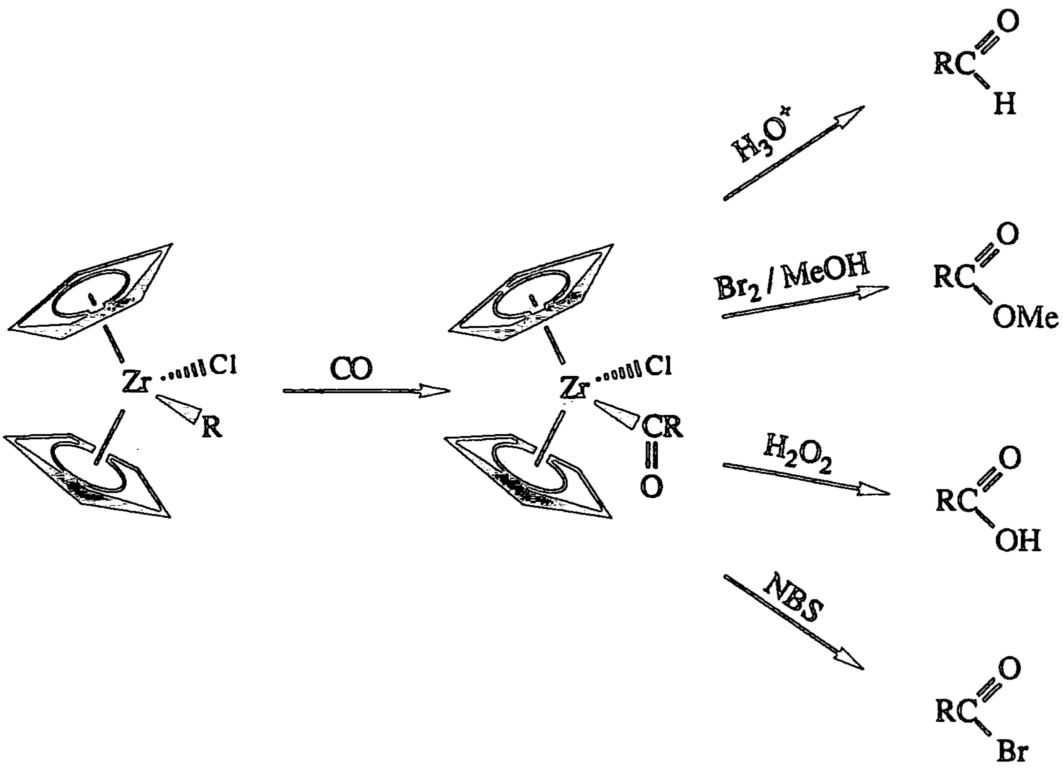


Figure 1.19

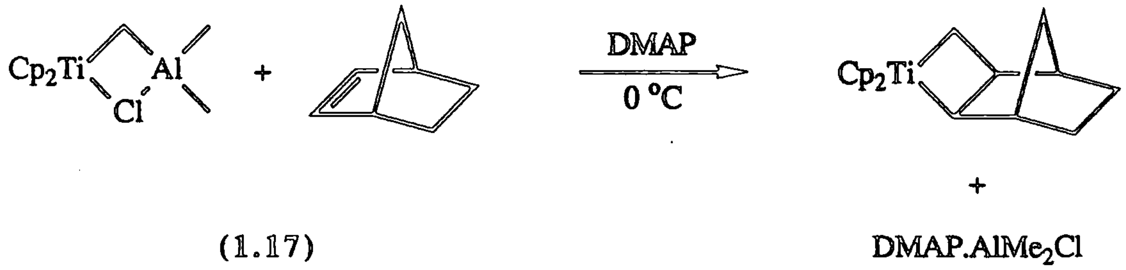
Carbon monoxide may be shown to insert into many alkyl, alkenyl or γ,δ-unsaturated (alkyl)zirconium(IV) complexes to generate stable acylzirconium species[98]. These acyls can then be converted into aldehydes, carboxylic acids, esters, or acyl halides according to Scheme 1.15.



Scheme 1.15 *The synthetic versatility of (acyl)zirconocene species.*

1.8.5 Metathesis Polymerisation.

Grubbs and co-workers have shown that titanacyclobutanes act as efficient initiators for the living ring-opening polymerisation of cyclic olefins[99]. Treatment of the Tebbe reagent, $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$ with norbornene and base (DMAP), for example affords a titanacyclobutane complex (Equation 1.17).



(1.17)

Subsequent thermolysis of this titanacyclobutane at 65°C in the presence of excess norbornene yields ring-opened polynorbornene of controlled molecular weight. Studies by Grubbs suggest that the mechanism of polymerisation is consistent with that outlined in Scheme 1.16. The metallacycle precursor can lead to a carbene-olefin complex in two possible ways. Path **a** is nonproductive, but rapidly reversible. Path **b** leads to a substituted titanacarbene which is trapped by norbornene forming a trisubstituted metallacycle. The metallacycle can be cleaved, and when trapped by norbornene again, yields a growing chain of ring-opened polynorbornene.

Furthermore, Grubbs has employed titanacyclobutane catalysts to prepare air-sensitive poly(3,4-diisopropylidenecyclobutene) with controlled molecular weight and little cross-linking[100] (Figure 1.20).

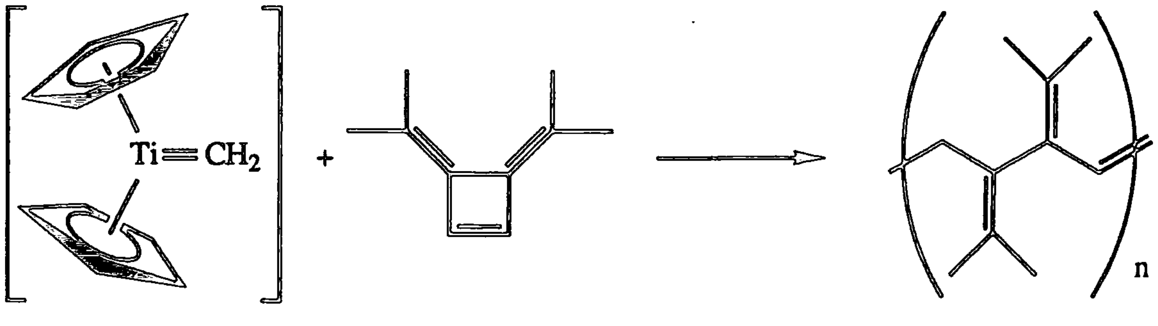
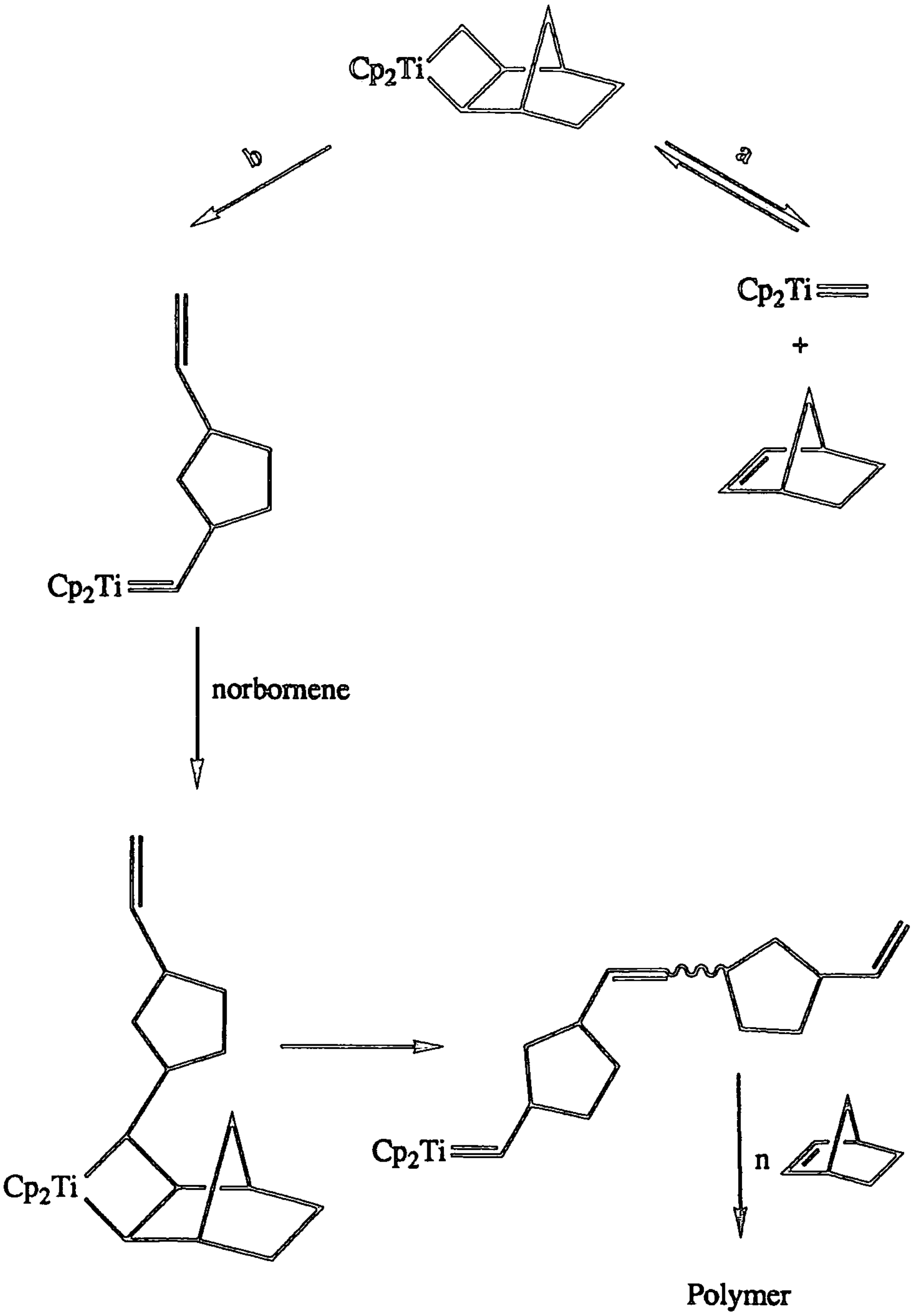


Figure 1.20 *Polymerisation of 3,4-diisopropylidenecyclobutene.*



Scheme 1.16 *The polymerisation of norbornene employing titanocyclobutane species.*

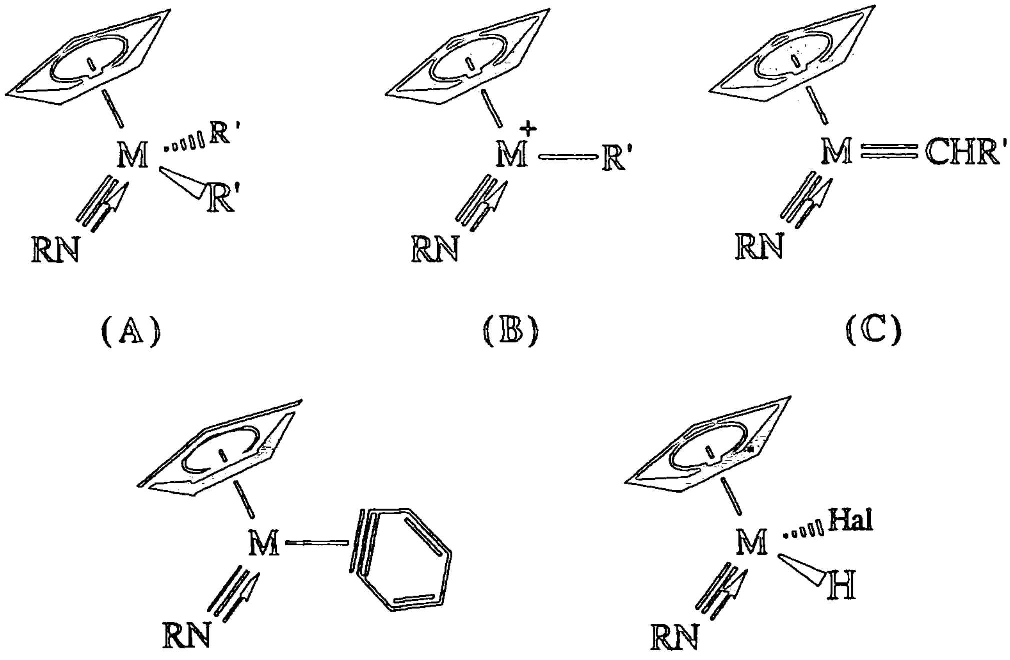
Oxidative doping of this polymer with iodine affords films which are shiny black and metallic in appearance. These materials exhibit conductivities from 10^{-3} to 10^{-4} Scm^{-1}, depending on the fabrication technique employed. The heavily oxidised polymer is brittle, but Grubbs has shown that block copolymers with norbornene can be prepared employing the titanocene catalyst which greatly improves the mechanical properties of the polymer, so making it more attractive for practical applications as a conducting polymer.

1.9 General Aims / Summary.

The combination of the isolobal and valence isoelectronic relationship between half-sandwich niobium and tantalum imido complexes and Group 4 metallocenes, together with our knowledge of the derivative chemistry of titanocene and zirconocene has enabled us to select attractive target molecules to pursue. Areas of interest include dialkyl species (**A**) as possible precursors to alkyl cations (**B**) suitable for Ziegler-Natta polymerisation, or alkylidene complexes (**C**) for acyclic and ring opening metathesis polymerisation. It is to be expected that ancillary multiply-bonded imido ligands would be ideally suited to the stabilisation of these types of high oxidation state complexes. Benzyne-containing species (**D**) and metal-hydrido complexes (**E**) could lead to novel reagents for various organic transformations such as C-C coupling reactions.

This chapter has highlighted important aspects of the vast range of transition metal imido chemistry studied to date. The occurrence and typical characterising data of imido complexes have been discussed, along with a number of applications of these species.

The relationship between imido and cyclopentadienyl ligands has been noted and the isolobal analogy has enabled areas of interest to be targeted based on consideration of Group 4 metallocene chemistry. The subsequent chapters of this thesis describe attempts to exploit this relationship through the synthesis, characterisation and reactivity studies on a variety of new early transition metal complexes.



(A) (B) (C)

(D) (E)

(M = Nb, Ta)

Figure 1.21 *Possible target molecules.*

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CHAPTER TWO

Synthesis and Characterisation of Half-Sandwich Imido Complexes of Niobium and Tantalum Containing Alkyl Ligands.

2.1 Introduction.

There is considerable interest in the half-sandwich imido compounds of niobium and tantalum of formula Cp'M(NR)X_2, (M = Nb, Ta), since they are formally isoelectronic with bent metallocenes of the type Cp'$_2$MX_2 (M = Ti, Zr, Hf)[1] (illustrated below for niobium and zirconium - Figure 2.1) Moreover, calculations have indicated that the frontier orbitals of the [Cp'M(NR)] (M = Group 5), and [Cp'$_2$M] (M = Group 4) fragments possess remarkably similar characteristics[1-3].

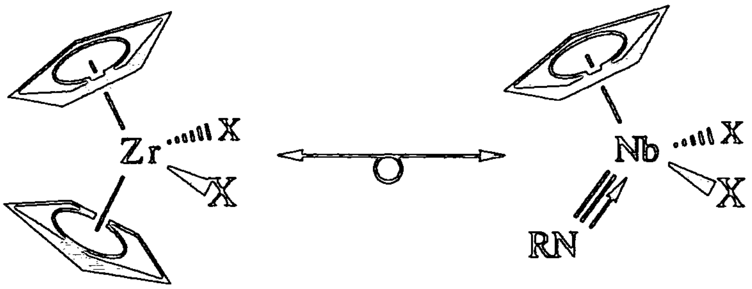


Figure 2.1 *Isolobal relationship between* Cp_2ZrX_2 *and* $CpNb(NR)X_2$.

Alkyl derivatives of titanocene and zirconocene are important both as stoichiometric and catalytic reagents for a variety of organic transformations[4] and have, for example, attracted much renewed interest due to their role in Ziegler-Natta polymerisations of α-olefins. This chapter describes convenient routes to the niobium and tantalum half-sandwich derivatives of the type Cp'M(NAr)Cl_2 (Cp' = Cp, M = Nb; Cp' = Cp*, M = Ta; Ar = 2,6-$^iPr_2$-C_6H_3). Hence, the synthesis and characterisation of a series of mono- and dialkyl complexes of the half-sandwich system are discussed as a prelude to an investigation of their stoichiometric and catalytic reactivity.

2.2 Synthesis of Complexes of the Form Cp'M(NR)Cl_2.

Recent work by Gibson and co-workers has described the synthesis of several half-sandwich imido compounds of niobium and tantalum[1,5]. Preliminary investigations of the reactivity of this class of compound suggests that a rich and varied derivative chemistry should be accessible[2].

The initial aim of this work was to develop improved synthetic routes to the convenient starting materials CpNb(NAr)Cl_2 and Cp^*Ta(NAr)Cl_2 which would act as the precursors for potentially useful synthetic reagents.

2.2.1 Preparation of CpNb(NAr)Cl_2 (1).

The established route to (1) involves the reaction of $CpNbCl_4$ with two equivalents of the silylated aniline ($Me_3SiNHAr$) in either 1,2-dichloroethane, dichloromethane, or toluene according to Equation 2.1. The subsequent removal of solvent, followed by washing with cold n-pentane and recrystallisation from a concentrated solution in n-pentane gave the product in good yield (80%).

$$CpNbCl_4 + 2Me_3SiNHAr \longrightarrow \underset{(1)}{CpNb(NAr)Cl_2} + 2Me_3SiCl + ArNH_2 \quad (2.1)$$

Two equivalents of silylated aniline are required for the preparation of (1); one equivalent leads to an insoluble yellow microcrystalline compound whose microanalysis corresponds to $[NHArSiMe_3][CpNb(NAr)Cl_3]$[2]. The 'waste' of one equivalent of silylated aniline is not desirable, since preparation and purification of $Me_3SiNHAr$ is laborious. Furthermore, the aniline liberated makes the product oily and so must be removed by repeated washing with cold n-pentane since it cannot be removed *in vacuo* due to its high boiling point (BP = 257 °C).

It was decided therefore to develop a new route to (1) which avoided the difficulties outlined above. Initial attempts to prepare (1) by the generation of silylated aniline *in situ* in the presence of base proved to be unsatisfactory.

$$\mathrm{CpNbCl_4} + \text{base} + \mathrm{Me_3SiCl} + \mathrm{ArNH_2} \longrightarrow$$

$$\underset{(1)}{\mathrm{CpNb(NAr)Cl_2}} + \text{base(HCl)} + \mathrm{Me_3SiCl} \quad (2.2)$$

(base = 2,6-lutidine)

A suspension of $\mathrm{CpNbCl_4}$ in dichloromethane was treated with excess base, 2,6-lutidine, followed by an excess of chlorotrimethylsilane. Upon subsequent addition of one equivalent of aniline in dichloromethane a purple solution was afforded. Removal of volatiles and extraction into diethylether gave a purple solution which, when reduced in volume afforded a red oil. Analysis by infrared spectroscopy confirmed that the oil contained the target molecule (1) and 2,6-lutidine. Attempted extraction of (1) from the oil was not successful, although it served to demonstrate that the silylated aniline could be generated and reacted with $\mathrm{CpNbCl_4}$ without having to be isolated.

As it could be shown that the target molecule (1) could be prepared utilising only one equivalent of silylated aniline an attempt was undertaken to optimise the conditions. To a suspension of $\mathrm{CpNbCl_4}$ in 1,2-dichloroethane was added one equivalent of base, (both triethylamine, and 2,6-lutidine were considered). To this mixture one equivalent of silylated aniline, $\mathrm{Me_3NHAr}$ in 1,2-dichloroethane,was then added. Stirring for *ca.* 12 hours gave a red solution in the case of the reaction involving 2,6-lutidine. No apparent reaction occured when triethylamine was employed as a base. Removal of the volatile components from the reaction employing 2,6-lutidine led to precipitation of the target molecule (1) which could be subsequently crystallised from a concentrated solution in n-pentane.

$$\mathrm{CpNbCl_4} + \mathrm{Me_3SiNHAr} + \text{base} \longrightarrow$$

$$\underset{(1)}{\mathrm{CpNb(NAr)Cl_2}} + \mathrm{Me_3SiCl} + \text{base(HCl)} \quad (2.3)$$

(base = 2,6-lutidine)

The above route has the advantage that the target species (1) is prepared in comparable yield to that of the established route. Moreover, the product is less oily due to the absence of free aniline. The availability of oil free (1) was subsequently found to be crucial in the success of alkylation reactions to give potential catalyst precursors.

Single crystal X-ray diffraction studies by this group on (1) show that the molecule is monomeric and isostructural with the earlier structurally characterised $CpNb(NMe)Cl_2$[5]. The Nb-N bond distance of 1.76(6)Å in (1) is consistent with a triply bonded imido ligand[6-8]. This is further substantiated by the Nb-N-C bond angle of 165.6(5)°, which lies at the low end of the range (161-180°)[9] typically observed for a terminal imido ligand containing an *sp* -hybridised nitrogen.

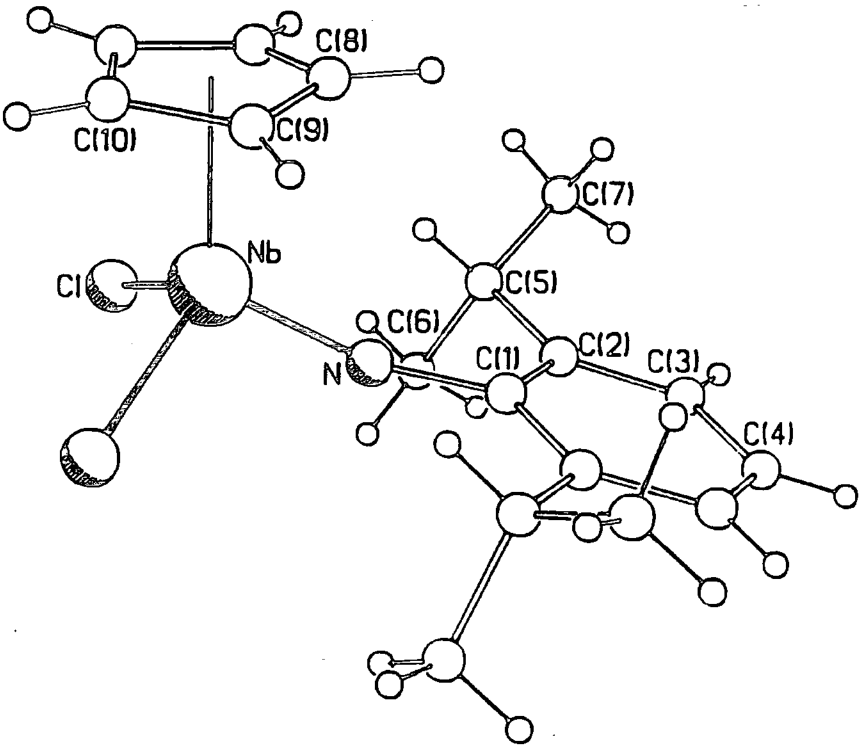


Figure 2.2 *Molecular structure of* $CpNb(NAr)Cl_2$.

The assignment of ^1H and ^{13}C NMR spectra are given in 5.2.2. For the imido moiety the assignments were made by comparison with other (aryl)imido complexes[10]. The ^1H coupled ^{13}C NMR spectrum of (1), and its alkylated derivatives show the Cp ring carbons not as the expected doublet, but as a doublet of pentets (Figure 2.3). The explanation for such a splitting pattern is that $^2J_{CH}$ and $^3J_{CH}$ coupling constants are identical, an effect which has been observed in other niobium species such as $Cp_2Nb(Et)(C_2H_4)$[11].

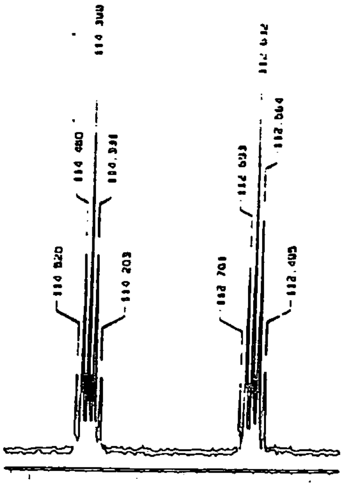


Figure 2.3 *100 MHz ^{13}C NMR spectrum (C_6D_6) of the Cp ring resonances of $CpNb(NAr)Cl_2$ (1).*

2.2.2. Preparation of $Cp^*Ta(NAr)Cl_2$ (2).

The synthetic route to (2) established by Mitchell[12] involved refluxing Cp^*TaCl_4 with two equivalents of silylated aniline, $Me_3SiNHAr$ in 1,2-dichloroethane at 70°C for 4 days (Equation 2.4). Subsequent recrystallisation from a concentrated solution in toluene afforded (2) as impure orange crystals in moderate yield (49%). Analysis by ^1H NMR spectroscopy showed the product to be contaminated with unreacted Cp^*TaCl_4. The reason for this unusually slow reaction is as yet not understood.

$$\overset{\circ}{\mathrm{Cp}}\mathrm{TaCl_4} + 2\mathrm{Me_3SiNHAr} \xrightarrow[70^{\circ}\mathrm{C}]{(\mathrm{CH_2Cl})_2} \overset{\circ}{\mathrm{Cp}}\mathrm{Ta(NAr)Cl_2} + 2\mathrm{Me_3SiCl} + \mathrm{ArNH_2} \quad (2.4)$$

(2)

It was found that the yield of (2) could be improved considerably by prolonged warming of the reaction mixture at 70°C for a period of 10 days. Extraction of the reaction mixture into toluene and subsequent recrystallisation at -78°C gives a 72% yield of analytically pure orange crystals.

Structural characterisation of (2) shows it to possess a similar three-legged piano stool geometry to that described for (1). The metal-nitrogen bond length (1.780(5)Å) is within the expected range for tantalum triple bonds[13-15], and the Ta-N-C angle of 171.4(5)° again is typical of a terminal imido ligand possessing a *sp* -hybridised nitrogen. The deviation from linearity of the Ta-N-C bond (8.6°) arises from a bending of the imido substituent towards the pentamethylcyclopentadienyl ring.

2.3 Reaction of Cp'M(NAr)Cl$_2$ with Tertiary Phosphines.

The half-sandwich imido species Cp'M(NAr)Cl$_2$ (M = Nb, Ta) are coordinatively unsaturated 16 electron species and therefore should bind donor solvents. They are similar to CpNb(NMe)Cl$_2$ in their inability to bind acetonitrile or THF strongly[5], but they do react with highly basic ligands such as trimethylphosphine to give the base adducts.

2.3.1 Preparation of CpNb(NAr)(PMe$_3$)Cl$_2$ (3).

Trimethylphosphine binds readily to (1) in toluene to yield CpNb(NAr)(PMe$_3$)Cl$_2$ (3) as a sparingly soluble yellow powder. This simple adduct is envisaged to form according to Equation 2.5. However, prolonged exposure to a dynamic vacuum leads to loss of phosphine. This lability is somewhat suprising considering the acidity of the niobium centre. For example, it has been found that

$CpNb(NMe)(PMe_3)Cl_2$ does not lose phosphine *in vacuo*. This suggests that although the relatively more electron-withdrawing (aryl)imido should favour phosphine addition compared with the (methyl)imido, $CpNb(NMe)Cl_2$, it is an over-riding steric influence that accounts for the lability of the phosphine.

$$\underset{(1)}{CpNb(NAr)Cl_2} + PMe_3 \underset{vacuo}{\rightleftharpoons} \underset{(3)}{CpNb(NAr)(PMe_3)Cl_2} \quad (2.5)$$

The lability of the phosphine in (3) is such that in THF solvent trimethylphosphine is displaced, and removal of the solvent under reduced pressure affords a significant fraction of base-free (1) in conjunction with (3).

2.3.2 Preparation of $Cp^*Ta(NAr)(PMe_3)Cl_2$ (4).

In toluene, (2) reacts cleanly with trimethylphosphine to afford a lemon yellow coloured solution. The 400 MHz ^1H NMR spectrum (C_7D_8) confirms that phosphine is bound to the metal centre $\delta(PMe_3)$ 0.92 ppm, (*cf.* free PMe_3 δ 0.87 ppm).

Attempted isolation of this adduct affords exclusively orange crystals of the phosphine free dichloride (2), even when the solvent is removed under reduced pressure at *ca.* -78°C. This may be attributed to the combination of sterically demanding Cp^* and (aryl)imido ligands and also the electron donating nature of the pentamethylcyclopentadienyl ligand.

$$\underset{(2)}{Cp^*Ta(NAr)Cl_2} + PMe_3 \underset{vacuo}{\rightleftharpoons} \underset{(4)}{Cp^*Ta(NAr)(PMe_3)Cl_2} \quad (2.6)$$

2.4 Preparation of Some Methyl Derivatives of $Cp'M(NAr)Cl_2$.

Alkyl derivatives of $Cp'M(NAr)Cl_2$ provide attractive precursors to zirconocene-like cationic alkyl target molecules. Initial attempts to alkylate $Cp'M(NAr)Cl_2$ centred on the preparation of the mono- and bis-methyl derivatives. It was then hoped that it would prove possible to use these alkyl derivatives to prepare cationic niobium and tantalum methyl species, as described by Jordan with Cp_2ZrMe_2 species[4b,16].

2.4.1 Preparation of CpNb(NAr)(Me)Cl (5).

Initial attempts to prepare the mono methyl derivative (5) employed diethylether solutions of MeMgI. These reactions, however, proved troublesome as they did not yield the expected niobium-imido alkyl species, but in all cases gave insoluble pale powders. Elemental analyses on these complexes indicated the presence of a substantial percentage of magnesium. It is believed that these products are complex niobium-magnesium adducts, presumably with iodides bridging the niobium and magnesium atoms. Since iodide is relatively soft, the harder chloro Grignard reagent was explored in an attempt to circumvent halide bridge formation.

Treatment of a diethylether solution of (1) with one equivalent of MeMgCl gave orange-red crystals of CpNb(NAr)(Me)Cl (5) upon subsequent recrystallisation from a concentrated solution in n-pentane (Equation 2.7).

$$\underset{(1)}{CpNb(NAr)Cl_2} + MeMgCl \xrightarrow{Et_2O} \underset{(5)}{CpNb(NAr)(Me)Cl} + MgCl_2 \quad (2.7)$$

The ^1H and ^{13}C NMR spectra were assigned by comparison with the NMR spectra of (1). The 100 MHz ^{13}C NMR spectrum of (5) shows a methyl resonance at δ 40.36 ppm which exhibits significant line broadening ($\upsilon^1/_2 = 65$ Hz), attributable to scalar coupling to the ^{93}Nb nucleus ($I = {}^9/_2$, 100% natural abundance), combined with a partial decoupling of the ^{93}Nb nucleus *via* quadropolar relaxation; such an effect has been observed for carbons attached to niobium for other species such as $Cp_2Nb(H)(C_2H_4)$[11].

$CpNb(NAr)Cl_2$ (1) reacts with two equivalents of MeMgCl to give an intractable oil, whose analysis was inconsistent with $CpNb(NAr)Me_2$. This intractability could possibly be a consequence of the absence of pπ donor ligands such as chloride which would tend to lend stability to the 16 electron complex *via* pπ-dπ donation.

2.4.2 Preparation of $CpNb(NAr)(PMe_3)(Me)Cl$ (6).

The mono-methyl, phosphine adduct (6) may be prepared by the reaction of one equivalent of MeMgCl with a diethylether suspension of (3), followed by recrystallisation from diethylether (Equation 2.8). Compound (6) may also be prepared by the reaction of trimethylphosphine with (5) (Equation 2.9).

$$\underset{(3)}{\mathrm{CpNb(NAr)(PMe_3)Cl_2}} + \mathrm{MeMgCl} \xrightarrow{\mathrm{Et_2O}} \underset{(6)}{\mathrm{CpNb(NAr)(PMe_3)(Me)Cl}} + \mathrm{MgCl_2} \tag{2.8}$$

$$\underset{(5)}{\mathrm{CpNb(NAr)(Me)Cl}} + \mathrm{PMe_3} \xrightarrow{\qquad} \underset{(6)}{\mathrm{CpNb(NAr)(PMe_3)(Me)Cl}} \tag{2.9}$$

The phosphine in (6) is much less labile than in (3); for example, it is found to be stable to prolonged exposure to dynamic vacuum. A possible explanation for this observation is the enhanced acidity of the niobium centre in (6) due to a reduction in the extent of pπ-dπ lone pair donation on replacement of one chloride ligand for a methyl group. However, the phosphine is still relatively weakly bound, since the 400 MHz ^1H NMR spectrum (C_6D_6) shows a resonance at δ 0.83 ppm for the PMe_3 methyls which is close to the chemical shift observed for free PMe_3, (δ 0.79 ppm).

Treatment of a suspension of (3) with two equivalents of MeMgCl failed to yield a tractable product. Thus, to date, the dimethyl derivative of (1) has not proven accessible either in a base-free or phoshine stabilised form.

2.4.3. Preparation of Cp*Ta(NAr)Me$_2$ (7).

Since the dimethyl derivative of CpNb(NAr)Cl$_2$ (1) proved inaccessible, interest turned to the possible dialkylation of Cp*Ta(NAr)Cl$_2$ (2). It has previously been demonstrated that Cp*Nb(NAr)Cl$_2$ may be cleanly dialkylated using MeMgCl[17]. Thus, replacement of the cyclopentadienyl ring for the more sterically demanding and electron donating pentamethylcyclopentadienyl ring appears to lead to the stabilisation of di-alkyl derivatives.

Treatment of a diethylether solution of (2) with an excess of MeMgCl gives a lemon yellow solution, which when extracted into n-pentane and recrystallised at -78°C, affords yellow-needle like crystals of Cp*Ta(NAr)Me$_2$ (7) in good yield (*ca.* 72%). (Equation 2.10).

$$\underset{(2)}{C\overset{*}{p}Ta(NAr)Cl_2} + 2MeMgCl \xrightarrow{Et_2O} \underset{(7)}{C\overset{*}{p}Ta(NAr)Me_2} + 2MgCl_2 \quad (2.10)$$

Although (7) is a 16 electron coordinatively unsaturated species, ^{1}H NMR spectroscopy shows there to be no interaction with the neutral L donor ligands PMe$_3$ and ethylene. This may be explained due to the sterically demanding and electron donating nature of the Cp* ligand.

2.4.4 Preparation of Cp*Ta(NAr)(Me)Cl (8).

Bercaw and co-workers[18] have shown that hydrogenation of Cp*Ta(NR)Me$_2$ with dihydrogen in the presence of phosphine affords tantalum-hydrido species according to Equation 2.11.

$$C\overset{*}{p}Ta(NR)Me_2 + 2H_2 + PMe_3 \longrightarrow$$

$$C\overset{*}{p}Ta(NR)(H)_2(PMe_3) + 2CH_4 \quad (2.11)$$

$$(R = CMe_3)$$

Isolation of the mono-methyl species (8) should prove to be an attractive precursor for the possible synthesis of $Cp^*Ta(NAr)(H)Cl$; this mono-hydrido tantalum complex would be an analogue of the synthetically useful 'Schwartz reagent', $Cp_2Zr(H)Cl$[4a].

Treatment of a diethylether solution of (2) with one equivalent of MeMgCl afforded an orange solution. Subsequent extraction and recrystallisation from a solution in n-pentane at -78°C gave an orange microcrystalline solid. Analysis by ^1H NMR spectroscopy showed the solid to be a mixture of the mono-methyl (8) with resonances at δ 0.83, 1.76, and 3.58 ppm attributable to methyl, Cp^* ring and isopropyl methine hydrogens respectively, but also the dichloride (2) and dimethyl (7) species. A subsequent ^1H NMR experiment involving mixing the dichloride (2) and dimethyl (7) tantalum species in C_6D_6 showed that chloro-methyl exchange occurs until equilibrium is attained after a few days at ambient temperature. A similar exchange reaction was observed when $Cp^*Nb(NAr)Cl_2$ and $Cp^*Nb(NAr)Me_2$ were mixed in an NMR tube[19]. Hence, the isolation of the niobium species (5) implies that the mono-methyl species was selectively crystallised out of an equilibrium mixture of $CpNb(NAr)Cl_2$ (1), CpNb(NAr)(Me)Cl (5) and $CpNb(NAr)Me_2$.

$$\underset{(2)}{Cp^*Ta(NAr)Cl_2} + Cp^*Ta(NAr)Me_2 \xrightleftharpoons{K} \underset{(8)}{2Cp^*Ta(NAr)(Me)Cl} \qquad (2.12)$$

$$K = 10.8(8)$$

2.5 Preparation of Some Neopentyl Derivatives of $CpNb(NAr)Cl_2$ (1).

As the dimethyl species $CpNb(NAr)Me_2$ cannot be isolated we sought to prepare sterically more demanding neopentyl derivatives of (1). We envisaged also that the bis-neopentyl niobium complex could provide a suitable precursor to a neopentylidene containing species ($Nb{=}CHCMe_3$) *via* an α-hydrogen abstraction process to eliminate neopentane[20]. Such an alklidene derivative would be of interest as a potential metathesis polymerisation catalyst.

2.5.1 Preparation of $CpNb(NAr)(CH_2CMe_3)Cl$ (9).

Treatment of a diethylether solution of (1) with one mole equivalent of Me_3CCH_2MgCl gave a red solution. Extraction into n-pentane afforded orange crystals of $CpNb(NAr)(CH_2CMe_3)Cl$ (9) upon prolonged cooling at -78°C. This reaction proceeds according to Equation 2.13. In contrast to the preparation of the mono-methyl tantalum complex (8), no equilibrium between $CpNb(NAr)Cl_2$ (1), $CpNb(NAr)(CH_2CMe_3)Cl$ (9) and a bis-neopentyl species is observed.

$$\underset{(1)}{CpNb(NAr)Cl_2} + Me_3CCH_2MgCl \xrightarrow{Et_2O} \underset{(9)}{CpNb(NAr)(CH_2CMe_3)Cl} + MgCl_2 \quad (2.13)$$

Compound (9) is soluble in aromatic, chlorocarbon and pentane solvents and has been characterised by elemental analysis, mass spectrometry, infrared and NMR spectroscopies.

Although a coordinatively unsaturated 16 electron compound, (9) shows no spectroscopic evidence for agostic interactions between the metal centre and the hydrogens of the α-carbon of the neopentyl group. In the 100 MHz ^{13}C NMR spectrum the α-carbon resonates at δ 86.31 ppm and is broadened ($\upsilon_{1/2}$ = 33 Hz) to such an extent that the value of the $^1J_{CH}$ coupling constant had to be acquired from the natural abundance ^{13}C satellites in the ^1H NMR spectrum. The $^1J_{CH}$ coupling constant of 123 Hz is not indicative of an agostic C-H bond[21]. A further point of interest is that the 400 MHz ^1H NMR spectrum (C_6D_6) shows that the methylene protons of the neopentyl group are diastereotopic, that is they have non-equivalent environments and so appear as two doublets δ 1.64, and 2.46 ppm; $^2J_{HH}$ = 12.5 Hz.

2.5.2 Preparation of $CpNb(NAr)(CH_2CMe_3)Br$ (**10**).

Treatment of a diethylether solution of (**1**) with one equivalent of bromo-neopentyl Grignard reagent and subsequent recrystallisation from a concentrated solution in n-pentane, afforded red crystals of $CpNb(NAr)(CH_2CMe_3)Br$ (**10**) in moderate yield (*ca.* 50%), (Equation 2.14). Analysis confirmed that quantitative halide exchange had occurred, a phenomenon also observed by Herrmann *et al* in the chemistry of half-sandwich rhenium imidos[22]. The 400 MHz ^1H NMR spectrum (C_6D_6) shows doublets at δ 1.34 and 2.54 ppm attributable to the diastereotopic methylene protons of the neopentyl group. The α-carbon $^1J_{CH}$ coupling constant of 122 Hz, again obtained from the ^{13}C satellites in the ^1H NMR spectrum, does not appear to be indicative of an agostic interaction between the methylene hydrogens of the neopentyl moiety and the metal centre.

$$\underset{(\mathbf{1})}{\mathrm{CpNb(NAr)Cl_2}} + \mathrm{Me_3CCH_2MgBr} \xrightarrow{\mathrm{Et_2O}} \underset{(\mathbf{10})}{\mathrm{CpNb(NAr)(CH_2CMe_3)Br}} + \mathrm{MgCl_2} \quad (2.14)$$

2.5.3 Preparation of $CpNb(NAr)(CH_2CMe_3)_2$ (**11**).

Initial attempts to prepare the bis-neopentyl, $CpNb(NAr)(CH_2CMe_3)_2$ (**11**), with two molar equivalents of Me_3CCH_2MgCl in diethylether solvent proved unsuccessful, yielding only the mono-neopentyl derivative (**9**). However, treatment of a diethylether solution of (**1**) with an excess of Me_3CCH_2MgCl (3.3 - 4 equivalents) gave an orange solution. After removal of the volatile components and recrystallisation of the residue from a concentrated solution in n-pentane yellow crystals of (**11**) were obtained in moderate yield (*ca.* 53%), (Equation 2.15).

$$\underset{(1)}{\mathrm{CpNb(NAr)Cl_2}} + \mathrm{2Me_3CCH_2MgCl} \xrightarrow{\mathrm{Et_2O}} \underset{(11)}{\mathrm{CpNb(NAr)(CH_2CMe_3)_2}} + \mathrm{2MgCl_2} \quad (2.15)$$

On standing at ambient temperature, a C_6D_6 solution of $CpNb(NAr)(CH_2CMe_3)_2$ (**11**) was found to decompose to liberate neopentane (^1H NMR δ 0.90) plus an unidentified paramagnetic niobium species, which may be responsible for the resultant black coloured solution. This decomposition is accelerated by heating. The liberation of neopentane suggests that initial decomposition may occur *via* a neopentylidene species, although none could be observed by ^1H NMR spectroscopy. The fact that no niobium-alkylidene is observed may not be suprising as Schrock *et al* have found that niobium-alkylidenes are often unstable[20,23]. However, the absence of signals in the olefin region of the ^1H NMR spectrum does not lend support to a decomposition pathway for (**11**) involving an alkylidene coupling reaction. Attempted trapping of a niobium-alkylidene species with PMe_3 proved unsuccessful. However, treatment of a solution of (**11**) with norbornene affords poly(norbornene) on standing at ambient temperature. This suggests that although no niobium-alkylidene is observed by ^1H NMR spectroscopy, there is evidence for initial decomposition generating a metathesis - active alkylidene *via* an α-hydrogen transfer.

2.5.3.1 The Molecular Structure of $CpNb(NAr)(CH_2CMe_3)_2$ (11).

A saturated n-pentane solution of (**11**) was cooled at -78°C over several days to afford yellow crystals. A crystal of suitable size was sealed in a Lindemann capillary and the X-ray crystal structure determination carried out by Dr. W. Clegg, Mr. D. C. R. Hockless, and Mr. P. A. O'Neil at the University of Newcastle-upon-Tyne. The structural parameters are collected in Appendix 1. The molecular structure is illustrated in Figure 2.4. Selected bond angles and lengths are collected in Table 2.1.

The Nb-N bond length of 1.788(2)Å lies within the range expected for niobium-imido compounds[6-8]. The Nb-N-C angle of 174.6(2)° is typical of those observed for a terminal imido ligand containing an *sp* -hybridised nitrogen[9]. The Nb-C_α distances of 2.215(3) and 2.174(3)Å, are comparable with the Nb-C_α distance (2.193(5)Å) found for the mono-methyl complex $CpNb(NCMe_3)(Me)Cl^2$. The Nb-Cp_{carbon} distances range from 2.403(5) to 2.564(4) Å.

The suprising feature of the crystal structure is that while the Cp and N-2,6-$^iPr_2$-C_6H_3 groups are quite normal, one of the α-hydrogens on each neopentyl group lies within close contact (av. 2.36 Å) of the metal centre with Nb-C-H_α bond angles of 87 and 89°. These parameters are consistent with weak agostic interactions, as first indicated by ^1H NMR and infrared spectroscopies.

Molecular modelling studies utilising COSMIC show that although one of the neopentyl groups approaches close to an isopropyl unit on the aryl imido of (11), (closest approach 1.43Å), there exists no close contacts for the the second neopentyl group. This suggests that steric congestion is an unlikely explanation for both agostic interactions.

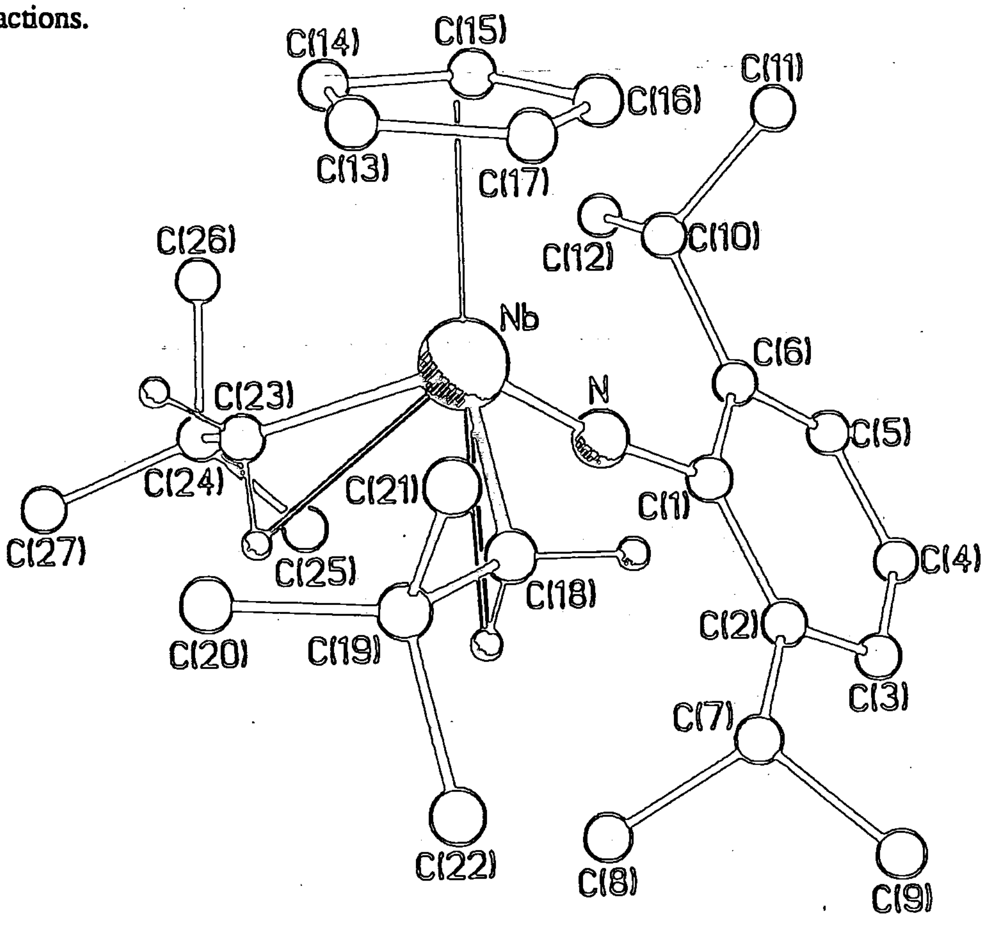


Figure 2.4 *Molecular structure of* $CpNb(NAr)(CH_2CMe_3)_2$ *(11).*

Nb - N	1.788(2)	Nb - C(13)	2.564(4)
Nb - C(14)	2.514(5)	Nb - C(15)	2.415(5)
Nb - C(16)	2.403(5)	Nb - C(17)	2.474(5)
Nb - C(18)	2.215(3)	Nb - H(18b)	2.405(33)
Nb - C(23)	2.174(3)	Nb - H(23b)	2.321(29)
N - C(1)	1.399(4)	C(1) - C(2)	1.416(5)
C(1) - C(6)	1.411(5)	C(2) - C(3)	1.404(6)
C(2) - C(7)	1.497(6)	C(3) - C(4)	1.350(9)
C(4) - C(5)	1.348(8)	C(5) - C(6)	1.402(7)
C(6) - C(10)	1.498(6)	C(7) - C(8)	1.518(6)
C(7) C(9)	1.538(6)	C(10) - C(11)	1.535(7)
C(10) - C(12)	1.535(7)	C(13) - C(14)	1.402(7)
C(13) - C(17)	1.395(7)	C(14) - C(15)	1.377(7)
C(15) - C(16)	1.383(8)	C(16) - C(17)	1.402(8)
C(18) - H(18a)	0.966(26)	C(18) - H(18b)	0.960(26)
C(18) - C(19)	1.544(5)	C(19) - C(20)	1.504(8)
C(19) - C(21)	1.512(7)	C(19) - C(22)	1.535(8)
C(23) - H(23a)	0.957(20)	C(23) - H(23b)	0.958(33)
C(23) - C(24)	1.535(5)	C(24) - C(25)	1.502(6)
C(24) - C(26)	1.503(8)	C(24) - C(27)	1.531(7)

N - Nb - C(13)	151.2(2)	N - Nb - C(14)	1.32.5(1)
C(13) - Nb - C(14)	32.0(2)	N - Nb - C(15)	102.2(1)
C(13) - Nb - C(15)	53.8(2)	C(14) - Nb - C(15)	32.4(2)
N - Nb - C(16)	97.2(2)	C(13) - Nb - C(16)	54.0(2)
C(14) - Nb - C(16)	54.1(2)	C(15) - Nb - C(16)	33.4(2)
N - Nb - C(17)	123.4(1)	C(13) - Nb - C(17)	32.1(2)
C(14) - Nb - C(17)	53.7(2)	C(15) - Nb - C(17)	54.9(2)
C(16) - Nb - C(17)	33.4(2)	N - Nb - C(18)	97.9(1)
C(13) - Nb - C(18)	94.7(2)	C(14) - Nb - C(18)	126.1(1)
C(15) - Nb - C(18)	140.5(1)	C(16) - Nb - C(18)	110.8(2)
C(17) - Nb - C(18)	85.7(2)	N - Nb - H(18b)	84.5(6)
C(13) - Nb - H(18b)	114.8(6)	C(14) - Nb - H(18b)	143.0(6)
C(15) - Nb - H(18b)	163.9(7)	C(16) - Nb - H(18b)	132.0(7)
C(17) - Nb - H(18b)	109.2(7)	C(18) - Nb - H(18b)	23.5(7)
N - Nb - C(23)	101.5(1)	C(13) - Nb - C(23)	99.9(2)
C(14) - Nb - C(23)	84.7(1)	C(15) - Nb - C(23)	103.3(2)
C(16) - Nb - C(23)	136.0(2)	C(17) - Nb - C(23)	132.0(2)
C(18) - Nb - C(23)	105.5(1)	H(18b) - Nb - C(23)	89.4(7)
N - Nb - H(23b)	97.0(9)	C(13) - Nb - H(23b)	110.3(9)
C(14) - Nb - H(23b)	104.8(9)	C(15) - Nb - H(23b)	127.4(8)
C(16) - Nb - H(23b)	158.8(9)	C(17) - Nb - H(23b)	139.1(9)
C(18) - Nb - H(23b)	82.6(8)	H(18b) - Nb - H(23b)	65.1(11)
C(23) - Nb - H(23b)	24.3(8)	Nb - N - C(1)	174.6(2)
N - C(1) - C(2)	118.5(3)	N - C(1) - C(6)	120.9(3)
C(2) - C(1) - C(6)	120.5(3)	C(1) - C(2) - C(3)	117.6(4)
C(1) - C(2) - C(7)	120.6(3)	C(3) - C(2) - C(7)	121.8(4)
C(2) - C(3) - C(4)	121.6(5)	C(3) - C(4) - C(5)	120.7(5)
C(4) - C(5) - C(6)	122.2(5)	C(1) - C(6) - C(5)	117.4(4)
C(1) - C(6) - C(10)	121.6(3)	C(5) - C(6) - C(10)	121.0(4)
C(2) - C(7) - C(8)	112.4(3)	C(2) - C(7) - C(9)	113.7(3)
C(8) - C(7) - C(9)	110.2(4)	C(6) - C(10) - C(11)	110.3(4)
C(6) - C(10) - C(12)	113.7(4)	C(11) - C(10) - C(12)	111.0(4)
Nb - C(13) - C(14)	72.0(2)	Nb - C(13) - C(17)	70.4(3)

C(14) - C(13) - C(17)	107.2(4)	Nb - C(14) - C(13)	75.9(3)
Nb - C(14) - C(15)	69.9(3)	C(13) - C(14) - C(15)	108.5(4)
Nb - C(15) C(14)	77.8(3)	Nb - C(15) - C(16)	72.8(3)
C(14) - C(15) - C(16)	108.4	Nb - C(16) - C(15)	73.8(3)
Nb - C(16) - C(17)	76.1(3)	C(15) - C(16) - C(17)	108.0(4)
Nb - C(17) - C(13)	77.5(3)	Nb - C(17) - C(16)	70.5(3)
C(13) - C(17) - C(16)	107.8(4)	Nb - C(18) - H(18a)	107.3(17)
Nb - C(18) - H(18b)	89.4(21)	H(18a) - C(18) - H(18b)	109.6(27)
Nb - C(18) - C(19)	131.2(2)	H(18a) - C(18) - C(19)	110.1(18)
H(18b) - C(18) - C(19)	106.0(18)	Nb - H(18b) - C(18)	67.0(18)
C(18) - C(19) - C(20)	110.7(4)	C(18) - C(19) - C(21)	111.7(3)
C(20) - C(19) - C(21)	110.5(4)	C(18) - C(19) - C(22)	107.2(4)
C(20) - C(19) - C(22)	108.9(4)	C(21) - C(19) - C(22)	107.7(4)
Nb - C(23) - H(23a)	107.0(20)	Nb - C(23) - H(23b)	86.5(17)
H(23a) - C(23) - H(23b)	105.3(32)	Nb - C(23) - C(24)	132.5(3)
H(23a) - C(23) - C(24)	106.9(22)	H(23b) - C(23) - C(24)	115.1(21)
Nb - H(23b) - C(23)	69.2(17)	C(23) - C(24) - C(25)	110.5(3)
C(23) - C(24) - C(26)	109.6(4)	C(25) - C(24) - C(26)	109.8(4)
C(23) - C(24) - C(27)	109.5(3)	C(25) - C(24) - C(27)	108.4(4)
C(26) - C(24) - C(27)	109.0(4)		

Table 2.1 *Bond distances (Å) and angles (°) for* $CpNb(NAr)(CH_2CMe_3)_2$ *(11).*

2.5.3.2 Spectroscopic Evidence for Agostic Interactions in $CpNb(NAr)(CH_2CMe_3)_2$ (11).

The 400 MHz ^1H NMR spectrum (C_6D_6) of (11) shows that only one of the diastereotopic methylene doublet resonances of the neopentyl ligand is observable at ambient temperature. The presence of a second neopentyl methylene doublet beneath the neopentyl t-butyl group (δ 1.12 ppm) was demonstrated by a homonuclear ^1H NMR decoupling experiment.

The α-carbon resonances of the neopentyl ligands are again found to be broadened through coupling to the quadropolar ^{93}Nb nucleus. The $^1J_{CH}$ coupling constant of 113 Hz for the methylenes of the neopentyl ligands has been obtained from the ^{13}C satellites in the ^1H NMR spectrum. The value of 113 Hz for the $^1J_{CH}$ coupling constant provides strong spectroscopic evidence for the presence of an α-agostic interaction in (11), and may be attributable to an average of a terminal *sp³* C-H bond (typically $^1J_{CH}$ = 120-130 Hz)[24] and the C-H coupling of a three-centre M-C-H (agostic) interaction (typically $^1J_{CH}$ = 70-100 Hz)[24,25]. Variable temperature ^1H NMR studies ($CDCl_3$, +50 to -50°C) on complex (11), failed to 'freeze out' the agostic structure at low temperature, but significant changes in the chemical shift of the methylene hydrogen resonances, (*ca.* 0.2 ppm), relative to the Cp and imido ligands were observed. This is again indicative of agostic interactions[25].

Difference NOE NMR experiments, ($CDCl_3$, -50°C), between each methylene resonance and the Cp and isopropyl groups of the (aryl)imido in (11) appear to indicate that the methylene hydrogens giving rise to the higher field signal, are on average, orientated toward the Cp ring, while its diastereotopic partner is directed towards the imido ligand. The same assignment of the orientation of the methylene hydrogen resonances can be made for the related complex $CpNb(NCMe_3)(CH_2CMe_3)_2$ (12).

Each methylene proton resonance will be an average of two hydrogen environments due to rotation of the neopentyl group about the Nb-C bond. This can be seen clearly from the idealised view below (Figure 2.5) where signals attributable to the

H_1/H_2 and H_3/H_4 pairs will be observed. Thus, on the basis of the NOE measurements, the high field signal can be assigned with some confidence to $(H_1/H_2)_{ave}$ with an averaged $^2J_{HH}$ of 11.8 Hz whilst the lower field doublet resonance is attributable to $(H_3/H_4)_{ave}$.

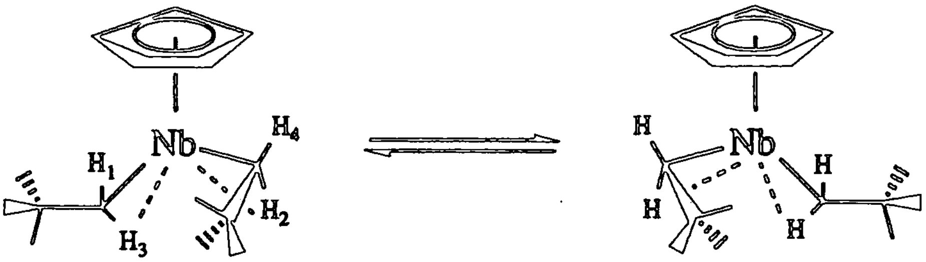


Figure 2.5

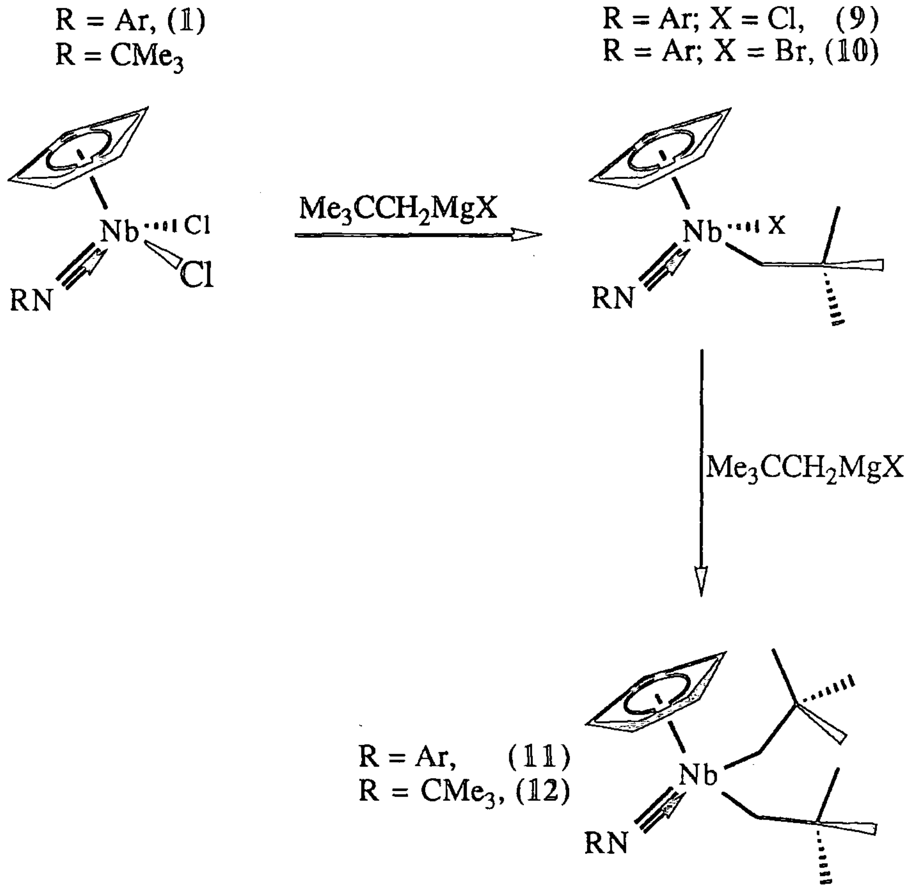
(H_2 and H_3 are the protons in relatively close contact with the metal centre indicated by dotted lines, while the imido ligand projects towards the rear and is not shown).

Further evidence for an α-agostic interaction comes from the infrared spectrum of (11) which reveals a broad absorption at 2700 cm^{-1} attributable to a bridging C-H stretch. This effect can be seen more effectively in the related complex $CpNb(NCMe_3)(CH_2CMe_3)_2$[26] (12) where, due to its low melting point (31.2 °C), the infrared spectrum can be taken from a thin film without the need for a mulling agent. Furthermore, a $^1J_{CH}$ coupling constant of 112 Hz is found for the neopentyl methylenes of $CpNb(NCMe_3)(CH_2CMe_3)_2$ (12) which is again consistent with the presence of an α-agostic interaction.

The only other niobium-neopentyl complex for which a $^1J_{CH}$ coupling constant has been reported is $Nb(\eta^1\text{-}CHCMe_3)(CH_2CMe_3)_3$ with a remarkably low value of 101 Hz[20b]. Related tantalum compounds are found to possess values over a considerable range (110-121Hz)[27] which may indicate that many of the compounds could possess agostic interactions of differing strengths.

In order to confirm the existence of α-agostic interactions in complexes of the type $CpNb(NR)(CH_2CMe_3)_2$ (R = CMe_3, 2,6-$^iPr_2$-C_6H_3), it was decided to undertake further spectroscopic studies on the neopentyl species so far discussed.

The preparation of these mono- and dialkyl derivatives of $CpNb(NR)Cl_2$, (R = CMe_3, 2,6-$^iPr_2$-C_6H_3) is summarised in Scheme 2.1 below:

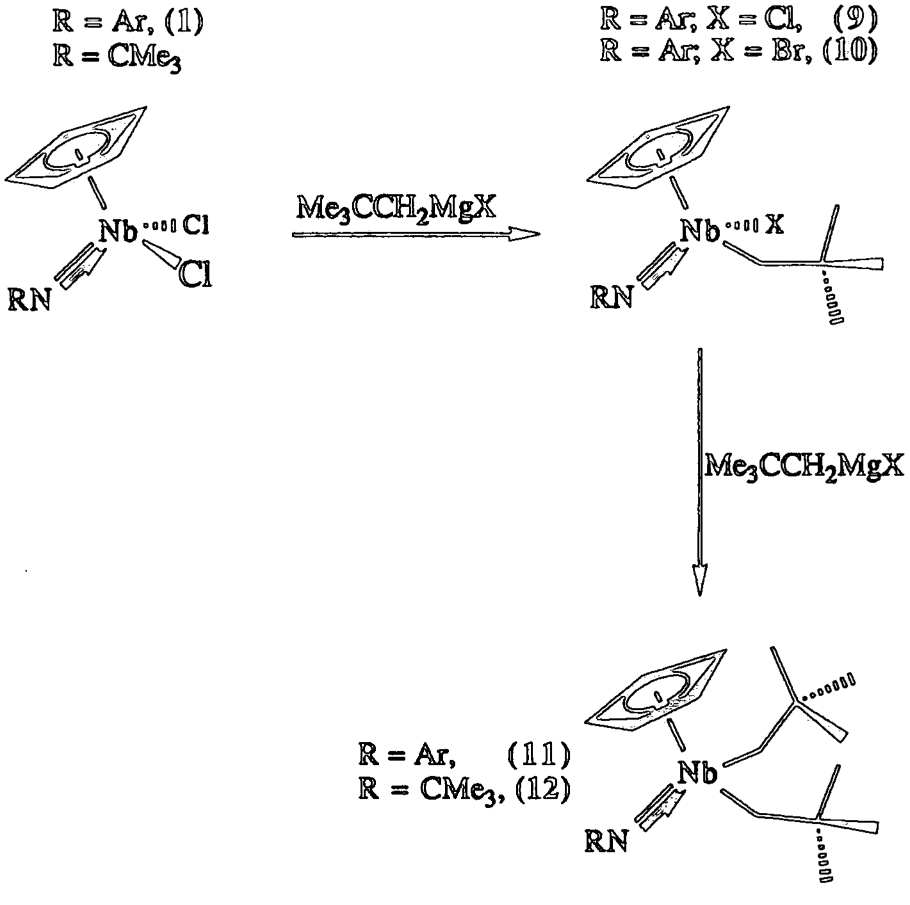


Scheme 2.1

2.6 Investigation of α-Agostic Interactions in Bis-neopentyl Derivatives of $CpNb(NR)Cl_2$.

Interactions of an alkyl ligand C-H bond with coordinatively unsaturated transition metal centres are now well-established[21,28]. However, multiple interactions at a single metal site as observed in the structure of the bis-neopentyl (**11**) are relatively uncommon. This type of interaction is at present restricted to very low electron count transition metal complexes such as $Cp^*Ti(CH_2Ph)_2$[29] (12 electrons) or complexes of the actinide elements such as $Cp^*_2Th(CH_2CMe_3)_2$[30]. All of these examples have been characterised by diffraction techniques.

The preparation of these mono- and dialkyl derivatives of $CpNb(NR)Cl_2$, (R = CMe_3, 2,6-$^iPr_2$-C_6H_3) is summarised in Scheme 2.1 below:



R = Ar, (1)
R = CMe_3

R = Ar; X = Cl, (9)
R = Ar; X = Br, (10)

R = Ar, (11)
R = CMe_3, (12)

Scheme 2.1

2.6 Investigation of α-Agostic Interactions in Bis-neopentyl Derivatives of $CpNb(NR)Cl_2$.

Interactions of an alkyl ligand C-H bond with coordinatively unsaturated transition metal centres are now well-established[21,28]. However, multiple interactions at a single metal site as observed in the structure of the bis-neopentyl (11) are relatively uncommon. This type of interaction is at present restricted to very low electron count transition metal complexes such as $Cp^*Ti(CH_2Ph)_2$[29] (12 electrons) or complexes of the rare earth elements such as $Cp^*{}_2Th(CH_2CMe_3)_2$[30]. All of these examples have been characterised by diffraction techniques.

A useful NMR method for identifying agostic C-H systems in solution is that of 'isotopic perturbation of resonance', first used by Shapley[31] for the osmium methyl compound $Os_3(CO)_{10}(Me)H$. He noted that the ^1H NMR chemical shifts and the value of the $^1J_{CH}$ coupling constants decrease in the order δ CH_3 > δ CH_2D > δ CHD_2. This phenomenon arises because of the thermodynamic preference for deuterium rather than hydrogen to occupy a terminal non-agostic site.This preference can be attributed to the smaller zero point energy difference between H and D in C-H-M and C-D-M bonds relative to the differences in non-agostic C-H and C-D bonds.

In order to further probe the presence of agostic interactions in solution of the neopentyl derivatives of $CpNb(NR)Cl_2$, it was decided to prepare partially deuterated analogues which would give characteristic isotopic shifts and temperature dependence when monitored by ^1H NMR spectroscopy.

2.6.1 Reaction of $CpNb(NR)Cl_2$ with an Excess of d_1-Neopentyl Grignard Reagent.

The labelled Grignard reagent, $BrMg(CHDCMe_3)$, was prepared by a conventional route[20b] (See 5.2.1). The partially deuterated compounds $CpNb(NR)(CHDCMe_3)_2$, (R = CMe_3[32], 2,6-$^iPr_2$-C_6H_3) were prepared *via* treatment of their respective dichlorides with excess $BrMg(CHDCMe_3)$.

The 250 MHz ^1H NMR spectrum of $CpNb(NCMe_3)(CHDCMe_3)_2$ (*d_2*-**12**) is shown in Figure 2.6b. It can be seen that the methylene resonances for the protio analogue (Figure 2.6a) are replaced by four broadened signals, each integrating as $^1/_2$ proton. These are four distinct signals rather than two doublets and their assignment as methylene protons geminal to deuterons was confirmed by deuterium decoupling experiments. In the case of the partially deuterated (*d_2*-**11**) a similar observation is noted. However, in (*d_2*-**11**) one of the methylene resonances is obscured, and so further discussion will focus on the bis-neopentyl species (**12**) and (*d_2*-**12**), containing the ancillary (t-butyl)imido ligand.

A rationalisation for the appearance of four signals is provided by considering the possible isomers of CpNb(NR)(CHDCMe$_3$)$_2$. Introducing two deuterium atoms at the α-carbon, generate two chiral centres. The four signals arise due to the possibility of four diastereoisomers illustrated below in Figure 2.7[33].

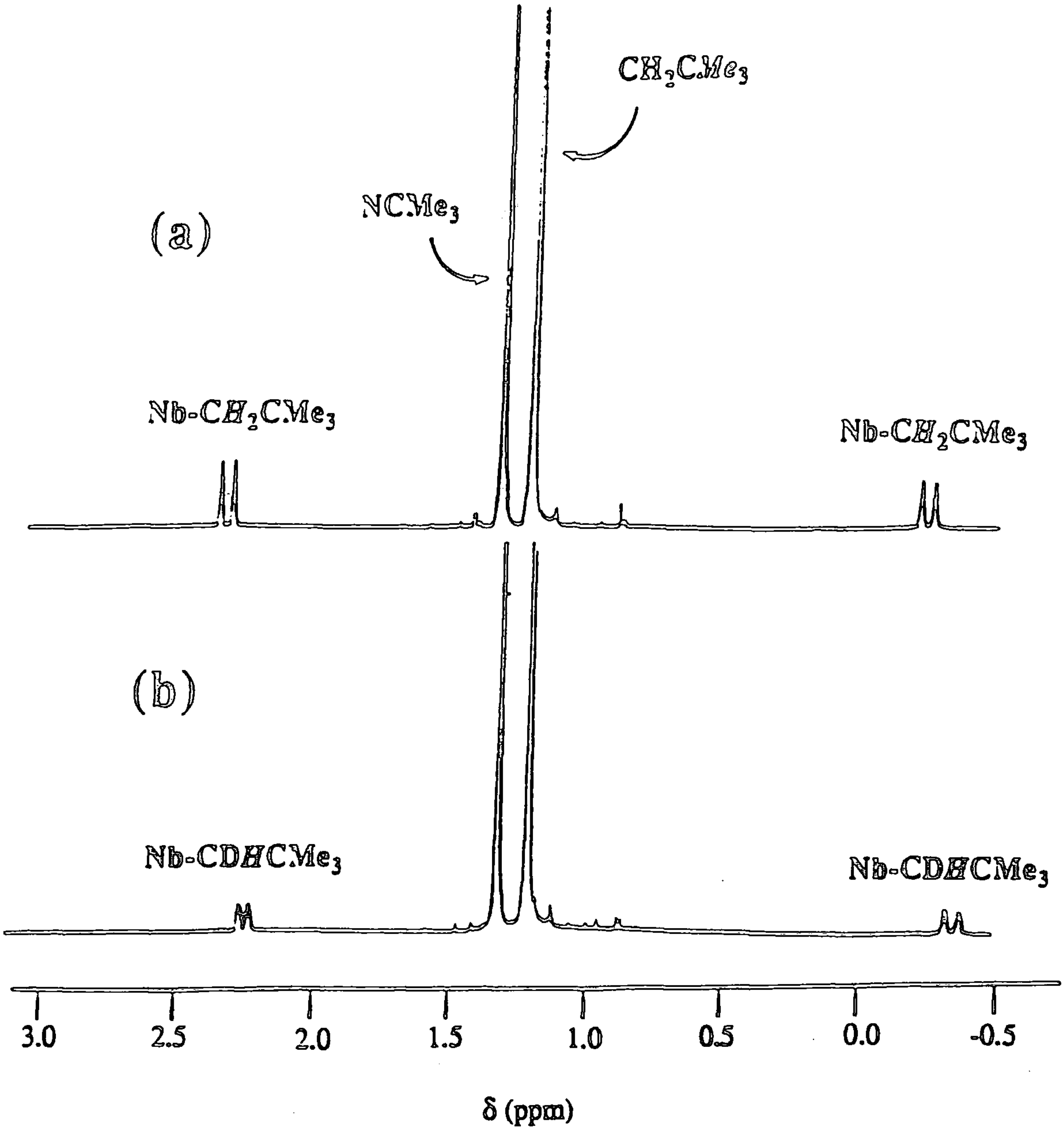
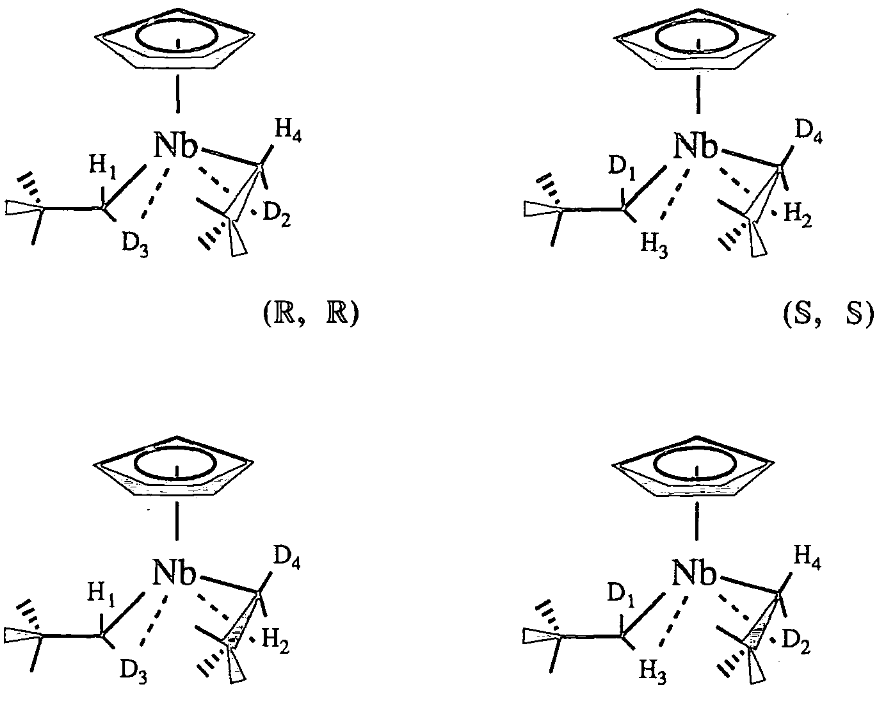


Figure 2.6 *250 MHz ^1H NMR spectrum (C_6D_6) of the alkyl region of a)12, and b) d_2- 12 at room temperature.*



(R, R) (S, S)

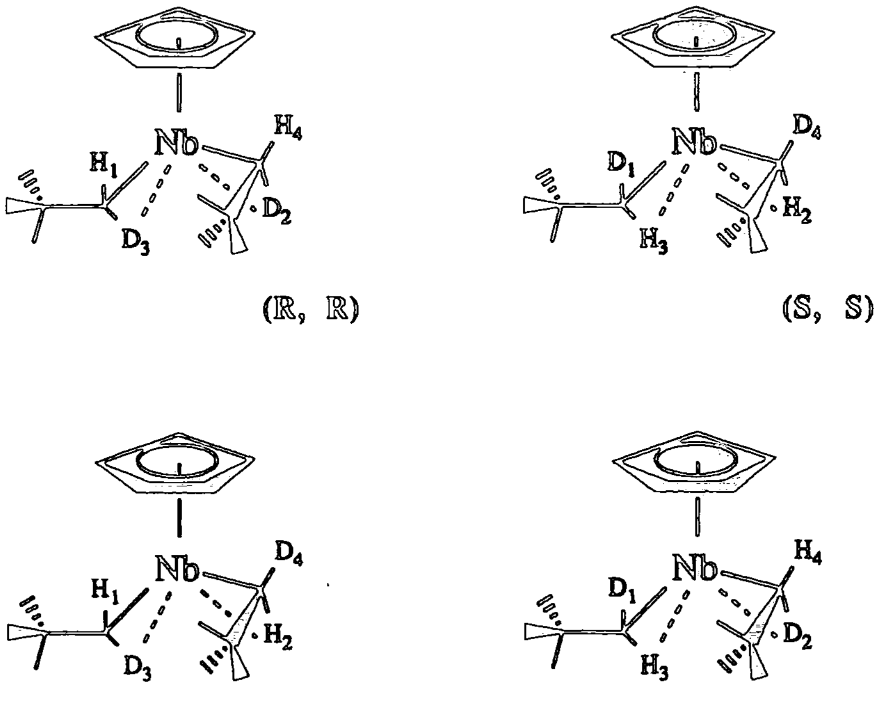
(R, S) (S, R)

Figure 2.7

The 'normal' isotopic shift upon partial deuteration for a n-alkane is *ca.* 0.01 - 0.02 ppm, 0.019ppm for CH_3D, for example. However, the isotope shift for protons attached to more electronegative elements is usually larger, (eg 0.03 ppm for HDO)[34,35]. It is , therefore, expected that the shift for CH(D) units attached to an electropositive metal such as niobium will be somewhat larger than normal due to substantial $Nb^{\delta+}$-$C^{\delta-}$ polarisation.

It is clear that one of the resonances in each pair experiences a greater upfield shift than its partner (*ca.* 0.11 ppm relative to the per-protio compound). This is consistent with the presence of agostic interactions in both the H_1/H_2 and H_3/H_4 interchanging pairs. This is in accordance with the solid state structure which shows that the agostic interactions occur for H_2 and H_3. On the other hand, the lower field resonances of each pair are shifted by *ca.* 0.06 ppm which is more consistent with simple isotopic substitution of a non-agostic C-H bond bound to an electropositive metal.

These observations can be understood by considering the exchange between agostic and non-agostic sites for each stereo-isomer. (Scheme 2.2). It is only in the



(R, R) (S, S)

(R, S) (S, R)

Figure 2.7

The 'normal' isotopic shift upon partial deuteration for a n-alkane is *ca.* 0.01 - 0.02 ppm, 0.019ppm for CH_3D, for example. However, the isotope shift for protons attached to more electropositive elements is usually larger, (eg 0.03 ppm for HDO)[34,35]. It is , therefore, expected that the shift for CH(D) units attached to an electropositive metal such as niobium will be somewhat larger than normal due to substantial $Nb^{\delta+}$-$C^{\delta-}$ polarisation.

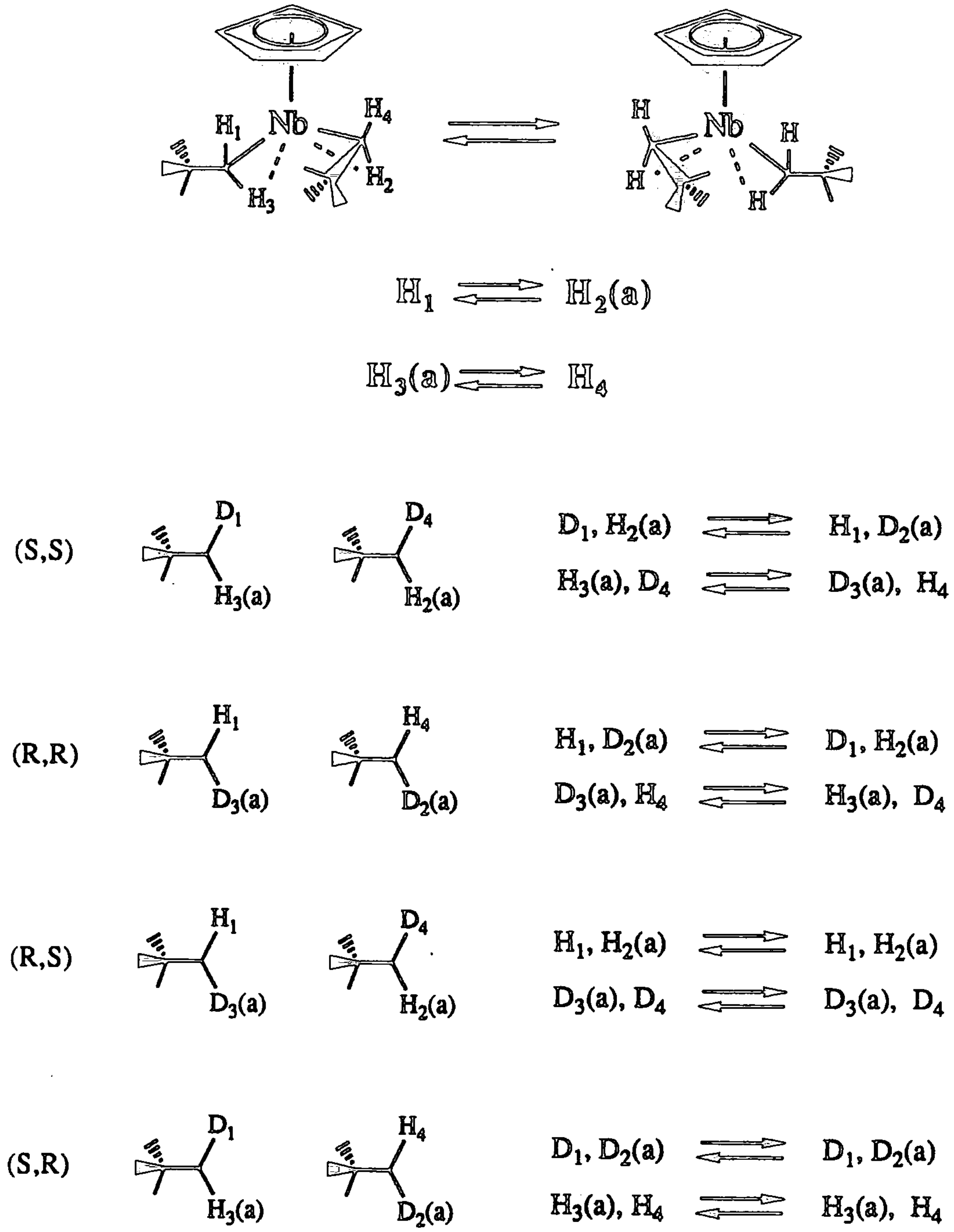
It is clear that one of the resonances in each pair experiences a greater upfield shift than its partner (*ca.* 0.11 ppm relative to the per-protio compound). This is consistent with the presence of agostic interactions in both the H_1/H_2 and H_3/H_4 interchanging pairs. This is in accordance with the solid state structure which shows that the agostic interactions occur for H_2 and H_3. On the other hand, the lower field resonances of each pair are shifted by *ca.* 0.06 ppm which is more consistent with simple isotopic substitution of a non-agostic C-H bond bound to an electropositive metal.

These observations can be understood by considering the exchange between agostic and non-agostic sites for each stereo-isomer. (Scheme 2.2). It is only in the enantiomeric (S,S) and (R,R) pair that exchange of H and D between agostic and non-agostic sites can occur, and therefore it is only for these isomers that isotopic perturbation of resonance is observed. Therefore, the resonances, in decreasing order of chemical shift may be assigned as $(H_3/H_4)_{ave}$ for S,R; $(H_3/H_4)_{ave}$ for the S,S/R,R pair; $(H_1/H_2)_{ave}$ for R,S; and $(H_1/H_2)_{ave}$ for the S,S/R,R pair.

There is also a marked temperature dependence of the ^1H NMR chemical shifts of the methylene resonances of (d_2-12). Whereas, the imido and Cp ring proton signals remain static over the temperature range, the two high field signals for (d_2-12) ($CDCl_3$) shift from δ -0.38 and -0.34 ppm at +40°C to δ -0.62 and -0.56 ppm repectively upon cooling to -50°C, whilst simultaneously, the lower field resonances at δ 2.16 and 2.19 ppm shift to δ 2.24 and 2.29 ppm respectively (Figure 2.8).

The per-protio compound (12) shows a similar temperature dependence of chemical shift (Figure 2.9). However, the shift difference between the methylene resonances of per-protio (12) and the CH(D) signals of (R,R) and (S,S) (d_2-12) increases as temperature is lowered, while the shift difference for the (R,S), and (S,R) CH(D) signals remain constant at *ca.* 0.06 ppm. This increase in separation is clearly discernable in Figure 2.8b.

The observation that the lowfield signals of (12) move to lower field upon cooling is intriguing as this is in the *opposite* direction to the shift observed upon isotopic substitution. This is consistent with a strengthening of the M-C-H interaction of one of the methylene orientations (the C-H bond closer to the Cp ring), at the expense of the agostic interaction of the other.



Scheme 2.2 *Interchange of the methylene H / D sites resulting from rotation of the neopentyl ligands.*

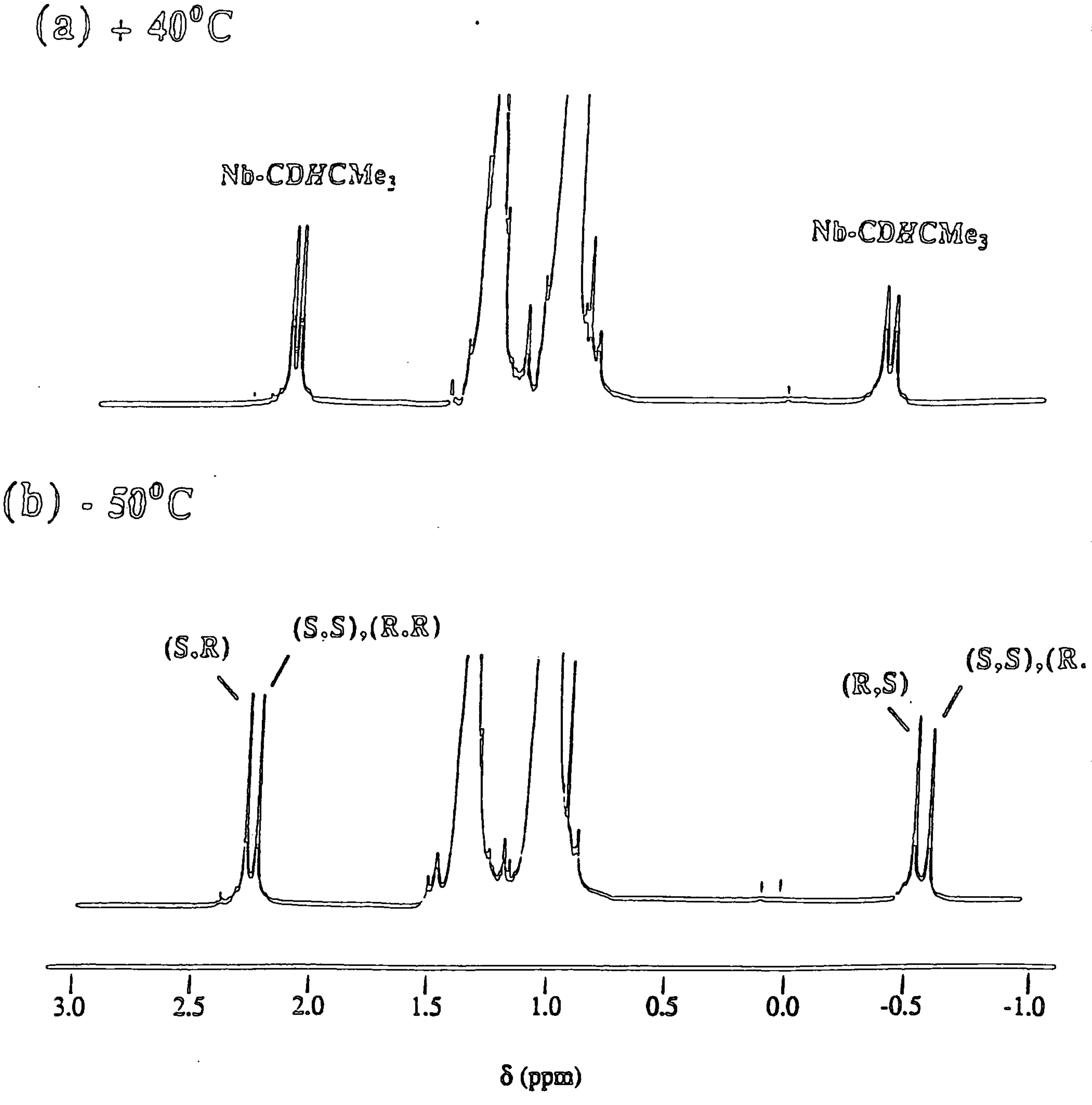


Figure 2.8 *400 MHz ^1H NMR spectra ($CDCl_3$) of the alkyl region of d_2-12 at a) +40 °C, and b) -50 °C.*

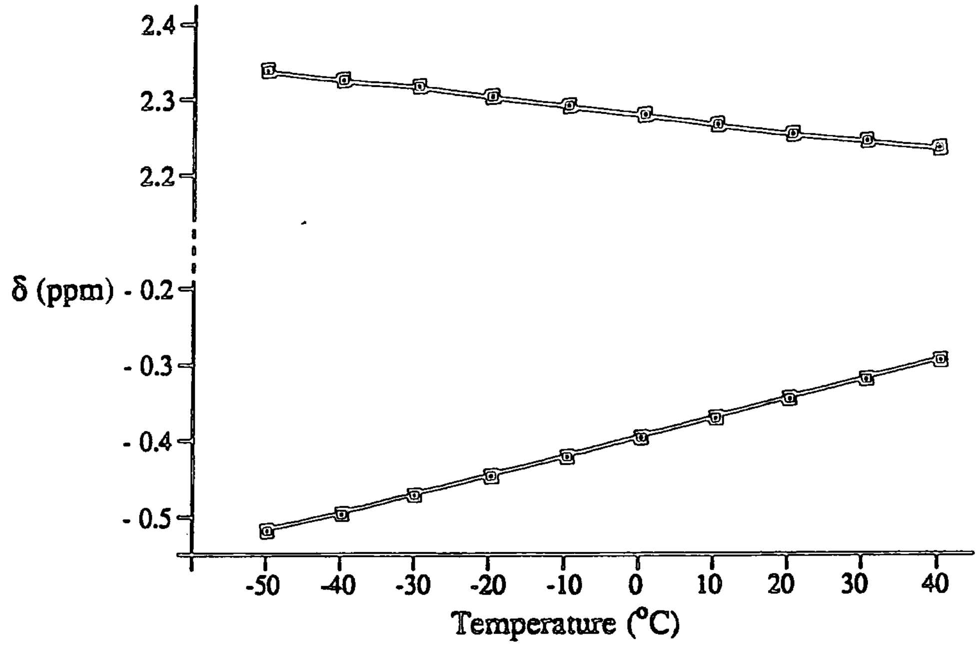


Figure 2.9 *Graph illustrating the temperature dependence of the methylene hydrogen ^{1}H NMR shifts (400 MHz, $CDCl_3$) of (12).*

2.6.2 Comments on the Relationship of the ^{1}H NMR Data to the X-ray Structure of $CpNb(NAr)(CH_2CMe_3)_2$ (11).

The crystal structure of $CpNb(NAr)(CH_2CMe_3)_2$ (11), (Figure 2.4), corresponds to the (S,S) form of (d_2-11) assuming the deuterons occupy their energetically preferred terminal sites. The agostic hydrogens H(18b) and H(23b) in then correspond to H_2 and H_3 in Figure 2.5.

The agostic hydrogen orientated towards the Cp ring interacts with the metal centre in close proximity to the plane containing Nb, C(18), and C(23); the deviation from this plane is 20.0°. This is expected to be a relatively strong interaction, since Fenske - Hall calculations show the LUMO of $CpNb(NR)(CH_2CMe_3)_2$ projects laterally and lies within this plane[1]. This is in agreement with the ^{1}H NMR data where the lower frequency methylene hydrogen resonance exhibits the greater upfield chemical shift change relative to the per-protio derivative upon partial deuteration. Its signals show the most significant temperature dependence in solution, suggesting that this methylene hydrogen interaction with the LUMO of $CpNb(NR)(CH_2CMe_3)_2$ predominates as the temperature is lowered.

The agostic hydrogen orientated towards the imido ligand interacts with the metal out of the Nb-C(18)-C(23) plane, (by 48.3°). Therefore, this agostic interaction is likely to be the weaker of the two. This is substantiated by a reduced chemical shift change upon partial deuteration and less significant temperature dependence of the signal in the ^1H NMR.

2.7 Preparation of Some Benzyl Derivatives of $Cp'M(NAr)Cl_2$.

It has been found that $CpNb(NAr)(CH_2CMe_3)_2$ (11) is unstable in solution, decomposing with slow loss of neopentane presumably *via* an unstable niobium neopentylidene species. The preparation therefore of the bis-benzyl species $Cp'M(NAr)(CH_2Ph)_2$, presented an opportunity to obtain a potential benzylidene metathesis polymerisation catalyst *via* elimination of toluene.

2.7.1 Preparation of $CpNb(NAr)(CH_2Ph)Cl$ (13).

A diethylether solution of $CpNb(NAr)Cl_2$ (1), when treated with one equivalent of potassium benzyl afforded a red-brown solution. Subsequent extraction and recrystallisation from a solution in n-pentane at -30°C gave yellow crystals of $CpNb(NAr)(CH_2Ph)Cl$ (13) in low yield (22%). The reaction is envisaged to occur according to Equation 2.16.

$$\underset{(1)}{CpNb(NAr)Cl_2} + KCH_2Ph \xrightarrow{Et_2O} \underset{(13)}{CpNb(NAr)(CH_2Ph)Cl} + KCl \quad (2.16)$$

(13) is very soluble in chlorocarbons, aromatic hydrocarbons and pentane. Its characterisation was provided by elemental analysis, mass spectrometry and infrared and NMR spectroscopies. In the 400 MHz ^1H NMR spectrum (C_6D_6), the α-

methylene hydrogens are observed as diastereotopic doublets at δ 2.85, and 3.29 ppm, whose coupling constant ($^1J_{CH}$ = 134 Hz) is not indicative of agostic an interaction[21]; however, deuterium labelling experiments would be necessary to confirm absence of such interactions. Furthermore, the $^1J_{CH}$ coupling constant of the benzyl ring ortho C-H bond was found to be 159 Hz. This $^1J_{CH}$ value does not suggest the presence of a γ-agostic interaction, as is observed in some zirconocene-benzyl complexes[36]. The mass spectrum reveals an envelope at m/z 459 (^{35}Cl) corresponding to the parent ion.

$\mathrm{CpNb(NAr)Cl_2}$ (1) reacted with two mole equivalents of potassium benzyl to give a yellow powder in low yield. Subsequent analysis by ^{1}H NMR spectroscopy revealed a complex mixture of products which were not readily identified. To date the bis-benzyl derivative of compound (1) has not proven accessible, possibly due to the bis-benzyl decomposing *via* an unstable benzylidene species.

2.7.2 Preparation of $\mathrm{Cp^{*}Ta(NAr)(CH_2Ph)_2}$ (14).

Treatment of a diethylether solution of (2) with two equivalents of potassium benzyl afforded a lemon-yellow solution which, on subsequent extraction and recrystallisation from a solution in n-pentane at -78°C, gave $\mathrm{Cp^{*}Ta(NAr)(CH_2Ph)_2}$ (14) in good yield.

$$\underset{(2)}{\mathrm{Cp^{*}Ta(NAr)Cl_2}} + 2\mathrm{KCH_2Ph} \xrightarrow{\mathrm{Et_2O}} \underset{(14)}{\mathrm{Cp^{*}Ta(NAr)(CH_2Ph)_2}} + 2\mathrm{KCl} \quad (2.17)$$

Elemental analysis confirms a stoichiometry consistent with the bis-benzyl complex (14). $\mathrm{Cp^{*}Ta(NAr)(CH_2Ph)_2}$ shows no clear spectroscopic evidence (NMR or infrared spectroscopies) for α-agostic interactions between the methylene hydrogens of the benzyl group and the metal centre. Neither the α-methylene $^1J_{CH}$ coupling constant (100 MHz, C_6D_6) of 120 Hz nor the corresponding proton shifts for the methylene hydrogens (400 MHz, C_6D_6) at δ 2.12 and 2.39 ppm offer an unambiguous indication of agostic interactions[21]. The possibility of γ-agostic interactions between the metal centre and the ortho C-H bonds of the benzyl ring as observed by Jordan in a zirconocene benzyl derivative seems less likely for steric reasons[36].

Intriguingly, mass spectrometry reveals no evidence of an envelope corresponding to the parent ion, (m/z 676, ^{181}Ta). However, a daughter fragment at m/z 584 (^{181}Ta) is observed consistent with the elimination of toluene from (14) to afford the benzylidene species, $Cp^{*}Ta(NAr)(\eta^{1}\text{-}CHPh)$.

The isolation of $Cp^{*}Ta(NAr)(CH_2Ph)_2$ again demonstrates the steric and electronic advantages of the replacement of Cp by Cp* rings, since $CpNb(NAr)(CH_2Ph)_2$ appear to be unstable.

2.8 Attempted Generation of Stable Benzylidene Complexes of Niobium and Tantalum.

In contrast to $CpNb(NAr)(CH_2CMe_3)_2$ (11) and $CpNb(NAr)(CH_2Ph)_2$, which appear to be unstable, $Cp^{*}Ta(NAr)(CH_2Ph)_2$ (14), and the analogous $Cp^{*}Nb(NAr)(CH_2Ph)_2$[37] are stable in solution, even at elevated temperatures. ^{1}H NMR experiments show that decomposition of the bis-benzyl complexes occurs only after prolonged exposure to a temperature of 120°C, yielding a mixture of unidentified products. However, the absence of toluene amongst these species indicates that any benzylidene which may be formed could not arise from an α-abstraction process.

Although $Cp^{*}M(NAr)(CH_2Ph)_2$ (M = Nb, Ta), can be warmed indefinitely at 100°C without decomposition, treatment of a sample of $Cp^{*}Nb(NAr)(CH_2Ph)_2$ (provided by Dr. U. Siemling) with excess trimethylphosphine at 70°C affords the benzylidene product $Cp^{*}Nb(NAr)(\eta^{1}\text{-}CHPh)(PMe_3)$ (15), with elimination of toluene. This phosphine assisted α-abstraction reaction is likely to arise due to the phosphine interacting with the laterally projecting LUMO of the bis-benzyl complex. This forces the two benzyl groups together, and hence permits extrusion of toluene. The benzylidene (15) can be envisaged to form as shown in Equation 2.18.

$$Cp^{*}Nb(NAr)(CH_2Ph)_2 + PMe_3 \xrightarrow{70^\circ C} \underset{(15)}{Cp^{*}Nb(NAr)(\eta^1\text{-}CHPh)(PMe_3)} + C_7H_8 \quad (2.18)$$

Schrock and Fellman have demonstrated that niobium alkylidenes are often considerably less stable than their tantalum analogues. The neopentylidene species $Nb(CH_2CMe_3)_3(\eta^1\text{-}CHCMe_3)$, for example, was shown to decompose readily in solution at ambient temperature, whereas, its tantalum counterpart $Ta(CH_2CMe_3)_3(\eta^1\text{-}CHCMe_3)$ demonstrated a much greater degree of thermal stability[20b]. In contrast to early work by Schrock[20c] where the half-sandwich niobium alkylidene $CpNb(\eta^1\text{-}CHCMe_3)Cl_2$ was found to be sufficiently stable to only permit characterisation by ^1H NMR spectroscopy, compound (15) exhibits suprising thermal stability. The use of ^1H NMR techniques show (15) to be indefinitely stable in aromatic hydrocarbon, and heptane solvents to temperatures of 90°C.

The 250 MHz ^1H NMR spectrum (C_6D_6) of (15) reveals a characteristic low field alkylidene proton resonance at δ 11.23 ppm, split by phosphorus coupling, ($^3J_{PH}$ = 5.4 Hz). ^{13}C NMR spectra (100 MHz, C_6D_6) shows a broadened resonance at δ 268.6 ppm ($\upsilon^1/_2$ = 35 Hz) corresponding to the benzylidene α-carbon. The benzylidene α-carbon resonance is only observed in the ^1H decoupled ^{13}C NMR spectrum; evidently it is too broad in the ^1H coupled ^{13}C NMR spectrum. The broadening of the signal is due to coupling of the α-carbon atom to ^{93}Nb. The fact that the benzylidene α-carbon atom resonance is significantly broader than the benzyl α-carbon resonance of $Cp^{*}Nb(NAr)(CH_2Ph)_2$ ($\upsilon^1/_2$ = 18 Hz) suggests it is more strongly coupled to ^{93}Nb, as one might expect for a π-bonded atom to niobium. The very low field value of the benzylidene α-carbon resonance of (15) is comparable with values recorded for a variety of d^0 alkylidene complexes of niobium and tantalum (Table 2.2).

Since the α-carbon resonance of the benzylidene moeity is broadened through coupling to the ^{93}Nb nucleus, the value of the $^1J_{CH}$ coupling constant had to be acquired from the natural abundance ^{13}C satellites in the ^{1}H NMR spectrum. The $^{1}J_{CH}$ coupling constant of 115 Hz is lower than expected for an *sp*^{2}- hybridised carbon, suggesting that the benzylidene ligand may be distorted through an agostic interaction between the α-hydrogen and the niobium. This suprisingly low $^{1}J_{CH}$ value is characteristic of many alkylidenes of the Group 5 triad[38].

Compound	δ C_α (ppm)	$^{1}J_{CH}$ (Hz)	Reference
$CpTa(\eta^1\text{-}CHCMe_3)Cl_2$	246	84	20a
$Nb(CH_2CMe_3)_3(\eta^1\text{-}CHCMe_3)$	246	101	20b
$Ta(CH_2CMe_3)_3(\eta^1\text{-}CHCMe_3)$	250	90	20b
$CpNb(\eta^1\text{-}CHCMe_3)Cl_2$	254	95	20c
$CpTa(\eta^1\text{-}CHCMe_3)Me_2$	231	78	20c
$Cp^*Ta(\eta^1\text{-}CHCMe_3)Cl_2$	242	83	20c
$CpTa(\eta^1\text{-}CHCMe_3)(PMe_3)Cl_2$	272	84	20c
$Ta(\eta^1\text{-}CHPh)(OR)_3(PMe_3)$	221	114	38
$Cp_2Nb(\eta^1\text{-}CHCMe_3)Cl$	299	131	41

Table 2.2 *^{13}C NMR data for niobium and tantalum alklidene complexes.*

The orientation of the benzylidene moeity within (15) has been investigated by solution NMR techniques. NOE NMR experiments show that the benzylidene α-hydrogen is orientated towards the Cp* ring and hence, the benzylidene phenyl group is directed towards the imido group.

The observation that a solution of norbornene in C_6D_6 is polymerised during the decomposition of $CpNb(NAr)(CHCMe_3)_2$ (11) led us to investigate the possible metathesis polymerisation activity of the well-defined niobium benzylidene (15). Treatment of $Cp^*Nb(NAr)(\eta^1\text{-}CHPh)(PMe_3)$ with three equivalents of norbornene afforded no reaction at ambient temperature. However, warming the solution to 90°C led to the generation of poly(norbornene) although no resonances assignable to propagating alkylidene species were observed in the ^{1}H NMR spectrum.

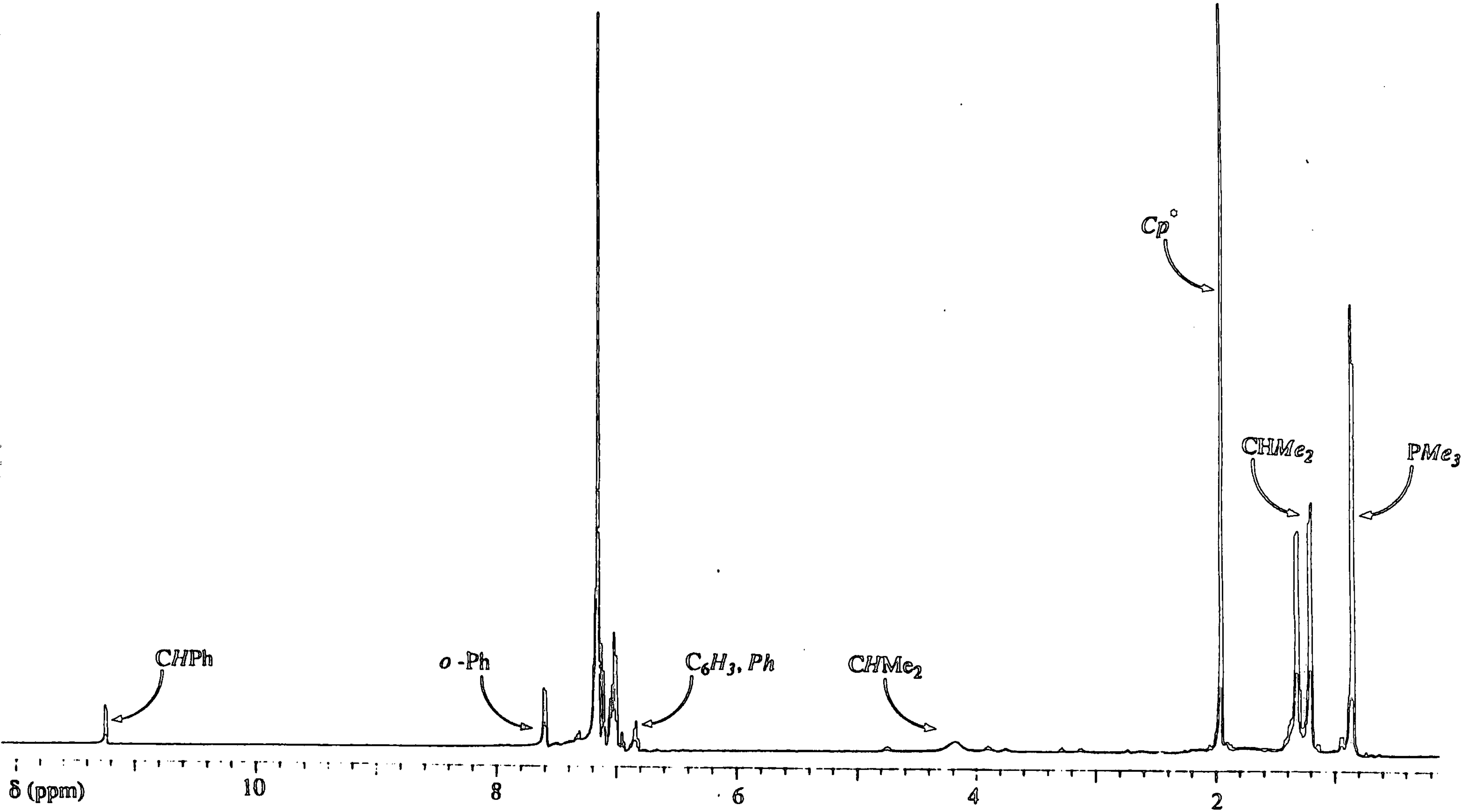


Figure 2.10 400 MHz ^1H NMR spectrum (C_6D_6) of Cp*Nb(NAr)(η^1-CHPh)(PMe$_3$) (15)

Since (**15**) is a coordinatively saturated complex, dissociation of phosphine is expected to be a pre-requiste for the alkylidene to polymerise cyclic olefins such as norbornene. The 250 MHz ^1H NMR spectrum (C_6D_6) of (**15**) revealed a signal attributable to the PMe_3 hydrogens at δ 0.83 ppm, close to the shift observed for free PMe_3 (δ 0.79 ppm). This suggests that the phosphine is either relatively weakly bound to the niobium, and/or the PMe_3 resonance is affected by the ring current of the benzylidene phenyl ring. ^1H NMR experiments show that phosphine dissociation from (**15**) is relatively slow at ambient temperature, as treatment of (**15**) with four equivalents of d_9-PMe_3 affords only *ca.* 50% exchange after one hour at this temperature. The reluctance of PMe_3 to dissociate from (**15**) therefore offers a possible explanation for the high temperatures necessary to initiate norbornene polymerisation.

In an attempt to overcome the inhibiting effect of phoshine on metathesis polymerisation activity, a study was undertaken to prepare a benzylidene in the presence of a more facile L-donor ligand. Work undertaken in collaboration with Miss. C. M. Langdale-Brown showed that treatment of $Cp^*Nb(NAr)(CH_2Ph)_2$ with one equivalent of THF at 90°C, afforded toluene and a number of unidentified species. Although liberation of toluene suggests that α-hydrogen abstraction may yield the desired benzylidene, THF appears not to be sufficiently basic to stabilise the niobium-alkylidene formed.

In order to prepare the tantalum analogue of (**15**), $Cp^*Ta(NAr)(\eta^1\text{-}CHPh)(PMe_3)$, a solution of $Cp^*Ta(NAr)(CH_2Ph)_2$ (**14**) and PMe_3 was warmed at 70°C until a purple colouration was afforded. The 250 MHz ^1H NMR spectrum (C_6D_6) of the solution revealed a low field doublet resonance (δ 9.85 ppm), attributed to a tantalum benzylidene α-hydrogen split by phosphorus coupling. However, the ^1H NMR spectrum suggested that generation of the benzylidene species was not clean (*cf.* the niobium benzylidene (**15**)) since further unidentified species were also observed. These additional species cannot be attributed to decomposition of the alkylidene complex, as ^1H NMR spectroscopy showed it to be indefinitely stable at temperatures up to 120°C. Moreover, ^1H NMR shows no evidence of stilbene, (PhCH=CHPh), and so coupling of the alkylidene units cannot account for unassigned species.

2.8.1 The Molecular Structure of $Cp^*Nb(NAr)(\eta^1-CHPh)(PMe_3)$ (15).

Yellow crystals of (15) were obtained by cooling a saturated heptane solution to -30°C overnight. A crystal of dimensions 0.20 x 0.25 x 0.55 mm was chosen for a crystallographic study and mounted in a Lindemann capillary tube under an inert atmosphere. The data was collected and the structure solved by Prof. J. A. K. Howard, Dr. J. K. Cockcroft and Miss C. Wilson within this department (Appendix 1). The molecular structure of (15) is illustrated in Figure 2.11 and selected bond angles and distances are given in Table 2.3.

We believe that (15) is only the third niobium alkylidene to be structurally characterised, the other two containing relatively unusual alkylidene ligand arrangements[39,40]. The metal-nitrogen bond length (1.812(3)Å) of (15) is slightly longer than is usually expected for a niobium - nitrogen triple bond (1.73 - 1.79Å)[6-8]. However, the imido unit is quasi-linear, the $Nb-N-C_{ipso}$ angle being 175.6(2)°, suggesting a terminal imido ligand possessing *sp* -hybridised nitrogen[9].

The Nb=C distance of 2.026(4)Å is comparable with the values found in the other two niobium structures and also compares favourably with related tantallocene derivatives[41], as expected for the similarly sized Nb(V) and Ta(V) centres. The α-benzylidene hydrogen of (15) projects towards the Cp^* ring, which is in agreement with NOE NMR experiments. The orientation of the benzylidene hydrogen and phenyl substituents, lying perpendicular to the P-Nb-C(1) plane, is consistent with the p orbital of the benzylidene carbon interacting with the metallocene-like π-symmetry orbitals of the $[Cp^*Nb(NAr)]$ fragment lending support to the metallocene analogy. The benzylidene ligand, however is distorted, the Nb-C(1)-C(2) angle being 136.3(4)°. Moreover, the Nb-C(1)-H(1) angle of 111.4(33)Å offers further evidence for a possible weak agostic interaction between the α-hydrogen atom and the metal centre.

Thus (**15**) may be regarded as a direct analogue of the zirconocene complex $Cp_2Zr(\eta^1$-$CHCH_2CMe_3)(PPh_3)$ described by Schwartz and co-workers[42].

The pentamethylcyclopentadienyl moiety appears not to be coordinated in an ideal η^5 fashion. Rather, a trend towards η^5/η^3 coordination (allyl-ene) is observed, leading to three short and two long Nb-Cp* ring carbon distances. The maximum deviation of the Nb-Cp* ring distance is 0.128Å, whilst the maximum deviation of inter-ring carbon distances is 0.025Å. This allyl-alkene type structure is similar to that found in previously studied niobium imido analogues[2] and $Cp^*Re(NCMe_3)Cl_2$ described by Herrmann[43]. A possible explanation for the non-ideal coordination of the Cp* ring is that ring slippage occurs to accommadate an agostic bond believed to be between the benzylidene α-hydrogen and the metal centre. Since, any such agostic interaction would cause the electron count of (**15**) to exceed 18 electrons (the effective atomic number rule)[9,44].

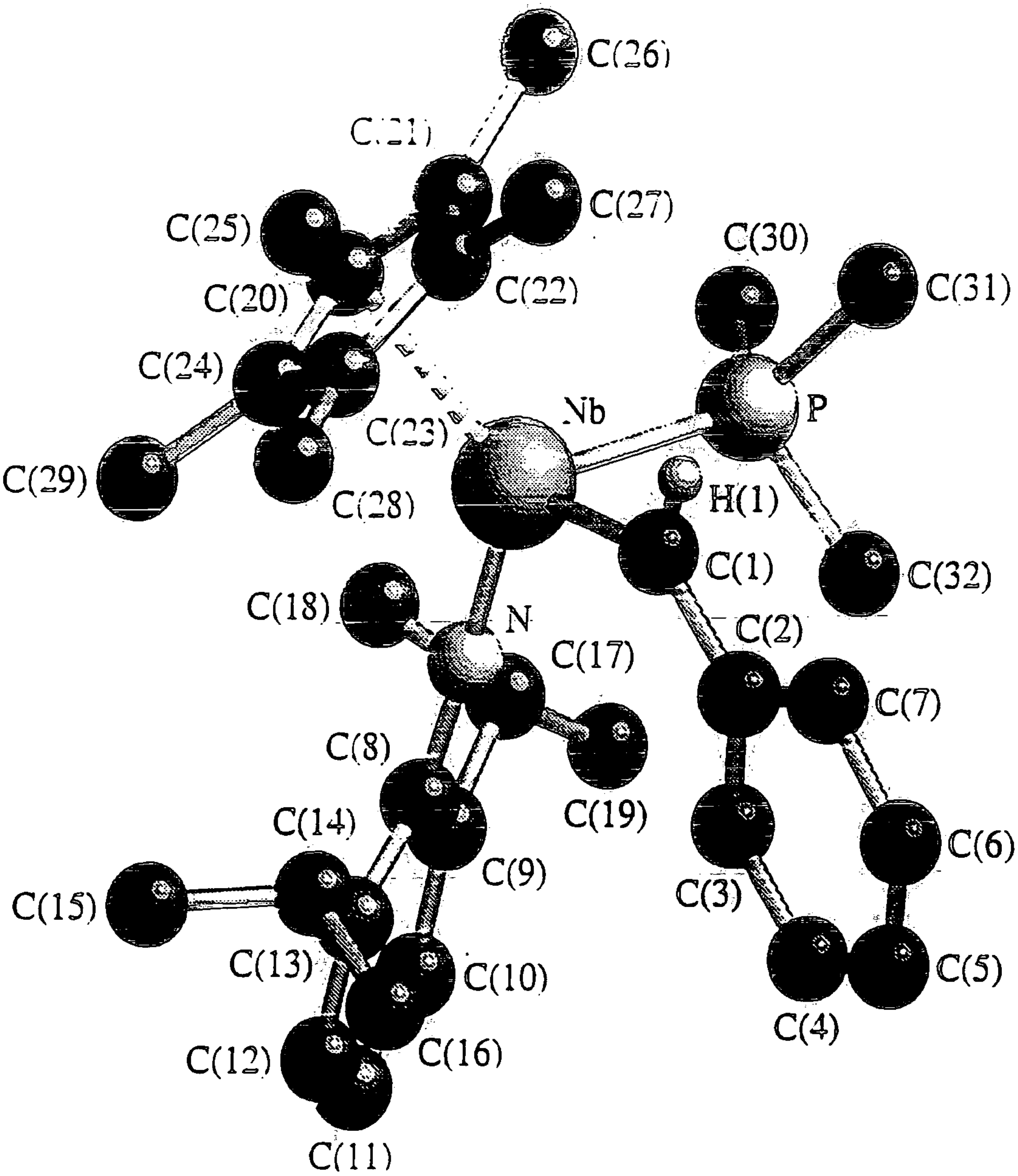


Figure 2.11 *Molecular structure of* $Cp^{*}Nb(NAr)(\eta^{1}\text{-}CHPh)(PMe_3)$ *(15).*

Nb - P	2.578(1)	Nb - N	1.812(3)
Nb - C(1)	2.026(4)	Nb - C(20)	2.471(4)
Nb - C(21)	2.553(5)	Nb - C(22)	2.548(5)
Nb - C(23)	2.442(4)	Nb - C(24)	2.425(4)
P - C(30)	1.838(6)	P - C(31)	1.815(6)
P(1) - C(32)	1.806(5)	N - C(8)	1.387(5)
C(1) - H(1)	0.856(58)	C(1) - C(2)	1.467(7)
C(2) - C(3)	1.400(8)	C(2) - C(7)	1.401(7)
C(3) - C(4)	1.387(8)	C(4) - C(5)	1.357(10)
C(5) - C(6)	1.370(12)	C(6) C(7)	1.408(9)
C(8) - C(9)	1.424(5)	C(8) - C(13)	1.421(6)
C(9) - C(10)	1.388(8)	C(9) - C(17)	1.513(7)
C(10) - C(11)	1.377(8)	C(11) - C(12)	1.369(7)
C(12) - C(13)	1.390(7)	C(13) - C(14)	1.515(6)
C(14) - C(15)	1.515(6)	C(14) - C(16)	1.540(7)
C(17) - C(18)	1.520(7)	C(17) - C(189)	1.526(7)
C(20) - C(21)	1.396(7)	C(20) - C(24)	1.410(6)
C(20) - C(25)	1.503(7)	C(21) - C(22)	1.408(7)
C(21) - C(26)	1.514(7)	C(22) - C(23)	1.421(7)
C(22) - C(27)	1.509(8)	C(23) - C(24)	1.409(7)
C(23) - C(28)	1.508(8)	C(24) - C(29)	1.500(7)

P - Nb - N	99.3(1)	P - Nb - C(1)	83.6(1)
N - Nb - C(1)	103.4(2)	P - Nb - C(20)	103.9(1)
N - Nb - C(20)	111.8(1)	C(1) - Nb - C(2))	142.0(2)
P - Nb - C(21)	90.0(1)	N - Nb - C(21)	143.7(1)
C(1) - Nb - C(21)	112.6(2)	C(20) - Nb - C(21)	32.2(2)
P - Nb - C(22)	108.3(1)	N - Nb C(22)	151.1(1)
C(1) - Nb - C(22)	88.2(2)	C(20) - Nb - C(22)	53.9(1)
C(21) - Nb - C(22)	32.0(2)	P - Nb - C(23)	141.1(1)
N - Nb - C(23)	118.5(1)	C(1) - Nb - C(23)	95.7(2)
C(20) - Nb - C(23)	55.1(2)	C(21) - Nb - C(23)	54.2(2)
C(22) - Nb - C(23)	33.0(2)	P - Nb - C(24)	137.4(1)
N - Nb - C(24)	98.8(1)	C(1) Nb - C(24)	128.5(2)
C(20) - Nb - C(24)	33.5(1)	C(21) - Nb - C(24)	54.4(1)
C(22) - Nb - C(24)	54.8(2)	C(23) - Nb - C(24)	33.6(2)
Nb - P - C(30)	121.2(2)	Nb - P - C(31)	115.0(2)
C(30) - P - C(31)	102.2(3)	Nb - P - C(32)	112.2(2)
C(30) - P - C(32)	102.3(3)	C(31) - P - C(32)	101.5(3)
Nb - N - C(8)	175.6(2)	Nb - C(1) - H(1)	111.4(33)
Nb - C(1) - C(2)	136.3(4)	H(1) - C(1) C(2)	112.3(33)
C(1) - C(2) - C(3)	122.5(4)	C(1) - C(2) - C(7)	120.9(5)
C(3) - C(2) - C7)	116.6(5)	C(2) - C(3) - C(4)	121.9(5)
C(3) - C(4) - C(5)	120.2(6)	C(4) - C(5) - C(6)	120.5(7)
C(5) - C(6) - C(7)	119.9(6)	C(2) - C(7) - C(6)	120.8(6)
N - C(8) - C(9)	119.9(4)	N - C(8) - C(13)	120.5(3)
C(9) - C(8) - C(13)	119.5(4)	C(8) - C(9) - C(10)	118.7(4)
C(8) - C(9) - C(17)	119.7(4)	C(10) - C(9) - C(17)	121.6(4)
C(9) - C(10) - C(11)	121.6(5)	C(10) - C(11) C(12)	119.8(6)
C(11) - C(12) - C(13)	122.0(5)	C(8) - C(13) - C(12)	118.4(4)
C(8) - C(13) - C(14)	121.8(4)	C(12) - C(13) - C(14)	119.7(4)
C(13) - C(14) - C(15)	111.3(4)	C(13) - C(14) - C(16)	112.6(4)
C(15) - C(14) - C(16)	109.3(4)	C(9) - C(17) - C(18)	110.1(4)
C(9) - C(17) C(19)	114.6(4)	C(18) - C(17) - C(19)	111.0(4)
Nb - C(20) - C(21)	77.2(3)	Nb - C(20) - C(24)	71.5(2)

C(21) - C(20) - C(24)	108.6(4)	Nb -C(20) C(25)	123.2(3)
C(21) - C(20) - C(5)	125.1(5)	C(24) - C(20) - C(25)	125.9(4)
Nb - C(21) - C(20)	70.6(3)	Nb - C(21) - C(22)	73.8(3)
C(20) - C(21) - C(22)	108.5(4)	Nb - C(21) - C(26)	129.3(3)
C(20) - C(21) - C(26)	125.8(5)	C(22) - C(21) C(26)	125.0(5)
Nb - C(22) - C(21)	74.2(3)	Nb - C(22) - C(23)	69.4(3)
C(21) - C(22) - C(23)	107.2(4)	Nb - C(22) - C(27)	125.0(3)
C(21) - C(22) C(27)	127.3(5)	C(23) - C(22) C(27)	125.3(5)
Nb - C(23) - C(22)	77.6(2)	Nb - C(23) C(24)	72.5(2)
C(22) - C(23) - C(24)	108.2(4)	Nb - C(23) - C(28)	122.2(3)
C(22) - C(23) - C(28)	125.0(5)	C(24) - C(23) - C(28)	126.3(5)
Nb - C(24) - C(20)	75.1(2)	Nb - C(24) - C(23)	73.9(2)
C(20) - C(24) - C(23)	107.4(4)	Nb - C(24) - C(29)	120.4(3)
C(20) - C(24) - C(29)	125.1(4)	C(23) - C(24) - C(29)	127.3(4)

Table 2.3 *Bond distances (Å) and angles (°) for $Cp^*Nb(NAr)(\eta^1\text{-}CHPh)(PMe_3)$ (15).*

2.9 Attempted Formation of Cationic Half-sandwich Imido Compounds of Niobium and Tantalum.

The work of Jordan, Turner and others has confirmed that d^0 cationic alkyls can act as well-defined catalysts for the Ziegler-Natta polymerisation of α-olefins[4b,45]. We have therefore focused attention on the possibility of preparing cationic derivatives of Cp'M(NAr)X_2 (Cp' = Cp, Cp*; M = Nb, Ta; X = halide, alkyl) employing a variety of well-established strategies.

2.9.1 Halide Abstraction Reactions.

The abstraction of a halide anion from neutral species is well documented. Jordan, for example, has succeeded in producing both mono- and dications from Cp_2ZrX_2 (X = Cl, Br, I), stabilised by the BPh_4 anion[16] (Equation 2.19 - 2.20).

$$Cp_2ZrX_2 + AgBPh_4 + 2CH_3CN \longrightarrow [Cp_2ZrX(CH_3CN)_2]BPh_4 + AgX \quad (2.19)$$

$$Cp_2ZrX_2 + 2AgBPh_4 + 3CH_3CN \longrightarrow [Cp_2Zr(CH_3CN)_3][BPh_4]_2 + 2AgX \quad (2.20)$$

Initial studies involved the treatment of CpNb(NAr)Cl_2 (1) with $AgBF_4$, well known for its ability for abstraction and displacement of a chloride from transition metal complexes, and subsequent stabilisation of the resulting cation with the BF_4 counter ion[46].

Treatment of a dichloromethane solution of (1) with $AgBF_4$ afforded a half-sandwich compound, the elemental analysis of which closely corresponded to $CpNbCl_2F_2$. Hence, it appears that instead of chloride abstraction there is an unexpected loss of the (aryl)imido ligand which may be isolated as the aniline and identified by ^1H NMR spectroscopy.

The loss of the imido ligand contrasts with the results obtained by Jordan who found that the acidic d^0 metal centre of the zirconocene system could abstract fluoride from the anion to yield a Zr-F bond[47] (Figure 2.12).

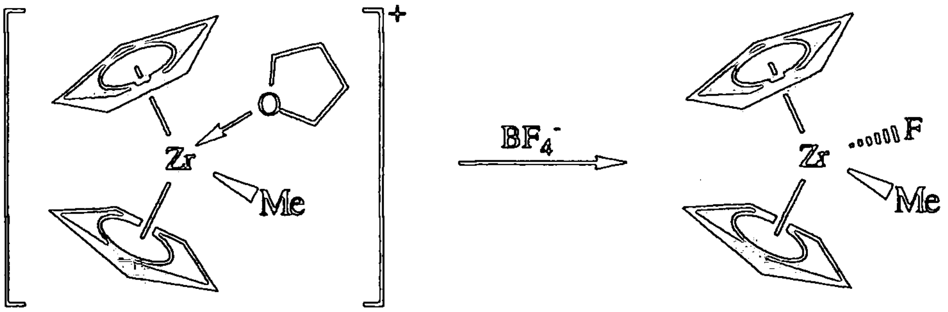


Figure 2.12

Since $CpNb(NAr)Cl_2$ (1) appeared to decompose the tetrafluoroborate anion, attention was then turned to the tetraphenylborate anion BPh_4^- since Jordan and others have shown that this counterion is better suited to stabilising reactive d^0 cationic zirconocene species[4b]. The enhanced stability of BPh_4^- salts has been attributed to a tetrahedral structure of the anion with a charged centre shielded by the sterically demanding phenyl groups, which results in increased stability towards acidic metal centres.

However, treatment of compound (1) with a variety of sources of the BPh_4 anion, (Cp_2FeBPh_4, $AgBPh_4$, $NaBPh_4$), afforded no reaction at ambient temperature. Moreover, warming to 70°C led only to the apparent decomposition of the anion to give BPh_3 as an isolatable white crystalline compound. The ^1H NMR spectrum of the residue revealed unreacted (1).

2.9.2 Alkyl Abstraction Reactions.

It is now well established that the one-electron oxidation of neutral Group 4 metallocene dialkyl complexes afford d^0 alkyl cations[4b]. In an attempt to undertake similar oxidation reactions, the dialkyl complexes $CpNb(NAr)(CH_2CMe_3)_2$ (11), $Cp^*Ta(NAr)Me_2$ (7), and $Cp^*Ta(NAr)(CH_2Ph)_2$ (14) were treated with $AgBPh_4$ or

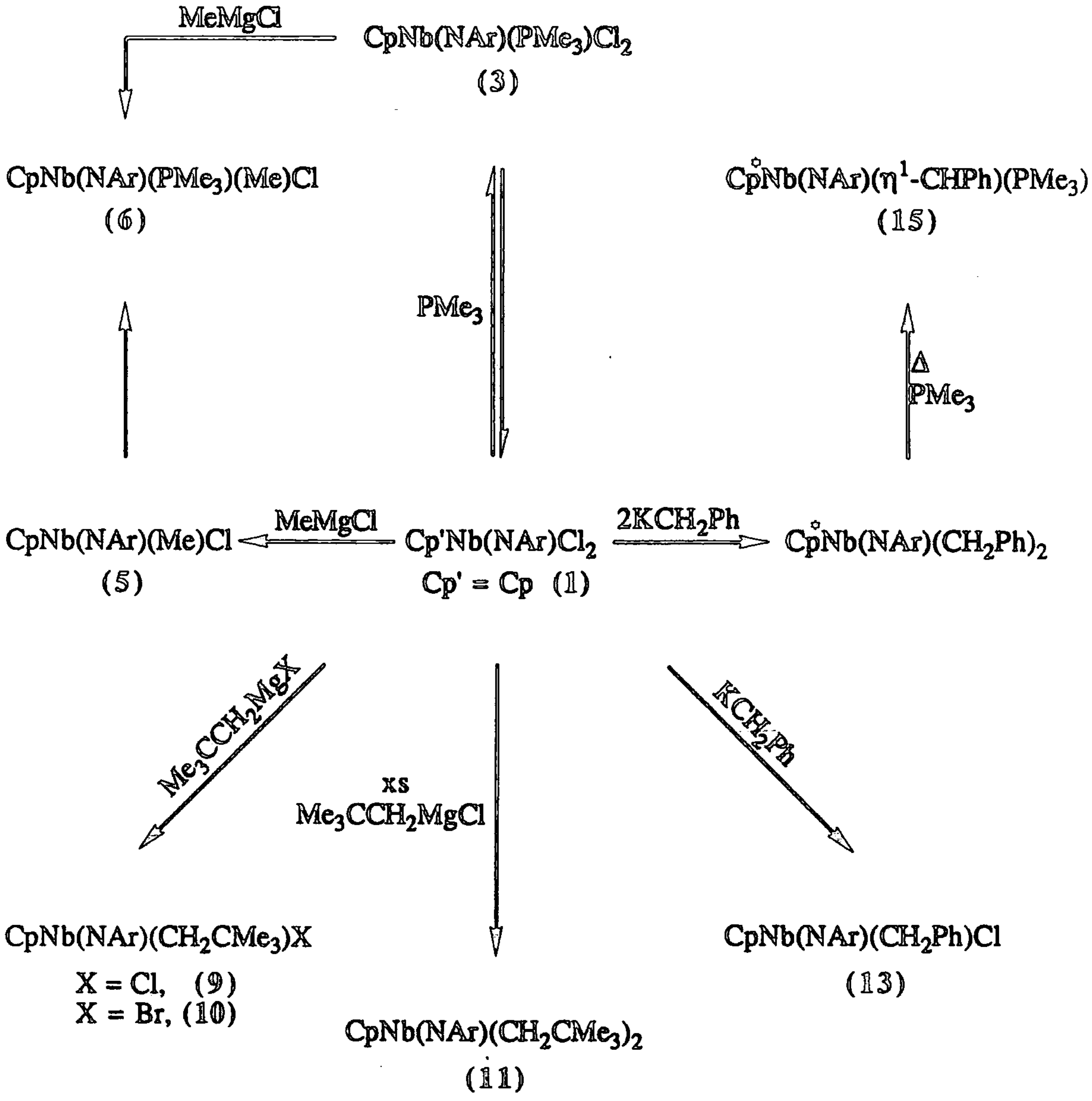
Cp_2FeBPh_4 under analogous conditions to those successfully employed by Bochmann[48] and Jordan[49,50] but no new organometallic species were isolated from the reaction mixtures.

Hlatky and Turner have shown that protonolysis of $Cp_2ZrMe_2$with $^nBu_3NHBPh_4$ generates ionic, base-free zirconocene catalysts for ethylene polymerisation[45]. Treatment of benzene solutions of the di-methyl complexes $Cp^*Nb(NAr)Me_2$ (supplied by Dr. U. Siemeling) and $Cp^*Ta(NAr)Me_2$ (7) with $^nBu_3NHBPh_4$ in an NMR tube however afforded no observable reaction at ambient temperature. Moreover, warming the NMR samples to 70°C led only to the appearance of ^1H NMR signals attributable to BPh_3 signifying the thermal decomposition of the trialkylammonium salt. The reason for the stability of the half-sandwich di-alkyl complexes towards alkyl cation formation is unclear but presumably a consequence of steric and electronic factors.

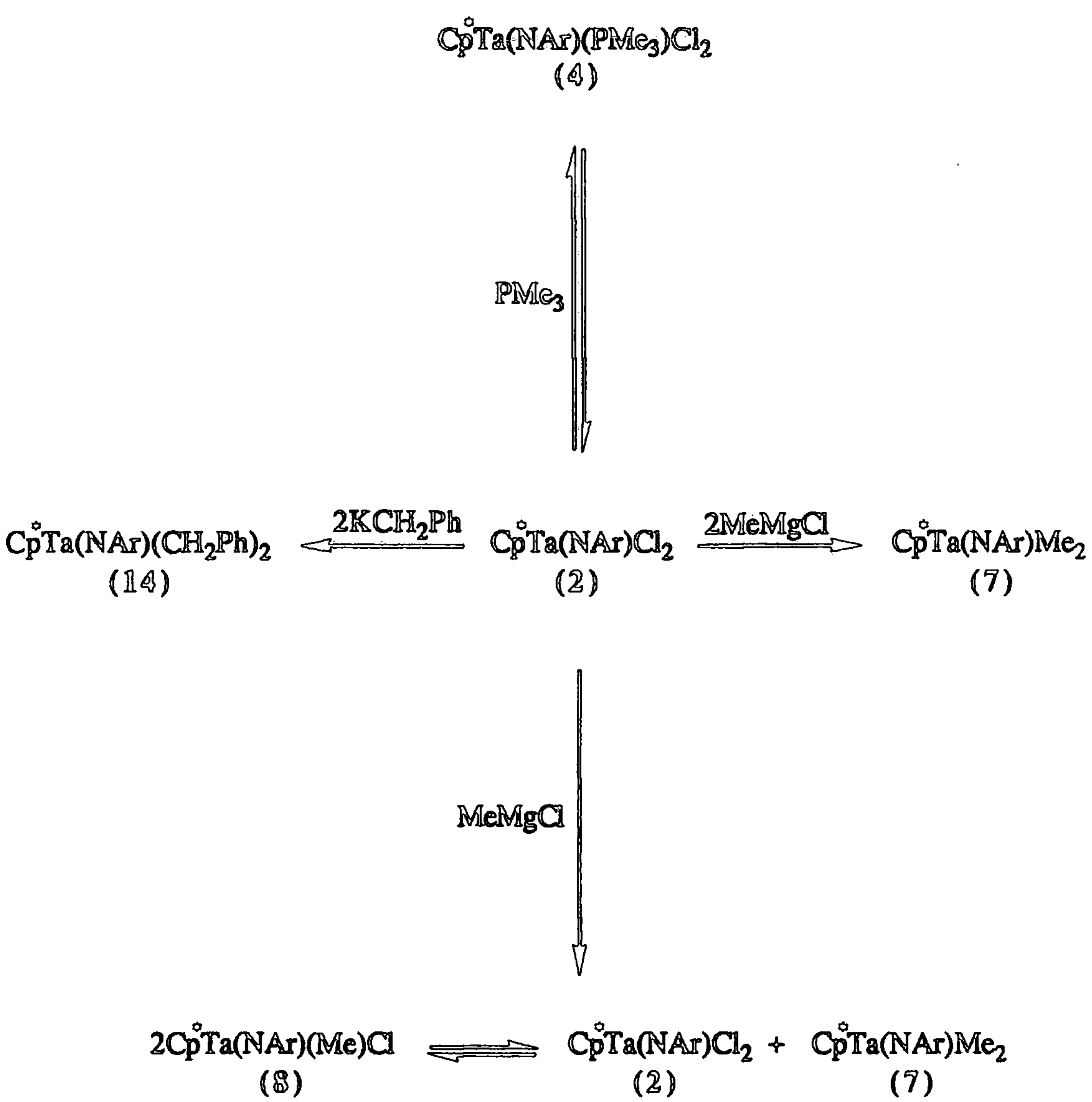
Thus, to date, no cationic half-sandwich niobium and tantalum species have been isolated. However, a further possible route that may be explored to potentially afford the target cationic-alkyl complexes has been very recently described by Bochmann. Group 4 metallocene alkyl cations have been prepared *via* the reaction of Cp'_2ZrMe_2 with triphenylcarbenium salts, the cations generated being stabilised with fluorinated anions such as $[B\{C_6H_3(CF_3)\}_4]^-$[51].

2.10 Summary.

A variety of half-sandwich imido complexes of niobium, and tantalum have been isolated and aspects of their derivative chemistry explored. These are summarised in Scheme 2.3 and 2.4. Of particular note are the benzylidene complex $Cp^*Nb(NAr)(\eta^2\text{-}CHPh)(PMe_3)$ and the bis-neopentyl species $CpNb(NAr)(CH_2CMe_3)_2$, whose single crystal structure determinations have been obtained. The structure of $CpNb(NAr)(CH_2CMe_3)_2$ revealed a multiple α-agostic interaction which has been further investigated through the employment of ^1H NMR spectroscopy.


MeMgCl
CpNb(NAr)(PMe3)Cl2
(3)
CpNb(NAr)(PMe3)(Me)Cl
(6)
PMe3
Cp*Nb(NAr)(η1-CHPh)(PMe3)
(15)
Δ
PMe3
CpNb(NAr)(Me)Cl
(5)
MeMgCl
Cp'Nb(NAr)Cl2
Cp' = Cp (1)
2KCH2Ph
Cp*Nb(NAr)(CH2Ph)2
Me3CCH2MgX
xs
Me3CCH2MgCl
KCH2Ph
CpNb(NAr)(CH2CMe3)X
X = Cl, (9)
X = Br, (10)
CpNb(NAr)(CH2CMe3)2
(11)
CpNb(NAr)(CH2Ph)Cl
(13)

Scheme 2.3



Scheme 2.4

2.11 References.

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CHAPTER THREE

Preparation and Reactivity of Half-Sandwich Niobium and Tantalum Imido Complexes Possessing Carbonyl, Phosphine, Olefin and other Related Ligands.

3.1 Introduction.

Transition metals are able to bind and activate a variety of unsaturated hydrocarbons. Recently, there has been considerable interest in the chemistry of complexes combining multiply-bonded imido ligands and neutral organic molecules at a single metal centre due to their relevance in a number of important catalytic processes including ammoxidation, amination, and oxyamination[1]. For metals of the Group 5 triad, such combinations are rare, presently being restricted to tantalum complexes of the type $Ta(NPh)Cl(PMe_3)_3(RCH{=}CH_2)$[2], and $Ta(NAr)X(py)_2(RC{\equiv}CR)$, ($Ar = 2,6\text{-}{}^iPr_2\text{-}C_6H_3$; $X = Cl, O\text{-}2,6\text{-}{}^iPr_2\text{-}C_6H_3$)[3].

The similariities between the frontier orbitals of [CpM(NR)], (M = V, Nb, Ta), and those of the bent metallocene [Cp_2M], (M = Ti, Zr, Hf)[4] indicated that it should prove possible to prepare half-sandwich imido complexes containing unsaturated hydrocarbon ligands.

3.2 Reaction of Cp'M(NAr)Cl_2 (M = Nb, Ta) with Ethyl Magnesium Chloride.

A general interest in comparing the chemistry of half-sandwich imido compounds of the Group 5 triad with that of Group 4 metallocenes prompted an investigation of the reaction of C_2H_5MgCl with $Cp'M(NAr)Cl_2$ (M = Nb, Ta). These reactions could possibly afford ethyl complexes which are of potential interest since they may be regarded as the 'first insertion' products of ethylene polymerisation by a metal hydride, and hence are plausible intermediates in a Ziegler-Natta type polymerisation process[5]. Alternatively, treatment of $Cp'M(NAr)Cl_2$ with C_2H_5MgCl could also afford metal-olefin complexes since Takahashi[6] and Waymouth[7] have shown that the reaction of $Cp_2ZrCl_2$with C_2H_5MgBr gives an (ethylene)zirconocene species which is of synthetic use for carbon-carbon bond forming reactions.

3.2.1 Preparation of $CpNb(NAr)(\eta^2\text{-}C_2H_4)(PMe_3)$ (1)

Initial attempts to alkylate $CpNb(NAr)Cl_2$ with C_2H_5MgCl in diethylether proved unsuccessful. Attempts to isolate the yellow crystalline product crystallised from n-pentane led only to decomposition when the solid was exposed to vacuum. Therefore, the reaction was repeated in the presence of the good donor ligand, trimethylphosphine.

Treatment of a diethylether solution of $CpNb(NAr)Cl_2$ with one molar equivalent of C_2H_5MgCl in the presence of an excess of trimethylphosphine gave a yellow solid which could be recrystallised in analytically pure form in moderate yield (*ca.* 40%) from a concentrated n-pentane solution at -78°C. The anticipated reaction is shown below in Equation 3.1.

$$CpNb(NAr)Cl_2 + PMe_3 + EtMgCl \xrightarrow{Et_2O} CpNb(NAr)(Et)(Cl)(PMe_3) + MgCl_2 \quad (3.1)$$

However, elemental analysis indicated that both halide ligands had been eliminated and the complex had a formulation consistent with $CpNb(NAr)(C_2H_5)(PMe_3)$ or $CpNb(NAr)(C_2H_4)(PMe_3)$.

The mass spectrum revealed an envelope at m/z 438 which would correspond to either the olefin or ethyl derivative above since it would not be unreasonable for the olefin complex to be readily protonated in the spectrometer. A daughter fragment at m/z 409 was also found to be present corresponding to $CpNb(NAr)(PMe_3)$.

The 400 MHz ^1H NMR spectrum showed a singlet at δ 5.40 ppm for the Cp ring, a septet at δ 3.64 ppm, and doublets at δ 1.17, 1.24 ppm attributable to the methine hydrogens and diastereotopic methyls of the (aryl)imido isopropyl groups. Resonances at δ 6.91, 7.00 ppm have been assigned to the aryl hydrogens, and a doublet at δ 0.96 ppm corresponds to coordinated trimethylphosphine. Also, complex multiplets at δ 0.58, 1.40, 1.64 ppm in the alkyl region were observed which did not appear characteristic of a simple ethyl ligand. (Figure 3.1).

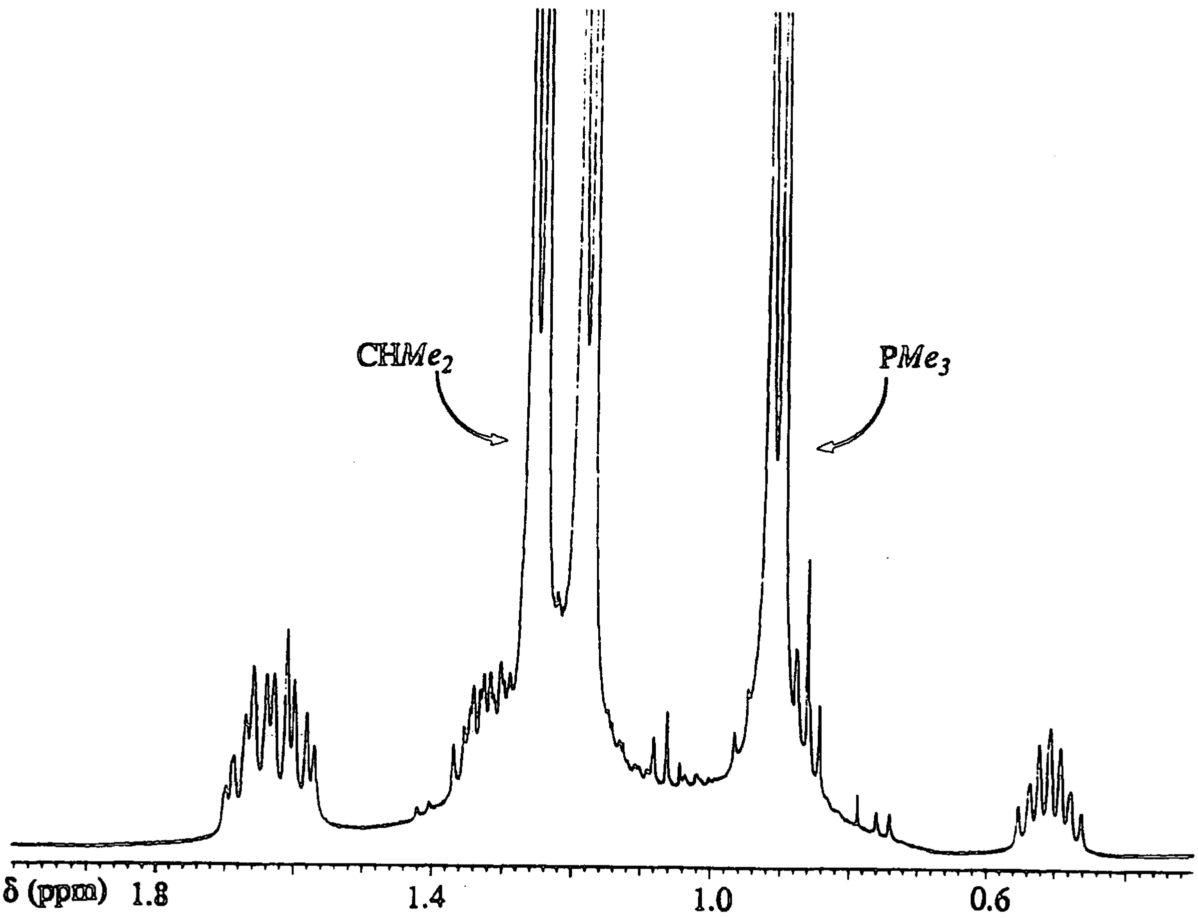

Figure 3.1 *400 MHz ^1H NMR spectrum (C_6D_6) of the alkyl region of (1).*

The ^{13}C NMR spectrum showed two broadened resonances attributable to a C-2 fragment, the broadening being attributable to the quadropolar effects of the niobium (I = $^9/_2$) nucleus. A DEPT NMR experiment confirmed that the C-2 fragment contained two *sp*^{2} - hybridised carbons, indicating that the fragment is an olefin rather than an ethyl group. Signals of significant intensity in the *sp*^{3} - carbon spectrum for the C-2 fragment, were also observed, possibly indicating that the olefin ligand experiences a significant degree of backbonding from the d^2 centre resulting in substantial metallacyclopropane character.

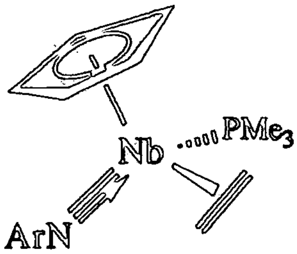

Figure 3.2 *CpNb(NAr)(η^2-C_2H_4)(PMe_3) (1).*

The complexity of the olefin signals in the ^1H NMR spectrum may be rationalised due to the presence of a chiral metal centre giving rise to an AA′MM′ spin system. Close inspection of the broadened ethylene resonances in the 100 MHz ^{13}C NMR spectrum revealed that the signal at δ 28.2 ppm exhibited coupling to phosphorus ($^2J_{CP}$ = 11.5 Hz) whereas the signal at δ 24.5 ppm showed no indication of coupling, a phenomenon also exhibited by Cp*Nb(NAr)(η^2-C_2H_4)(PMe_3)[8]. Attempts to assign the hydrogens of the ethylene ligand by NOE NMR experiments proved unsuccessful not only due to the low intensity of the signals, but also due to different T_1 relaxation times for each proton environment.

The rotational barrier of the ethylene ligand could not be determined by ^{13}C NMR techniques since the ethylene carbon environments are not averaged up to 90°C. Displacement of ethylene by *d4*- ethylene, however, was observed by ^1H NMR spectroscopy upon prolonged warming at 60°C indicating that dissociation of the ethylene ligand occurs in solution.

Subsequent preparation of (1) employing an excess of C_2H_5MgCl rather than one molar equivalent afforded an improved yield (61%).

3.2.2 Preparation of Cp*Ta(NAr)(η^2-C_2H_4)(PMe_3) (2).

Treatment of a diethylether solution of Cp*Ta(NAr)Cl_2 with an excess of C_2H_5MgCl in the presence of trimethylphosphine, yielded lemon-yellow crystals of the ethylene adduct Cp*Ta(NAr)(η^2-C_2H_4)(PMe_3) (2).

Compound (**2**) is soluble in aromatic and low polarity hydrocarbon solvents such as n-pentane. However, unlike the niobium derivative (**1**) which is stable indefinitely in halogenated solvents, Cp*Ta(NAr)(η^2-C_2H_4)(PMe_3) quickly affords free ethylene and Cp*Ta(NAr)Cl_2(PMe_3) upon exposure to chlorocarbons.

Elemental analysis confirms the stoichiometry of $C_{27}H_{45}TaNP$, whilst mass spectrometry shows envelopes at m/z 567, and 519 (^{181}Ta) attributable to the fragments Cp*Ta(NAr)(PMe_3) and Cp*Ta(NAr)(η^2-C_2H_4) respectively. The 400 MHz ^1H NMR spectrum (C_6D_6) reveals complex multiplets at δ -0.14, 0.93, and 1.60 ppm consistent with an AA'MM' spin system for a static ethylene ligand in a chiral environment which is analogous to that observed for the species CpNb(NAr)(η^2-C_2H_4)(PMe_3) (**1**). The 100 MHz ^{13}C NMR spectrum (C_6D_6) exhibits resonances due to the ethylene carbons at δ 29.61, and 35.66 ppm, with coupling to phosphorus of 1.9 and 11.1 Hz respectively.

3.3 Reaction of Cp'M(NAr)Cl_2 (M = Nb, Ta) with n-Propyl Magnesium Chloride.

The observation that treatment of Cp'M(NAr)Cl_2 (M = Nb, Ta) with an excess of ethyl Grignard reagent in the presence of phosphine affords the ethylene complexes (**1**) and (**2**) in good yield prompted an investigation into the possibility of preparing substituted olefin derivatives.

3.3.1 Preparation of CpNb(NAr)(η^2-C_3H_6)(PMe_3) (3).

The propylene derivative (**3**) was prepared by the reaction of a diethylether solution of CpNb(NAr)Cl_2 with an excess of n-C_3H_7MgCl, in the presence of trimethylphosphine. Subsequent recrystallisation from a concentrated solution in n-pentane gave a moderate yield of orange-red crystals. (Yield, 55%).

Compound (**3**) is extremely air-sensitive and highly soluble in hydrocarbon and polar solvents. Elemental analysis confirms the stoichiometry of $C_{23}H_{37}NNbP$ and the

Attempts to assign the four rotamers of the propylene ligand by NOE NMR techniques were unsuccessful since T_1 proton relaxation measurements have shown that the quadrupolar ^{93}Nb nucleus in each of the four different rotamers has a different quadrupolar effect upon the relaxation times of the hydrogens of the different groups within the molecule. This can be clearly seen for the propylene methyl proton resonances in Figure 3.6.

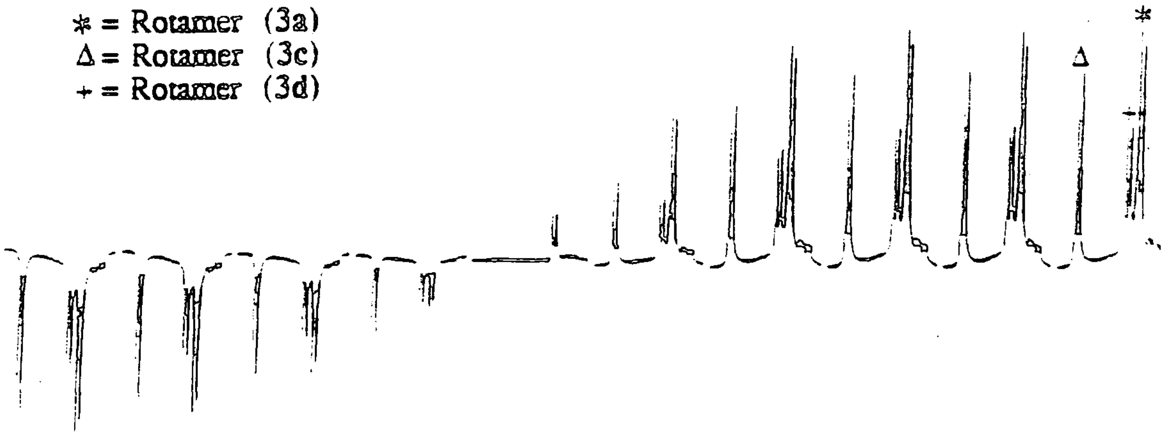

Figure 3.6

3.3.1.1 The Molecular Structure of CpNb(NAr)(η^2-C_3H_6)(PMe_3) (3).

A saturated n-pentane solution of (3) was cooled at -78°C over several days to afford red crystals. A crystal of suitable dimensions was chosen for a crystallographic study and mounted in a Lindemann capillary tube under an inert atmosphere. The data was collected and the structure solved by Dr. W Clegg at the University of Newcastle-upon-Tyne (Appendix 1). The molecular structure is illustrated in Figure 3.7 and selected bond angles and distances are given in Table 3.2.

Attempts to assign the four rotamers of the propylene ligand by NOE NMR techniques were unsuccessful since T_1 proton relaxation measurements have shown that the quadropolar ^{93}Nb nucleus in each of the four different rotamers has a different quadropolar effect upon the relaxation times of the hydrogens of the different groups within the molecule. This can be clearly seen for the propylene methyl proton resonances in Figure 3.6.

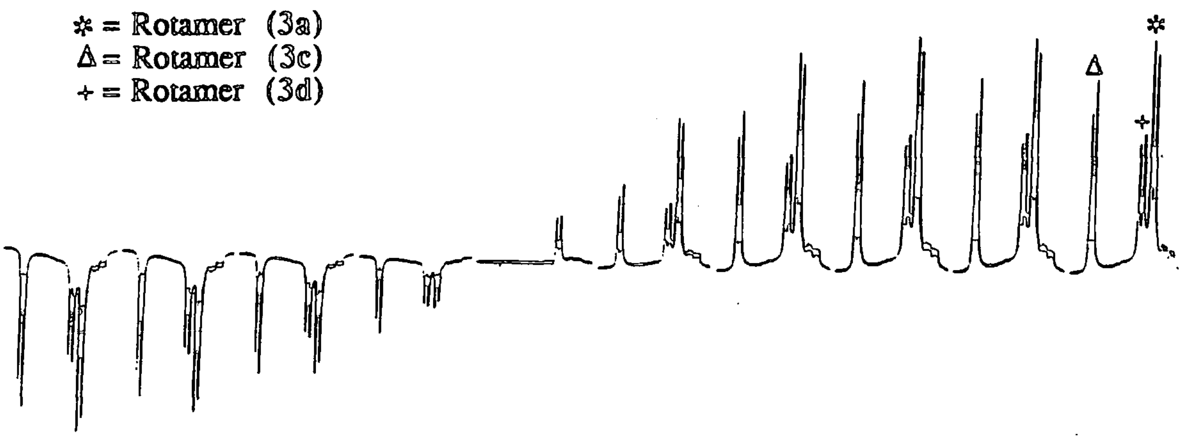

Figure 3.6

3.3.1.1 The Molecular Structure of CpNb(NAr)(η^2-C_3H_6)(PMe_3) (3).

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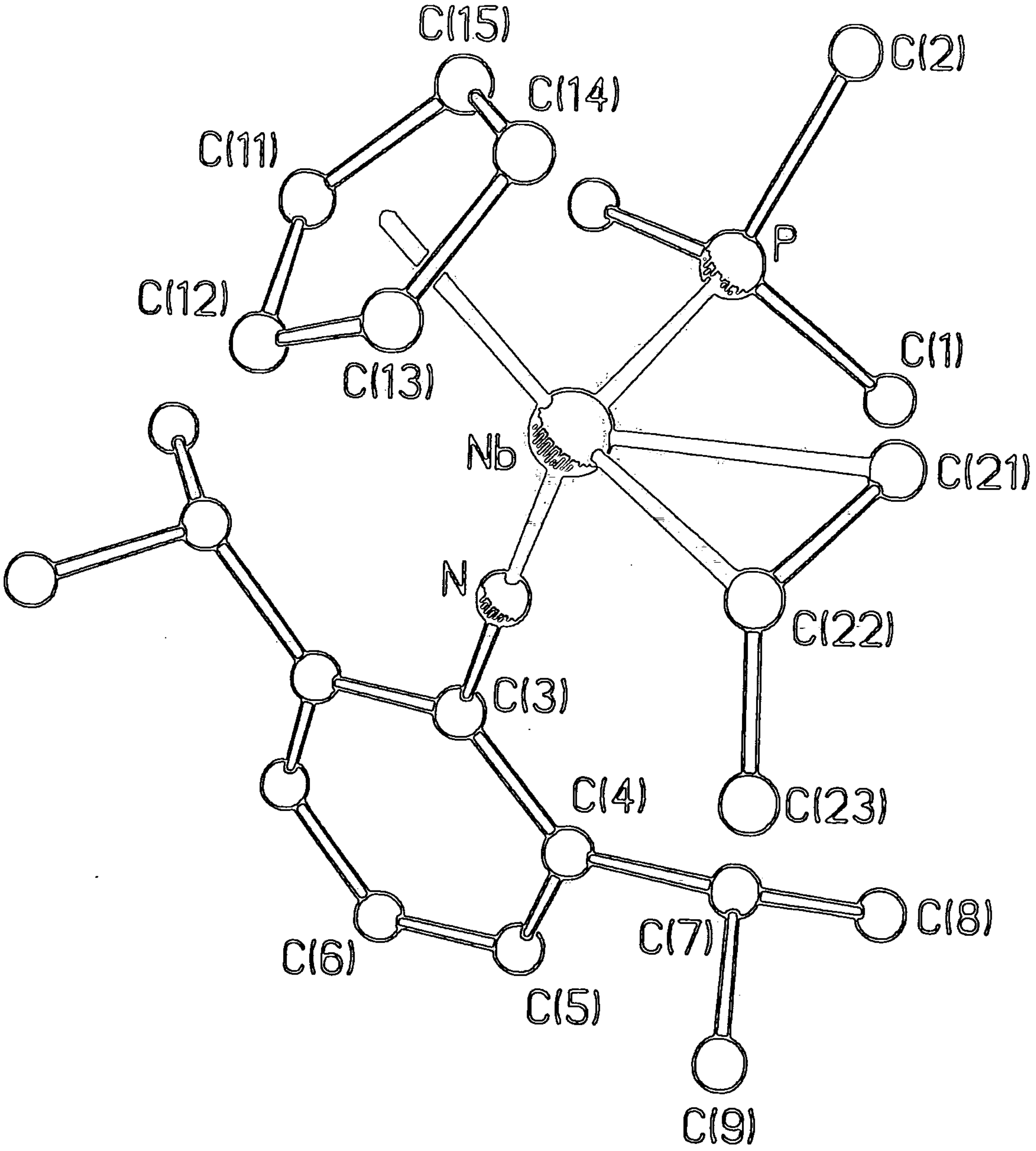


Figure 3.7 *The molecular structure of CpNb(NAr)(η^2-C_3H_6)(PMe_3) (3).*

Nb - P	2.514(4)	Nb - N	1.793(11)
Nb - C(11)	2.482(19)	Nb - C(12)	2.470(18)
Nb - C(13)	2.517(16)	Nb - C(14)	2.557(16)
Nb - C(15)	2.536(18)	Nb - C(21)	2.386(28)
Nb - C(22)	2.276(28)	P - C(1)	1.824(16)
P - C(2)	1.809(17)	C(3) - C(4)	1.412(13)
C(3) - N	1.429(18)	C(4) - C(5)	1.377(16)
C(4) - C(7)	1.507(17)	C(5) - C(6)	1.265(16)
C(7) - C(8)	1.530(18)	C(7) - C(9)	1.542(19)

P - Nb - N	88.6(4)	P - Nb - C(11)	94.6(4)
N - Nb - C(11)	104.8(4)	P - Nb - C(12)	128.0(4)
N - Nb - C(12)	102.5(4)	C(11) - Nb - C(12)	33.3(2)
P - Nb - C(13)	133.7(4)	N - Nb - C(13)	129.2(5)
C(11) - Nb - C(13)	54.7(4)	C(12) - Nb - C(13)	33.1(2)
P - Nb - C(14)	102.5(4)	N - Nb - C(14)	156.5(5)
C(11) - Nb - C(14)	54.2(4)	C(12) - Nb - C(14)	54.4(4)
C(13) - Nb - C(14)	32.5(2)	P - Nb - C(15)	81.0(4)
N - Nb - C(15)	133.7(4)	C(11) - Nb - C(15)	32.9(2)
C(12) - Nb - C(15)	54.6(4)	C(13) - Nb - C(15)	54.1(3)
C(14) - Nb - C(15)	32.4(2)	P - Nb - C(21)	78.5(6)
N - Nb - C(21)	113.2(5)	C(11) - Nb - C(21)	141.1(7)
C(12) - Nb - C(21)	136.4(6)	C(13) - Nb - C(21)	103.4(6)
C(14) - Nb - C(21)	89.5(7)	C(15) - Nb - C(21)	108.7(7)
P - Nb - C(22)	117.6(9)	N - Nb - C(22)	107.3(8)
C(11) - Nb - C(22)	134.3(7)	C(12) - Nb - C(22)	107.2(8)
C(13) - Nb - C(22)	79.7(8)	C(14) - Nb - C(22)	86.0(8)
C(15) - Nb - C(22)	117.5(8)	C(21) - Nb - C(22)	39.4(11)
Nb - P - C(1)	113.8(4)	Nb - P - C(2)	119.5(6)
C(1) - P - C(2)	102.5(6)	C(1) - P - C(1')	102.7(9)
C(4) - C(3) - N	119.8(7)	C(4) - C(3) - C(4')	120.3(13)
C(3) - C(4) - C(5)	118.0(11)	C(3) - C(4) - C(7)	121.0(9)
C(5) - C(4) - C(7)	121.0(11)	C(4) - C(5) - C(6)	121.6(12)
C(5) - C(6) - C(5')	120.1(15)	C(4) - C(7) - C(8)	113.2(9)
C(4) - C(7) - C(9)	110.7(10)	C(8) - C(7) - C(9)	110.4(11)
Nb - N - C(3)	176.6(10)	Nb - C(11) - C(12)	72.9(4)
Nb - C(11) - C(15)	75.7(4)	Nb - C(12) - C(11)	73.8(4)
Nb - C(12) - C(13)	75.3(4)	Nb - C(13) - C(12)	71.6(4)
Nb - C(13) - C(14)	75.3(4)	Nb - C(14) - C(13)	72.2(4)
Nb - C(14) - C(15)	73.0(4)	Nb - C(15) - C(11)	71.5(4)
Nb - C(15) - C(14)	74.6(4)	Nb - C(21) - C(22)	66.5(14)
Nb - C(22) - C(21)	74.1(15)	Nb - C(22) - C(23)	121.4(24)
C(21) - C(22) - C(23)	126.3(27)		

Table 3.2 *Bond distances (Å) and angles (°) for* $CpNb(NAr)(\eta^2\text{-}C_3H_6)(PMe_3)$ *(3).*

The diffraction studies reveal that only one rotamer is found in the crystal investigated, the methyl group of the propylene is orientated towards the imido unit and away from the Cp ring, corresponding to isomer (3a). Stereochemical models show that this is the least hindered environment for the propylene ligand. Rotation of the propylene moiety by 180° places the methyl unit in close proximity to both PMe_3 and Cp units, the least favoured of the four possible C_3H_6 orientations. Thus, the rotamer observed by diffraction studies may be tentatively assigned to the more intense signal of pair A.

The metal-nitrogen distance, at 1.793(11)Å, is at the long end of the range observed for Nb-N(imido) bond lengths, and compares with a metal-nitrogen distance of 1.761(6)Å in the starting dichloride, $CpNb(NAr)Cl_2$[4]. This slight increase in Nb-N bond length for (3a) is attributed to its lower formal oxidation state, (regarding propylene as a neutral two electron donor). The metal carbon distances for the methylene and methine carbons are 2.39(3) and 2.28(3)Å respectively with a C-C distance of 1.58(4)Å. Caution is required in the interpretation of these bond parameters due to disorder in the propylene and Cp ligands which superimpose on each other across a mirror plane containing the Nb, N, and P atoms[11].

The orientation of the propylene group is of considerable interest as there is expected to be a close similarity between (3) and metallocenes such as Negishi's $Cp_2Zr(PhC{\equiv}CPh)(PMe_3)$[12] and Buchwald's (hexyne)zirconocene complex $Cp_2Zr(CH{\equiv}C^nBu)(PMe_3)$[13]. Pseudo metallocene character for (3) would require the C(21)-C(22) bond of the propylene ligand to lie co-planar with the phosphine to allow favourable overlap with metallocene-like frontier orbitals of the [CpNb(NAr)] fragment. The Nb-P bond is found to lie only 7.1° out of the Nb-C(21)-C(22) plane which does indeed lend further support to the metallocene analogy.

3.3.2 Preparation of $Cp^*Ta(NAr)(\eta^2-C_3H_6)(PMe_3)$ (4).

The propylene derivative $Cp^*Ta(NAr)(\eta^2-C_3H_6)(PMe_3)$ was prepared by the treatment of a diethylether solution of $Cp^*Ta(NAr)Cl_2$ with an excess of n-propyl Grignard reagent and trimethylphosphine. Subsequent extraction into n-pentane and prolonged cooling at -40°C gave a moderate yield (41%) of analytically pure orange crystals.

Compound (4) is very soluble in hydrocarbon solvents; however, as for $Cp^*Ta(NAr)(\eta^2-C_2H_4)(PMe_3)$ (2), treatment with chlorocarbons affords $Cp^*Ta(NAr)Cl_2(PMe_3)$ and free propylene. The 400 MHz ^1H NMR spectrum shows four isomers in varying concentrations which is consistent with slow rotation of the C_3H_6 unit about the metal propylene axis, making the four possible orientations of the propylene ligand observable. Furthermore, attempts to assign propylene orientation through NOE NMR techniques proved unsuccessful due to different T_1 relaxation times for each rotamer (*cf.* analogous niobium complex (3) described earlier).

The four isomers (4a - 4d) again may be conveniently divided into rotamer pairs (A and B) related by a 180° rotation of the propylene ligand; the ratios of the rotamers within each pair are invariant in solution NMR spectra. Moreover, the A to B ratio is found to depend upon the temperature of the solution. However, in contrast to the niobium-propylene species (2) which is unstable in solution at ambient temperature, compound (4) can be warmed indefinitely at 60°C in C_6D_6 without decomposition. This observation is intriguing since steric considerations lead to the conclusion that the Cp^* ring would make the propylene unit more labile than in the Cp complex (2). However, increased electron donation by the Cp^* ring can in turn lead to greater back donation to the propylene carbons leading to greater stability through increased metallacyclopropane character.

Examination of stereochemical models indicate that orientation of the propylene towards the imido unit and away from the Cp^* ring again affords the least hindered orientation, whereas rotation of the propylene moiety by 180° places the methyl unit in close contact with both phosphine and Cp^* units, the least favoured orientation. Thus, the rotamer pair which exists as a 4.2 : 1 ratio may be tentatively be assigned to pair A. Comparison with the analogous rotamer pair of the niobium species (3), where a 2.8 : 1 ratio is found, clearly indicates the increased steric constraints imposed upon the propylene unit by replacement of Cp by Cp°.

Pair B of compound (4) shows a 2.8 : 1 ratio (*cf.* 1.4 : 1 ratio for the niobium analogue). Moreover, as observed for (3), the proportion of pair B in a given solution of (4) increases gradually over a period of several weeks on warming at 60°C.

3.4 Mechanism of Formation of the Niobium and Tantalum(III) Olefin Derivatives.

The mechanism of formation of these olefin derivatives has been probed, in order to elucidate which of two likely mechanisms leads to the formation of these species.

The first mechanism involves the formation of the mono-alkyl derivative Cp'M(NAr)(R)Cl followed by subsequent elimination of HCl and stabilisation of the resultant olefin species by phosphine, the HCl being "mopped-up" as $PMe_3H^+Cl^-$. An alternative mechanism involves the reaction proceeding *via* β-hydride elimination with loss of alkane from a dialkyl intermediate.

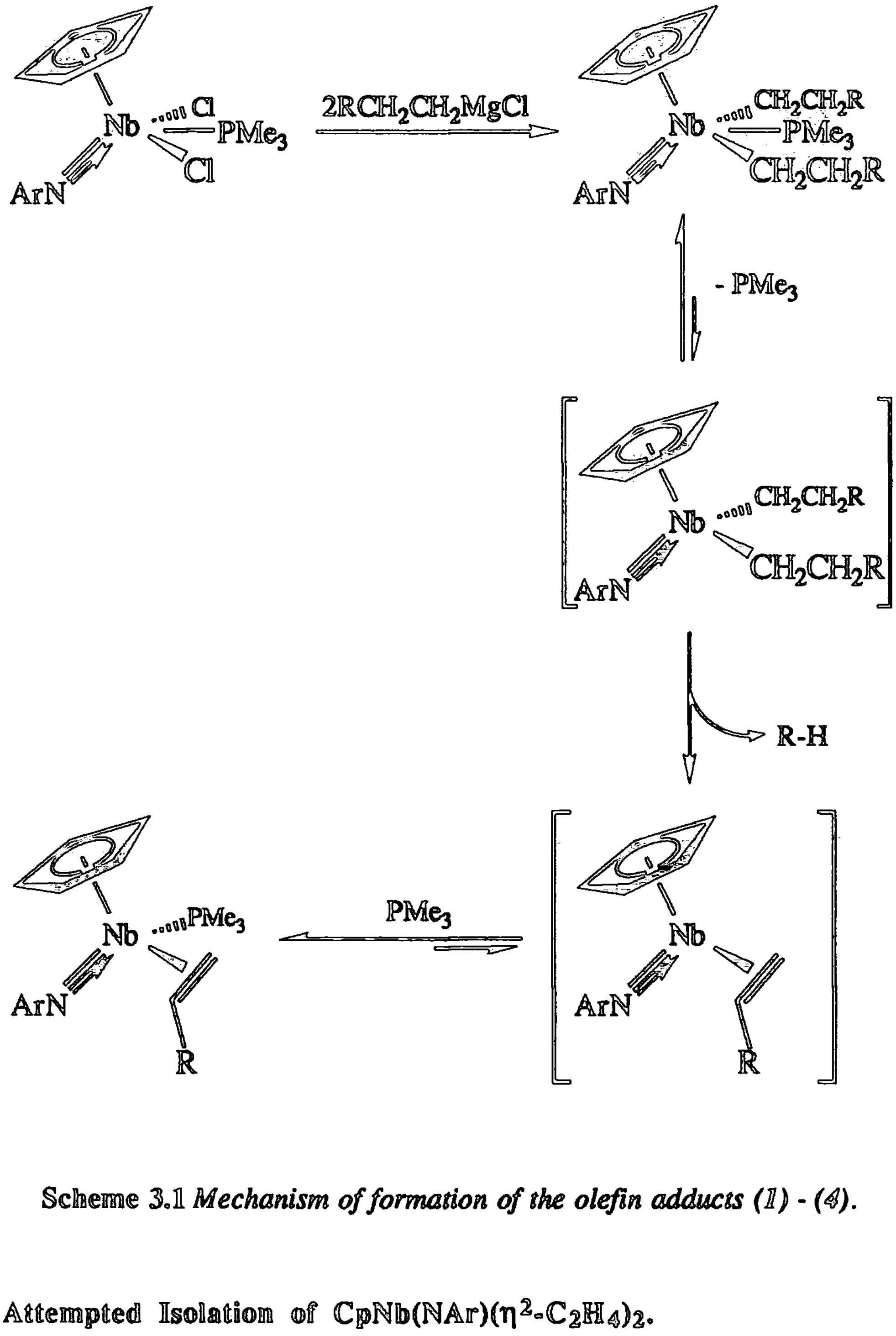
No $PMe_3H^+Cl^-$ was observed by infrared spectroscopy[14] in the insoluble residues of the reaction. Mass spectrometry of the volatile components of the reaction mixture showed the presence of propane (m/z 42) from a reaction of a diethylether solution of $CpNb(NAr)Cl_2$ with $n\text{-}C_3H_7MgCl$ and PMe_3. Furthermore, when a 2:1 mixture of $CpNb(NAr)Cl_2$ and $(Et_2AlCl)_2$ is sealed in an NMR tube, (C_6D_6), in the presence of PMe_3 and monitored by ^1H NMR spectroscopy (250 MHz), the olefin derivative (1) is obtained along with ethane (δ 0.79 ppm) *via* an intermediate species that we have tentatively assigned as $CpNb(NAr)(Et)_2(PMe_3)$. This intermediate complex exhibits resonances at δ 6.08, 1.53, and 1.02 ppm attributable to the Cp ring, ethyl β-hydrogen, and PMe_3 hydrogens respectively. Moreover, a doublet at δ 1.21 ppm has been assigned to the (aryl)imido isopropyl methyl hydrogens indicating that the phosphine is presumably located symmetrically between the ethyl units. (See Scheme 3.1).

The mechanism of formation can therefore be thought most likely to proceed *via* an unstable dialkyl phosphine complex, which on dissociation of PMe_3 allows elimination of alkane and generation of the olefin adduct stabilised with phosphine. This mechanism for the preparation of an olefin complex is not uncommon; Buchwald[13], for example, noted that warming $Cp_2Zr(n\text{-}Bu)_2$in the presence of PMe_3 afforded $Cp_2Zr(1\text{-butene})(PMe_3)$ and n-butane. The olefin adducts (1)-(4) can therefore be envisaged to form according to Equation 3.2 and Scheme 3.1.

$$Cp'M(NAr)Cl_2 + 2RCH_2CH_2MgCl + PMe_3 \xrightarrow{Et_2O}$$

$$Cp'M(NAr)(\eta^2\text{-}CH_2CHR)(PMe_3) + 2MgCl_2 + R\text{-}H \quad (3.2)$$

(M = Nb, Ta)



Scheme 3.1 *Mechanism of formation of the olefin adducts (1) - (4).*

3.5 Attempted Isolation of CpNb(NAr)(η^2-C_2H_4)$_2$.

An attempt to isolate the diethylene derivative, CpNb(NAr)(η^2-C_2H_4)$_2$ was undertaken *via* the reaction of excess ethyl magnesium chloride with CpNb(NAr)Cl_2 in diethylether in the presence of an ethylene atmosphere. However, this reaction did not afford a tractable product, indicating that any diethylene (or metallacyclopentane) species formed is too unstable to allow its isolation.

An alternative route *via* displacement of the tertiary phosphine from CpNb(NAr)(η^2-C_2H_4)(PMe$_3$) (1) using a 20 fold excess of ethylene also proved unsuccessful. However, treatment of CpNb(NAr)Cl$_2$ with (Et$_2$AlCl)$_2$ and ethylene in an NMR tube afforded but-1-ene and a number of unidentified organometallic species on standing at ambient temperature. The formation of but-1-ene, *via* a β-hydrogen elimination is a characteristic reaction of metallacyclopentanes, numerous examples having been reported, for example in Ni(II) and Pd(II) complexes (Figure 3.8)[15]. This observation may suggest that the metallacycle complex $\mathrm{Cp\overline{Nb(NAr)((CH_2)_3C}H_2)}$, has been generated. The thermal instability of this species is not unexpected as early work by Schrock showed that niobium metallacycles are in general unstable[16].

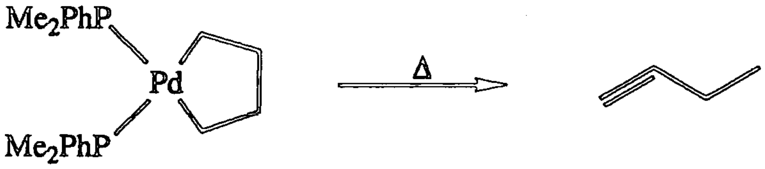
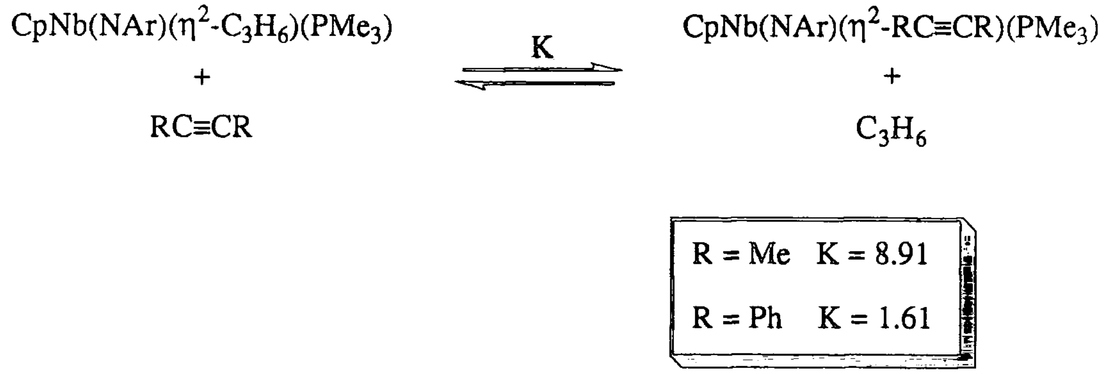


Figure 3.8

3.6 Displacement Reactions of the Olefin Derivatives CpNb(NAr)(η^2-C_2H_3R)(PMe$_3$) (R = H (1); Me (3)).

As anticipated, the sterically hindered propylene ligand in complex (3) is sufficiently labile to be readily and cleanly displaced by ethylene in benzene solvent, slowly at ambient temperature and rapidly at 60°C.

Displacement of the propylene unit in Cp(NAr)(η^2-C_3H_6)(PMe$_3$) (3) with the disubstituted acetylenes MeC≡CMe and PhC≡CPh does not lead to quantitative conversion to the corresponding disubstituted acetylene complexes but to equilibrium mixtures with the acetylene complexes (Figure 3.9).



$$\mathrm{CpNb(NAr)(\eta^2\text{-}C_3H_6)(PMe_3)} + \mathrm{RC{\equiv}CR} \overset{K}{\rightleftharpoons} \mathrm{CpNb(NAr)(\eta^2\text{-}RC{\equiv}CR)(PMe_3)} + \mathrm{C_3H_6}$$

R = Me K = 8.91

R = Ph K = 1.61

Figure 3.9

The but-2-yne derivative CpNb(NAr)(η^2-MeC≡CMe)(PMe$_3$) (5) can be observed by ^{1}H NMR spectroscopy to exist in two distinct forms of equal proportions below room temperature with resonances attributable to the Cp ring hydrogens at δ 6.40 and 6.62 ppm, and septet resonances at δ 3.47 and 3.59 ppm corresponding to (aryl)imido isopropyl methine hydrogens (400 MHz, CDCl$_3$). However, at higher temperatures only an averaged signal is observed for the Cp ring hydrogens, seen as a singlet at δ 6.41ppm, while the isopropyl methine hydrogens are found at δ 3.64 ppm.. The coalescence temperature and rate of interconversion between the two forms are found to be 28°C, and 195 Hz respectively.

Likewise, (3) reacts with diphenylacetylene at elevated temperature (60°C) in benzene to afford an equilibrium mixture of starting olefin complex and a diphenylacetylene species which again exists in two isomeric forms in ambient temperature solution. The 250 MHz ^{1}H NMR spectrum (C_6D_6) of CpNb(NAr)(η^2-PhC≡CPh)(PMe$_3$) (6) showed singlets at δ 5.76 and 5.82 ppm for the Cp ring hydrogens and septet resonances at δ 3.85 and 3.90 ppm assigned to the methine hydrogens of the aryl(imido) isopropyl groups.

The observation that two forms of the complexes CpNb(NAr)(η^2-RC≡CR)(PMe$_3$) exist may be explained through steric considerations. The pseudo metallocene character of the [CpNb(NAr)] fragment would favour the acetylene ligand bonding to the niobium centre so as to be co-planar with the phosphine. Examination of molecular models, however, indicates that such a conformation would not be favoured since an acetylene substituent (*ie* methyl, or phenyl) would then be in close contact with the phosphine ligand. One possibility for alleviating this unfavourable interaction would be for the acetylene to rotate to a position where its substituents could lie either side of the PMe_3. (See Figure 3.10) The equal proportions of each isomer indicates no steric preference for either rotamer. The coalescence observed for the but-2-yne complex may be attributed to averaging of signals at elevated temperatures. However, significant steric congestion in the diphenylacetylene complex CpNb(NAr)(η^2-PhC≡CPh)(PMe_3) (6) prevents any such averaging of the isomers from occurring. The mechanism of the observed averaging of the two CpNb(NAr)(η^2-MeC≡CMe)(PMe_3) isomers has yet to be established since (5) has been characterised exclusively by ^1H NMR spectroscopy.

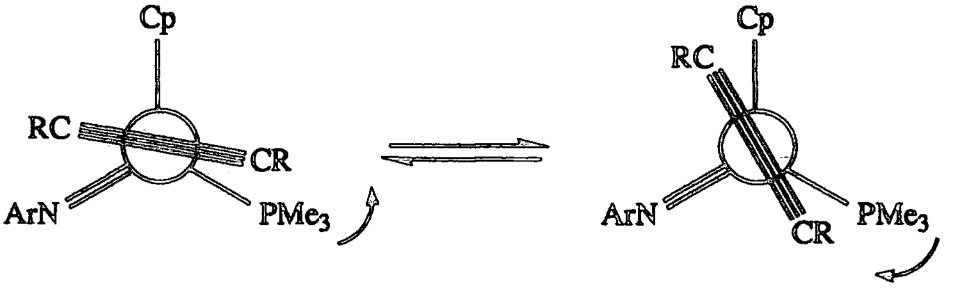
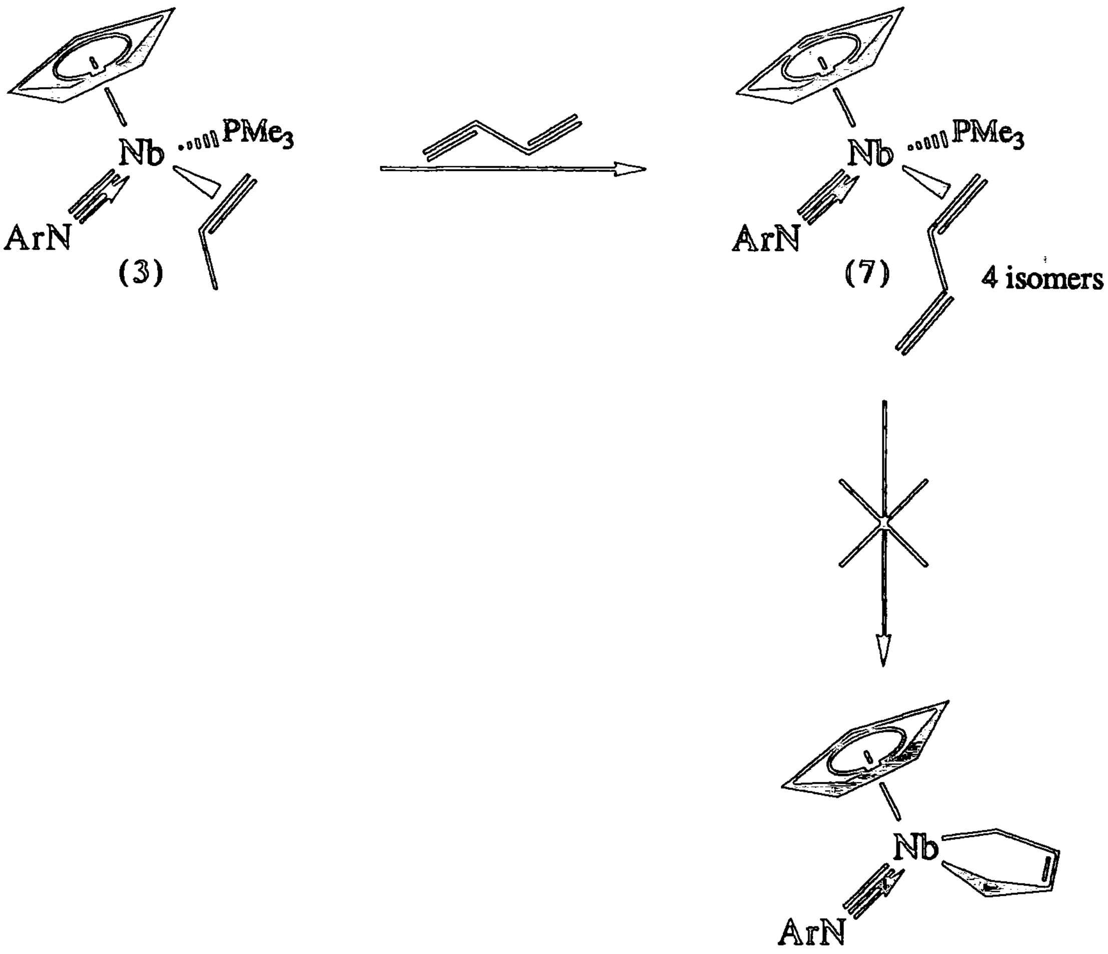


Figure 3.10 *Newman projections of the two proposed forms of the acetylene adducts (5) and (6).*

In recent years there has been growing interest in the chemistry of metal-diene complexes such as Cp_2M(diene) (M = Ti, Zr, Hf), which furnish synthetically useful selective carbon-carbon bond-forming reactions[17,18].

Interest therefore focused on the possibility of producing metallocene-diene analogues through the displacement of olefin and phosphine from CpNb(NAr)(η^2-C_3H_6)(PMe_3) (3) with 1,3-butadiene. Compound (3) and a 10 fold excess of 1,3-butadiene were sealed in an NMR tube and monitored by 250 MHz ^1H NMR spectroscopy (C_6D_6). Although no free PMe_3 was subsequently detected, a mixture of four new half-sandwich species, with Cp ring hydrogen resonances in the range δ 5.71

- 5.89 ppm, and resonances due to bound PMe_3 between δ 0.83 - 0.91 ppm, were observed. Moreover, ^1H NMR spectroscopy revealed signals attributable to free propylene. The four new species have been assigned to the four rotamers of the η^2-butadiene complex $CpNb(NAr)(\eta^2\text{-}C_4H_6)(PMe_3)$ (7). Subsequent warming of the sample to 60°C did not lead to dissociation of phosphine to afford a niobium metallacyclopentene complex, rather decomposition occurred to afford a number of unidentified black paramagnetic species.



Scheme 3.2 *Reaction of (3) with 1,3-butadiene.*

3.6.1 Preparation of $CpNb(NAr)(CO)(PMe_3)$ (8).

Treatment of $CpNb(NAr)(\eta^2\text{-}C_3H_6)(PMe_3)$ (3) with carbon monoxide quickly and cleanly liberated propylene in hydrocarbon solvent at ambient temperature to yield the carbonyl compound $CpNb(NAr)(CO)(PMe_3)$ (8). Compound (8) was subsequently isolated as red air-sensitive crystals from concentrated solutions in n-pentane at -78°C. The reaction can be envisaged to proceed according to Equation 3.3. Carbonylation of the ethylene complex (1) was found to occur only upon prolonged warming at 60°C. This observation can be attributed to the greater lability of the monosubstituted olefin of (3) compared with the ethylene ligand in (1).

$$\underset{(3)}{CpNb(NAr)(\eta^2\text{-}C_3H_6)(PMe_3)} + CO \xrightarrow{\text{n-pentane}} \underset{(8)}{CpNb(NAr)(CO)(PMe_3)} + C_3H_6 \quad (3.3)$$

Compound (8) gives an absorption in the infrared spectrum at 1870 cm^{-1} which is indicative of a $\upsilon(CO)$ stretching vibration for a terminal carbonyl ligand, where the carbonyl experiences considerable back-donation from the niobium(III) centre. Mass spectrometry reveals envelopes at m/z 361, 332, 275 that are attributable to the fragments CpNb(NAr)(CO), CpNb(NAr), and $CpNb(CO)(PMe_3)$ respectively. The ^{13}C NMR spectrum does not reveal a resonance attributable to the carbonyl unit due to the close proximity of the quaternary carbonyl carbon to the quadrupolar ^{93}Nb nucleus ($I = {}^9/_2$, 100% natural abundance).

3.7 Reaction of $CpNb(NAr)(\eta^2\text{-}C_2H_3R)(PMe_3)$ with $HBF_4.Et_2O$ (R = H, (1); Me, (3)).

Brookhart has demonstrated that with a strong acid such as $HBF_4.Et_2O$ half-sandwich olefin compounds of cobalt can be protonated to give cationic alkyls which show ethylene polymerisation activity[19].

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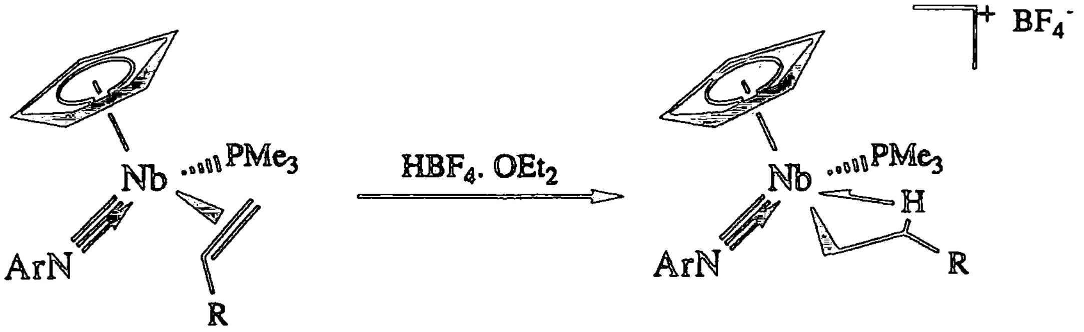
Compound (8) gives an absorption in the infrared spectrum at 1870 cm^{-1} which is indicative of a υ(CO) stretching vibration for a terminal carbonyl ligand, where the carbonyl experiences considerable back-donation from the niobium(III) centre. Mass spectrometry reveals envelopes at m/z 361, 332, 275 that are attributable to the fragments CpNb(NAr)(CO), CpNb(NAr), and CpNb(CO)(PMe$_3$) respectively. The ^{13}C NMR spectrum does not reveal a resonance attributable to the carbonyl unit due to the close proximity of the quaternary carbonyl carbon to the quadropolar ^{93}Nb nucleus (I = $^9/_2$, 100% natural abundance).

3.7 Reaction of CpNb(NAr)(η^2-C_2H_3R)(PMe$_3$) with HBF$_4$.Et$_2$O (R = H, (1); Me, (3)).

Brookhart has demonstrated that with a strong acid such as HBF$_4$.Et$_2$O half-sandwich olefin compounds of cobalt can be protonated to give cationic alkyls which show ethylene polymerisation activity[19].

Through our interest in preparing potential initiators for Ziegler-Natta activity, HBF_4. Et_2O was mixed with the previously described ethylene and propylene adducts (1) and (3) in diethylether in an attempt to afford phosphine-stabilised alkyl cations, as shown below in Figure 3.11:



R = H, (1)
R = Me, (3)

Figure 3.11

Treatment of diethylether solutions of the olefin adducts (1) and (3) with dilute solutions of $HBF_4.OEt_2$ at -30°C afforded pale precipitates instantaneously, in conjunction with the decolourisation of the orange solutions. However, within minutes of warming to ambient temperature the solid darkened to afford an air-sensitive paramagnetic grey solid, indicating that decomposition had probably occurred.

The reason for this thermal instability is at present unclear, it is possible that any alkyl cation generated is unstable, potentially decomposing *via* attack on the BF_4^- counterion, or else protonation may be occurring at the nitrogen of the ancillary imido ligand, rather than the desired olefin site, which may destabilise the complex.

3.8 Displacement Reactions of the Olefin Derivatives $Cp^{*}Ta(NAr)(\eta^2-C_2H_3R)(PMe_3)$ (R = H, (2); Me, (4)).

The variety of displacement reactions displayed by the niobium olefin derivatives (1) and (3) prompted an investigation of the analogous tantalum ethylene and propylene species, (2) and (4) respectively.

Upon treatment of $Cp^{*}Ta(NAr)(\eta^2-C_3H_6)(PMe_3)$ (4) with ethylene it was anticipated that the less sterically congested ethylene adduct (2) would be afforded, according to Equation 3.4.

$$\underset{(4)}{Cp^{*}Ta(NAr)(\eta^2-C_3H_6)(PMe_3)} + C_2H_4 \longrightarrow \underset{(2)}{Cp^{*}Ta(NAr)(\eta^2-C_2H_4)(PMe_3)} + C_3H_6 \quad (3.4)$$

Intriguingly, however, when an equimolar mixture of $Cp^{*}Ta(NAr)(\eta^2-C_3H_6)(PMe_3)$ (4) and ethylene was sealed in an NMR tube and monitored by ^1H NMR spectroscopy (C_6D_6), no free propylene was observed. Rather, the ^1H NMR resonances attributable to (4) were replaced by four equally abundant isomers of a new species; all of the ethylene was consumed and a doublet resonance at δ 0.79 attributable to free PMe_3 was observed. The ^1H NMR spectrum therefore indicated that the anticipated displacement of propylene by ethylene had not occurred, but rather displacement of the phosphine to give the ethylene-propylene derivative $Cp^{*}Ta(NAr)(\eta^2-C_2H_4)(\eta^2-C_3H_6)$ (9), which is more likely to exist as a tantallacyclopentane as noted by Schrock[20]. Moreover, it is of interest that the ethylene component of (9) did not exchange with the bound propylene, thus suggesting that (9) has significant metallacycle character. This reaction can be envisaged to take place as shown in Equation 3.5.

$$\underset{(4)}{\mathrm{Cp^*Ta(NAr)(\eta^2\text{-}C_3H_6)(PMe_3)}} + \mathrm{C_2H_4} \xrightarrow{\text{benzene}} \underset{(9)}{\mathrm{Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)(\eta^2\text{-}C_3H_6)}} + \mathrm{PMe_3} \quad (3.5)$$

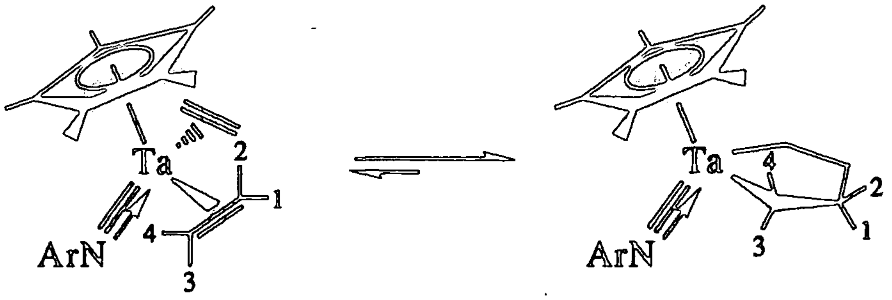


Figure 3.12 *The significant metallacyclopentane character of $Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)(\eta^2\text{-}C_3H_6)$ (9).*

$Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)(\eta^2\text{-}C_3H_6)$ (9) was characterised by ^1H NMR spectroscopy (400 MHz, C_6D_6) with four singlet resonances of equal intensity between δ 1.73 - 1.74 ppm corresponding to the Cp* rings of the four possible metallacycle isomers. Complex overlapping multiplets at δ 0.60, 1.96, 2.50 ppm and a doublet at δ 1.36 ppm are attributable to the tantallacycle ring and methyl substituent hydrogens respectively. Furthermore, four septets between δ 3.72 - 3.73 and doublets between δ 1.38 - 1.39 ppm correspond to the methine hydrogens and diastereotopic methyl substituents of the (aryl)imido isopropyl groups respectively, resonances in the range δ 6.99 - 7.24 ppm being assigned to the (aryl)imido hydrogens. The observation that the four isomers of (9) exist in equal concentrations in solution indicates that there is no energetic preference for one form.

Treatment of $Cp^*Ta(NAr)(\eta^2\text{-}C_3H_6)(PMe_3)$ with one equivalent of propylene and subsequent monitoring by ^1H NMR spectroscopy afforded the dipropylene complex $Cp^*Ta(NAr)(\eta^2\text{-}C_3H_6)_2$ (10) and free trimethylphosphine, according to Equation 3.6.

$$\underset{(4)}{Cp^*Ta(NAr)(\eta^2\text{-}C_3H_6)(PMe_3)} + C_3H_6 \xrightarrow{\text{benzene}} \underset{(10)}{Cp^*Ta(NAr)(\eta^2\text{-}C_3H_6)_2} + PMe_3 \quad (3.6)$$

The 400 MHz ^1H NMR spectrum reveals a mixture of ten isomers in differing concentrations corresponding to all possible configurations for the metallacycle. However, two isomers predominate, with Cp^* ring hydrogen resonances at δ 1.40 and 1.43 ppm, and isopropyl methyl and methine signals at δ 1.36, 1.38, and 3.90, 4.01 ppm repectively. The two favoured configurations of the tantallacycle presumably correspond to the species possessing the least steric hindrance, in contrast to the half-sandwich tantalum metallacycles described by Schrock and co-workers[20,21] which preferentially adopt a trans-ββ' substitution pattern . (Figure 3.13).

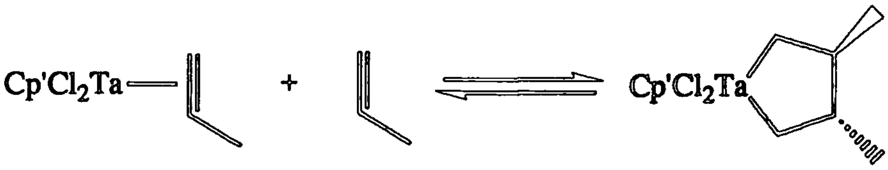


Figure 3.13

The displacement of tertiary phosphine from tantalum-olefin species suggest that analogues of the synthetically useful metallocene-diene complexes Cp_2M(diene) (M = Ti, Zr, Hf) may be accessible through reaction of (2) or (4) with a diene. Such species would be of interest, since Nakamura has found other tantalum diene species to possess unusual ligand bonding modes[22].

In contrast to the reaction of (3) with 1,3-butadiene, treatment of a benzene solution of $Cp^*Ta(NAr)(\eta^2\text{-}C_3H_6)(PMe_3)$ (4) with 1,3-butadiene in an NMR tube and subsequent warming to 60°C did not afford free propylene. Rather, monitoring by ^1H NMR spectroscopy (250 MHz, C_6D_6) revealed that dissociation of phosphine had occurred. Ten new Cp^* methyl hydrogen signals were resolved in the range δ 1.65 - 1.85 ppm consistent with all the possible tantallacycle isomers of the propylenebutadiene tantalum complex $Cp^*Ta(NAr)(\eta^2\text{-}C_4H_6)(\eta^2\text{-}C_3H_6)$ (11). Moreover, resonances in the ranges δ 1.12 - 1.37 ppm and δ 3.80 - 4.22 ppm were assigned to the aryl(imido) isopropyl methyl and methine hydrogens respectively. Prolonged warming at 100°C did not yield the desired tantallacyclopentene *via* loss of propylene (Equation 3.7). This may be indicative of the groundstate of $Cp^*Ta(NAr)(\eta^2\text{-}C_4H_6)(\eta^2\text{-}C_3H_6)$ (11) being more metallacyclopentane-like rather than diolefin.

$$\begin{tikzcd} \underset{(4)}{Cp^*Ta(NAr)(\eta^2\text{-}C_3H_6)(PMe_3)} + C_4H_6 \arrow[r, "60^\circ C", "-PMe_3"'] & \underset{(11)}{Cp^*Ta(NAr)(\eta^2\text{-}C_4H_6)(\eta^2\text{-}C_3H_6)} \arrow[d, "100^\circ C"', "-C_3H_6", "\times" marking] \\ & Cp^*Ta(NAr)(\eta^4\text{-}C_4H_6) \end{tikzcd}$$

(3.7)

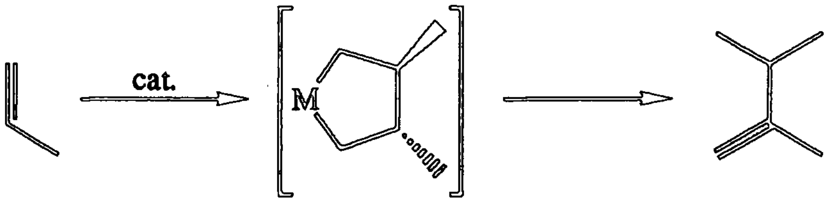
The NMR monitored reaction of $Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)(PMe_3)$ (2) with ethylene at 60°C afforded an equilibrium mixture of (2) and the diethylene species $Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)_2$ (12) whose characterising data are discussed in 3.8.1 below. In contrast to the displacement reactions of the propylene derivative (4) with olefin where loss of tertiary phosphine is quantitative, the equilibrium observed between the ethylene and diethylene derivatives (2) and (4) is at first surprising. This may arise due to the larger size of the propylene ligand in (4) compared with the ethylene unit in (2) leading to less favourable steric interactions in the former.

$$\underset{(2)}{Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)(PMe_3)} + C_2H_4 \xrightleftharpoons[60^\circ C]{\text{benzene}} \underset{(12)}{Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)_2} + PMe_3 \quad (3.8)$$

3.8.1 Preparation of $Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)_2$ (12).

The half-sandwich tantalum complex $CpTaCl_2(RCH{=}CH_2)_2$ has been shown to be an efficient catalyst for the selective dimerisation of ethylene and propylene to but-1-ene and 2,3-dimethyl-but-1-ene respectively[21,23]. Spectroscopic studies have shown the mechanism of dimerisation to involve metallacyclic intermediates (Figure 3.14) where high head-to-head selectivity is found in the formation of the tantallacycles.

The surprising observation that tantallacycles are afforded through treatment of (2) and (4) with olefins led us to attempt to isolate such complexes as potential α-olefin dimerisation catalysts.



cat. = $CpTaCl_2(RCH{=}CH_2)_2$

Figure 3.14

As the diethylene complex (12) cannot be prepared quantitatively through the reaction of $Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)(PMe_3)$ (2) with ethylene, an attempt to isolate (12) was undertaken *via* the reaction of an excess of ethyl Grignard reagent and ethylene with $Cp^*Ta(NAr)Cl_2$.

Treatment of a diethylether solution of $Cp^*Ta(NAr)Cl_2$ with an excess of C_2H_5MgCl in the presence of an ethylene atmosphere afforded a lemon-yellow solution of $Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)_2$ and $MgCl_2$. (Equation 3.9).

$$Cp^*Ta(NAr)Cl_2 + 2EtMgCl + C_2H_4 \xrightarrow{Et_2O}$$

$$\underset{(12)}{Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)_2} + 2MgCl_2 + C_2H_6 \quad (3.9)$$

Compound (12) can be isolated as yellow needle-like crystals upon prolonged cooling of a concentrated diethylether solution at -78°C. These moisture sensitive crystals are soluble in aromatic and low polarity hydrocarbon solvents, and are indefinitely stable in chlorocarbons. This indicates that (12) is likely to possess significant metallacyclopentane character, since the diethylene form would be anticipated to react with chlorocarbons to afford the dichloride $Cp^{*}Ta(NAr)Cl_2$ and free ethylene (*cf.* compound (2)). A further indication of the metallacycle character of (12) is provided by very slow exchange with d_4-ethylene which occurs only over several days at 60°C.

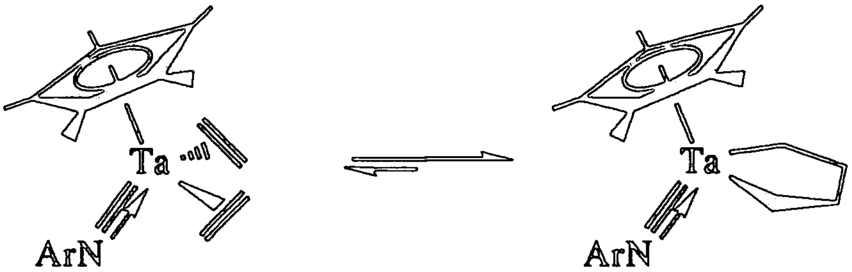
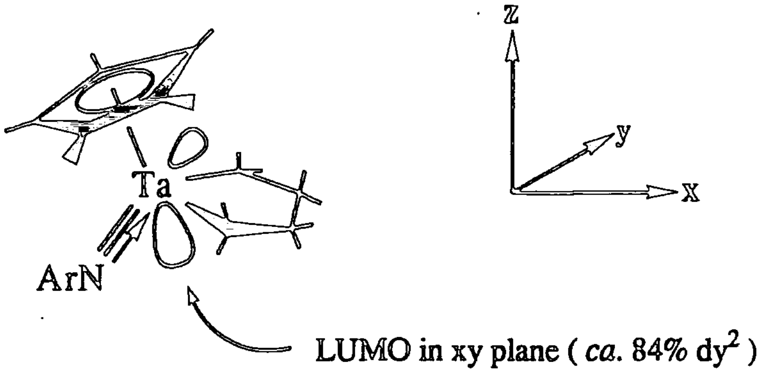


Figure 3.15 *Significant metallacyclopentane character of* $Cp^{*}Ta(NAr)(\eta^2\text{-}C_2H_4)_2$ *(12).*

The 400 MHz ^1H NMR spectrum reveals complex multiplets at δ 0.96, 1.68, 2.22, 2.48 ppm attributable to the tantallacycle ring methylene hydrogens. NOE NMR techniques show that the protons giving rise to the resonances at δ 1.68 and 2.22 ppm are orientated towards the Cp* ring, whereas the resonances at δ 0.96 and 2.48 ppm are due to protons directed towards the ancillary imido unit. Unfortunately, since crystals suitable for X-ray diffraction have proven elusive, the absolute conformation of the tantallacycle ring remains to be determined. The 100 MHz ^{13}C NMR spectrum (C_6D_6) shows resonances at δ 16.20 and 53.54 ppm which may be assigned to the metallacycle ring carbons. The $^1J_{CH}$ coupling constants of 133 and 129 Hz respectively are characteristic of those expected for sp^3- hybridised methylene units[24]. Mass spectrometry reveals an envelope at m/z 548 (^{181}Ta) corresponding to the protonated parent ion and daughter fragments at m/z 519 and 491 (^{181}Ta) are attributable to Cp*Ta(NAr)(C_2H_4) and Cp*Ta(NAr) respectively.

Compound (12) is thermally robust, being stable indefinitely at 120°C with no elimination of but-1-ene. A possible contributory factor in this stability lies in the directional properties of the LUMO for the [Cp*Ta(NAr)] fragment which is orientated in the xy plane (Figure 3.16) and so β-hydrogen elimination, a prerequisite for elimination of but-1-ene, may not be favourable.

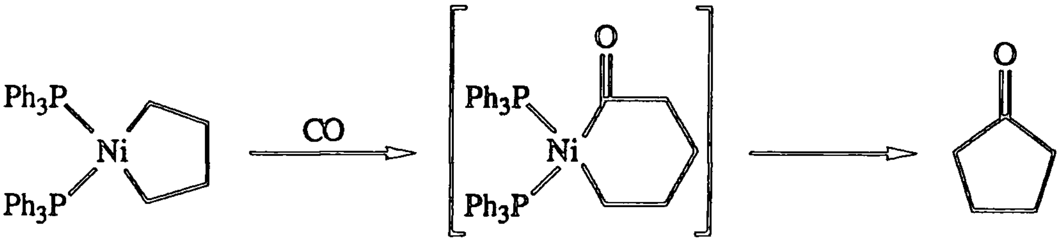


LUMO in xy plane (*ca.* 84% dy^2)

Figure 3.16 *Orientation of the LUMO in the tantallacycle (12).*

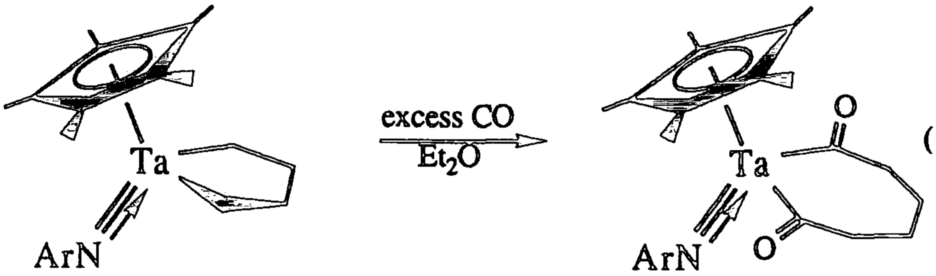
3.8.2 Preparation of Cp*Ta(NAr)$\overline{[C(O)C_4H_8C(O)]}$ (13).

Like other transition metal-carbon bonds, the metal-carbon bonds in metallacyclopentanes insert carbon monoxide to afford acyl derivatives, which may liberate cyclic ketones on decomposition, a feature demonstrated by Grubbs^{25} with the Ni(II) phosphine complex in Scheme 3.3.



Scheme 3.3

Treatment of a diethylether solution of the diethylene complex (12) with an excess of carbon monoxide readily afforded an orange solution of $Cp^*\overline{Ta(NAr)[C(O)C_4H_8C}(O)]$ (13) at ambient temperature. (Equation 3.10). The diacyl complex (13) was subsequently isolated as a microcrystalline orange solid upon prolonged cooling at -40°C. Diacylation of (12) has been shown to be rapid as spectroscopic investigations (^1H NMR) failed to reveal any evidence of a mono-insertion product.



(12) (13) (3.10)

Elemental analysis confirms a stoichiometry consistent with $C_{28}H_{40}NO_2Ta$. Moreover, mass spectrometry reveals an envelope at m/z 603 (^{181}Ta) corresponding to the parent ion. Infrared spectroscopy shows a weak band at 1630 cm^{-1} which has been assigned to an acyl υ(CO) stretching vibration, the position of which is intermediate between those observed for η^1- and η^2-acyl species[26]. The 250 MHz ^1H NMR spectrum (C_6D_6) shows complex multiplets due to the metallacycle methylene hydrogens at δ 1.40, 1.65, 2.35, and 2.65 ppm; these resonances are shifted upfield by 0.2 - 0.5 ppm relative to those of the 'diethylene' complex (12). The 100 MHz ^{13}C NMR spectrum reveals a resonance at δ 133.74 ppm corresponding to the quaternary acyl carbons, and resonances at δ 23.03 and 28.94 ppm which are attributable to the methylene carbon resonances of the metallacycloheptadione ring. The ^{13}C shift of the acyl carbon is diagnostic of its bonding mode, for although η^1-acyl resonances fall over a very wide range, the acyl carbon resonances expected for η^2-acyl containing complexes are restricted to values between δ 248 - 392 ppm[26]. Thus, the acyl bonding mode in (13) can be assigned tentatively as being an η^1-acyl. This is in contrast to many Group 4 metallocene species which exhibit η^2-acyl bonding modes[17,26]. A plausible rationalisation for the η^1-acyl bonding in (13) may be found in the geometric constraints of the tantallocycloheptadione ring such that the acyl oxygens are unable to approach the electron deficient metal centre.

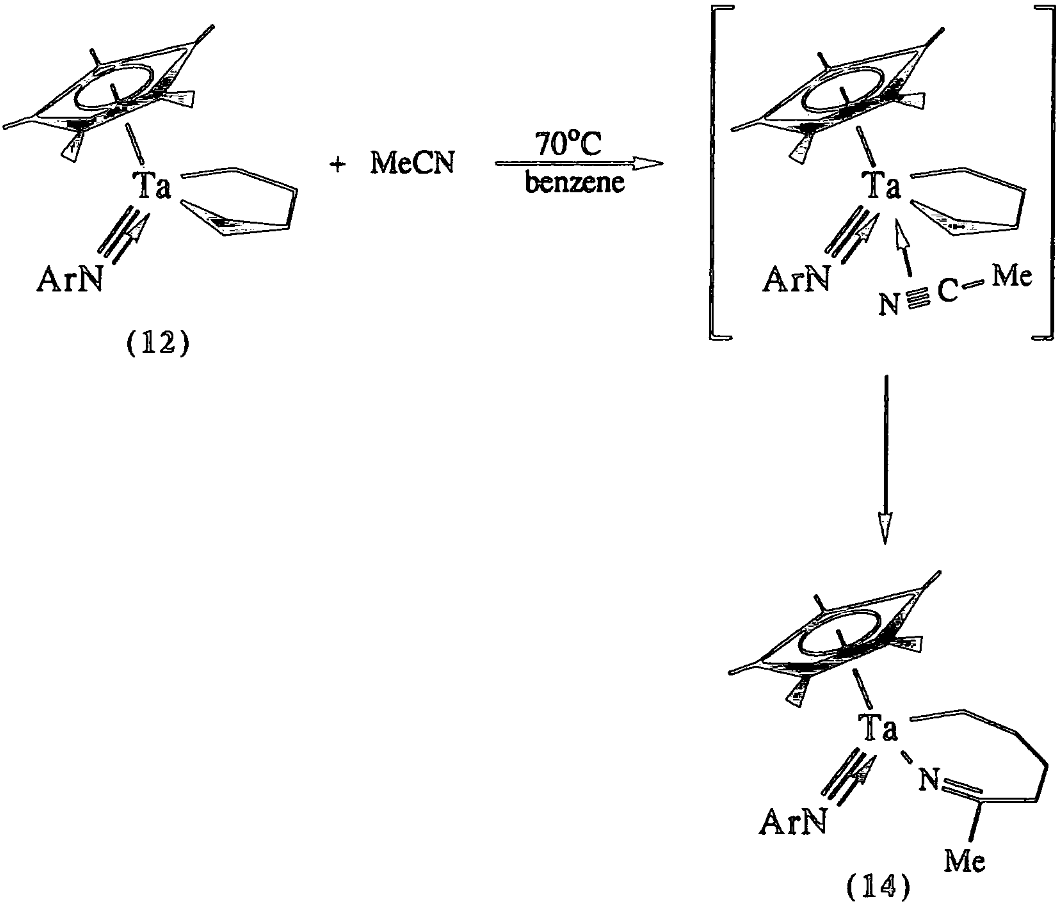
3.8.3 Reaction of $Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)_2$ (12) with Acetonitrile.

Since carbon monoxide readily inserts into the tantalum-carbon bonds of (12), the possibility of incorporating heteroatoms into metallacycle rings was addressed. This is of some interest as Buchwald has demonstrated that zirconocene-induced coupling of benzyne with nitriles affords azametallacycles which can be used to generate aromatic ketones and/or other heteroatom containing species upon hydrolysis[27,28].

Treatment of the 'diethylene' complex (12) with two mole equivalents of acetonitrile in a sealed NMR tube (C_6D_6), gave no reaction at ambient temperature when monitored by ^1H NMR spectroscopy. However, warming of the solution at 70°C resulted in a slow reaction of one mole equivalent of acetonitrile with the metallacycle (12) affording the metallacycloimine $Cp^*\overline{Ta(NAr)[N{=}C(Me)C_3H_6CH_2}]$ (14).

Characterisation by NMR spectroscopy (C_6D_6) indicates that there is a unique mode of insertion of the acetonitrile into the metallacycle ring of (12), presumably attributable to steric interactions in the acetonitrile-adduct intermediate prior to insertion, as commented on previously for the zirconocene system by Buchwald[24]. The 250 MHz ^1H NMR spectrum reveals a single resonance corresponding to Cp^* ring hydrogens at δ 1.83 ppm, a septet at δ 3.85 ppm and doublets at δ 1.33 and 1.41 ppm attributable to the methine hydrogens and diastereotopic methyls of the (aryl)imido isopropyl groups respectively, and four complex multiplets between δ 0.90-2.50 ppm due to the metallacycle methylene hydrogens. A singlet at δ 1.60 ppm is assignable to the methyl substituent of the azatantallacycle ring, subsequent employment of NOE NMR techniques show this methyl group to be orientated toward the (aryl)imido unit which may reflect steric considerations during the formation of the nitrogen containing metallacycle. (Scheme 3.4). The 100 MHz ^{13}C NMR spectrum shows a lowfield resonance at δ 184.6 ppm attributable to the *sp*^{2} -hybridised azametallacycle ring carbon where the nitrile has inserted to form a Ta-N bond[30].

The metallacycloimine is suprisingly stable, decomposition occurring only after warming to 100°C for many days to afford a number of products whose identities have yet to be established.



Scheme 3.4

3.8.4 Preparation of $Cp^*Ta(NAr)(CO)(PMe_3)$ (15).

Treatment of $Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)(PMe_3)$ (2) with an excess of carbon monoxide in n-pentane afforded a brown solution which, on subsequent recrystallisation at -30°C, yielded a yellow-brown crystalline solid. The infrared spectrum showed the presence of a terminal CO ligand (υ(CO) = 1860 cm^{-1}). However, analysis by ^{1}H NMR spectroscopy shows that quantitative conversion to the carbonyl complex $Cp^*Ta(NAr)(CO)(PMe_3)$ (15) has not occurred unlike for its niobium analogue (8); the majority of the species present is the olefin starting complex $Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)(PMe_3)$ (2). Subsequent ^1H NMR reactions show that there is competition between the CO and C_2H_4 for a coordination site, as shown in Equation 3.11. This non-quantitative conversion to (15) may reflect a reluctance of the tantalum centre to adopt a more reduced form in the carbonyl, *ie* Ta(III), compared with the Ta(V) metallacyclopropane (2).

$$\underset{(2)}{Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)(PMe_3)} + CO \rightleftharpoons \underset{(15)}{Cp^*Ta(NAr)(CO)(PMe_3)} + C_2H_4 \quad (3.11)$$

3.9 Reduction of Cp'M(NAr)Cl$_2$ (M = Nb, Ta) in the Presence of PMe$_3$.

Both the versatile precusors $Cp_2Ti(PMe_3)_2$ and $Cp_2Zr(PMePh_2)_2$ have been shown to react with alkynes to form synthetically useful metallacyclopentadienes *via* intermediate $Cp_2M(PMe_3)$(alkyne) complexes that can often be observed spectroscopically[31,32]. Hence, work was undertaken to prepare niobium and tantalum analogues which may prove to be synthetically versatile.

3.9.1 Preparation of CpNb(NAr)(PMe$_3$)$_2$ (16).

$CpNb(NAr)(PMe_3)_2$ (16) may be isolated as a black solid *via* magnesium reduction of a THF solution of $CpNb(NAr)Cl_2$ in the presence of trimethylphosphine. (Equation 3.12).

$$CpNb(NAr)Cl_2 + 2PMe_3 + Mg \xrightarrow{THF} \underset{(16)}{CpNb(NAr)(PMe_3)_2} + MgCl_2 \quad (3.12)$$

Whereas, the related $Cp^{*}Nb(NAr)(PMe_3)_2$ is stable to prolonged exposure to a dynamic vacuum[8], (16) is found to readily lose phosphine under similar conditions. Compound (16) has been characterised by its mass, infrared, and NMR spectra. However, variable elemental analyses were obtained due to the extreme lability of the trimethylphosphine ligands. This lability of the phosphine is demonstrated clearly in the reactivity of (16) towards a variety of reagents. Treatment of the bisphosphine (16) with ethylene and carbon monoxide gases at ambient temperature readily affords the previously characterised ethylene and carbonyl complexes (1) and (8) respectively. This contrasts with the analogous displacement reactions of $Cp^{*}Nb(NAr)(PMe_3)_2$, where extended warming at 85°C is required to effect similar transformations.

Siemeling has shown that treatment of $Cp^{*}Nb(NAr)(PMe_3)_2$ with dihydrogen at 60°C affords the colourless niobium(V) dihydride $Cp^{*}Nb(NAr)(H)_2(PMe_3)$[8]. A similar reaction of compound (16) with dihydrogen immediately afforded a pale solution of $CpNb(NAr)(H)_2(PMe_3)$ (17) at ambient temperature. Whereas solutions of $Cp^{*}Nb(NAr)(H)_2(PMe_3)$ are stable to 60°C, compound (17) rapidly decomposes in ambient temperature solution to afford dark paramagnetic products. Isolation of this dihydride has not proven possible, and hence it has been characterised by ^1H NMR spectroscopy only. In the 250 MHz ^1H NMR spectrum of $CpNb(NAr)(H)_2(PMe_3)$ (17) the Cp ring hydrogens are found as a singlet at δ 5.87 ppm whereas the trimethylphosphine appears as a doublet at δ 1.17 ppm. The hydride resonances have not been located, possibily broadened due to their proximity to the niobium ($I = {}^9/_2$) centre. However, their presence has been confirmed as treatment of (17) with chloroform affords the previously described species $CpNb(NAr)Cl_2(PMe_3)$. Moreover, the methyl substituents on the (aryl)imido isopropyl groups appear as diastereotopic doublets, δ 1.28 and 1.34 ppm, indicating that the hydrides are not disposed symmetrically on either side of the P-Nb-N plane as observed for $Cp^{*}Nb(NAr)(H)_2(PMe_3)$[8]. The reactivity of the bisphosphine complex (16) is illustrated in Scheme 3.5.

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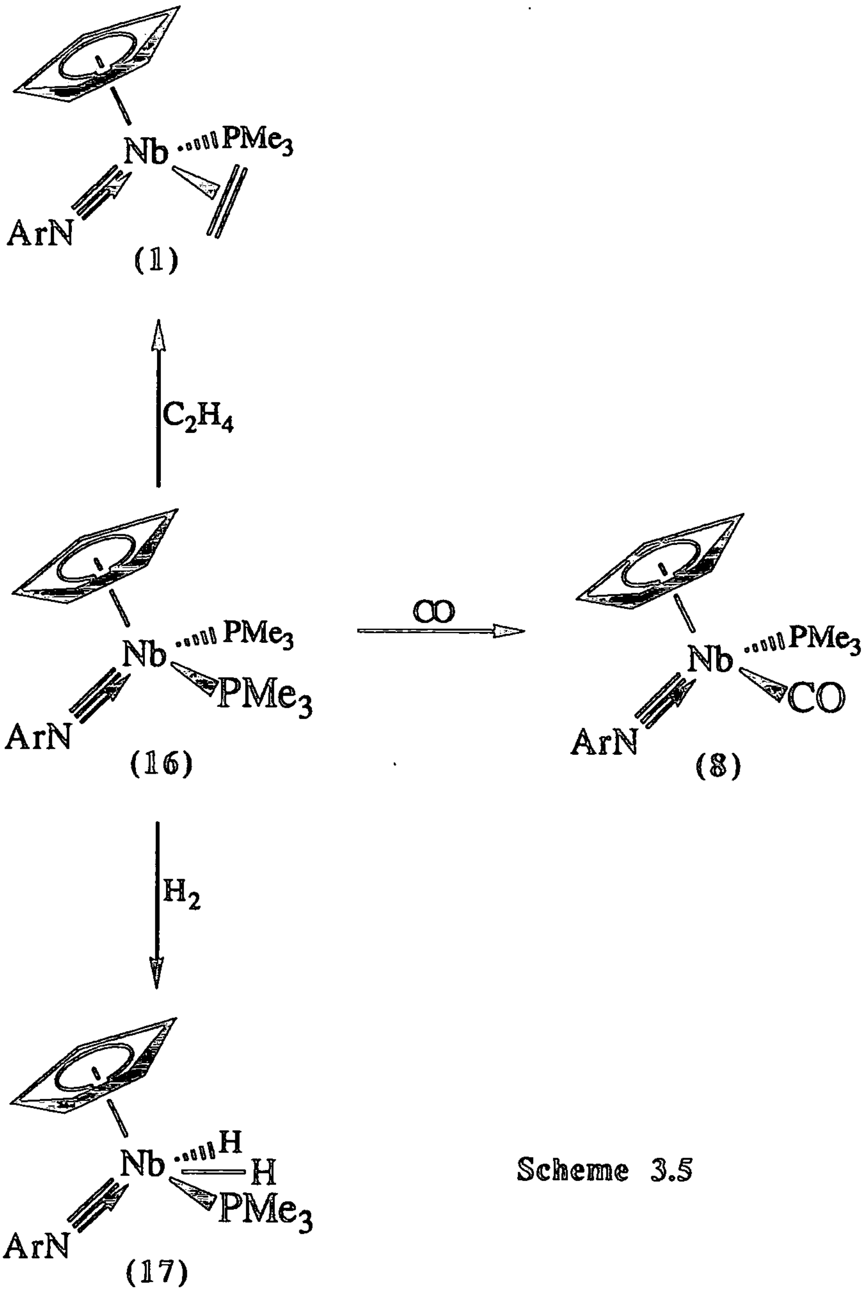
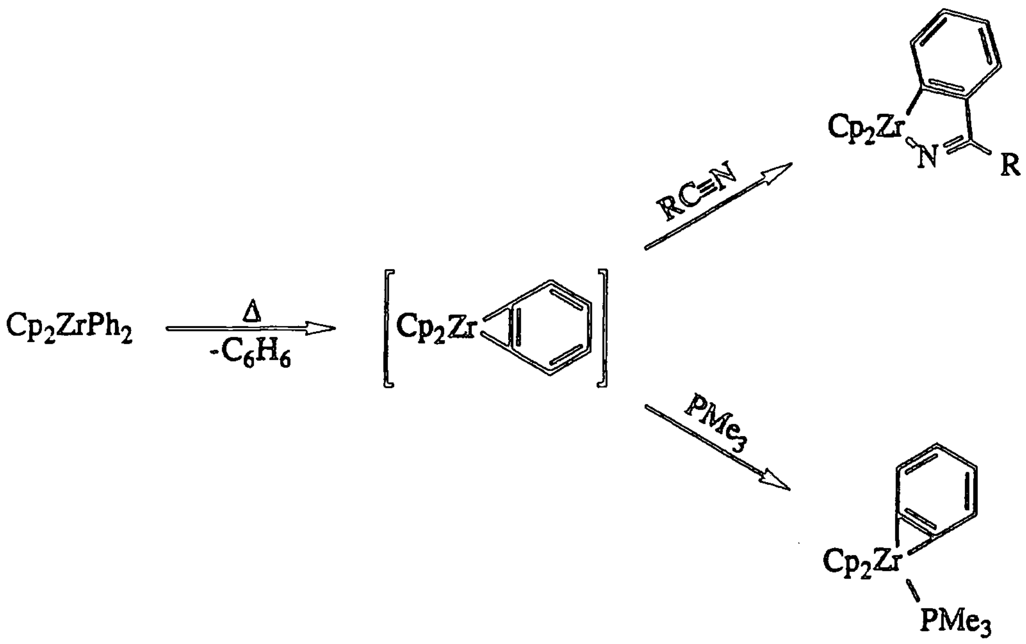
Treatment of a THF solution of $Cp^*Ta(NAr)Cl_2$ with magnesium in the presence of PMe_3 afforded a purple solution and $MgCl_2$ upon stirring at ambient temperature. However, attempted isolation of the target bisphosphine complex proved unsuccessful, affording only a purple intractable oil whose ^1H NMR spectrum revealed a number of unidentified species. The instability of $Cp^*Ta(NAr)(PMe_3)_2$ may possibly be attributed to the steric crowding of the Cp^* ring and the preference for the metal to adopt a Ta(V) oxidation state.



Scheme 3.5

3.10 Reaction of Cp'M(NAr)Cl_2 (M = Nb, Ta) with Phenyl Magnesium Chloride.

Buchwald and Erker have demonstrated that phenyl derivatives of the Group 4 bent metallocenes are precursors to benzyne complexes *via* the elimination of benzene[33]. These benzyne complexes may either be isolated as nitrile coupled products[27], or as phosphine adducts[28] or used *in situ* for carbon-carbon coupling reactions.



Scheme 3.6 *Generation and stabilisation of (benzyne)zirconocene species.*

We therefore embarked on a programme of study to prepare the analogous phenyl derivatives of Cp'M(NAr)Cl_2 (M = Nb, Ta) since the preparation of a benzyne complex through a β-hydrogen abstraction from a diphenyl intermediate would represent one of a number of attractive targets.

3.10.1 Preparation of CpNb(NAr)Ph$_2$(PMe$_3$) (18).

Treatment of a diethylether solution of CpNb(NAr)Cl$_2$ with two equivalents of PhMgCl in the presence of trimethylphosphine afforded an orange solution of CpNb(NAr)Ph$_2$(PMe$_3$) (18). Large orange, cubic crystals of (18) were subsequently isolated upon prolonged cooling of the diethylether solution at -40°C.

$$\mathrm{CpNb(NAr)Cl_2 + 2PhMgCl + PMe_3 \xrightarrow{Et_2O} \underset{(18)}{CpNb(NAr)Ph_2(PMe_3)} + 2MgCl_2} \quad (3.13)$$

Compound (18) is soluble in hydrocarbon and chlorocarbon solvents. Its characterisation was provided by elemental analysis, mass spectrometry, infrared and NMR spectroscopies. In the ^{1}H NMR spectrum (400 MHz, C_6D_6) the phosphine methyl hydrogen resonance is found as a doublet at δ 0.60 ppm, ($^2J_{PH}$ = 5.9 Hz), upfield of free trimethylphosphine (δ 0.79 ppm); this is presumed to result from ring current effects associated with the phenyl groups. Furthermore, since only one set of phenyl resonances is observed and the methyl resonances of the isopropyl groups appear as a doublet at δ 1.32 ppm, the phosphine may be regarded as being located symmetrically between the two phenyl units. The 100 MHz ^{13}C NMR spectrum reveals a severely broadened resonance at δ 177.6 ppm ($\upsilon^1/_2$ = 80.5 Hz), due to coupling of the ^{93}Nb nucleus to the *ipso-* carbon of the phenyl ring. The mass spectrum interestingly shows an envelope at m/z = 485 corresponding to CpNb(NAr)(C_6H_4)(PMe$_3$); this indicates that although the diphenyl (18) may be isolated, subsequent elimination of benzene could be sufficiently facile to afford the benzyne target molecule.

3.10.2 Preparation of Cp*Ta(NAr)(Ph)Cl (19).

The reaction of Cp*Ta(NAr)Cl$_2$ with one molar equivalent of PhMgCl in diethylether afforded an orange solution. After removal of solvent and extraction into n-pentane, orange crystals of Cp*Ta(NAr)(Ph)Cl (19) could be isolated in moderate yield (62%) upon prolonged cooling at -78°C. The reaction is envisaged to proceed according to Equation 3.14.

$$\mathrm{Cp^{*}Ta(NAr)Cl_2 + PhMgCl \xrightarrow{Et_2O} \underset{(19)}{Cp^{*}Ta(NAr)(Ph)Cl} + MgCl_2} \quad (3.14)$$

Cp*Ta(NAr)(Ph)Cl (19) can be isolated as analytically pure crystals which contrasts with the preparation of the analogous mono-methyl complex Cp*Ta(NAr)(Me)Cl. Mass spectrometry reveals an envelope for the parent ion at m/z 604 (^{181}Ta), and fragments at m/z 567 and 527 (^{181}Ta), attributable to Cp*Ta(NAr)(Ph) and Cp*Ta(NAr)Cl, respectively.

It was hoped that successful hydrogenation of compound (19) might afford the mono-hydrido tantalum complex Cp*Ta(NAr)(H)Cl (Equation 3.15) a direct analogue of the 'Schwartz reagent' $Cp_2Zr(H)Cl$[34].

$$\mathrm{\underset{(19)}{Cp^{*}Ta(NAr)(Ph)Cl} + H_2 \xrightarrow{\Delta} Cp^{*}Ta(NAr)(H)Cl + C_6H_6} \quad (3.15)$$

Prolonged warming of a toluene solution of (19) with dihydrogen at 85°C slowly afforded benzene and an insoluble yellow powder which may be a polynuclear form of Cp*Ta(NAr)(H)Cl with bridging hydride and/or chloride ligands.

3.10.3 Preparation of Cp*Ta(NAr)Ph_2 (20).

Treatment of a diethylether solution of Cp*Ta(NAr)Cl_2 with an excess of PhMgCl and PMe_3 afforded a red solution. Subsequent removal of solvent and extraction into n-pentane gave red crystals of the base free complex Cp*Ta(NAr)Ph_2 (Equation 3.16) on prolonged cooling at -25°C. The surprising absence of tertiary phosphine in (20) reflects the high degree of steric crowding around the tantalum centre.

$$\mathrm{Cp^{*}Ta(NAr)Cl_2 + 2PhMgCl \xrightarrow[PMe_3]{Et_2O} \underset{(\mathbf{20})}{Cp^{*}Ta(NAr)Ph_2} + 2MgCl_2} \quad (3.16)$$

The 400 MHz ^1H NMR spectrum of (**20**) reveals doublet resonances at δ 7.76 ppm ($^3J_{HH}$ = 7.9 Hz) corresponding to the *ortho-* hydrogen signals of the phenyl moeities where little thermal motion appears to be experienced. This contrasts with the *ortho-* hydrogen signals of the mono-phenyl derivative (**19**) where substantial ring motion on the NMR timescale is indicated by broadening of the corresponding resonances. The 100 MHz ^{13}C NMR spectrum shows a very lowfield singlet resonance at δ 198.0 ppm attributable to the *ipso-* carbon of the phenyl rings; the remaining phenyl carbon signals are found in the region δ 127.4-136.4 ppm. A parent ion is observed in the mass spectrum at m/z 645 (^{181}Ta); however, more intriguingly an envelope at 567 (^{181}Ta) corresponds to expulsion of benzene from the parent ion to afford the fragment $Cp^*Ta(NAr)(C_6H_4)$.

3.11 Attempted Preparation of Benzyne Derivatives of Niobium and Tantalum.

Benzyne (C_6H_4) and its derivatives can act as η^2-ligands donating between two and four electrons in monomeric transition-metal complexes. Such compounds are still relatively rare, todate being restricted to Zr[28], Nb[35,36], Ta[35,36], Re[37], Ru[38], and Ni[39], although the intermediacy of such species has been postulated by Vol'pin[40] and others[41]. Moreover, benzyne derivatives of the Group 5 triad are restricted to Power's Nb and Ta dibenzynes[36] prepared through the reaction of $NbCl_5$ and $TaCl_5$ with phenyl lithium in THF, and Schrock's $Cp^*M(C_6H_4)Me_2$ (M = Nb, Ta)[35] afforded *via* the decomposition of $Cp^*M(Ph)Me_3$ (Figure 3.17).

$$Cp^{*}Ta(NAr)Cl_2 + 2PhMgCl \xrightarrow[PMe_3]{Et_2O} \underset{(20)}{Cp^{*}Ta(NAr)Ph_2} + 2MgCl_2 \quad (3.16)$$

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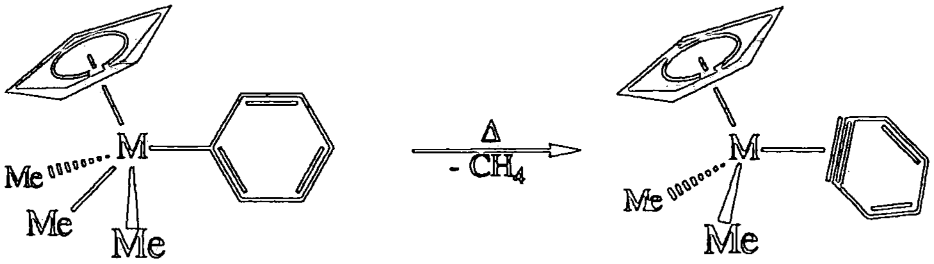


(M = Nb, Ta)

Figure 3.17 *Formation of* $Cp^{*}M(\eta^2\text{-}C_6H_4)Me_2$ *(M = Nb, Ta).*

In an attempt to prepare a niobium benzyne analogous to $Cp_2Zr(\eta^2\text{-}C_6H_4)(PMe_3)$[28], an n-heptane solution of $CpNb(NAr)Ph_2(PMe_3)$ (18) was warmed at 70°C to slowly afford a deep red solution. Subsequent extraction into diethylether, followed by prolonged cooling at -40°C gave yellow-green plates of $CpNb(NAr)(\eta^2\text{-}C_6H_4)(PMe_3)$ (21) in good yield (78%). Compound (21) is envisaged to form *via* elimination of one mole equivalent of benzene from (18) according to Equation 3.17.

$$\underset{(18)}{CpNb(NAr)Ph_2(PMe_3)} \xrightarrow[\text{n-heptane}]{70^\circ C} \underset{(21)}{CpNb(NAr)(\eta^2\text{-}C_6H_4)(PMe_3)} + C_6H_6 \quad (3.17)$$

^1H NMR experiments with added PMe_3 indicate that loss of PMe_3 from (18) is rate determining. This observation is not suprising as the transition state for β-hydrogen abstraction will demand a vacant orbital at the metal centre if the hydrogen transfer process is to be mediated by the niobium.

Compound (21) is very soluble in low polarity hydrocarbons, donor solvents and chlorocarbons. Moreover, (21) is stable to aromatic hydrocarbons such as toluene; this contrasts with work by Erker who demonstrated that $Cp_2Zr(\eta^2\text{-}C_6H_4)$ activates aromatic solvents to reform (diaryl)zirconocenes[37].

Elemental analysis confirms a stoichiometry consistent with the benzyne complex (21), and the mass spectrum reveals an envelope at m/z 485 corresponding to the parent ion. The 400 MHz ^1H NMR spectrum shows a doublet resonance at δ 1.13 ppm

($^2J_{PH}$ = 8.0 Hz) assignable to PMe_3 strongly bound to the niobium centre. A septet signal at δ 3.56 ppm and doublets at δ 0.97, 1.16 ppm are attributable to the methine and diastereotopic methyls of the isopropyl substituents respectively. The benzyne hydrogen resonances of (21) are found as four distinct signals at δ 7.53, 7.60, 7.71, and 8.30 ppm in an AMNX splitting pattern, corresponding to the four hydrogens of a static benzyne ligand bound to a chiral metal centre (Figure 3.18).

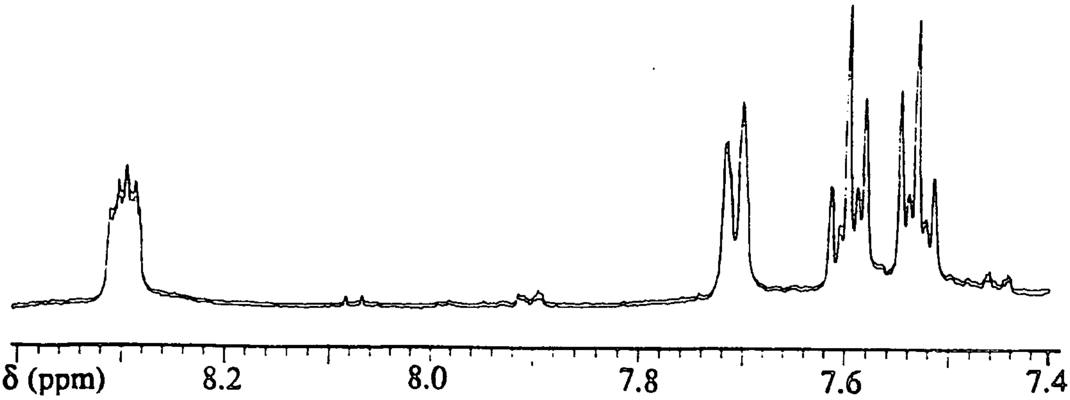


Figure 3.18 *400 MHz ^1H NMR spectrum (C_6D_6) of the aryne region of (21).*

The resonances at δ 7.71 ($^3J_{HH}$ = 6.0 Hz) and 8.30 ppm ($^3J_{HH}$ = 6.0 Hz, $^3J_{PH}$ = 0.9 Hz) have been assigned to the β-hydrogens of the aryne ligand, whereas, the second order multiplets at δ 7.53 and 7.60 ppm have been shown to correspond to the hydrogens attached to the γ-carbons. COSY ^1H NMR experiments have enabled the assignment of the βγ-hydrogen pairs illustrated in Figure 3.21. However, NOE NMR techniques have been unable to obtain the absolute assignment of the benzyne hydrogens.

The 100 MHz ^{13}C NMR spectrum (C_6D_6) reveals a broad signals at δ 153.73 and 162.7 ppm attributable to the α-carbon atoms of the benzyne which are coupled to the quadropolar ^{93}Nb nucleus. Furthermore, two-dimensional heteronuclear correlation (HETCOR) NMR spectra have allowed assignment of four resonances between δ 130.2-132.1 ppm to the β and γ carbon atoms of the aryne ring. (Figure 3.19; Table 3.3).

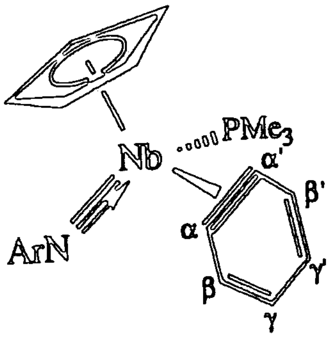


Figure 3.19

Assignment	^{1}H NMR δ (ppm)	^{13}C NMR δ (ppm)
α, α '	-	153.73, 162.67 (br)
β	7.71 (d)	130.83 (d)
γ	7.53 (m)	130.16 (d)
β '	8.30 (dd)	132.10(d)
γ '	7.60 (m)	130.63 (d)

Table 3.3 *^1H / ^{13}C NMR correlation of the aryne resonances of (21).*

In general, benzyne complexes are highly reactive toward organic reagents, Bergman and co-workers[38] for example, have shown that the (benzyne)ruthenium complex $(PMe_3)_4Ru$ (η^2-C_6H_4) will activate C-C, C-H, N-H, and O-H bonds. Schrock[35a] and others[33], have shown that aryne complexes readily react with ethylene to afford benzometallacyclopentenes. However, this contrasts with the reactivity of complex (21) which demonstrates suprising stability towards a range of substrates. For example, (21) is stable in the presence of ethylene even when warmed at 120°C. Treatment of $CpNb(NAr)(\eta^2\text{-}C_6H_4)(PMe_3)$ (21) with carbon monoxide or acetonitrile does not readily afford insertion products, although prolonged warming to 80°C does result in the generation of a number of black paramagnetic species. Hydrogenation of (21) at 60°C results in the liberation of benzene and no new diamagnetic organometallic species. This is most likely due to the formation of unstable niobium dihydrido complex $CpNb(NAr)(H)_2(PMe_3)$ (17) which we have shown to decompose at room temperature (Equation 3.18).

$$\underset{(21)}{CpNb(NAr)(\eta^2\text{-}C_6H_4)(PMe_3)} + 2H_2 \xrightarrow{60^\circ C} \underset{(17)}{[CpNb(NAr)(H)_2(PMe_3)]} + C_6H_6 \quad (3.18)$$

Attempts to prepare the (benzyne)tantalum complex $\mathrm{Cp^*Ta(NAr)(\eta^2\text{-}C_6H_4)(PMe_3)}$ have to date proven unsuccessful. Equimolar quantities of the base-free diphenyl complex (20) and trimethylphosphine were warmed to 100°C in a sealed NMR tube; subsequent monitoring by ^{1}H NMR spectroscopy revealed that, although elimination of benzene occurred, a complex mixture of unidentified products was afforded. This suggests that stabilisation utilising tertiary phosphine of the (benzyne)tantalum complex may be prevented through the steric restrictions imposed by the Cp* ring.

Buchwald and co-workers have demonstrated that metallocene benzyne complexes may be prepared *via* the α–elimination of methane from a mixed (methyl-phenyl)zirconocene complex[42]. We therefore envisaged that Cp*Ta(NAr)(Ph)(Me) might eliminate benzene in the presence of trimethylphosphine to afford a tantalum-benzyne species according to Equation 3.19.

$$\mathrm{Cp^*Ta(NAr)(Ph)(Me)} + \mathrm{H_2} + \mathrm{PMe_3} \xrightarrow{\Delta} \mathrm{Cp^*Ta(NAr)(\eta^2\text{-}C_6H_4)(PMe_3)} + \mathrm{CH_4} \quad (3.19)$$

Treatment of Cp*Ta(NAr)(Ph)Cl (19) with an excess of methyl Grignard reagent in diethylether afforded yellow crystals upon subsequent recrystallisation from a concentrated solution in n-pentane. However, ^{1}H NMR spectroscopy indicated that alkyl metathesis had occurred, yielding the previously characterised dimethyl complex $\mathrm{Cp^*Ta(NAr)Me_2}$. Thus, to date the methyl-phenyl tantalum species Cp*Ta(NAr)(Ph)(Me) and hence the target (benzyne)tantalum complex have not been prepared.

3.11.1 The Molecular Structure of CpNb(NAr)(η^2-C_6H_4)(PMe_3) (21).

Large yellow-green crystals of (21) were obtained by cooling a saturated diethylether solution at -30°C. A crystal of dimensions 0.30 x 0.15 x 0.35 mm was selected for study and sealed in a Lindemann capillary tube under an inert atmosphere. The data was collected and the structure solved by Prof. J. A. K. Howard, and Ms C. Wilson within this department. The molecular structure of (13) is illustrated in Figure 3.20 and selected bond angles and distances are collected in Table 3.4.

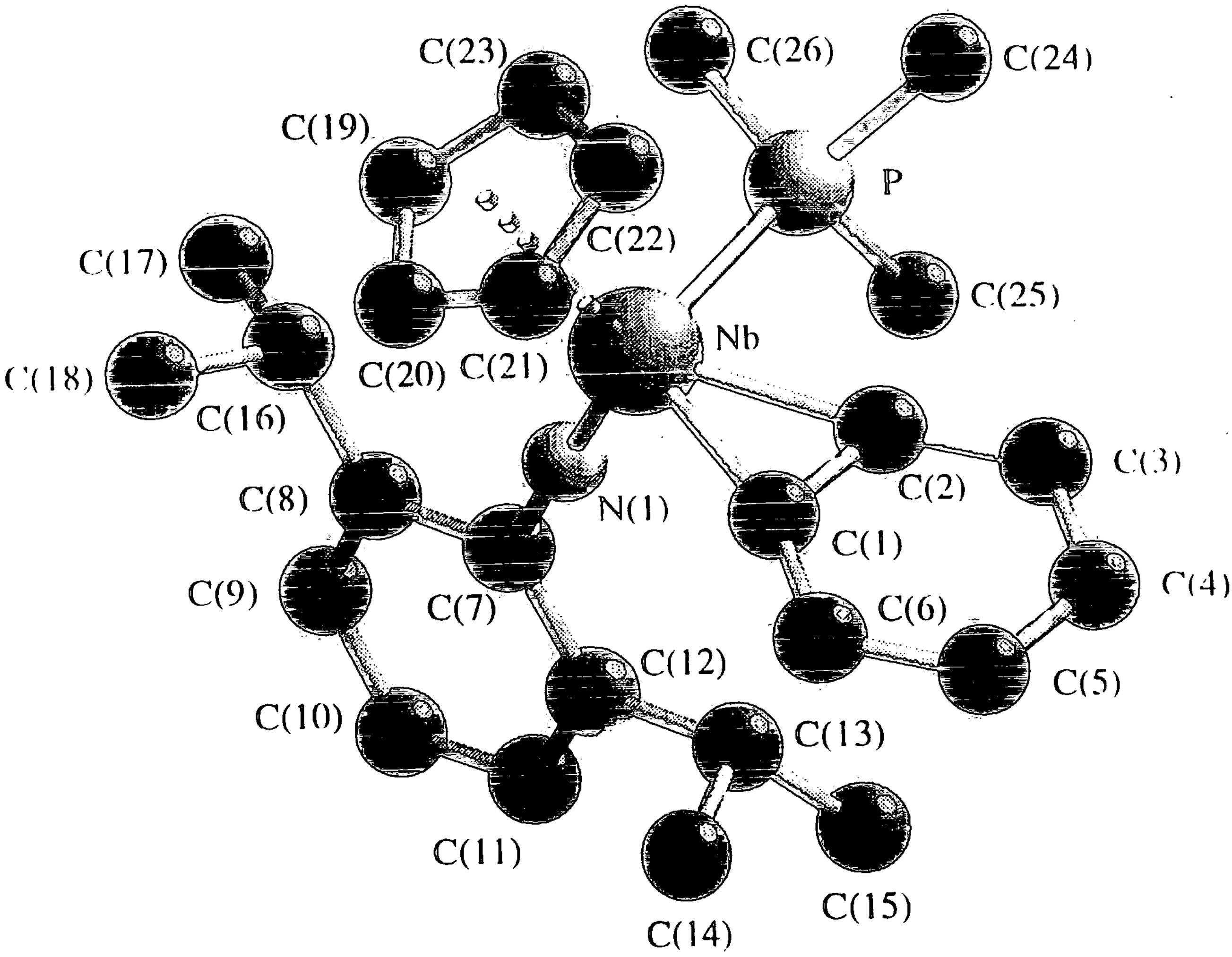


Figure 3.20 *The moecular structure of CpNb(NAr)(η^2-C_6H_4)(PMe_3) (21).*

Nb - C(1)	2.138(7)	Nb - C(2)	2.190(8)
Nb - N	1.809(6)	Nb - C(19)	2.440(9)
Nb - C(20)	2.401(9)	Nb - C(21)	2.471(9)
Nb - C(22)	2.510(11)	Nb - C(23)	2.481(11)
Nb - P	2.528(3)	C(1) - C(2)	1.342(11)
C(1) - C(6)	1.396(11)	C(2) - C(3)	1.394(12)
C(3) - C(4)	1.393(13)	C(4) - C(5)	1.357(15)
C(5) - C(6)	1.384(14)	N - C(7)	1.398(9)
C(7) - C(8)	1.425(10)	C(7) - C(12)	1.434(10)
C(8) - C(9)	1.399(11)	C(8) - C(16)	1.507(11)
C(9) - C(10)	1.378(12)	C(10) - C(11)	1.386(12)
C(11) - C(12)	1.392(10)	C(12) - C(13)	1.515(10)
C(13) - C(14)	1.506(12)	C(13) - C(15)	1.525(13)
C(16) - C(17)	1.507(11)	C(16) - C(18)	1.498(12)
C(19) - C(20)	1.372(15)	C(19) - C(23)	1.398(16)
C(20) - C(21)	1.397(15)	C(21) - C(22)	1.368(17)
C(22) - C(23)	1.390(16)	P - C(24)	1.815(9)
P - C(25)	1.794(9)	P - C(26)	1.829(9)

C(1) - Nb - C(2)	36.1(3)	C(1) - Nb - N	102.9(3)
C(2) - Nb - N	107.1(3)	C(1) - Nb - C(19)	135.8(3)
C(2) - Nb - C(19)	150.0(3)	N - Nb - C(19)	102.9(3)
C(1) - Nb - C(20)	105.2(3)	C(2) - Nb - C(20)	134.2(3)
N - Nb - C(20)	105.3(2)	C(19) - Nb - C(20)	32.9(3)
C(1) - Nb - C(21)	81.6(3)	C(2) - Nb - C(21)	102.4(3)
N - Nb - C(21)	134.4(3)	C(19) - Nb - C(21)	54.9(3)
C(20) - Nb - C(21)	33.3(4)	C(1) - Nb - C(22)	93.3(3)
C(2) - Nb - C(22)	95.7(3)	N - Nb - C(22)	156.9(3)
C(19) - Nb - C(22)	54.5(4)	C(20) - Nb - C(22)	53.9(4)
C(21) - Nb - C(22)	31.9(4)	C(1) - Nb - C(23)	125.5(3)
C(2) - Nb - C(23)	119.2(3)	N - Nb - C(23)	129.9(3)
C(19) - Nb - C(23)	33.0(4)	C(20) - Nb - C(23)	54.0(4)
C(21) - Nb - C(23)	53.6(4)	C(22) - Nb - C(23)	32.3(4)
C(1) - Nb - P	114.0(4)	C(2) - Nb - P	78.0(2)
N - Nb - P	90.7(2)	C(19) - Nb - P	100.9(3)
C(20) - Nb - P	132.9(3)	C(21) - Nb - P	129.5(3)
C(22) - Nb - P	97.7(3)	C(23) - Nb - P	81.7(3)
Nb - C(1) - C(2)	74.0(5)	Nb - C(1) - C(6)	163.1(6)
C(2) - C(1) C(6)	122.8(8)	Nb - C(2) - C(1)	69.8(5)
Nb - C(2) - C(3)	169.6(6)	C(1) - C(2) - C(3)	120.3(7)
C(2) - C(3) - C(4)	117.1(8)	C(3) - C(4) - C(5)	122.1(9)
C(4) - C(5) - C(6)	120.7(9)	C(1) - C(6) - C(5)	116.9(8)
Nb - N - C(7)	179.7(5)	N - C(7) - C(8)	121.1(6)
N - C(7) - C(12)	118.1(6)	C(8) - C(7) - C(12)	120.8(6)
C97) - C(8) - C(9)	117.4(7)	C(7) - C(8) - C(16)	120.6(6)
C(9) - C(8) - C(16)	122.0(7)	C(8) - C(9) - C(10)	122.5(7)
C(9) - C(10) - C(11)	119.4(8)	C(10) - C(11) - C(12)	122.1(7)
C(7) - C(12) - C(11)	117.7(7)	C(7) - C(12) - C(13)	121.1(6)
C(11) - C(12) - C(13)	121.2(7)	C(12) - C(13) - C(14)	110.5(7)
C(12) - C(13) - C(15)	112.8(7)	C(14) - C(13) - C(15)	108.8(7)
C(8) - C(16) - C(17)	114.7(7)	C(8) - C(16) - C(18)	110.5(7)
C(17) - C(16) - C(18)	109.1(7)	Nb - C(19) - C(20)	72.0(5)
Nb - C(19) - C(23)	75.1(6)	C(20) - C(19) - C(23)	106.3(9)
Nb - C(20) - C(19)	75.1(5)	Nb - C(20) - C(21)	76.1(5)
C(19) - C(20) - C(21)	109.5(10)	Nb - C(21) - C(20)	70.6(5)

Nb - C(21) - C(22)	75.6(6)	C(20) - C(21) - C(22)	107.4(9)
Nb - C(22) - C(21)	72.5(6)	Nb - C(22) - C(23)	72.7(6)
C(21) - C(22) - C(23)	108.0(10)	Nb - C(23) - C(19)	71.9(6)
Nb - C(23) - C(22)	75.0(6)	C(19) - C(23) - C(22)	108.7(10)
Nb - P - C(24)	116.7(4)	Nb - P - C(25)	111.6(3)
C(24) - P - C(25)	104.7(5)	Nb - P - C(26)	116.8(3)
C(24) - P - C(26)	103.1(4)	C(25) - P - C(26)	102.3(5)

Table 3.4 *Bond distances (Å) and angles (°) for CpNb(NAr)(η^2-C_6H_4)(PMe_3) (21).*

To our knowledge, (21) is only the second (benzyne)niobium complex to be structurally characterised, the only other being the unusual lithiated species $[Nb(C_6H_4)_2Ph_3(LiPh.THF)(LiTHF)_4].0.5THF.0.5C_6H_{14}$[36].

The metal-nitrogen distance of (21), at 1.809(6)Å, is at the long end of the range observed for the Nb-N(imido) bond lengths[4] and reflects the formal Nb(III) oxidation state. The linear (179.7(5)°) Nb-N-C bond angle is consistent with a terminal imido ligand containing an *sp* -hybridised nitrogen[43].

The benzyne ligand interacts with the niobium 'end-on' in an analogous fashion to that observed in the isolobal zirconocene derivative $Cp_2Zr(\eta^2-C_6H_4)(PMe_3)$[28]. There are also similarities in the structural parameters associated with the metal-benzyne moieties in these two complexes. For example, the C(1)-C(2) bond length in (21) (1.342(11)Å) is comparable with the distance of 1.364(8)Å found in the zirconocene complex, and the C-C distances within the benzyne rings of both complexes are equivalent within experimental error, consistent with a delocalised aromatic structure arising from a high degree of back-bonding from the metal to the π^* orbital of the benzyne. Thus, the benzyne unit in (21) may be regarded as a 2 electron ligand resulting in an overall 18 electron count for the complex. Contrastingly, the benzyne ligand in $Cp^*Ta(\eta^2-C_6H_4)Me_2$[35] possesses alternating C-C bond lengths most likely reflecting electron pair donation from both of the filled orthogonal π-orbitals of the benzyne ligand (ie a 4 electron donor situation). Of particular significance, the Nb-P bond lies only 4.4° out of the Nb-C(1)-C(2) plane which is in accordance with metallocene-like frontier orbitals for the [CpNb(NAr)] fragment.

3.12 Summary.

This chapter has demonstrates that in analogy to the chemistry of zirconocene, treatment of Cp'M(NAr)Cl_2 (M = Nb, Ta) with β-hydrogen containing Grignard reagents, gives unstable dialkyl species. These dialkyl species readily decompose *via* loss of alkane to afford niobium(III) and tantalum(III) olefin complexes which may be isolated and characterised through trapping with trimethylphosphine.

A single crystal structure determination on CpNb(NAr)(η^2-C_3H_6)(PMe_3) (3) has been undertaken, the propylene ligand being found to be co-planar with the phosphine which does indeed lead further support to the metallocene analogy. The ethylene ligand in (1) is not displaced by substituted olefins and exchanges only slowly with carbon monoxide. The propylene derivative (3) however, is carbonylated rapidly and reacts with ethylene to give (1). This is attributed to the greater lability of the monosubstituted olefin in (3) compared with the ethylene ligand in (1). Moreover, substituted acetylene complexes have been shown to be accessible *via* treatment of the propylene derivative with MeC≡CMe or PhC≡CPh, leading to equilibrium mixtures of (3) with (5) and (6) respectively.

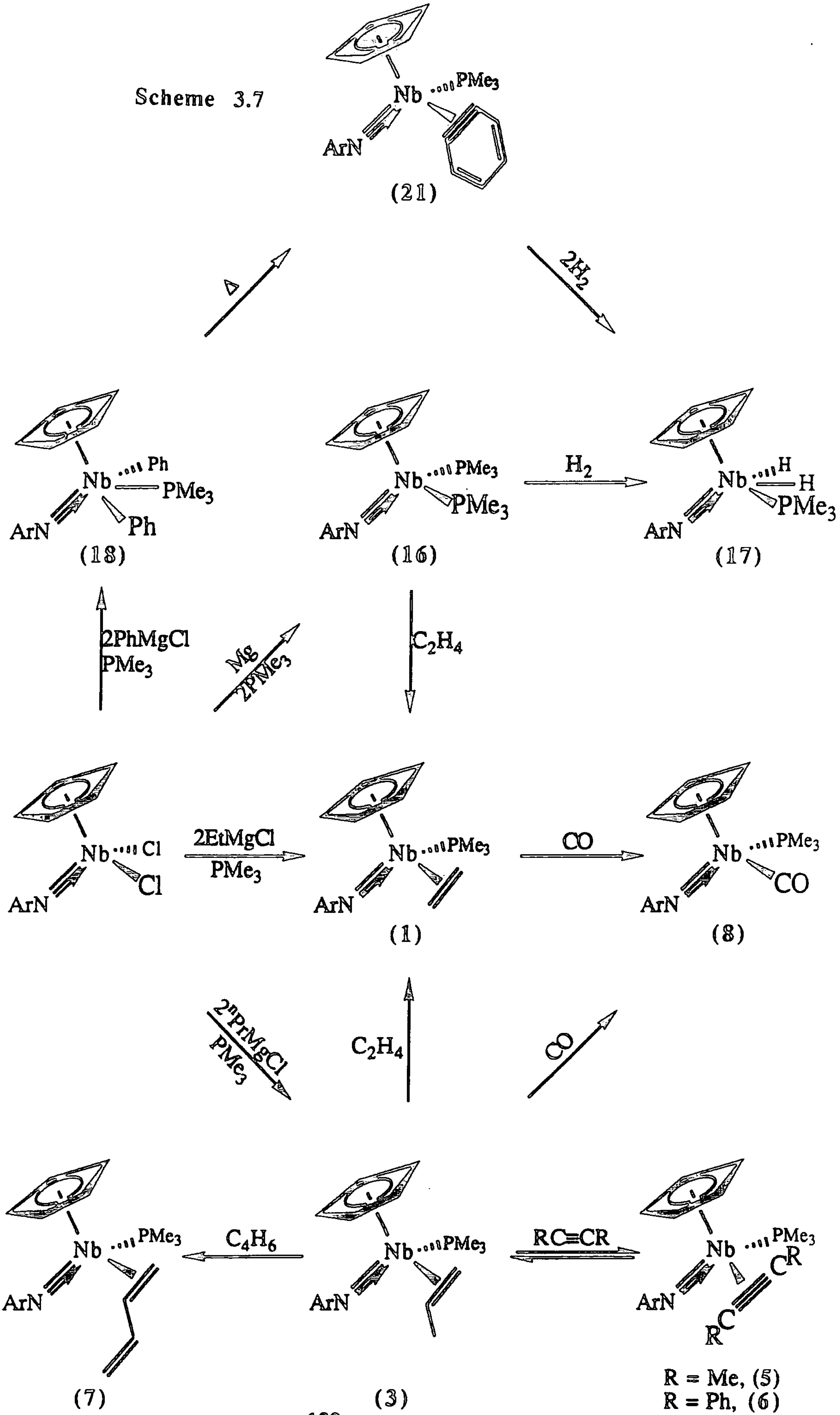
The tantalum olefin complexes (2) and (4) are thermally robust being less prone to decomposition *via* loss of olefin than their niobium analogues. This is a reflection of increased backbonding to the olefin by tantalum, thus enhancing the metallacyclopropane character of the bond. In contrast to (1) and (3), treatment of the tantalum ethylene and propylene derivatives (2) and (4) with a variety of α-olefins leads to dissociation of phosphine and the generation of tantallacycle species. Investigation of the metallacycle ring configurations of these complexes suprisingly reveals that there is often little energetic preference for one form. The insertion of carbon monoxide and acetonitrile into the metallacycle ring of (12) affords the novel, suprising stable metallacycloheptadione and azametallacycle complexes (13) and (14) repectively.

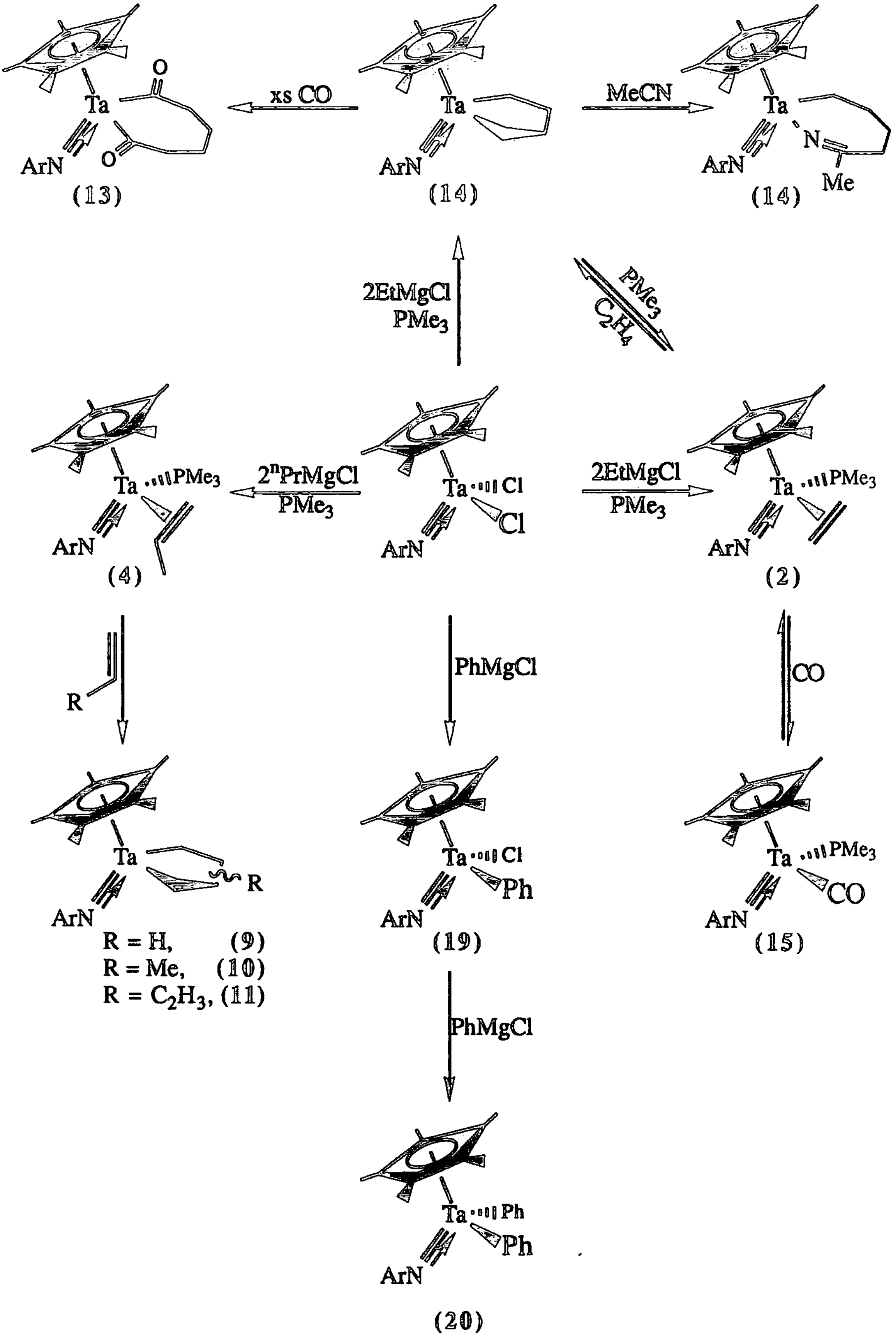
Reduction of $CpNb(NAr)Cl_2$ with magnesium in the presence of trimethylphosphine affords the bisphosphine $CpNb(NAr)(PMe_3)_2$ (16), an analogue of the synthetically versatile $Cp_2Ti(PMe_3)_2$[31] and $Cp_2Zr(PMePh_2)_2$[32]. Spectroscopic investigations (^1H NMR) reveal (16) to be highly reactive towards C_2H_4, CO, and H_2 affording $CpNb(NAr)(\eta^2\text{-}C_2H_4)(PMe_3)$, $CpNb(NAr)(CO)(PMe_3)$, and the unstable $CpNb(NAr)(H)_2(PMe_3)$ respectively. However, in contrast to the Group 4 metallocene analogues, olefins do not displace a second phosphine from (16) to afford metallacycle containing species.

Warming a solution of the diphenyl complex (18) eliminates benzene *via* a β-hydrogen abstraction process to afford the benzyne(niobium) species $CpNb(NAr)(\eta^2\text{-}C_6H_4)(PMe_3)$ (21). The molecular structure of (21) reveals similarities in the structural parameters of the niobium-benzyne unit with those of the isolobal zirconocene derivative $Cp_2Zr(\eta^2\text{-}C_6H_4)(PMe_3)$[28]. Whereas, (benzyne)zirconocene species demonstrate a diverse range of synthetically useful reactions, $CpNb(NAr)(\eta^2\text{-}C_6H_4)(PMe_3)$ is suprisingly unreactive when treated with a variety of substrates. The stability of (21) presumably reflecting the strength of the Nb-P bond and the steric crowding around the metal centre. However, attempts to prepare the analogous tantalum complex $Cp^*Ta(NAr)(\eta^2\text{-}C_6H_4)(PMe_3)$ have been unsuccessful, since the sterically demanding Cp^* ring appears to prohibit stabilisation of any (benzyne)tantalum species by trimethylphosphine.

In conclusion a series of imido complexes of niobium(III) and tantalum(III) have been synthesised containing a variety of ancillary ligands including olefins, acetylenes, and tertiary phosphines which are illustrated in Scheme 3.7 and 3.8.

Scheme 3.7


Nb
PMe3
ArN
(21)
Δ
2H2
Ph
PMe3
Ph
(18)
PMe3
PMe3
(16)
H2
H
H
PMe3
(17)
2PhMgCl
PMe3
Mg
2PMe3
C2H4
Cl
Cl
2EtMgCl
PMe3
(1)
CO
CO
(8)
2nPrMgCl
PMe3
C2H4
CO
C4H6
(7)
(3)
RC≡CR
CR
RC
R = Me, (5)
R = Ph, (6)


O
Ta
ArN
O
(13)
xs CO
Ta
ArN
(14)
MeCN
Ta
N
ArN
Me
(14)
2EtMgCl
PMe$_3$
PMe$_3$
C$_2$H$_4$
Ta PMe$_3$
ArN
(4)
2^{n}PrMgCl
PMe$_3$
Ta Cl
Cl
ArN
2EtMgCl
PMe$_3$
Ta PMe$_3$
ArN
(2)
R
PhMgCl
CO
Ta
R
ArN
R = H, (9)
R = Me, (10)
R = C$_2$H$_3$, (11)
Ta Cl
Ph
ArN
(19)
Ta PMe$_3$
CO
ArN
(15)
PhMgCl
Ta Ph
Ph
ArN
(20)

Scheme 3.8

3.13. References.

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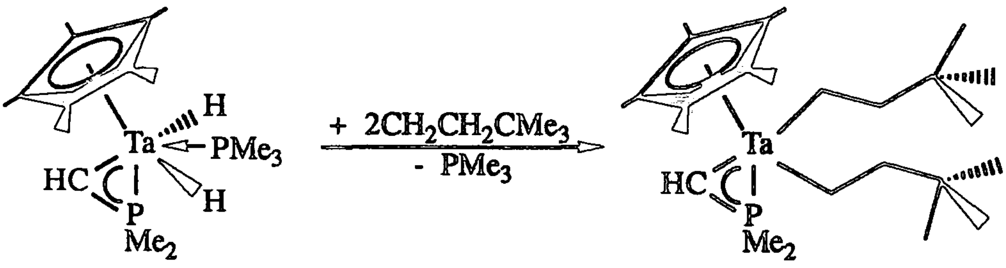
CHAPTER FOUR

An Investigation of the Reactivity of Group 5 Half-Sandwich Imido and Phosphino-Carbene Complexes with α-Olefins.

4.1 Introduction.

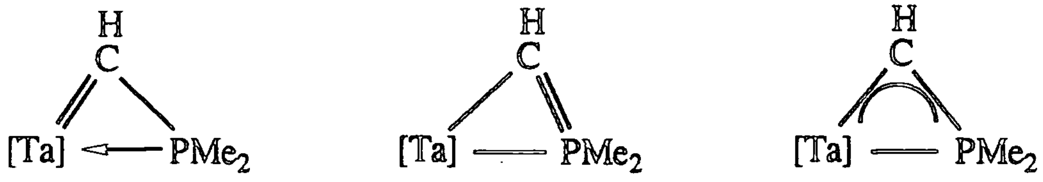
Coordinatively unsaturated transition metal hydride and alkyl complexes are important intermediates in the catalytic dimerisation, oligomerisation and polymerisation of alkenes[1]. Although these species are traditionally generated *in situ* through treatment of an appropriate transition metal halide with a Lewis acid co-catalyst, there has been growing interest in the development of single component, Lewis acid-free catalysts, particularly for alkene polymerisation[2].

Recently, Kee has demonstrated that neohexene inserts into the Ta-H bonds of the half-sandwich tantallacycle $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)$ to give the stable sixteen-electron dialkyl $Cp^*Ta(\eta^2\text{-}CHPMe_2)(CH_2CH_2CMe_3)_2$[3], (Equation 4.1). Furthermore, $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)$ has been shown to catalytically oligomerise ethylene and propylene to a complex mixture of tantalum alkyls and higher alkenes[4].



(4.1)

Scrutiny of the bond lengths in the $Ta(\eta^2\text{-}CHPMe_2)$ metallacycle show that they are consistent with contributions from canonical forms (II) and (III) (Figure 4.1)[5], with calculations suggesting that (II) is the most appropriate representation of the bonding[6]. Canonical form (II) can be regarded as a four electron phosphino-carbene and bears some resemblance to an imido group, the lone pair now effectively located on the remote phosphorus atom. Moreover, Fenske-Hall calculations considering the frontier orbitals of the $[Cp^*Ta(\eta^2\text{-}CHPMe_2)]$ fragment suggest that a relationship exists with the [CpM(NR)] (M = Nb, Ta) fragment[7].



(I) (II) (III)

Figure 4.1 *Canonical forms of metal-(η^2-$CHPMe_2$) ligand bonding.*

In order to further probe the isolobal analogy between these two classes of half-sandwich Group 5 complex, we set out to compare the reactivity of a variety of hydrido derivatives of the form $Cp^*Ta(E)(H)(X)(PMe_3)$, ($E = NAr$, η^2-$CHPMe_2$; $X = H$, halide) with a number of α-olefins.

Moreover, since it has long been known that titanocene and zirconocene derivatives are efficient catalysts in the Ziegler-Natta polymerisation of α-olefins[8], a study has been undertaken to investigate possible catalytic activity of derivatives of $Cp'M(NR)Cl_2$ ($M = Nb, Ta$) with α-olefins under industrially relevant conditions.

4.2 Oligomerisation Reactions of $Cp^*Ta(\eta^2$-$CHPMe_2)(H)_2(PMe_3)$.

4.2.1 Preparation of $Cp^*Ta(\eta^2$-$CHPMe_2)(H)_2(PMe_3)$ (1).

Treatment of Cp^*TaCl_4 with an excess of sodium sand in neat trimethylphosphine solvent for four days afforded a black solution from which $Cp^*Ta(\eta^2$-$CHPMe_2)(H)_2(PMe_3)$ (1) may be isolated in moderate yield (*ca.* 40%) (Equation 4.2).

$$\overset{*}{C}pTaCl_4 + 2PMe_3 + 4Na \longrightarrow \underset{(1)}{\overset{*}{C}pTa(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)} + 4NaCl \quad (4.2)$$

Compound (1) was first prepared by Dr. T. P. Kee[5] in this laboratory as moisture sensitive crystals which are soluble in hydrocarbon solvents. The 400 MHz

^1H NMR spectrum of (1) reveals a lowfield signal at δ 9.19 ppm corresponding to the phosphino-carbene methine hydrogen. Furthermore, a resonance at δ 3.87 ppm split by two inequivalent phosphorus signals ($^2J_{PH}$= 54.9 Hz; $^2J_{PH}$ = 17.9 Hz) is attributable to two hydrides disposed either side of a PMe_3 unit (Figure 4.2). The results of Fenske-Hall calculations indicate that lateral bonding of the tertiary phosphine moeity should be observed[7], as is revealed in the single crystal structure determination of the related $CpNb(NMe)Cl_2(PMe_3)$ complex[9]. However, the crystal structure of $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)$ (1) shows that the PMe_3 ligand occupies the central site[5], presumably for thermodynamic reasons.

4.2.2 Mechanistic Study of the Insertion Chemistry of $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)$ (1).

In general, it is found that high oxidation-state alkyl complexes of the early transition metals catalyse alkene oligomerisation and polymerisation *via* a direct insertion (Cossee - Arlman - type) mechanism[10], rather than one involving metallacycle intermediates as observed initially by Schrock *et al* in a tantalum system[11].

An investigation into the initial insertion products arising from the reaction of $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)$ (1) with terminal olefins has been conducted, along with the olefin oligomerisation products generated, in order to gain insight into the mechanism operating in this system.

The insertion of olefins into the Ta-H bonds of $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)$ (1) leads to a complex mixture of products with partially obscured resonances in the alkyl region of the ^1H NMR spectra making assignments difficult. However, the metallacycle methine hydrogen and Cp* ring methyl hydrogen resonances in the ^1H NMR spectra are sufficiently unambiguous to enable the oligomerisation processess to be monitored.

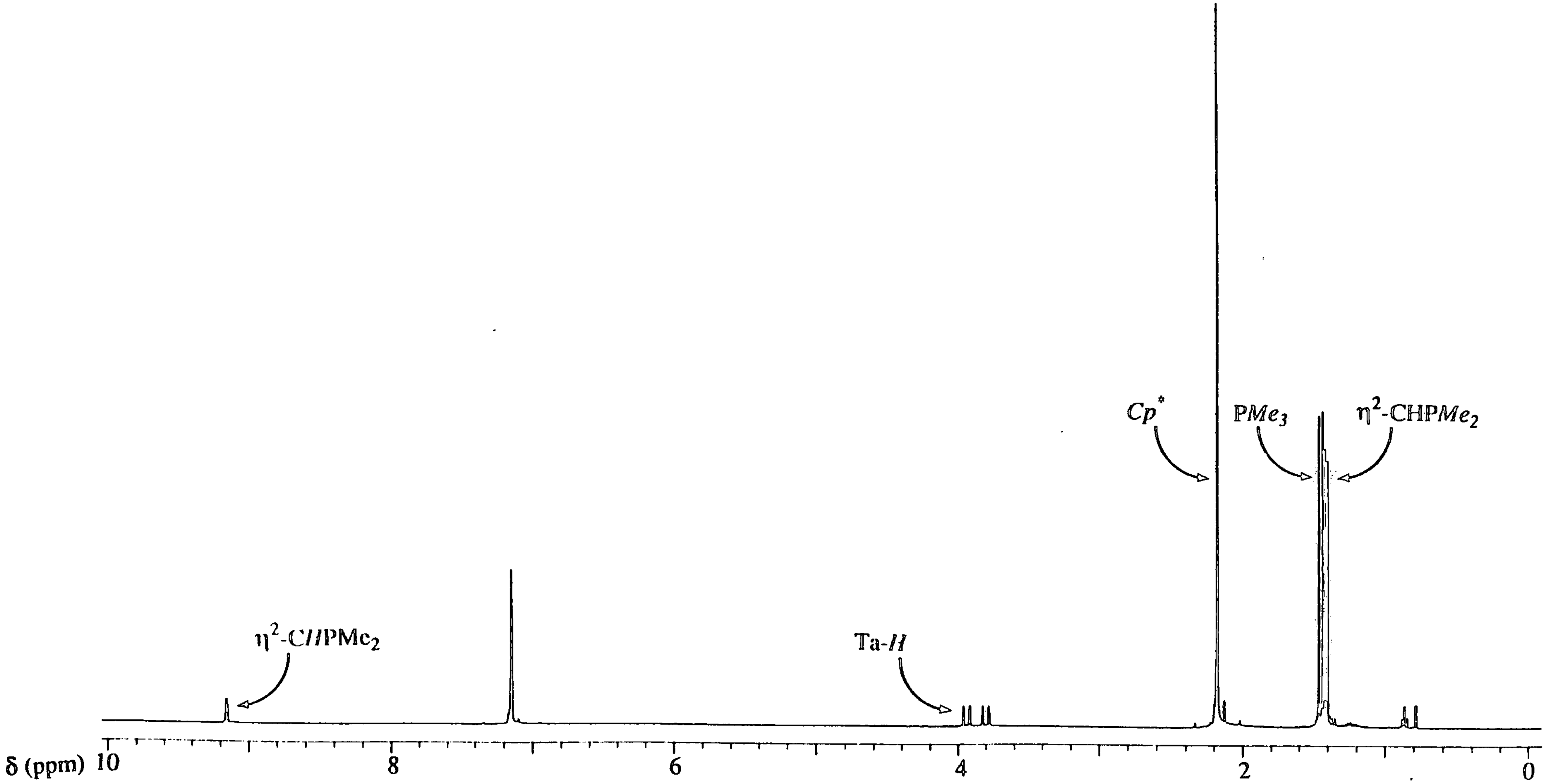
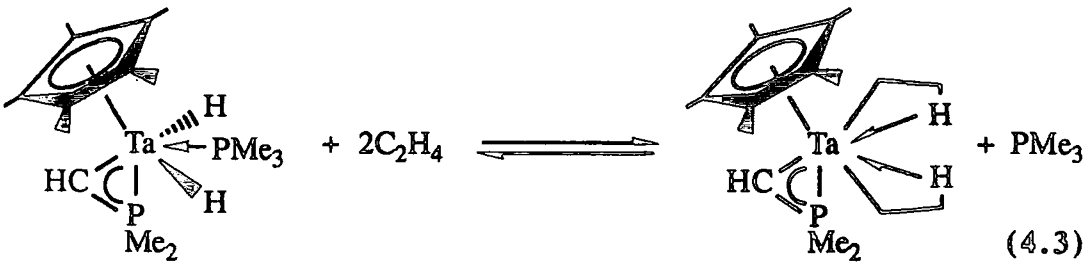


Figure 4.2 *400 MHz ^1H NMR spectrum (C_6D_6) of $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)$ (1)*

4.2.3 Reaction of Cp*Ta(η^2-CHPMe$_2$)(H)$_2$(PMe$_3$) (1) with Ethylene.

Monitoring of the reaction of Cp*Ta(η^2-CHPMe$_2$)(H)$_2$(PMe$_3$) (1) with an excess of ethylene in benzene by ^{1}H NMR spectroscopy (250 MHz) shows that ethylene is consumed to afford new resonances at δ 1.81, 1.33 and 9.41 ppm attributable to the Cp* ring, metallacycle methyl and methine hydrogen resonances respectively, of the dialkyl species Cp*Ta(η^2-CHPMe$_2$)Et$_2$ (2). Complex (2) has been characterised by ^{1}H NMR spectroscopy only; attempts to isolate this compound were unsuccessful. The ^{1}H NMR spectrum of the reaction mixture shows no evidence of new tantalum-hydride signals suggesting that a monoethyl-hydride species of the type Cp*Ta(η^2-CHPMe$_2$)(H)(Et), or Cp*Ta(η^2-CHPMe$_2$)(H)(Et)(PMe$_3$) are too short-lived to be observed.

The absence of bound phosphine in the observed initial insertion product Cp*Ta(η^2-CHPMe$_2$)Et$_2$ (2) is of interest and may possibly reflect agostic interactions involving hydrogens on the β-carbons of the ethyl groups stabilising the 16-electron cooordinatively unsaturated complex. It was hoped that confirmation of the presence of agostic interactions would be possible through the preparation of the deuterium labelled ethyl ligand (-CD$_2$CD$_2$H) *via* treatment of compound (1) with two equivalents of *d*$_4$-ethylene. However, ^{1}H and ^{2}H NMR spectroscopies reveals that insertion of ethylene into the Ta-H bonds is rapidly reversible so as to afford hydrogen/deuterium scrambling in the ethyl groups. Moreover, further reaction of (2) with excess ethylene to generate a number of unidentified complexes leads to further complications in the assignment of resonances in the ^{1}H NMR spectrum.

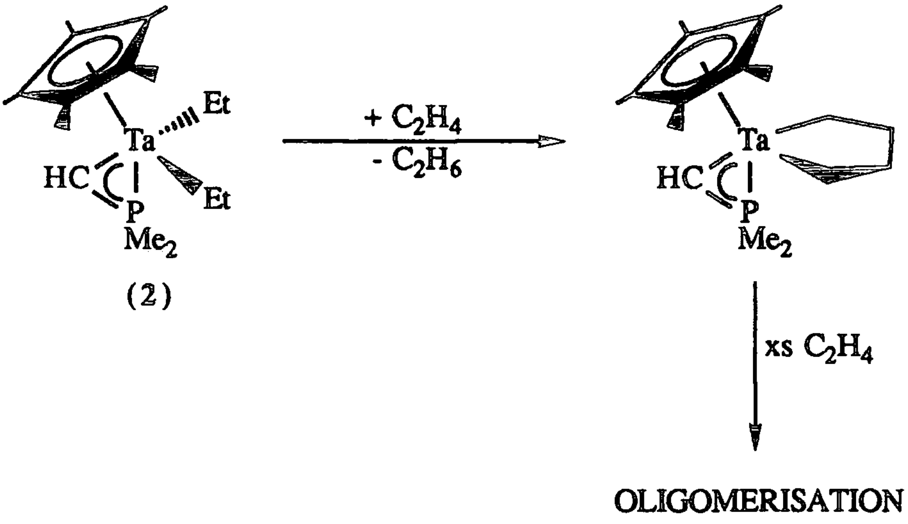


(4.3)

(1) (2)

The identification of Cp*Ta(η^2-CHPMe$_2$)Et$_2$ (2) unfortunately does not give any indication of the oligomerisation mechanism. Moreover, treatment of a benzene solution of the dihydride (1) with an excess of d_4 -ethylene and subsequent monitoring by ^{2}H NMR spectroscopy (61 MHz), reveals a number of resonances in the region δ 0.69-0.73 ppm which are attributable to partially deuterated ethanes[12]. The ^{2}H NMR spectrum shows also a singlet at δ 1.29 ppm corresponding to a per-deuterio species containing equivalent deuteron environments; this has been cautiously assigned to a rapidly rotating per-deuterio ethylene ligand bound to tantalum. A similar singlet resonance (δ 1.30 ppm) is resolved in the ^{1}H NMR spectrum (400 MHz, C_6D_6) of the reaction of (1) with C_2H_4, this again has been tentatively assigned to an ethylene ligand bound to the metal centre.

Thus, it is thought likely that oligomerisation proceeds *via* loss of alkane to generate a coordinated olefin which then combines with more olefin to generate a tantallacyclopentane species (Scheme 4.1).



Scheme 4.1

The instability of the dialkyl complex Cp*Ta(η^2-CHPMe$_2$)Et$_2$ (2) is analogous to the behaviour of the related CpNb(NAr)Et$_2$ species which is unstable to loss of ethane affording an olefin derivative which can be isolated as the phosphine adduct CpNb(NAr)(η^2-C_2H_4)(PMe$_3$)[13]. Intriguingly, Kee[3] has demonstrated that the bis-neohexyl complex $Cp^*Ta(\eta^2\text{-}CHPMe_2)(CH_2CH_2CMe_3)_2$ may be isolated. This suprising stability may be attributed to the sterically demanding neohexyl ligands preventing the attainment of a favourable configuration for β-elimination of 2, 2-dimethylbutane.

Since NMR spectroscopy did not facilitate identification of all the oligomerisation products of (1) with ethylene, alternative analytical techniques were considered. Treatment of a solution of $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)$ (1) in toluene with a large excess of ethylene at ambient temperature and subsequent analysis of the volatile material by G.C. mass spectrometry did lead to the identification of olefins and saturated hydrocarbons including ethane and butane.

Analysis of the mass spectrometry fragmentation patterns of the olefin fractions indicates the presence of both (E) and (Z) forms of but-2-ene; two C_6 isomers and a C_8 olefin in the reaction mixture. Since the reaction appears to proceed*via* a mechanism involving metallacycle species, the absence of 1-butene from the reaction mixture is somewhat suprising[14]. This observation however, can be rationalised as $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)(Br)(PMe_3)$ has been shown to cleanly dimerise ethylene to but-1-ene, and once all the ethylene has been consumed, but-1-ene is then isomerised to the internal olefin, but-2-ene[15]. Indeed, ^1H NMR spectroscopy shows that 1-butene is generated in the reaction of ethylene with compound (1). Thus, the but-1-ene formed may be subsequently isomerised to the internal olefin and so is not observed by G.C. mass spectrometry. Alternatively, rather than the isomerisation of but-1-ene, the C_4 olefin may couple with further ethylene units to yield the higher C_6 and C_8 olefins. However, no higher olefins than C_8 were detected by G.C mass spectrometry.

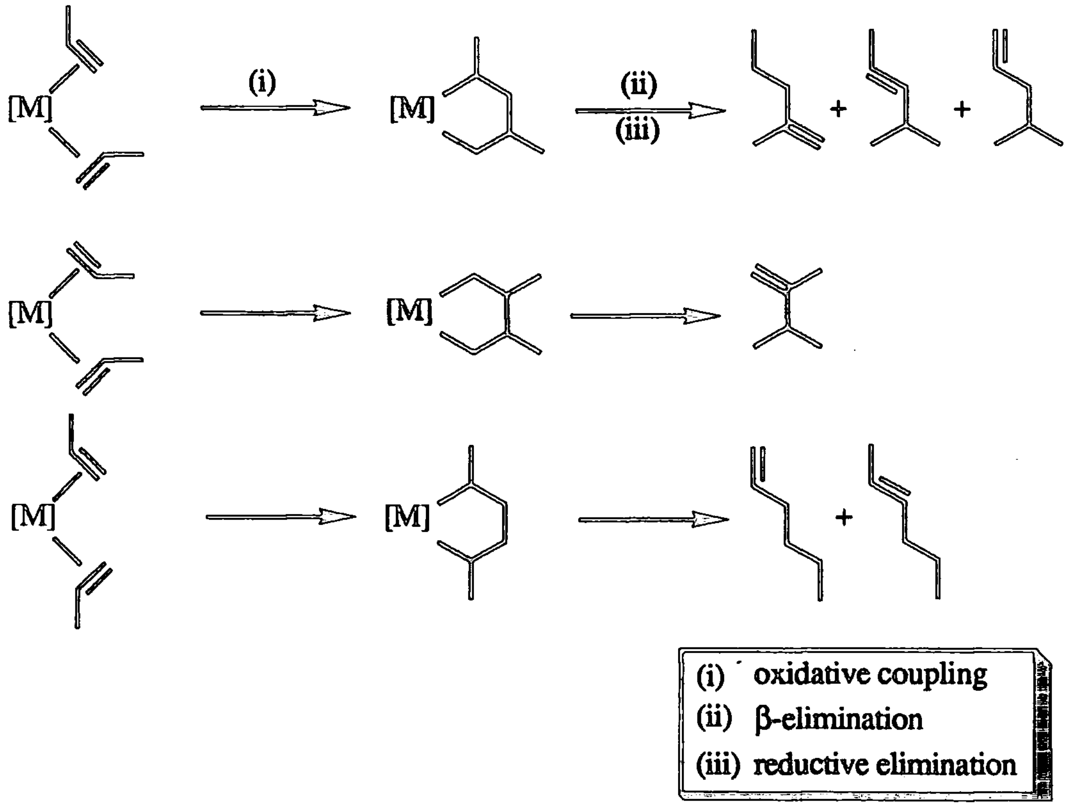
As a metallacycle mechanism is suspected for the oligomerisation process the presence of ethane in the reaction mixture can be explained by β-elimination of alkane from the unstable (diethyl)tantalum complex (2), whereas the observed higher saturated hydrocarbons may result from hydrogenation of the higher olefins possibly catalysed by decomposition products.

4.2.4 Reaction of Cp*Ta(η^2-CHPMe$_2$)(H)$_2$(PMe$_3$) (1) with Propylene.

The investigation of the oligomerisation products arising from the treatment of (1) with propylene offers a further opportunity for determining whether a Cossee-Arlman or a metallacycle mechanism predominates.

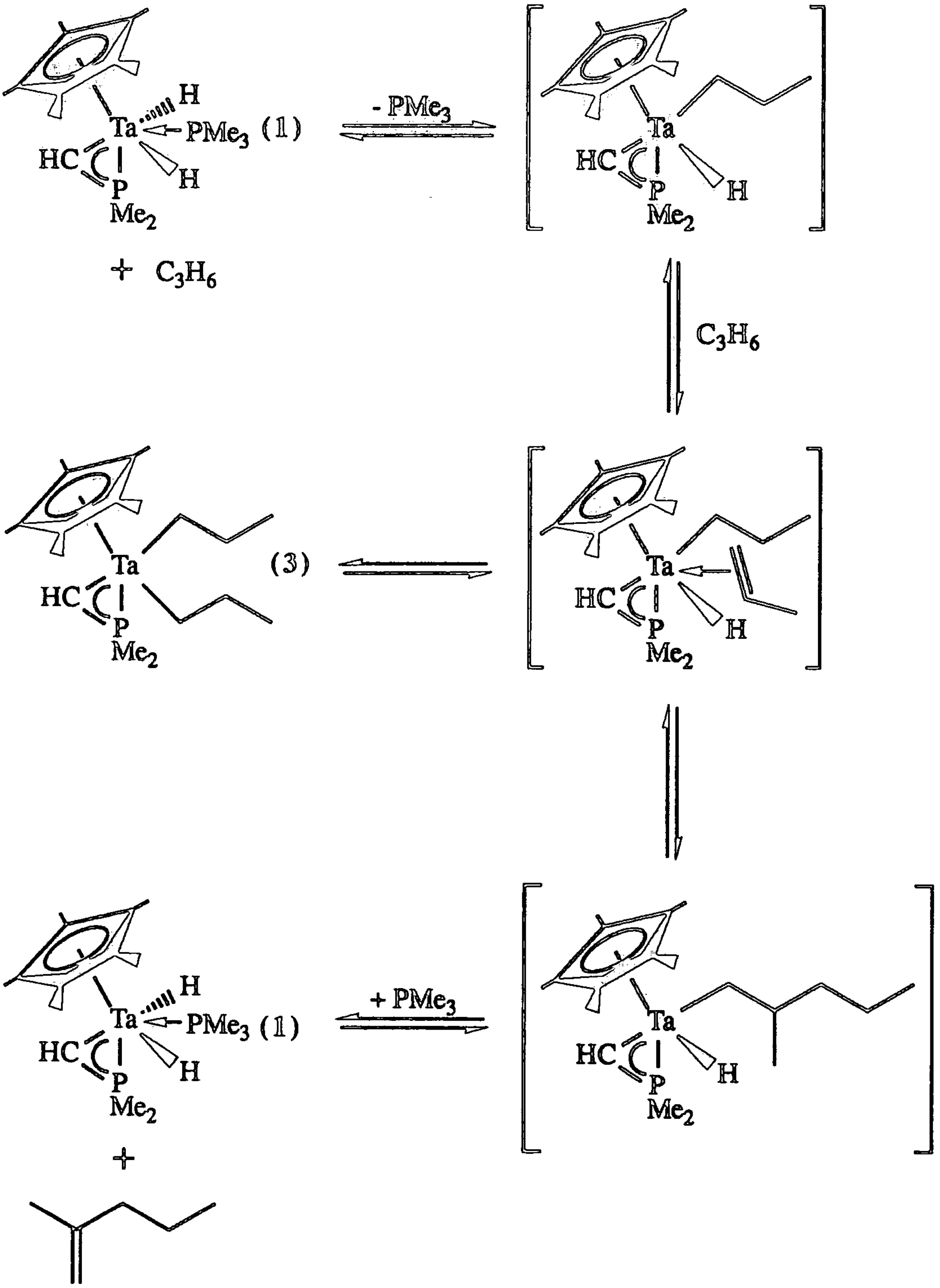
The Cossee-Arlman mechanism may give 2-methylpent-1-ene, hex-1-ene, or hex-2-ene as the initial dimerisation products, depending upon which way around the propylene inserts into the metal-propyl unit. However, formation of 2-methylpent-1-ene is expected to be favoured for steric and electronic[16] reasons (Scheme 4.2).

The alternative metallacycle mechanism, as observed by Schrock *et al* [11], can potentially give a number of propylene dimers dependent upon steric crowding within the metallacycle. Three of these dimers are identical to the products of the direct-insertion mechanism. Moreover, it is not unreasonable to anticipate a variety of dimerisation products, as it has been demonstrated that preparation of the related tantallacycle Cp*Ta(NAr)(η^2-C$_3$H$_6$)$_2$ affords all ten possible metallacycle isomers[13].



(i) oxidative coupling
(ii) β-elimination
(iii) reductive elimination

Scheme 4.3 *Potential propylene dimers generated via a metallacycle mechanism.*



Scheme 4.2 *Dimerisation of propylene to 2-methylpent-1-ene by (1) via a Cossee-Arlman mechanism.*

The initial insertion product of the treatment of $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)$ (1) with propylene has been observed by ^1H NMR spectroscopy. The 250 MHz ^1H NMR spectrum (C_6D_6) indicates insertion into both Ta-H bonds and liberation of phosphine to afford the dialkyl species $Cp^*Ta(\eta^2\text{-}CHPMe_2)(^nPr)_2$ (3), with Cp^* ring metallacycle methine and methyl hydrogen resonances at δ 1.77, 9.12 and 1.64 ppm repectively, (Equation 4.4). This reaction is slower than that observed for the reaction of the dihydride (1) with ethylene, 0.43 insertions per hour for a 4 fold excess (*cf.* 0.63 insertions per hour), which is presumably a consequence of steric factors.

$$\underset{(1)}{Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)} + 2C_3H_6 \rightleftharpoons \underset{(3)}{Cp^*Ta(\eta^2\text{-}CHPMe_2)(^nPr)_2} + PMe_3 \quad (4.4)$$

Further studies employing ^1H NMR spectroscopy have been undertaken to identify the C_6 olefins generated in this reaction and reveal that a number of propylene dimers are afforded. Comparison with C_6 olefin standards show that the dimers observed in the ^1H NMR cannot be solely attributed to hex-1-ene, hex-2-ene, and 2-methyl-pent-1-ene the C_6 dimers of a direct insertion mechanism. Moreover, the observed C_6 olefins are unlikely to be attributable to isomerisation products of a Cossee-Arlman type mechanism since an excess of propylene is present during the reaction. Attempts to identify the C_6 isomers by G.C. mass spectrometry have however failed to reveal their identities.

Since ^1H NMR experiments show that the propylene dimerisation does not afford one C_6 isomer selectively, work was undertaken to investigate the reactivity of compound (1) towards a mixture of ethylene and propylene. Treatment of the dihydride (1) with equimolar amounts of these gases in an NMR tube, and subsequent monitoring by 250 MHz ^1H NMR spectroscopy revealed a metallacycle methine hydrogen at δ 9.41 ppm, indicating that the initial product of this reaction is exclusively

$Cp^*Ta(\eta^2\text{-}CHPMe_2)Et_2$ (2). This is to be expected given the faster insertion rate of ethylene over propylene. Moreover, there is no measurable consumption of propylene until the majority (*ca.* 80%) of the free ethylene available has been dimerised by (1) to but-1-ene.

4.2.5 Reaction of $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)$ (1) with But-1-ene.

Treatment of a solution of (1) with a 10-fold excess of but-1-ene leads to slow insertion into both Ta-H bonds, *ca.* 0.92 insertions per hour, to generate a yellow solution of $Cp^*Ta(\eta^2\text{-}CHPMe_2)(^nBu)_2$ (4). Again, no monohydrido-alkyl species are observed by ^1H NMR spectroscopy. The 250 MHz ^1H NMR spectrum reveals a metallacycle methine hydrogen singlet at δ 9.11 ppm and a singlet resonance at δ 1.79 ppm assignable to the Cp^* methyl hydrogens of the di-insertion product.

Continued monitoring by ^1H NMR spectroscopy reveals the generation of new olefin signals, however, these new species cannot be identified by ^1H NMR .

R	$\eta^2\text{-}CH\,PMe_2$ δ (ppm)	C_5Me_5 δ (ppm)
Et	9.41	1.81
^{n}Pr	9.12	1.77
^{n}Bu	9.11	1.79

Table 4.1 *Selected 250 MHz ^1H NMR resonances (C_6D_6) of $Cp^*Ta(\eta^2\text{-}CHPMe_2)R_2$ (R = Et, (2); ^{n}Pr, (3); ^{n}Bu, (4)).*

4.2.6 Alkylation of $Cp^*Ta(\eta^2\text{-}CHPMe_2)I_2$ (5).

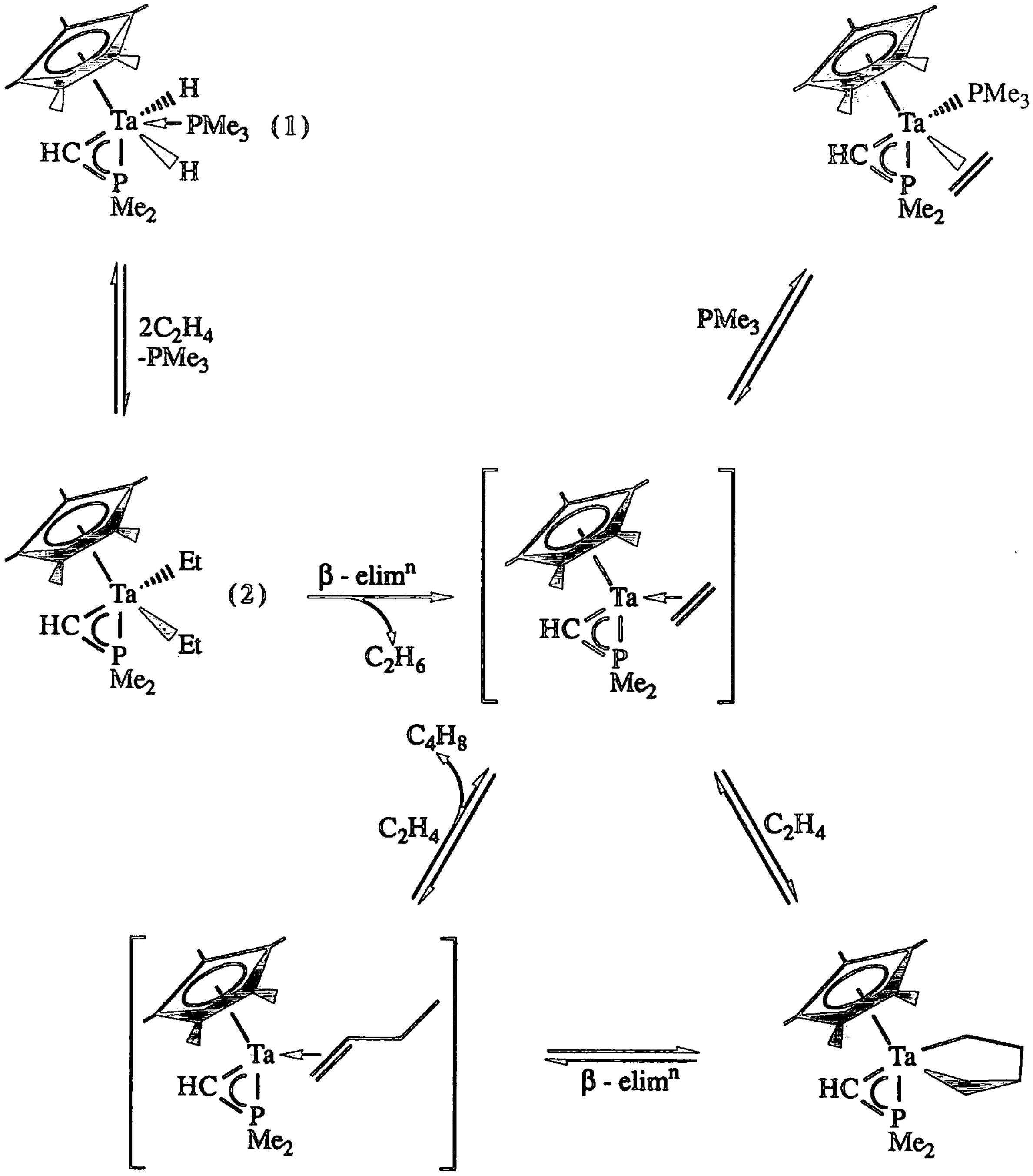
Kee has shown that reaction of an n-pentane solution of the dihydride (1) with an excess of methyl iodide affords a purple solution of the (diiodo)tantalum complex $Cp^*Ta(\eta^2\text{-}CHPMe_2)I_2$ (5), and free tertiary phosphine which is precipitated as the phosphonium halide $PMe_4{}^+I^-$[5,6] (Equation 4.5).

$$\underset{(1)}{Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)} + 3MeI \longrightarrow \underset{(5)}{Cp^*Ta(\eta^2\text{-}CHPMe_2)I_2} + [PMe_4]^+I^- + 2CH_4 \quad (4.5)$$

The diiodide $Cp^*Ta(\eta^2\text{-}CHPMe_2)I_2$ (5) was mixed with 0.5 equivalents of $[Et_2AlCl]_2$ in C_6D_6 at room temperature. An immediate reaction ensued affording a brown solution, the ^1H NMR spectrum of which revealed a methine hydrogen resonance at δ 10.43 ppm (*cf.* $Cp^*Ta(\eta^2\text{-}CHPMe_2)I_2$ methine resonance δ 11.28 ppm) in conjunction with free ethane.

Since the alkylation of (5) affords free ethane, presumably through the β-elimination of alkane from an unstable diethyl species, this offers further support for the ethylene oligomerisation cycle proceeding *via* a metallacycle mechanism. The new species described above is not however observed in the catalytic oligomerisation of ethylene by (1), suggesting that an interaction with the Lewis acid could be occuring, rather than with the PMe_3 that is present in the catalytic cycle involving $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)$ (1).

In conclusion, investigations primarily employing NMR spectroscopies have indicated that the catalytic oligomerisation of olefins by $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)$ (1) most probably proceed *via* metallacycle mechanisms.



Scheme 4.4 *A possible catalytic cycle for ethylene dimerisation by (1) via a metallacycle mechanism.*

4.3 Reaction of $Cp^*Ta(NAr)(H)_2(PMe_3)$ with α-Olefins.

Mayer and Bercaw[17] have previously described the synthesis of the dihydride $Cp^*Ta(NCMe_3)(H)_2(PMe_3)$ *via* hydrogenation of the dimethyl precursor $Cp^*Ta(NCMe_3)Me_2$. Hence, the preparation of the (dimethyl)tantalum complex $Cp^*Ta(NAr)Me_2$[18], afforded an opportunity to access the reactivity of the dihydride species $Cp^*Ta(NAr)(H)_2(PMe_3)$ towards α-olefins, thus facilitating a comparison with the related $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)$ (**1**).

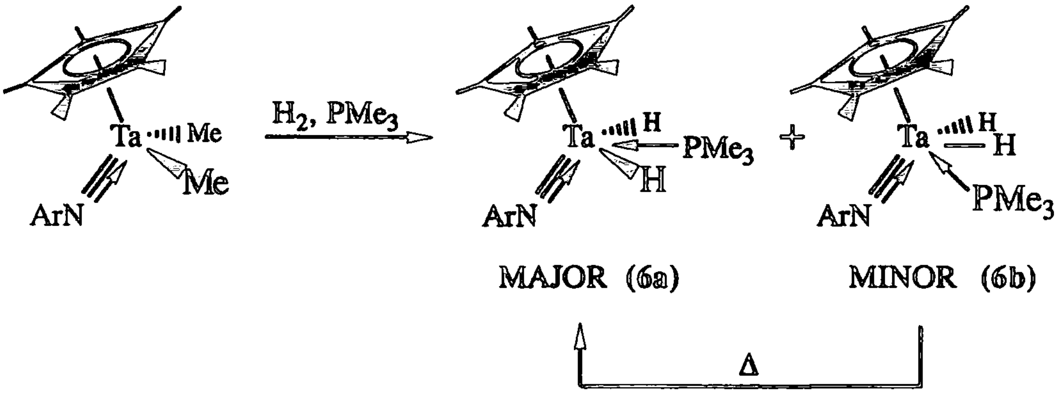
4.3.1 Preparation of $Cp^*Ta(NAr)(H)_2(PMe_3)$ (6).

Treatment of a toluene solution of $Cp^*Ta(NAr)Me_2$ with an excess of dihydrogen and trimethylphosphine, proceeded slowly at 100°C over a period of 20 days to afford a pale solution. Extraction into n-pentane gave white crystals of $Cp^*Ta(NAr)(H)_2(PMe_3)$ (**6**) upon prolonged cooling at -78°C.

$$\overset{*}{Cp}Ta(NAr)Me_2 + 2H_2 + PMe_3 \xrightarrow[100^{\circ}C]{toluene} \underset{(6)}{\overset{*}{Cp}Ta(NAr)(H)_2(PMe_3)} + 2CH_4 \quad (4.6)$$

Compound (**6**) is soluble in aromatic, and low polarity hydrocarbons such as pentanes. However, treatment with chlorocarbons readily affords the phosphino-dichloride $Cp^*Ta(NAr)(PMe_3)Cl_2$. Characterisation is provided by elemental analysis, mass spectrometry, infrared and NMR spectroscopies. The infrared spectrum reveals bands at 1665 and 1710 cm^{-1}, which are assigned to υ(Ta-H) stretching vibrations. Mass spectrometry shows an envelope at m/z 569 (^{181}Ta) corresponding to the parent ion, and daughter ions at m/z 567 and 491 attributable to the fragments $Cp^*Ta(NAr)(PMe_3)$ and $Cp^*Ta(NAr)$ respectively. Intriguingly ^1H NMR spectroscopy (C_6D_6) reveals a mixture of two isomers of the dihydride complex (**6a** + **6b**) in a relative ratio of 6:1. The 400 MHz ^1H NMR spectrum of the predominant isomer (6a) shows a singlet resonance at δ 2.10 ppm and a doublet at δ 1.16 ppm ($^2J_{PH}$ = 7.6 Hz) assignable to the Cp* ring hydrogens and a strongly coordinating PMe_3 ligand respectively. The hydride ligands are found as a lowfield doublet resonance at δ 7.18 ppm ($^2J_{PH}$ = 60 Hz). They are thus presumed to be disposed symmetrically either side of the P-Ta-N plane, as illustrated in Scheme 4.5.

The ^1H NMR spectrum of (6b) reveals inequivalent hydride environments at δ 8.77 and 8.87 ppm in an AB spin system. Isomer (6b) is therefore assigned to the kinetic product of the hydrogenation of Cp*Ta(NAr)Me_2, *ie* with PMe_3 bonded laterally as observed in CpNb(NMe)(PMe_3)Cl_2[9]. Consistently prolonged warming of a mixture of (6a + 6b) at *ca.* 100°C exclusively affords the thermodynamic isomer (6a).



Scheme 4.5 *Preparation of Cp*Ta(NAr)(H)$_2$(PMe$_3$) (6).*

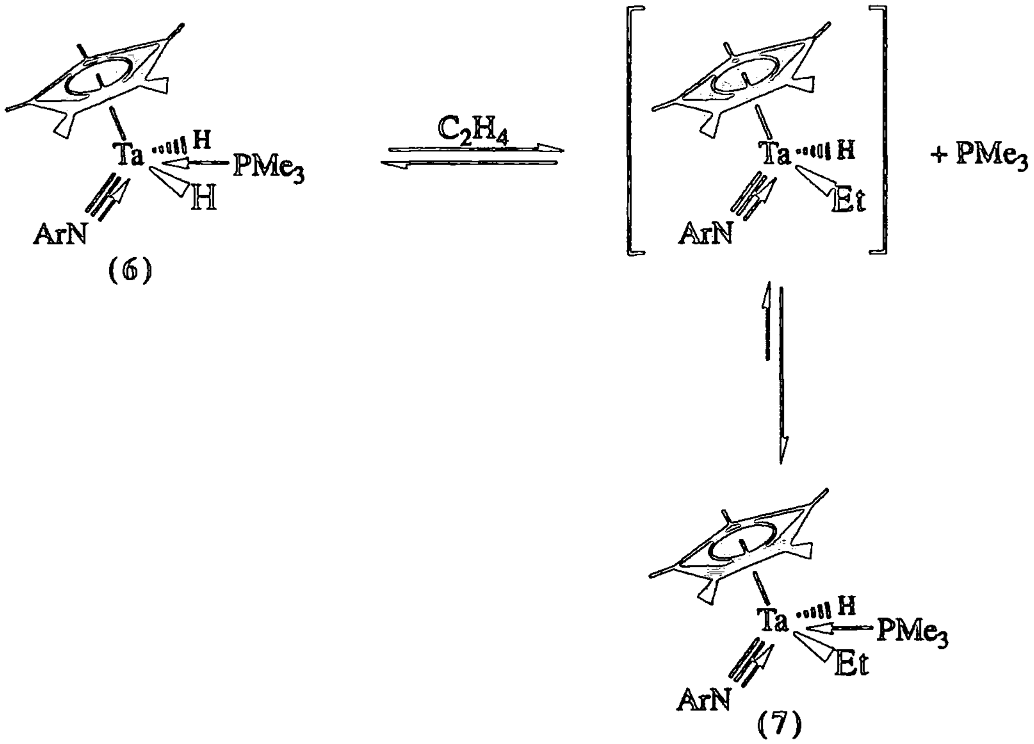
Attempts were made to prepare the base free dihydride Cp*Ta(NAr)(H)$_2$ which could provide a relatively sterically uncongested site for attack by organic substrates, and so offer a potent catalyst for the oligomerisation or polymerisation of olefins.

Hydrogenation of a toluene solution of Cp*Ta(NAr)Me_2 in the absence of PMe_3 at 100°C afforded a pale solution, which when allowed to cool below *ca.* 70°C precipitated a colourless microcrystalline solid. Characterisation by infrared spectroscopy shows a strong band at 1705 cm^{-1} associated with vibrations of a Ta-H bond. Moreover, high temperature ^1H NMR spectroscopy (400 MHz, C_7D_8, 90°C) reveals very low field signals at δ 14.97 and 15.59 ppm attributable to hydride resonances. Two singlets of equal intensity at δ 1.89 and 2.00 ppm are assigned to the hydrogens of a Cp* ring and four equally intense septets at δ 3.64, 3.67, 4.05 and 4.52 ppm corresponding to (aryl)imido isopropyl methine hydrogens, suggest that the complex may be a cluster species. Furthermore, a singlet resonance at δ 0.41 ppm is assigned to a methyl group indicating that hydrogenation of all the Ta-Me units has not occurred and hence, this complex cannot be regarded as a "$Cp^*Ta(NAr)H_2$" cluster species. To date, further identification of this complex has not proven possible, due in part to its insolubility and involatility.

4.3.2 Reaction of $Cp^*Ta(NAr)(H)_2(PMe_3)$ (6) with Ethylene.

Mayer and Bercaw reported that treatment of the tantalum species $Cp^*Ta(NCMe_3)(H)_2(PMe_3)$ with an excess of ethylene afforded a complex mixture of products that were not readily identifiable[17]. The preparation of the analogous compound (**6**) and other derivatives of the synthetically versatile dichloride $Cp^*Ta(NAr)Cl_2$ has allowed us to investigate this reaction with a modified imido derivative in order to elucidate the mechanism of olefin insertion .

When the dihydride $Cp^*Ta(NAr)(H)_2(PMe_3)$ (**6**) and a 4-fold excess of ethylene are sealed in an NMR tube (C_6D_6), and monitored by 200 MHz ^1H NMR spectroscopy, a new hydride doublet resonance at δ 8.80 ppm ($^2J_{PH}$ = 60 Hz) is soon observed. Furthermore, the ^1H NMR spectrum reveals other new signals including a singlet at δ 2.07 ppm and a triplet resonance at δ 1.15 ppm ($^3J_{HH}$ = 6.4 Hz) attributable to Cp* ring hydrogens and hydrogens attached to the β-carbon of an ethyl group, respectively. This first insertion product is assigned as the (monohydrido)tantalum complex $Cp^*Ta(NAr)(H)(Et)(PMe_3)$ (**7**). Moreover, the ^1H NMR shows no free trimethylphosphine (δ 0.79 ppm) to be present, indicating that the product of ethylene insertion into the Ta-H bond of $Cp^*Ta(NAr)(H)_2(PMe_3)$ (**6**) is trapped out rapidly by PMe_3 (Scheme 4.6).



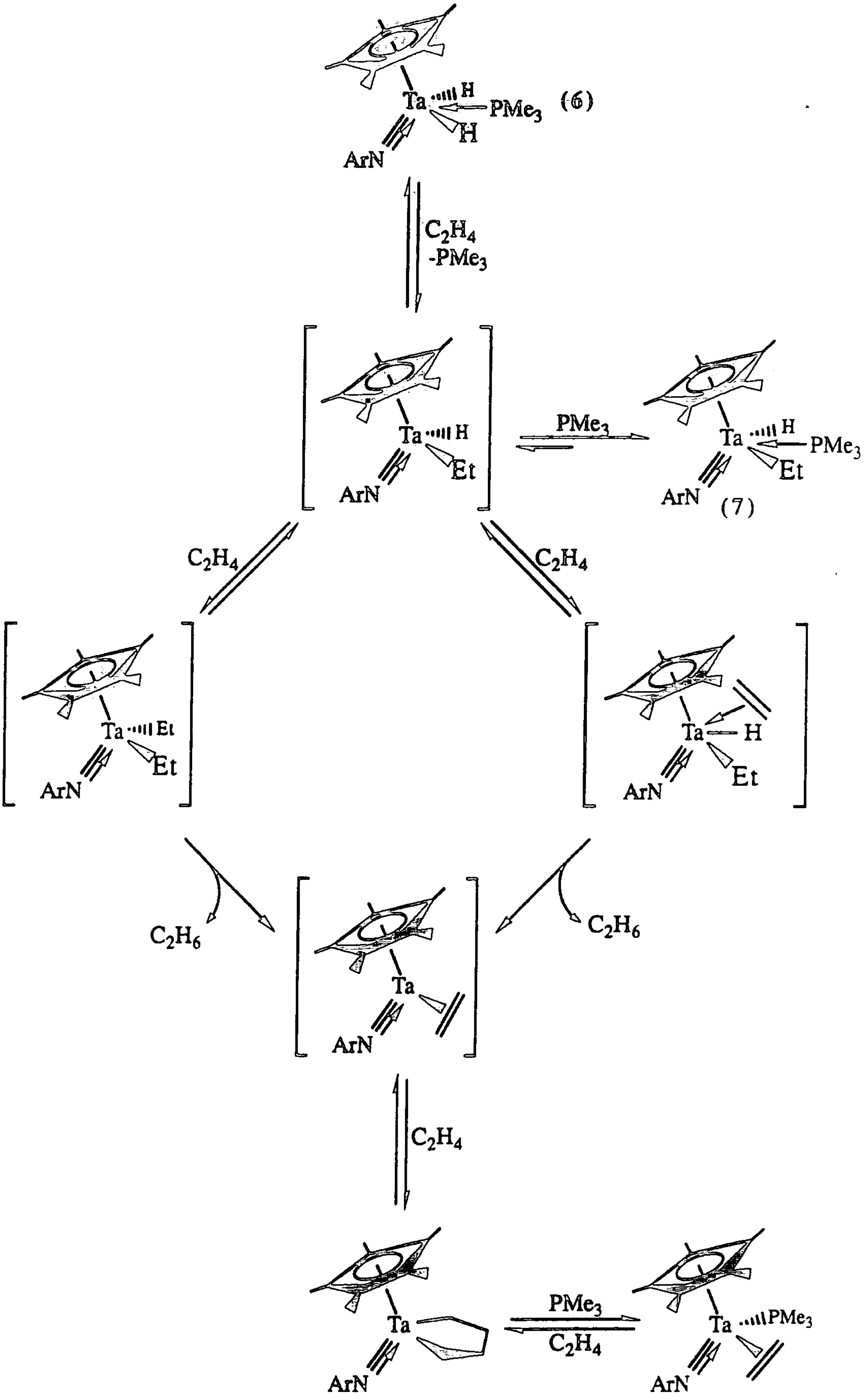
Scheme 4.6 *Reaction of* $Cp^{*}Ta(NAr)(H)_2(PMe_3)$ *(6) with ethylene.*

Insertion of a further equivalent of ethylene into (7) is slow, affording free trimethylphosphine, ethane and a mixture of the previously characterised 'diethylene' and 'ethylene' derivatives $Cp^{*}Ta(NAr)(\eta^2\text{-}C_2H_4)_2$ and $Cp^{*}Ta(NAr)(\eta^2\text{-}C_2H_4)(PMe_3)$, in a 10 : 1 ratio respectively[13]. The mechanism of ethane elimination could not be elucidated since ^1H NMR spectroscopy does not reveal whether extrusion occurs from a (diethyl)- or (monoethyl-hydrido)tantalum species (Scheme 4.7). This is in contrast to the treatment of (1) with ethylene where $Cp^{*}Ta(\eta^2\text{-}CHPMe_2)(Et)_2$ (2) may be observed by ^1H NMR spectroscopy.

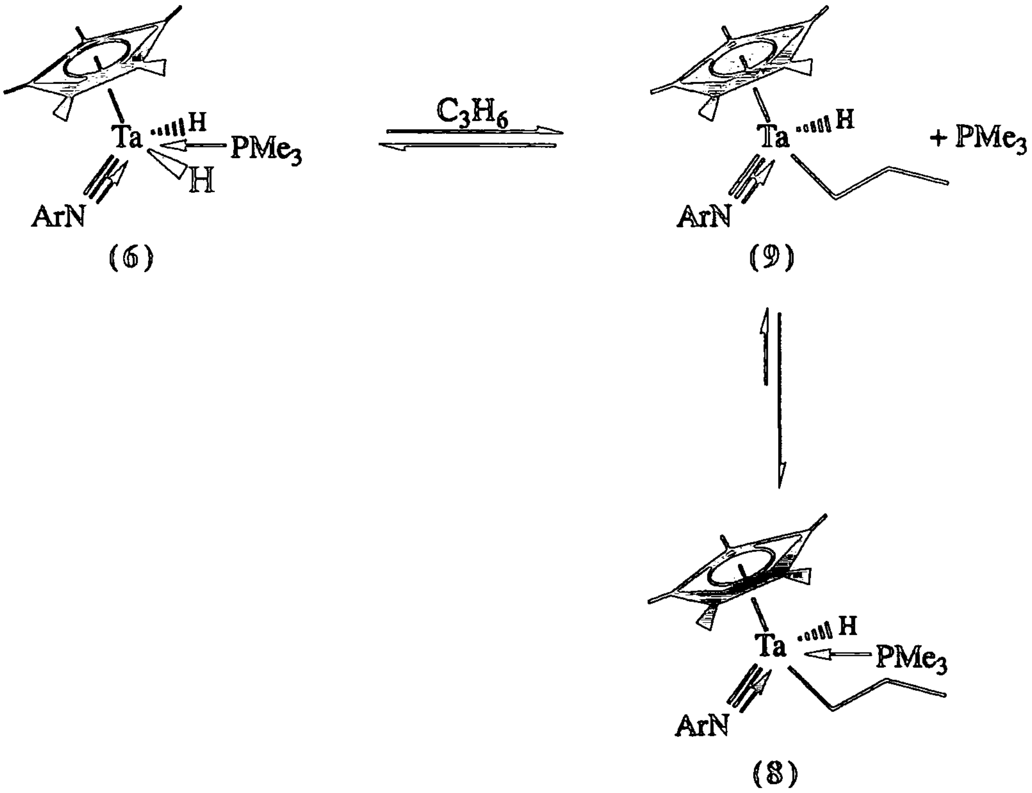
Monitoring of the $Cp^{*}Ta(NAr)(\eta^2\text{-}C_2H_4)(PMe_3)$ / $Cp^{*}Ta(NAr)(\eta^2\text{-}C_2H_4)_2$ mixture over a period of several days reveals a slow increase in the concentration of the (olefin)tantalum complex $Cp^{*}Ta(NAr)(\eta^2\text{-}C_2H_4)(PMe_3)$ at the expense of $Cp^{*}Ta(NAr)(\eta^2\text{-}C_2H_4)_2$. The initial predominance of $Cp^{*}Ta(NAr)(\eta^2\text{-}C_2H_4)_2$ may be rationalised by a preference for ethylene over phosphine in the competition for the available coordination site on tantalum, made available on elimination of ethane from any unstable (diethyl)- or (monoethyl-hydrido)tantalum species. The subsequent increase in the concentration of Cp*Ta(NAr)(η^2-C_2H_4)(PMe_3) can then be attributable to attainment of the previously described equilibrium between Cp*Ta(NAr)(η^2-C_2H_4)(PMe_3) and Cp*Ta(NAr)(η^2-C_2H_4)$_2$[13]. Warming of the mixture to 100°C affords no new olefin signals, again demonstrating the suprising stability of the complex Cp*Ta(NAr)(η^2-C_2H_4)$_2$, which is derived through this metallacycle mechanism.

4.3.3 Reaction of Cp*Ta(NAr)(H)$_2$(PMe_3) (6) with Propylene.

Treatment of a benzene solution of the dihydride Cp*Ta(NAr)(H)$_2$(PMe_3) (6) with an excess of propylene (4 fold) in a sealed NMR tube gives a slow reaction at ambient temperature. A 200 MHz ^{1}H NMR spectrum of the solution reveals a lowfield doublet resonance at δ 8.81 ppm ($^2J_{PH}$ = 60 Hz) attributable to a new (hydrido)tantalum species. Furthermore, a doublet resonance at δ 1.06 ppm is assigned to coordinated phosphine, with only trace amounts of free phosphine being found in solution. This new species is tentatively assigned as Cp*Ta(NAr)(^{n}Pr)(H)(PMe_3) (8), the first insertion product of the reaction between (6) and propylene. The slow rate of propylene insertion, $t^1/_2$ *ca.* 24 hours (*cf.* $t^1/_2$ *ca.* 12 hours for insertion of ethylene; assuming first order kinetics) being attributed to steric considerations. Moreover, careful scrutiny of the ^{1}H NMR spectrum reveals a low concentration of a further (hydrido)tantalum species. A low intensity singlet resonance at δ 8.90 ppm is assigned to a hydride experiencing no coupling to phosphorus. A singlet at δ 1.72 ppm for Cp* ring hydrogens, a septet at δ 3.98 ppm and doublets at δ 1.38, and 1.41 ppm corresponding to the methine and diastereotopic methyls of an aryl isopropyl respectively are also observed. This complex is cautiously assigned to the base free monohydride Cp*Ta(NAr)(^{n}Pr)(H) (9), its apparent stability possibly reflecting steric congestion of the n-propyl group hindering binding of the phosphine base. The initial insertion of propylene into the Ta-H bond of (6) is illustrated in Scheme 4.8.



Scheme 4.7 *Possible mechanism for the formation of* $Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)(PMe_3)$ *and* $Cp^*Ta(NAr)(\eta^2\text{-}C_2H_4)_2$ *from the reaction of (6) with ethylene.*



Scheme 4.8

Further monitoring of the reaction mixture by ^1H NMR spectroscopy reveals that after a period of one week the signals corresponding to the monohydride species can no longer be detected. Rather, signals representing the isomers of the 'dipropylene' tantalum complex Cp*Ta(NAr)(η^2-C_3H_6)$_2$ in conjunction with traces of the complex Cp*Ta(NAr)(η^2-C_3H_6)(PMe_3) are found. By analogy with the reaction of compound (6) with ethylene, ^1H NMR spectroscopy reveals no evidence for dialkyl intermediates; moreover, as for ethylene, propylene binds preferentially to the metal centre to afford 'diolefin' species on elimination of alkane from the tantalum intermediates.

Investigation of the Cp*Ta(NAr)(η^2-C_3H_6)$_2$ complexes generated shows that two isomers predominate in the mixture, presumably reflecting steric constraints within the tantallacycle ring. These are the same two preferred isomers that are found when Cp*Ta(NAr)(η^2-C_3H_6)(PMe_3) is treated with an excess of propylene[13]. This contrasts with the work of Schrock where 'dipropylene' metallacycles were shown to form one isomer adopting a trans ββ' configuration[19].

Unfortunately no new olefin species could be detected on warming the reaction mixture to *ca.* 100°C indicating that the tantallacycles has not oligomerised propylene to higher olefins. To conclude, the employment of NMR techniques reveal that the consumption of α-olefins by the (dihydrido)tantalum complex (6) proceeds *via* a metallacycle mechanism. However, in contrast to (1) where catalytic oligomerisation of olefins is observed, the metallacycle derivatives of (6) are stable and thermally robust.

4.4 Catalytic Dimerisation of α-Olefins by $Cp^*Ta(\eta^2$-$CHPMe_2)(H)(I)(PMe_3)$ (3).

It has been demonstrated that reaction of the dihydride (1) with an excess of α-olefin affords a complex mixture of tantalum alkyls and higher alkenes. It was envisagedthat exchange of one of the hydrides of $Cp^*Ta(\eta^2$-$CHPMe_2)(H)_2(PMe_3)$ for a halide, would moderate its reactivity towards α-olefins so allowing clean and selective dimerisation reactions to be undertaken.

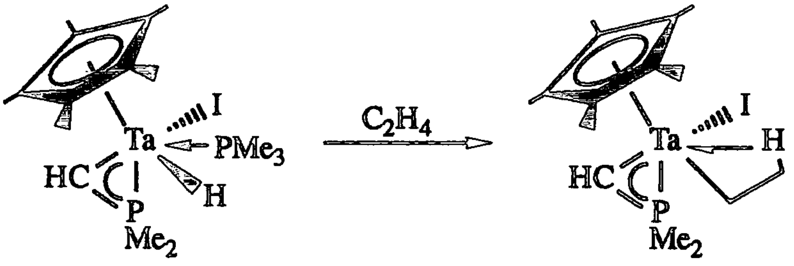
4.4.1 Preparation of $Cp^*Ta(\eta^2$-$CHPMe_2)(H)(I)(PMe_3)$ (10).

$Cp^*Ta(\eta^2$-$CHPMe_2)(H)(I)(PMe_3)$ (10) has been described previously by Kee[5,6] and is accessible *via* treatment of $Cp^*Ta(\eta^2$-$CHPMe_2)(H)_2(PMe_3)$ (1) with a molar equivalent of methyl iodide (Equation 4.7).

$$\underset{(1)}{Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)_2(PMe_3)} + MeI \longrightarrow \underset{(10)}{Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)(I)(PMe_3)} + CH_4 \quad (4.7)$$

4.4.2 Reaction of Cp*Ta(η^2-CHPMe$_2$)(H)(I)(PMe$_3$) (10) with Ethylene and Propylene.

Treatment of a benzene solution of the mono-iodide Cp*Ta(η^2-CHPMe$_2$)(H)(I)(PMe$_3$) (10) with excess ethylene in a sealed NMR tube at room temperature established an equilibrium mixture of the compound (10) and the alkyl derivative Cp*Ta(η^2-CHPMe$_2$)(Et)(I) (11). Characterisation by ^{1}H NMR spectroscopy (400 MHz, C_6D_6) of (11) reveals a metallacycle methine hydrogen singlet at δ 9.85 ppm and a triplet at δ 0.82 ppm ($^3J_{HH}$ = 8.0 Hz) attributable to the β-hydrogens of the ethyl ligand.The (monoethyl)tantalum complex is a coordinatively unsaturated 16 electron species and so may possibly possess a β-agostic interaction between the ethyl ligand and the metal centre (Figure 4.3).



(10) (11)

Figure 4.3 *Reaction of (10) with ethylene to afford (11), potentially possessing a β-agostic interaction.*

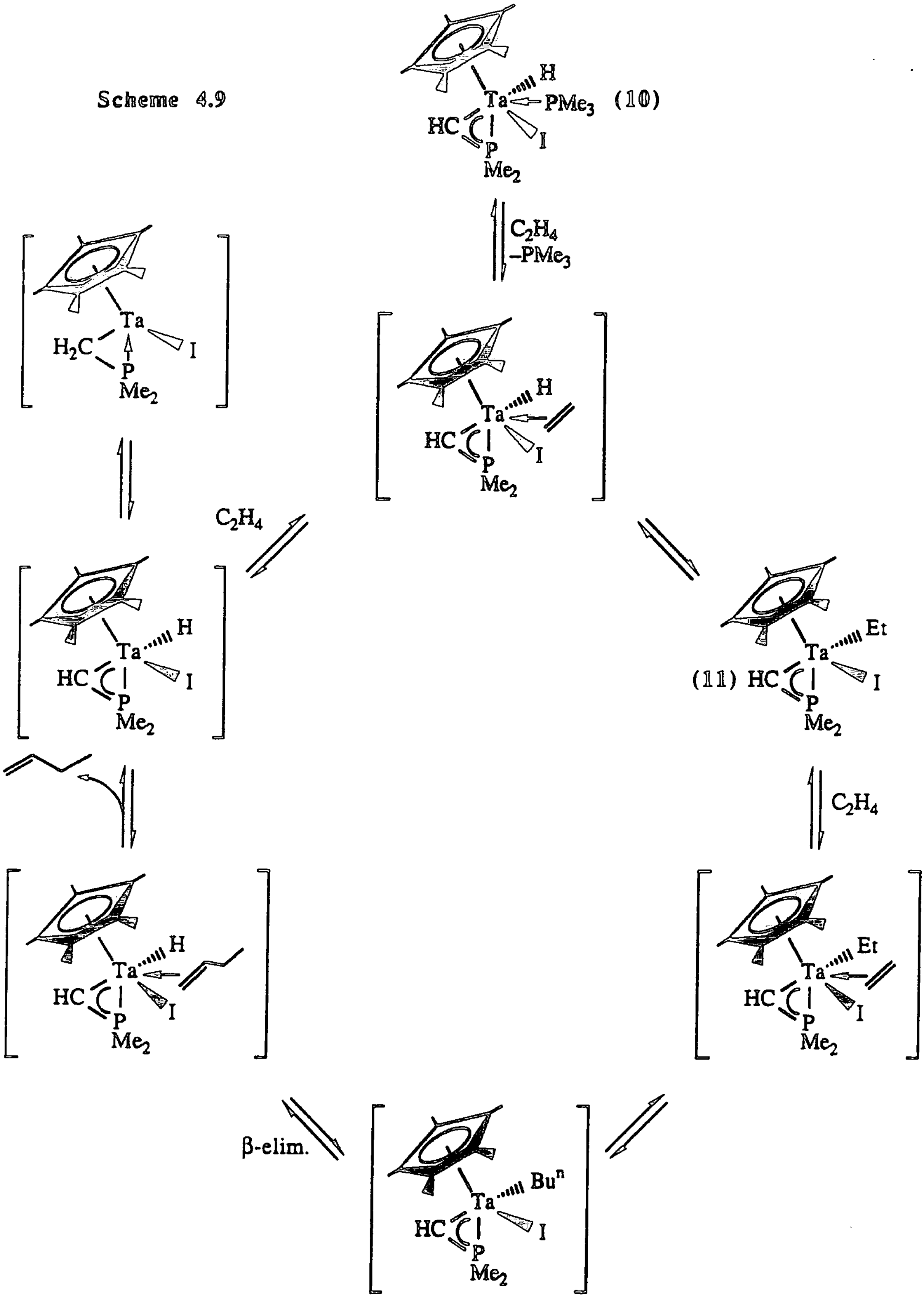
In order to probe this, (3) was treated with *d$_4$* -ethylene in an NMR tube (C_6D_6), to afford the partially deuterated species Cp*Ta(η^2-CHPMe$_2$)(CD$_2$CD$_2$H)(I) (*d$_4$*-11), subsequent monitoring by 250 MHz ^{1}H NMR spectroscopy reveals an upfield shift of the β-hydrogen of the ethyl ligand to δ 0.80 ppm consistent with the normal isotope shift on deuterium substitution. Moreover, variable temperature ^{1}H NMR experiments show the chemical shift of this resonance to be invariant over the temperature range -50°C to +20°C and therefore is unlikely to be indicative of a hydrogen atom experiencing an agostic interaction with a metal centre[20]. A possible rationalisation for the absence of β-agostic stabilisation in (**11**) may be that the metal centre could receive sufficient electron density from the attendant soft iodide ligand.

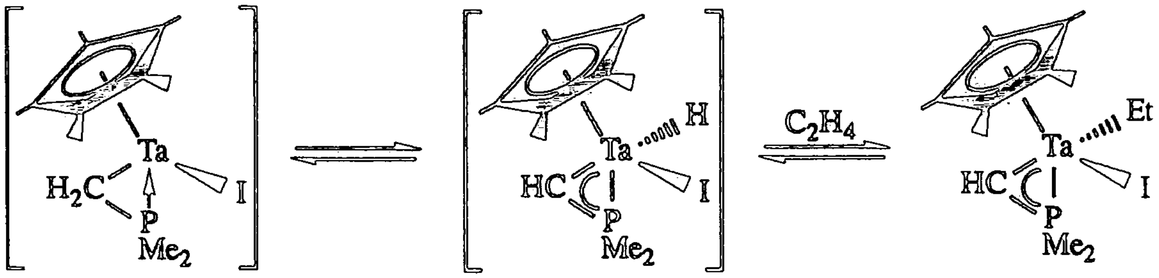
Although (**10**) was found not to oligomerise ethylene at ambient temperature, warming of a solution of (**10**) at 70°C in the presence of an excess of ethylene resulted in a clean and selective dimerisation of ethylene to but-1-ene, when monitored by ^1H NMR spectroscopy. This reaction is catalytic, but slow giving *ca.* 4 turnovers in 21 hours for an 8 fold excess of ethylene. A possible catalytic cycle for this reaction involving a direct insertion mechanism is shown in Scheme 4.9

To date the mechanism of this dimerisation remains unclear. Neither intermediate n-butyl-Ta species nor the metal alkene adducts attributable to the Cossee-Arlman mechanism described in Scheme 4.9 are observed *via* ^1H NMR spectroscopy under these conditions, since they may be either too unstable or too labile.

An alternative pathway involving tantallacycles cannot be ruled out, since the reaction of $Cp^*Ta(\eta^2\text{-}CHPMe_2)(H)(I)(PMe_3)$ with d_4-ethylene results in deuterium incorporation into the methine hydrogen site of the phosphino-carbene. This implies an equilibrium between (**10**) and a $Ta(CH_2PMe_2)$ species (Scheme 4.10), thus allowing for the possibility of an alkene coupling pathway[11,19,21] *via* $Cp^*Ta(\eta^2\text{-}CH_2PMe_2)(I)$.

Scheme 4.9





(11)

Scheme 4.10

The eventual appearance of but-2-ene in the reaction mixture is found only after complete consumption of free ethylene. This suggests that but-2-ene either does not compete effectively with ethylene for the vacant coordination site of the base free hydrido-iodide Cp*Ta(η^2-CHPMe$_2$)(H)(I), and/or that the insertion of but-1-ene into the Ta-H bond to give a secondary Ta-alkyl is disfavoured.

Compound (10) was treated with a 10 fold excess of propylene, as identification of any dimerisation products would aid in the elucidation of whether a Cossee-Arlman or metallacycle mechanism predominated.

The ^{1}H NMR spectrum (250 MHz, C$_6$D$_6$) reveals an ambient temperature equilibrium between the mono-hydride Cp*Ta(η^2-CHPMe$_2$)(H)(I)(PMe$_3$) (10) and the base-free alkyl derivative Cp*Ta(η^2-CHPMe$_2$)(^{n}Pr)(I) (12) which exhibits singlet resonances at δ 1.86 and 9.33 ppm corresponding to the Cp* ring and metallacycle methine hydrogens repectively. However, warming of the mixture to *ca.* 70°C affords no propylene dimer species presumably since a further equivalent of propylene is unable to bind to the vacant orbital on the sterically congested tantalum centre. Thus, the olefin dimerisation mechanism of (10) has yet to be revealed.

4.5 Reaction of Cp*Ta(NAr)(H)(I)(PMe$_3$) with α-Olefins.

Since it is unclear whether the dimerisation of ethylene by Cp*Ta(η^2-CHPMe$_2$)(H)(I)(PMe$_3$) (**10**) occurs *via* either a direct insertion or metallacycle mechanism, interest focused on the reaction of (mono-hydrido)tantalum imido species with ethylene. Assuming the ancillary imido unit remained as a four electron donor to the tantalum any dimerisation of ethylene would be anticipated to proceed *via* a direct insertion mechanism.

4.5.1 Preparation of Cp*Ta(NAr)(H)(I)(PMe$_3$) (13).

Treatment of Cp*Ta(NAr)(H)$_2$(PMe$_3$) (**6**) with one molar equivalent of methyl iodide in n-pentane afforded a yellow solution, which on subsequent recrystallisation at -78°C gave Cp*Ta(NAr)(H)(I)(PMe$_3$) (**13**) in low yield (38%). The reaction is believed to occur according to Equation 4.8.

$$\underset{(\mathbf{6})}{\overset{*}{\mathrm{Cp}}\mathrm{Ta(NAr)(H)_2(PMe_3)}} + \mathrm{MeI} \xrightarrow[\mathrm{RT}]{\text{n-pentane}} \underset{(\mathbf{13})}{\overset{*}{\mathrm{Cp}}\mathrm{Ta(NAr)(H)(I)(PMe_3)}} + \mathrm{CH_4} \quad (4.8)$$

Characterisation of (**13**) is provided by elemental analysis, mass spectrometry, infrared and NMR spectroscopies. The infrared spectrum reveals a band at 1750 cm^{-1} attributable to the υ(Ta-H) stretching vibration and a weak band is seen for υ(Ta-I) at 355 cm^{-1}. Fragments at m/z 619 and 569 (^{181}Ta, ^{127}I) in the mass spectrum are assigned to the daughter ions [Cp*Ta(NAr)(H)(I)]$^+$ and [Cp*Ta(NAr)(H)]$^+$ respectively. In the 250 MHz ^{1}H NMR spectrum (C$_6$D$_6$) the hydride resonance is found as a low field doublet at δ 7.99 ppm ($^2J_{PH}$ = 73 Hz). A doublet at δ 1.27 ppm ($^2J_{PH}$ = 8 Hz) indicates the presence of a strongly bound PMe$_3$ ligand, which is confirmed by a doublet at δ 18.70 ppm (J_{CP} = 27 Hz) in the 100 MHz ^{13}C NMR spectrum.

4.5.2 Reaction of $Cp^*Ta(NAr)(H)(I)(PMe_3)$ (13) with Ethylene.

The reaction of an n-pentane solution of the (monohydrido)tantalum complex (13) with an excess of ethylene yielded an orange solution on stirring at room temperature for 24 hours. Subsequent removal of volatile components afforded the base free $Cp^*Ta(NAr)(Et)(I)$ (14) as an orange microcrystalline solid (Equation 4.9).

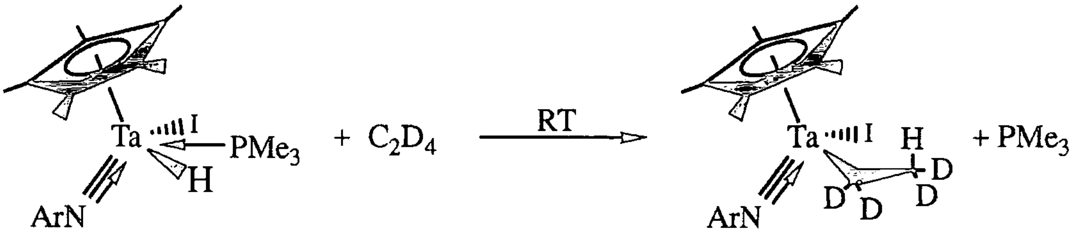
$$\underset{(13)}{Cp^*Ta(NAr)(H)(I)(PMe_3)} + C_2H_4 \xrightarrow[RT]{\text{n-pentane}} \underset{(14)}{Cp^*Ta(NAr)(Et)(I)} + PMe_3 \quad (4.9)$$

The absence of bound tertiary phosphine in (14) is suprising since this (ethyl)tantalum complex is formally a 16 electron coordinatively unsaturated species. It was initially believed that in solution PMe_3 would bind weakly to the metal centre, and hence would be removed when (14) was dried *in vacuo*. However, ^1H NMR experiments reveal that $Cp^*Ta(NAr)(Et)(I)$ does not interact with phosphine in solution, even when cooled to a temperature of -50°C.

Green and Brookhart[20] have noted that agostic C-H groups have infrared bands in the region υ(C-H) *ca.* 2350 - 2700 cm^{-1} as a consequence of the decreased force constant of agostic C-H bonds. Interestingly, the infrared spectrum of compound (14) reveals a broad absorption at 2350 cm^{-1} that could offer the intriguing possibility of an agostic interaction in (14). This would rationalise the suprising reluctance of PMe_3 to interact with the metal centre.

The 250 MHz ^1H NMR spectrum (C_6D_6) of (14) reveals multiplets at δ 0.90 and 0.77 ppm and a triplet resonance at δ 1.92 ppm ($^3J_{HH}$ = 8 Hz) corresponding to diastereotopic methylene hydrogens and methyl hydrogens of the ethyl ligand respectively. The ^{13}C NMR spectrum (100 MHz, C_6D_6) shows signals at δ 67.61 ppm (J_{CH} = 123 Hz) and δ 15.41 ppm (J_{CH} = 126 Hz) attributable to the α and β ethyl carbons, neither of these resonances show J_{CH} coupling constants characteristic of agostic interactions[20].

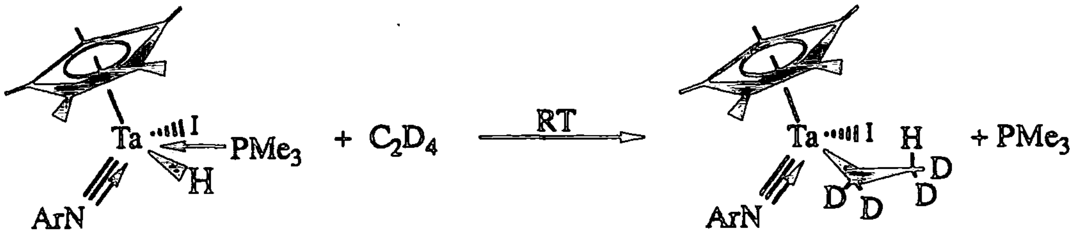
Cp*Ta(NAr)(Et)(I) (14) does not readily undergo the reverse β-hydrogen elimination to afford the starting hydride compound. For example, monitoring of a reaction of (14) with *d*$_4$-ethylene by ^{1}H NMR spectroscopy shows that no deuterium incorporation into (14) occurs below *ca.* 70°C. This observation allowed us to ascertain whether a β-agostic bond between the ethyl group and the metal centre was present since a partially deuterated Ta-ethyl ligand ($TaCD_2CD_2H$), could be prepared with no subsequent deuterium scrambling within the ethyl ligand at ambient temperature. (Equation 4.10).



(13) (*d*$_4$ -14) (4.10)

It was anticipated that if a β-agostic interaction were present the β-carbon J_{CH} coupling constant of 126 Hz previously determined for (14) would be dramatically reduced in magnitude on partial deuteration through the 'isotopic perturbation of resonance' phenomenon[22]. However, a deuterium decoupled 150 MHz ^{13}C NMR spectrum of Cp*Ta(NAr)(CD_2CD_2H)(I) (*d*$_4$ -14) (C_6D_6) acquired by Dr. J. A. Parkinson at the Edinburgh University Ultra High Field NMR Service, reveals that although the β-carbon of interest shifts up field to δ 14.60 ppm, a shift consistent with the isotopic substitution of two deuterons, the J_{CH} coupling constant remains unchanged at 126 Hz corresponding to the presence of a normal C-H bond. Furthermore, the 400 MHz ^{1}H NMR spectrum shows that the ethyl β-hydrogen resonance of (*d*$_4$ -14) demonstrates an isotopic shift of 0.065 ppm on partial deuteration the magnitude of which is invariant over the temperature range +50°C to -50°C, again suggesting the absence of an agostic interaction.

Cp*Ta(NAr)(Et)(I) (14) does not readily undergo the reverse β-hyudrogen elimination to afford the starting hydride compound. For example, monitoring of a reaction of (14) with d_4-ethylene by ^{1}H NMR spectroscopy shows that no deuterium incorporation into (14) occurs below *ca.* 70^{o}C. This observation allowed us to ascertain whether a β-agostic bond between the ethyl group and the metal centre was present since a partially deuterated Ta-ethyl ligand (TaCD_2CD_2H), could be prepared with no subsequent deuterium scrambling within the ethyl ligand at ambient temperature. (Equation 4.10).



(13) (d_4-14) (4.10)

It was anticipated that if a β-agostic interaction were present the β-carbon J_{CH} coupling constant of 126 Hz previously determined for (14) would be dramatically reduced in magnitude on partial deuteration through the 'isotopic perturbation of resonance' phenomenon^{22}. However, a deuterium decoupled 150 MHz ^{13}C NMR spectrum of Cp*Ta(NAr)(CD_2CD_2H)(I) (d_4-14) (C_6D_6) acquired by Dr. J. A. Parkinson at the Edinburgh University Ultra High Field NMR Service, reveals that although the β-carbon of interest shifts up field to δ 14.60 ppm, a shift consistent with the isotopic substitution of two deuterons, the J_{CH} coupling constant remains unchanged at 126 Hz corresponding to the presence of a normal C-H bond. Furthermore, the 400 MHz ^{1}H NMR spectrum shows that the ethyl β-hydrogen resonance of (d_4-14) demonstrats an isotopic shift of 0.65 ppm on partial deuteration the magnitude of which is invariant over the temperature range +50^{o}C to -50^{o}C, again suggesting the absence of an agostic interaction.

Variable temperature 400 MHz ^{1}H NMR experiments (C_7D_8) reveal that cooling a solution of the per-protio (ethyl)tantalum species (14) to -50°C intriguingly results in one of the ethyl ligand diastereotopic methylene hydrogen resonances changing to afford a quartet structure, whilst its geminal partner is severely broadened. Moreover, the resonances of the ethyl CH_3 group occur as two overlapping triplets at -50°C indicating the possibility of two inequivalent environments for the ethyl ligand in (14). However, no such resolution is observed for the methylene resonances (Figure 4.4).

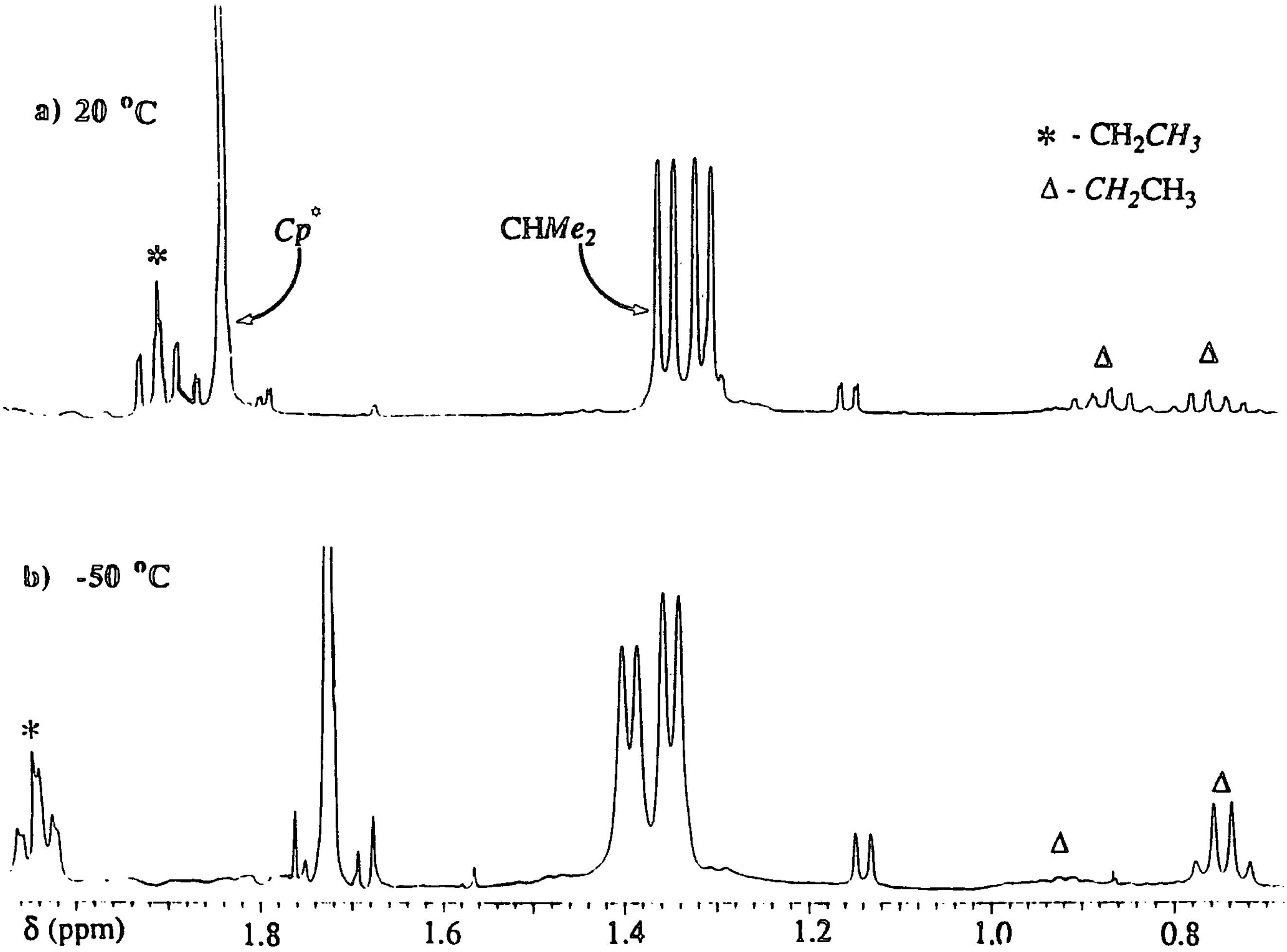


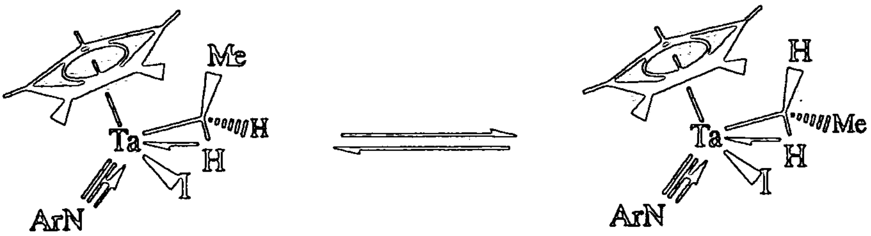
Figure 4.4 *400 MHz ^{1}H NMR spectrum (C_7D_8) of the alkyl region of Cp*Ta(NAr)(Et)(I) (14) a) at 20 °C and b) -50 °C.*

Recently, work by Erker and co-workers[23] has suggested that a number of (alkenyl)zirconocene complexes, $Cp_2Zr(alkenyl)X$ (X = Cl, Br, I), may possess weak α-agostic interactions in preference to those involving β-hydrogens. Hence, the low temperature ^1H NMR spectrum of the related complex $Cp^{*}Ta(NAr)(Et)(I)$ (14) could correspond to α-agostic interactions being 'frozen out' between the ethyl ligand and the tantalum centre. The anticipated β-agostic interaction possibily is disfavoured due to steric congestion attributable to the large ancillary iodide ligand. The severe broadening demonstrated by one of the methylene hydrogens is believed to arise due to through-bond quadropolar relaxation by iodine[24]. Hence, if α-agostic interactions are present it is the hydrogen corresponding to the broadened methylene resonance that is interacting with the tantalum since it will experience a greater coupling to iodine.

Furthermore, the quartet structure of the remaining visible methylene hydrogen indicates that geminal coupling between the α-hydrogens of the ethyl unit is very small corresponding to distortion of an sp^3 -hybridised C-H bond[25], a phenomenon which would arise through an α-agostic interaction. The triplet structure of the β-hydrogen resonances of the ethyl unit indicates that coupling ($^3J_{HH}$) to the two methylene hydrogens is coincident rather than showing that the methylene hydrogens are equivalent.

An alternative explanation to describe the low temperature ^1H NMR spectrum of complex (14) involves the formation of a weak interaction between a methylene hydrogen of the ethyl group and the iodine ligand, either independently, or in conjunction with an α-agostic C-H-Ta interaction. At low temperature such an interaction will severely broaden one methylene resonance preferentially, while potentially locking the ethyl ligand in one of two possible orientations as observed in the ^1H NMR spectrum. If a methylene hydrogen-iodine rather than an α-agostic interaction were to be present this could rationalise the absence of a temperature dependent chemical shift for the methylene hydrogen resonances of (14)[20] Establishing the precise nature of the ethyl ligand binding mode will undoubtedly require a crystal structure determination.

(4.5a)



(4.5b)

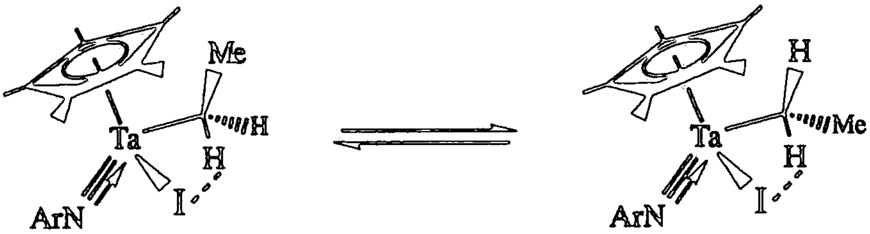


Figure 4.5 *a)Possible α-agostic interactions in (14).*

b) Potential H-I interactions in (14).

Treatment of a benzene solution of Cp*Ta(NAr)(Et)(I) (14) with an excess of ethylene, and subsequent monitoring by 250 MHz ^{1}H NMR spectroscopy, reveals no consumption of ethylene, even when the solution is warmed for prolonged periods at *ca.* 100°C. The reluctance of ethylene to insert directly into the Ta-C bond may be attributed to either the strength of the Ta-C bond already present, or more likely to steric crowding around the metal centre. Since ^{1}H NMR studies suggest that in contrast to the phosphino-carbene Cp*Ta(η^2-CHPMe$_2$)(H)(I)(PMe$_3$) (10), compound (13) will not dimerise ethylene, no reactions of the (monohydrido)tantalum complex (13) with other α-olefins were investigated.

4.6 Study of the Reactivity of Group 5 Half-Sandwich Imido Complexes with α-Olefins Through Industrial Placements within B.P. Chemicals Ltd.

For many years it has been known that the soluble bis-cyclopentadienyl complexes Cp_2MCl_2 (M = Ti, Zr) in the presence of aluminium alkyl co-catalysts polymerise ethylene[8]. Recent versions of this catalyst system incorporating chiral zirconocene complexes and aluminoxane co-catalysts, have been shown to polymerise propylene to highly isotactic polypropylene[26].

Through our understanding of the isolobal relationship between Cp and imido units it was envisaged that a number of the Group 5 half-sandwich imido complexes described within this thesis may offer potential catalysts for the oligomerisation or polymerisation of α-olefins. Hence, a programme of work was undertaken utilising the polymerisation bench reactors at B.P. Chemicals sites at Grangemouth and Hull to investigate a variety of complexes for possible catalytic activity with olefin feedstocks.

The types of potential catalyst system studied fall into three distinct categories:

(a) Classical homogeneous catalyst systems analogous to the well-established Ziegler-Natta systems such as Cp_2TiCl_2 / $EtAlCl_2$[8].

(b) Coordinatively unsaturated niobium and tantalum alkyl complexes both with or without co-catalyst.

(c) Single component catalysts which avoid the necessity to employ co-catalysts.

4.6.1 Results.

(a) Attempts to afford a classical homogeneous catalyst system for α-olefin oligomerisation/polymerisation reactions focused on the treatment of the dichlorides $CpNb(NMe)Cl_2$[27], $CpNb(NAr)Cl_2$, and $Cp^{*}Ta(NAr)Cl_2$ with a variety of alkylating agents: diethylaluminium chloride, dimethylaluminium chloride, triethylboron, (octyl-butyl)magnesium and methylaluminoxane.

The Cp'M(NR)Cl_2/alkylating agent systems under investigation were treated with ethylene, propylene and but-1-ene feedstocks under a variety of temperature (0 - 110°C) and pressure (150 - 600psi) regimes.

However, detailed analysis employing G.C., G.C. mass spectrometry, infrared and NMR spectroscopies of a variety of liquid and gas samples obtained from reaction runs failed to provide conclusive evidence for oligomerisation or polymerisation of the olefin feedstock.

(b) The 16 electron coordinatively unsaturated dialkyl species Cp*M(NAr)Me_2 (M = Nb[28], Ta) both in the presence of, and in the absence of co-catalyst, failed to afford any evidence of olefin oligomerisation / polymerisation activity when treated with ethylene (90°C; 600 psi). This observation is in agreement with previous ^{1}H NMR reactions where ethylene has been shown not to insert into the M-C bonds of Cp*Ta(NAr)Me_2[27].

(c) Cp*Ta(NAr)(η^2-C_2H_4)$_2$ may be regarded as a possible intermediate in a catalytic cycle and hence no co-catalyst is required. Moreover, since Schrock[11,19,21] has previously shown that olefins may be catalytically dimerised *via* tantallacycle species, it was hoped that Cp*Ta(NAr)(η^2-C_2H_4)$_2$ may demonstrate similar activity.

However, monitoring of the treatment of Cp*Ta(NAr)(η^2-C_2H_4)$_2$ with ethylene at high temperature (120 °C) and pressure (600 psi), failed to afford conclusive proof of oligomerisation or polymerisation of the olefin feedstock. This is presumably a reflection of the stability of the tantallacycle complex employed, since previous investigations described within this thesis have shown Cp*Ta(NAr)(η^2-C_2H_4)$_2$ to be stable in the presence of olefins.

Consideration of the isoelectronic relationship between the fragments [Cp'M(NR)] (M = Nb, Ta) and [Cp_2M] (M = Ti, Zr, Hf) would suggest that the half-sandwich imido complexes described herein may be expected to couple olefins together. A number of factors may contribute to the lack of reactivity of the niobium- and tantalum(imido) complexes investigated. Steric congestion around the metal centre could prevent attack at vacant sites by olefin substrates. Moreover, when treated with an alkylating agent, the complexes under consideration could potentially decompose as

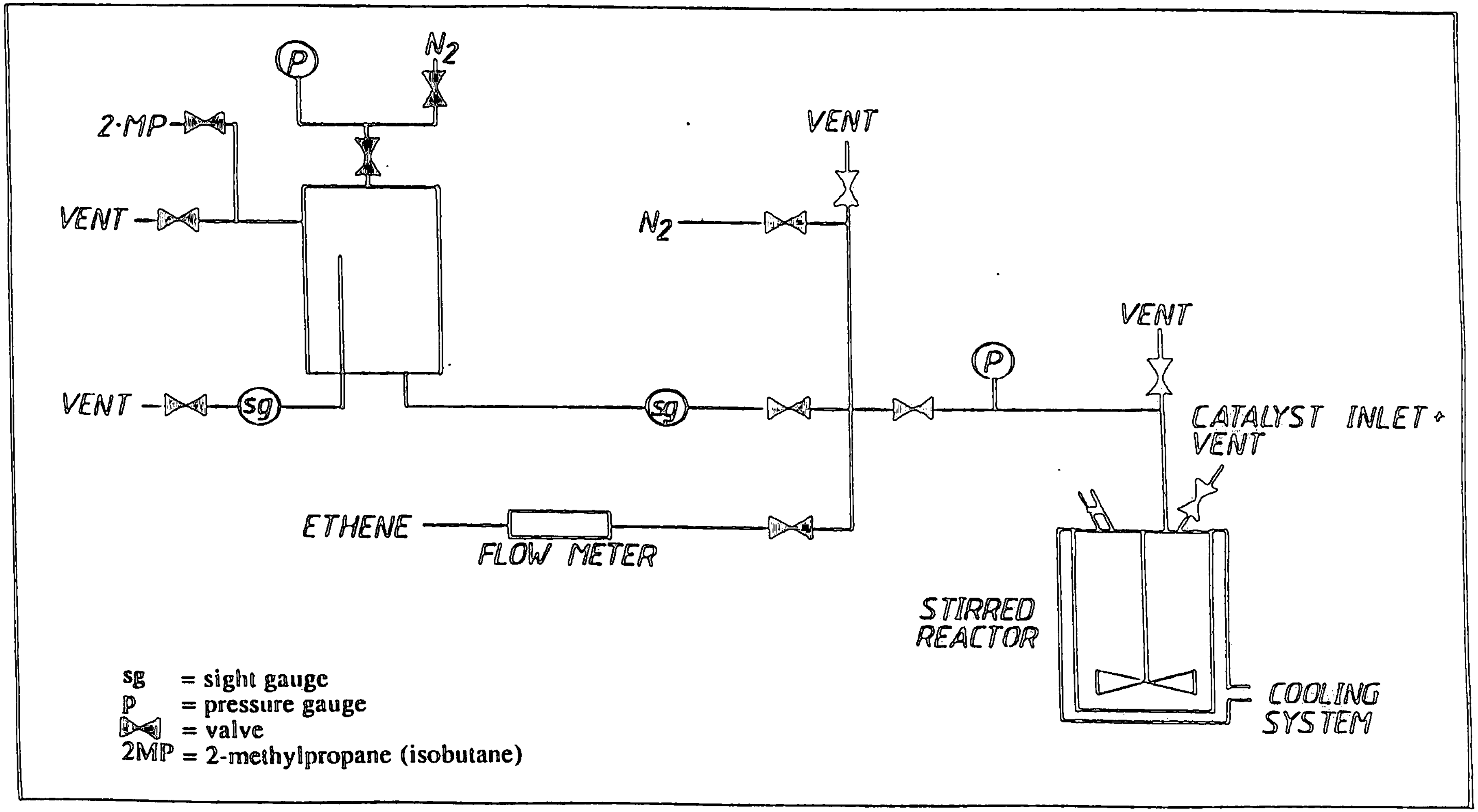


Figure 4.6 *Schematic representation of the bench reactor used within B.P. Chemicals Ltd.*

a consequence of an interaction between the ancillary imido group and the Lewis Acid co-catalyst.

4.7 Summary.

Catalytic oligomerisation of the olefins ethylene, propylene, and but-1-ene is observed with Cp*Ta(η^2-CHPMe$_2$)(H)$_2$(PMe$_3$) (1). The initial insertion products of these may be identified by ^{1}H NMR spectroscopy as the base-free (dialkyl)tantalum species Cp*Ta(η^2-CHPMe$_2$)R$_2$ (R = Et (2); ^{n}Pr (3); ^{n}Bu (4)). Investigation into the mechanism of the oligomerisation reactions primarily employing NMR spectroscopy reveal that a pathway involving metallacycle intermediates is most probable. Treatment of the related dihydride Cp*Ta(NAr)(H)$_2$(PMe$_3$) (6) with ethylene or propylene however affords only slow consumption of α-olefins *via* a metallacycle mechanism. In contrast to compound (1), the tantallacycle derivatives of Cp*Ta(NAr)(H)$_2$(PMe$_3$) (6) demonstrate remarkable thermal stability, not readily affording higher olefins.

The reactivity of Cp*Ta(η^2-CHPMe$_2$)(H)$_2$(PMe$_3$) (1) can be moderated by generation of the mono-halide derivative Cp*Ta(η^2-CHPMe$_2$)(H)(I)(PMe$_3$) (10), where clean dimerisation of ethylene to but-1-ene is observed by ^{1}H NMR spectroscopy. However, it has not proved possible to elucidate the dimerisation mechanism with certainty. Treatment of the (monohydrido)tantalum complex Cp*Ta(NAr)(H)(I)(PMe$_3$) (13) with an excess of ethylene affords the thermally stable monoethyl species Cp*Ta(NAr)(Et)(I) (14), which on addition of excess ethylene fails to insert further olefin into the Ta-C bond *via* a Cossee-Arlman type mechanism. A reaction pathway involving metallacycle species derived from (13) is disfavoured for the consumption of ethylene, as the imido moeity of Cp*Ta(NAr)(Et)(I) is anticipated to remain as a four electron donor to the tantalum.

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CHAPTER FIVE

Experimental Details

5.1 General.

5.1.1 Experimental Techniques.

All manipulations of air and / or moisture sensitive materials were performed on a conventional vacuum / inert atmosphere (nitrogen or argon) line using standard Schlenk and cannular techniques, or in an inert atmosphere (nitrogen or argon) filled glove box.

Elemental analyses were performed by the microanalytical services of this department.

Infrared spectra were recorded on Perkin-Elmer 577 and 457 grating spectrophotometers using CsI windows. Absorbtions abbreviated as: vs (very strong), s (strong), m (medium), w (weak), br (broad), sh (shoulder).

Mass spectra were recorded on a VG 7070E Organic Mass Spectrometer.

NMR spectra were recorded on the following instruments, at the frequencies listed, unless stated otherwise: Bruker AMX500 ^{1}H (500.14 MHz), ^{31}P (202.46 MHz); Varian VXR400, ^{1}H (399.95 MHz), ^{2}H (61.40 MHz), ^{13}C(100.58 MHz); Bruker AC 250, ^{1}H (250.13 MHz), ^{13}C (62.90 MHz), ^{31}P (101.26 MHz); Varian Gemini 200, ^{1}H (199.98 MHz), ^{13}C (50.29 MHz).The following abbreviations have been used for band multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet). Chemical shifts are quoted as δ in ppm with respect to the following references, unless stated otherwise: ^{31}P (dilute aq. H_3PO_4, 0 ppm); ^{13}C (C_6D_6, 128.0 ppm, $CDCl_3$, 77.0 ppm, C_7D_8, 125.2 ppm); ^{1}H (C_6D_6, 7.15 ppm, $CDCl_3$, 7.24 ppm, C_7D_8, 6.98 ppm, CD_2Cl_2, 5.35 ppm).

5.1.2 Solvents and Reagents

The following NMR solvents were dried by vacuum distillation from a suitable drying agent (in parentheses) and stored under nitrogen or vacuum prior to use: d_6-benzene (phosphorus (V) oxide), d_8-toluene (phosphorus (V) oxide), d-chloroform (phosphorus (V) oxide), d_2-dichloromethane (phosphorus (V) oxide).

The following solvents were dried by prolonged reflux over a suitable drying agent, being freshly distilled and deoxygenated before use (drying agent in parentheses): toluene (sodium metal), petroleum ether (40-60°C) (lithium aluminium hydride), pentane (lithium aluminium hydride), heptane (sodium metal), octane (lithium aluminium hydride), tetrahydrofuran (sodium benzophenone ketyl), acetonitrile (calcium hydride), dichloromethane (calcium hydride), 1,2-dichloroethane (calcium hydride), carbon tetrachloride (calcium hydride) and diethylether (lithium aluminium hydride).

The following chemicals were prepared by previously published procedures: NaC_5H_5[1], PMe_3[2], $CpNbCl_4$[3], Cp^*TaCl_4[4], Me_3SiNHR[5], Cp_2FeBPh_4[6], R_3NHBPh_4[7], $^nBu_3SnCp$[8], Me_3CCH_2MgCl[9].

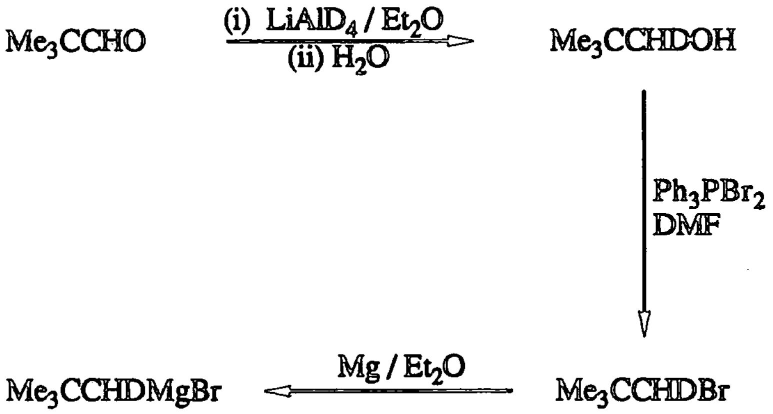
The following chemicals were obtained commercially and used as recieved unless stated otherwise: tantalum pentachloride (Aldrich), niobium pentachloride (Aldrich), but-2-yne (Aldrich), triphenylphosphine (BDH), chloromethylsilane (Aldrich, distilled before use), heptamethyldisazane (Aldrich, dried and stored over 4Å molecular sieves), n-butyl lithium (Aldrich, 1.6M in hexanes), 2,6-diisopropylphenylaniline (Aldrich, distilled before use), 2,6-lutidine (Aldrich, distilled before use), triethylamine (Aldrich), triphenylphosphoniumbromide (Aldrich), lithium aluminium deuteride (MSD Isotopes), neopentyl chloride (Aldrich), neopentyl bromide (Aldrich), methylmagnesium chloride 3.0M in THF (Aldrich), ethylmagnesium chloride 2.0M in diethylether (Aldrich), n-propylmagnesium chloride 2.0M in diethylether (Aldrich), phenylmagnesium chloride 2.0M in THF (Aldrich), magnesium turnings (Aldrich), sodium (Aldrich), methyl iodide (Aldrich), ethylene (Air Products), d^4 -ethylene (MSD

Isotopes), propylene (Aldrich), but-1-ene (Aldrich), oct-1-ene (Aldrich), hydrogen (Aldrich), carbon monoxide (Aldrich), tetrafluoroboric acid (Aldrich, diethylether complex 85%), silver tetrafluoroborate (Aldrich), silver triflate (Aldrich), sodium tetraphenylborate (Aldrich).

5.2 Experimental Details to Chapter 2.

5.2.1 Preparation of d_1-Neopentyl Magnesium Bromide ($Me_3CCDHMgBr$):

The synthetic transformations involved are outlined in Scheme 5.1[10].



Scheme 5.1

5.2.1.a Preparation of $Me_3CCDHOH$.

Pivaldehyde (20.0g, 0.232 moles), is added to a stirring suspension of $LiAlD_4$ (5.0g, 0.120 moles) in dry diethylether (400 mL) in a 1L round bottom flask cooled to *ca.* -78°C *via* a pressure equalizing dropping funnel. An immediate exothermic reaction ensued, and the solution was stirred for a further 6 hrs. Addition of water (32.4g, 1.8 moles) to consume excess $LiAlD_4$ afforded a white suspension which was then filtered and the supernatant solution dried over $MgSO_4$ for 1 hr. The diethylether was then removed under reduced pressure to afford a white solid, which was distilled to purity, (112-4°C, 760 mmHg). Yield, 8.61g, 42%.

5.2.1.b Preparation of $Me_3CCDHBr$.

Neopentyl alcohol (8.6g, 0.10 moles) in dry DMF (40 mL) was added to a stirring suspension of Ph_3PBr_2 (55.0g, 0.13 moles) in dry DMF (200 mL) in a 1L round bottom flask at RT *via* a pressure equalizing dropping funnel. An immediate reaction ensued resulting in the consumption of the Ph_3PBr_2 suspension and the formation of a brown solution. The volatile components were distilled off the residues (80-160°C, 760 mmHg) and transferred to a 2L seperating funnel containing water (200 mL). The organic phase was subsequently collected and distilled to purity (106°C, 760 mmHg). Yield, 6.60g, 45%.

5.2.1.c Preparation of $Me_3CCDHMgBr$.

A solution of $Me_3CCDHBr$ (6.60g, 39 mmol) in diethylether (20 mL) was added dropwise to the stirring suspension of activated magnesium turnings (2.0g, 83 mmol), in diethylether (50 mL) to afford a grey suspension. After stirring for a further 12 hr the supernatant solution was filtered off the Mg residues to afford a yellow-brown grignard solution. The molarity of the grignard solution then being assertained *via* titration against butan-2-ol[11].

5.2.2 Reaction of $CpNbCl_4$ with $Me_3SiNH(2,6\text{-}^iPr_2C_6H_3)$:

Preparation of $CpNb(NAr)Cl_2$ (1) ($Ar = 2,6\text{-}^iPr_2C_6H_3$).

To a stirred suspension of $CpNbCl_4$ (0.50g, 1.67 mmol) in dichloromethane (50 mL) at 0°C, was added 2,6-lutidine (0.18g, 1.67 mmol) *via* syringe. To this was added dropwise a solution of $Me_3SiNH(2,6\text{-}^iPr_2C_6H_3)$ (0.41g, 3.3mmol) in dichloromethane (20 mL). The mixture was stirred at RT for 12 hrs to afford a deep red solution. The solvent was removed under reduced pressure to give a red solid which was extracted from the 2,6-lutidinium hydrochloride with diethylether (2 x 100 mL). The diethylether was then removed under reduced pressure to yield an oily red solid which was subsequently washed with petroleum ether (40/60), (2 x 10 mL) at *ca.* -78°C. The residue was then recrystallised from a concentrated n-pentane solution (50 mL) to yield deep red needle-like crystals. Yield, 0.55g, 81%.

Elemental analysis for $C_{17}H_{22}NCl_2Nb$ Found (Required): %C, 50.1 (50.5); %H, 5.3 (5.5); %N, 3.1 (3.5); %Cl, 17.8 (17.5); %Nb 22.0 (23.0).

Infrared data (Nujol, CsI, cm^{-1}): 3052(w), 3029(w), 1622(w), 1588(w), 1425(w), 1350(w), 1310(w,sh), 1332(m), 1285(m), 1114(w), 1024(w), 986(w), 934(w), 856(m), 843(w), 831(w), 819(s), 798(s), 758(vs), 457(w), 402(m), 382(m), 321(w).

Mass spectral data (CI, isobutane carrier gas, m/z, ^{35}Cl): 403 $[M]^+$, 388 $[M-Me]^+$, 368 $[M-Cl]^+$, 228 $[M-NAr]^+$.

^1H NMR data (250MHz, d_6-benzene, 298K): 1.24 (d, 12, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 3.72 (sept., 2, $^3J_{HH}$ = 6.9 Hz, $CHMe_2$), 5.82 (s, 5, C_5H_5), 6.88 (t, 1, $^3J_{HH}$ = 6.6 Hz, *p*-C_6H_3), 6.98 (d, 2, $^3J_{HH}$ = 7.5 Hz, *m*-C_6H_3).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 24.07 (q, J_{CH} = 126 Hz, $CHMe_2$), 28.52 (d, J_{CH} = 128 Hz, $CHMe_2$), 113.52 (d, J_{CH} = 178 Hz, C_5H_5), 122.82 (d, J_{CH} = 158 Hz, *m*-C_6H_3), 126.65 (d, J_{CH} = 159 Hz, *p*-C_6H_3), 145.49 (s, *o*-C_6H_3), 152.01 (s, *ipso* -C_6H_3) .

5.2.3 Reaction of $Cp^{\circ}TaCl_4$ with $Me_3SiNH(2,6\text{-}^iPr_2C_6H_3)$:

Preparation of $Cp^{\circ}Ta(NAr)Cl_2$ *(2) (Ar =* $2,6\text{-}^iPr_2C_6H_3$*).*

To a stirred suspension of $Cp^{\circ}TaCl_4$ (7.64g, 16.69 mmol) in dichloroethane (100 mL) at 70°C, was added $Me_3SiNH(2,6\text{-}^iPr_2C_6H_3)$ (8.36g, 33.38 mmol) *via* syringe. The yellow suspension was consumed over a period of 10 days to yield an orange-red solution. Removal of the volatile components under reduced pressure, followed by washing with cold n-pentane (15 mL) to remove amine afforded an orange powder. Extraction of the solid with toluene (100 mL) follwed by concentration and cooling to *ca.* -78°C afforded orange moisture sensitive crystals. Yield, 6.80g, 73%.

Elemental analysis for $C_{22}H_{32}NCl_2Ta$ Found (Required): %C, 46.5 (47.0); %H, 5.8 (5.7); %N, 2.3 (2.5).

Infrared data (Nujol, CsI, cm^{-1}): 2920(br, s), 2850(s), 1460(s), 1445(sh, m), 1380(s), 1350(s), 1300(w), 1105(w), 1030(br, w), 980(w), 805(m), 765(s), 720(br, m), 375(m), 355(s), 350(m).

Mass spectral data (EI, m/z, ^{35}Cl, ^{181}Ta): 561 $[M]^+$, 546 $[M\text{-}Me]^+$, 386 $[M\text{-}NAr]^+$.

^1H NMR data (400MHz, d_6-benzene, 298K): 1.33 (d, 12, $^3J_{HH}$ = 7.2 Hz, $CHMe_2$), 1.85 (s, 15, C_5Me_5), 3.53 (sept., 2, $^3J_{HH}$ = 7.2 Hz, $CHMe_2$), 6.88 (t, 1, $^3J_{HH}$ = 6.8 Hz, *p*-C_6H_3), 7.16 (d, 2, $^3J_{HH}$ = 6.8 Hz, *m*-C_6H_3).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 11.22 (q, J_{CH} = 128 Hz, C_5Me_5), 24.44 (q, J_{CH} = 130 Hz, $CHMe_2$), 28.16 (d, J_{CH} = 127 Hz, $CHMe_2$), 121.39 (s, C_5Me_5), 122.25 (d, J_{CH} = 144 Hz, *m*-C_6H_3), 124.97 (d, J_{CH} = 158 Hz, *p*-C_6H_3), 145.46 (s, *o*-C_6H_3), 148.28 (s, *ipso* -C_6H_3).

5.2.4 Reaction of $CpNb(NAr)Cl_2$ with Trimethylphosphine:

Preparation of $CpNb(NAr)(PMe_3)Cl_2$ *(3) (Ar =* $2,6\text{-}^iPr_2C_6H_3$*).*

Trimethylphosphine (0.26g, 3.38 mmol) was condensed onto a frozen solution of $CpNb(NAr)Cl_2$ (1.01g, 2.47 mmol) in toluene (50 mL), at -196°C. After warming to RT and stirring for 30 mins a yellow suspension was formed. Removal of solvent under reduced pressure afforded a yellow powder. Yield, 0.91g, 77%.

Elemental analysis for $C_{20}H_{31}NCl_2NbP$ Found (Required): %C, 53.2 (50.0); %H, 6.8 (6.3); %N, 2.6 (2.9).

Note: Consistently high carbon analyses were obtained due to the lability of the PMe_3 ligand when $CpNb(NAr)Cl_2$ is dried *in vacuo*.

Infrared data (Nujol, CsI, cm^{-1}): 3120(w), 3090(w), 3050(w), 2850(s), 1460(s), 1420(m), 1380(m), 1330(m), 1290(m), 1280(m), 1020(m), 960(s), 820(s), 760(s), 370(w), 330(w), 300(m).

Mass spectral data (EI m/z, ^{35}Cl): 404 $[M - PMe_3]^{+\cdot}$

^1H NMR data (400MHz, d_8-toluene, 328K): 1.23 (d, 12, $^3J_{HH}$ = 6.0 Hz), ($CHMe_2$), 3.87 (sept., 2, $^3J_{HH}$ = 6.0 Hz, $CHMe_2$), 6.03 (s, 5, C_5H_5), 6.87 (t, 1, $^3J_{HH}$ = 8.4 Hz, *p*-C_6H_3), 6.99 (d, 2, $^3J_{HH}$ = 8.4 Hz, *m*-C_6H_3).

^{13}C NMR data (100MHz, d_8-toluene, 328K): 24.35 ($CHMe_2$), 27.88 ($CHMe_2$), 113.96 (C_5H_5), 123.11 (*m*-C_6H_3), 126.39 (*p*-C_6H_3), 145.03 (*o*-C_6H_3), not resolved (*ipso*-C_6H_3).

5.2.5 Reaction of $Cp^*Ta(NAr)Cl_2$ with Trimethylphosphine:

Preparation of $Cp^*Ta(NAr)(PMe_3)Cl_2$ (4) (Ar = 2,6-$^{i}Pr_2C_6H_3$).

Onto a frozen orange solution of $Cp^*Ta(NAr)Cl_2$ (29mg, 0.05 mmol) in d_8-toluene (0.7 mL) in an NMR tube was condensed trimethylphosphine (4mg, 0.05 mmol) at -196°C. After being sealed, the NMR tube was warmed to RT to afford a yellow solution of $Cp^*Ta(NAr)(PMe_3)Cl_2$.

Attempted isolation of $Cp^*Ta(NAr)(PMe_3)Cl_2$ afforded only $Cp^*Ta(NAr)Cl_2$ due to the lability of the trimethylphoshine when $Cp^*Ta(NAr)(PMe_3)Cl_2$ was dried *in vacuo*.

^{1}H NMR data (400MHz, d_8-toluene, 298K): 0.92 (d, 9, $^{2}J_{PH}$ = 1.2 Hz, P*Me$_3$*), 1.37 (d, 12, $^{3}J_{HH}$ = 6.8 Hz, CH*Me$_2$*), 1.95 (s, 15, C_5*Me$_5$*), 3.59 (sept., 2, $^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 6.90 (t, 1, $^{3}J_{HH}$ = 7.6 Hz, *p*-C_6H_3), 7.17 (d, 2, $^{3}J_{HH}$ = 7.6 Hz, *m*-C_6H_3).

^{13}C NMR data (100MHz, d_8-toluene, 298K): 11.24 (q, J_{CH} = 128 Hz, C_5*Me$_5$*), 16.22 (qd, J_{CH} = 127 Hz, J_{CP} = 9 Hz, P*Me$_3$*), 24.51 (q, J_{CH} = 126 Hz, CH*Me$_2$*), 28.02 (d, J_{CH} = 128 Hz, *C*HMe$_2$), 121.15 (s, *C$_5$*Me$_5$), 122.26 (d, J_{CH} = 153 Hz, *p*-C_6H_3), 129.21 (d, J_{CH} = 164 Hz, *m*-C_6H_3), 144.99 (s, *o*-C_6H_3), 148.02 (s, *ipso* -C_6H_3).

^{31}P NMR data (101MHz, d_8-toluene, 298K): -57.47.

5.2.6 Reaction of $CpNb(NAr)Cl_2$ with MeMgCl:

Preparation of $CpNb(NAr)(Me)Cl$ (5) (Ar = 2,6-$^{i}Pr_2C_6H_3$).

To a stirring solution of $CpNb(NAr)Cl_2$, (1.00g, 2.48 mmol) in diethylether (50 mL) at -78°C was added MeMgCl as a 3M solution in THF (0.82mL, 2.28mmol) *via* syringe. The solution was allowed to stir at RT for 2 hrs to give an orange-red suspension. Filtration of the supernatant solution and removal of the solvent under reduced pressure yielded an oily-orange solid. The solid was washed with cold n-pentane (2 x 5 mL) to give an orange solid which when extracted into n-pentane as a concentrated solution, afforded orange crystals on cooling to *ca.* -78°C. Yield, 0.33g, 35%.

Elemental analysis for $C_{18}H_{25}NClNb$ Found (Required): %C, 56.2 (56.3); %H, 6.4 (6.6); %N, 3.2 (3.6).

Infrared data (Nujol, CsI, cm^{-1}): 3030(w), 2940(s), 2900(s), 2860(s), 1620(w), 1460(s), 1430(m), 1380(m), 1330(m), 1280(m), 800(m), 750(s), 480(w), 390(m).

Mass spectral data (EI, m/z, ^{35}Cl): 383 $[M]^+$, 368 $[M-Me]^+$.

^1H NMR data (250MHz, d_6-benzene, 298K): 1.27 (d, 12, $^3J_{HH}$ = 7.5 Hz, $CHMe_2$), 1.34 (s, 3, *Me*), 3.80 (sept., 2, $^3J_{HH}$ = 7.5 Hz, $CHMe_2$), 5.64 (s, 5, C_5H_5), 6.97 (t, 1, $^3J_{HH}$ = 5.0 Hz, *p*-C_6H_3), 7.06 (d, 2, $^3J_{HH}$ = 5.0 Hz, *m*-C_6H_3).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 24.37 (q, J_{CH} = 131 Hz, $CHMe_2$), 28.47 (d, J_{CH} = 126 Hz, $CHMe_2$), 40.36 (br, $\upsilon^{1/2}$ = 65 Hz, *Me*), 110.00 (d, J_{CH} = 176 Hz, C_5H_5), 122.65 (d, J_{CH} = 156 Hz, *m*-C_6H_3), 125.22 (d, J_{CH} = 160 Hz, *p*-C_6H_3), 144.62 (s, *o*-C_6H_3), 152.23 (s, *ipso* -C_6H_3).

5.2.7 Reaction of $CpNb(NAr)(PMe_3)Cl_2$ with MeMgCl:

Preparation of $CpNb(NAr)(PMe_3)(Me)Cl$ (6) (Ar = 2,6-$^iPr_2C_6H_3$).

To a stirring suspension of $CpNb(NAr)(PMe_3)Cl_2$, (0.39g, 8.13 mmol) in diethylether (70 mL), at *ca.* -78°C, was added MeMgCl as a 3M solution in THF (0.27

mL, 8.13 mmol) *via* syringe. The suspension was filtered to leave the $MgCl_2$ residue, and the solvent removed under reduced pressure to afford a yellow solid. The solid was washed with cold n-pentane (2 x 5 mL) and extracted into diethylether as a concentrated solution and recrystallised as yellow-orange crystals at *ca.* -78°C. Yield, 0.12g, 33%.

Elemental analysis for $C_{21}H_{34}NClNbP$ Found (Required): %C, 54.5 (54.9); %H, 7.5 (7.5); %N, 2.6 (3.0).

Infrared data (Nujol, CsI, cm^{-1}): 3020(m), 2900(s), 2840(s), 1580(w), 1420(s), 1380(m), 1330(s), 1280(m), 1130(s), 1020(w), 950(s), 800(s), 780(s), 750(m).

Mass spectral data (EI, m/z, ^{35}Cl): 383 $[M-PMe_3]^+$, 368 $[M-Me-PMe_3]^+$.

^{1}H NMR data (400MHz, d_6-benzene, 298K): 0.83 (d, 9, $^2J_{PH}$ = 3.0 Hz, P*Me$_3$*), 1.19, 1.30 (d, 12, $^3J_{HH}$ = 7.0 Hz, CH*Me$_2$*), 1.44 (s, 3, *Me*), 3.91 (sept., 2, $^3J_{HH}$ = 7.0 Hz, C*H*Me$_2$), 5.75 (s, 5, C_5*H$_5$*), 6.92 (t, 1, $^3J_{HH}$ = 7.0 Hz, *p*-C_6H_3), 7.15 (d, 2, $^3J_{HH}$ = 7.0 Hz, *m*-C_6H_3).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 15.02 (q, J_{CH} = 129 Hz, P*Me$_3$*), 24.30, 24.80 (q, J_{CH} = 126 Hz, CH*Me$_2$*), 27.64 (d, J_{CH} = 129 Hz, *C*HMe$_2$), 32.42 (br, $\upsilon^1/_2$ = 32 Hz, *Me*), 108.15 (d, J_{CH} = 177 Hz, *C$_5$*H$_5$), 123.01 (d, J_{CH} = 177 Hz, *m*-C_6H_3), 124.70 (d, J_{CH} = 160 Hz, *p*-C_6H_3), 144.91 (s, *o*-C_6H_3), 151.15 (s, *ipso* -C_6H_3).

5.2.8 Reaction of $Cp^*Ta(NAr)Cl_2$ with an Excess of MeMgCl :

Preparation of $Cp^*Ta(NAr)Me_2$ (7) (Ar = 2,6-$^iPr_2C_6H_3$).

Diethylether (40 mL), was condensed onto a mixture of $Cp^*Ta(NAr)Cl_2$ (0.90g, 1.60 mmol), and MeMgCl (0.36g, 4.80mmol) in an ampoule cooled at -196°C. On allowing the mixture to warm to RT an immediate reaction ensued leading to the formation of a lemon yellow solution and a pale precipitate, which after the introduction of one atmosphere of nitrogen was stirred for a further 1 hr. The supernatant solution was filtered from the $MgCl_2$ residue and the solvent removed under reduced pressure to afford a yellow solid, which was dried *in vacuo* for 2 days. Extraction of the solid into n-pentane (50 mL), and prolonged cooling to *ca.* -78°C to gave lemon-yellow needles. Yield, 0.66g, 79%.

Elemental analysis for $C_{24}H_{38}NTa$ Found (Required): %C, 55.2 (55.2); %H, 7.6 (7.3); %N, 2.6 (2.7).

Infrared data (Nujol, CsI, cm^{-1}): 2955(s), 2910(s), 2855(s), 1595(w), 1465(s), 1440(m), 1385(s), 1300(m), 1260(w), 1160(m), 1110(w), 1030(br, w), 990(w), 800(br, w), 760(s), 750(m), 720(br, w), 720(br, w), 505(m), 470(br, m), 360(br, w).

Mass spectral data (EI, m/z, ^{181}Ta): 521 $[M]^+$, 506 $[M-Me]^+$, 489 $[M-C_2H_8]^+$.

^1H NMR data (400MHz, d_6-benzene, 298K): 0.30 (s, 6 *Me*), 1.37 (d, 12, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$), 1.71 (s, 15, C_5Me_5), 3.69 (sept., 2, $^3J_{HH}$ = 6.8 Hz, *CH*Me$_2$), 6.98 (t, 1, $^3J_{HH}$ = 7.6 Hz, *p*-C_6H_3), 7.23 (d, 2, $^3J_{HH}$ = 7.6 Hz, *m*-C_6H_3).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 10.62 (q, J_{CH} = 127 Hz, C_5Me_5), 24.30 (q, J_{CH} = 126 Hz, CH*Me*$_2$), 28.09 (d, J_{CH} = 128 Hz, *C*HMe$_2$), 48.44 (q, J_{CH} = 118 Hz, *Me*), 116.01 (s, C_5Me$_5$), 122.20 (d, J_{CH} = 153 Hz, *m*-C_6H_3), 122.48 (d, J_{CH} = 157 Hz, *p*-C_6H_3), 144.11 (s, *o*-C_6H_3), 151.48 (s, *ipso* -C_6H_3).

5.2.9 Reaction of $Cp^*Ta(NAr)Cl_2$ with MeMgCl :

Preparation of $Cp^*Ta(NAr)(Me)Cl$ *(8) (Ar =* $2,6\text{-}^iPr_2C_6H_3$*).*

Diethylether (30 mL) was condensed into an ampoule containing a mixture of $Cp^*Ta(NAr)Cl_2$ (0.80g, 1.42 mmol) and MeMgCl (0.11g, 1.42 mmol) at -196°C. The mixture was allowed to warm over 3 hrs to RT and stirred for a further 12 hrs to afford an orange suspension. The supernatant solution was filtered off the residues and concentrated to half volume and subsequent cooling to *ca.* -78°C afforded orange crystals. Spectroscopic analysis (^1H NMR) showed the crystals to be a mixture of $Cp^*Ta(NAr)Cl_2$, $Cp^*Ta(NAr)(Me)Cl$ and $Cp^*Ta(NAr)Me_2$.

^{1}H NMR data (400MHz, d_6-benzene, 298K): 0.83 (s, 3 *Me*), 1.33, 1.37 (d, 12, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 1.76 (s, 15, C_5Me_5), 3.58 (sept., 2, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 6.93 (t, 1, $^3J_{HH}$ = 7.6 Hz, *p*-C_6H_3), 7.19 (d, 2, $^3J_{HH}$ = 7.6 Hz, *m*-C_6H_3).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 10.82 (q, J_{CH} = 127 Hz, C_5Me_5), 24.38 (q, J_{CH} = 126 Hz, $CHMe_2$), 28.16 (d, J_{CH} = 124 Hz, $CHMe_2$), 42.66 (q, J_{CH} = 121 Hz, *Me*), 118.13 (s, C_5Me_5), 122.19 (d, J_{CH} = 159 Hz, *m*-C_6H_3), 123.67 (d, J_{CH} = 157 Hz, *p*-C_6H_3), 144.43 (s, *o*-C_6H_3), 149.93 (s, *ipso* -C_6H_3).

5.2.10 Reaction of $CpNb(NAr)Cl_2$ with Me_3CCH_2MgCl:

Preparation of $CpNb(NAr)(CH_2CMe_3)Cl$ *(9) (Ar =* $2,6\text{-}^iPr_2C_6H_3$*).*

To a stirring solution of $CpNb(NAr)Cl_2$, (1.02g, 2.48mmol) in diethylether (50 mL), at *ca.* -78°C was added Me_3CCH_2MgCl as a 2.1M solution in diethylether (1.15 mL, 2.48 mmol), *via* syringe. The solution was warmed to RT and stirred for 2 hrs until an orange-brown colouration was afforded. The solution was filtered from the $MgCl_2$ residue and the solvent removed under reduced pressure to give an oily orange-red solid. The oil was extracted with cold n-pentane (2 x 5 mL) and the residue recrystallised from a concentrated solution of n-pentane to yielding red crystals upon prolonged cooling to *ca.* -78°C. Yield, 0.59g, 54%.

Elemental analysis for $C_{22}H_{33}NClNb$ Found (Required): %C, 60.0 (60.1); %H, 7.8 (7.6); %N, 3.1 (3.2).

Infrared data (Nujol, CsI, cm^{-1}): 3010(w), 2910(s), 2860(s), 1460(s), 1440(m), 1380(m), 1360(m), 1330(s), 1290(s), 1230(w), 1100(br), 1020(br), 980(m), 820(s), 760(s), 460(br), 380(m), 360(m).

Mass spectral data (EI, m/z, ^{35}Cl): 369 $[M\text{-}Cl\text{-}CH_2CMe_3]^+$.

^{1}H NMR data (250MHz, d_6-benzene, 298K): 1.15 (s, 9, $CH_2C\mathit{Me}_3$), 1.18, (d, 12, $^3J_{HH}$ = 7.5 Hz, $CH\mathit{Me}_2$), 1.64, 2.46 (d, 2, $^2J_{HH}$ = 12.5 Hz, $C\mathit{H}_2CMe_3$), 3.99 (sept., 2, $^3J_{HH}$ = 7.5 Hz, $C\mathit{H}Me_2$), 5.74 (s, 5, $C_5\mathit{H}_5$), 6.95 (t, 1, $^3J_{HH}$ = 7.5 Hz, *p*-C_6H_3), 7.06 (d, 2, $^3J_{HH}$ = 7.5 Hz, *m*-C_6H_3).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 23.99, 24.76 (q, J_{CH} = 126 Hz, $CH\mathit{Me}_2$), 28.07 (d, J_{CH} = 127 Hz, $\mathit{C}HMe_2$), 34.59 (q, J_{CH} = 124 Hz, $CH_2C\mathit{Me}_3$), 36.31 (s, CH_2CMe_3), 86.31 (br, $\upsilon^1/_2$ = 33 Hz, J_{CH} = 123 Hz*, $\mathit{C}H_2CMe_3$), 110.47 (d, J_{CH} = 176 Hz, C_5H_5), 123.09 (d, J_{CH} = 156 Hz, *m*-C_6H_3), 125.42 (d, J_{CH} = 160 Hz, *p*-C_6H_3) 145.73 (s, *o*-C_6H_3), 151.77 (s, *ipso* -C_6H_3).

*- Coupling constants obtained from ^{13}C satellites in ^{1}H NMR spectra.

5.2.11 Reaction of $CpNb(NAr)Cl_2$ with Me_3CCH_2MgBr: *Preparation of $CpNb(NAr)(CH_2CMe_3)Br$ (10) (Ar = 2,6-$^iPr_2C_6H_3$).*

A 0.31M diethylether solution of Me_3CCH_2MgBr (3.2mL, 1.0 mmol), was added dropwise to a stirred solution of $CpNb(NAr)Cl_2$ (0.40g, 1.0 mmol), in cold diethylether (30 mL) at *ca.* -78°C. On allowing to warm to RT the suspension adopted a red-brown colouration. After stirring for a further 9 hrs the supernatant solution was filtered off the residues and the solvent removed under reduced pressure to afford a red-brown solid. The solid was subsequently dissolved in n-pentane (10 mL) and cooled to *ca.* -78°C to yield orange-red crystals, which were collected and dried *in vacuo*. Yield, 0.17g, 35%.

Elemental analysis for $C_{22}H_{33}NBrNb$ Found (Required): %C, 54.4 (54.4); %H, 6.8 (6.8); %N, 2.7 (2.9).

Infrared data (Nujol, CsI, cm^{-1}): 2920(br, s), 2840(s), 2700(br, w), 1620(w), 1495(sh, m), 1460(s),1380(s), 1370(sh, m), 1330(m),1285(m), 1230(w), 1100(br, w), 1020(br, w), 975(w), 930(w), 815(sh, m), 805(s), 795(sh, m), 755(s), 730(m), 720(m), 370(br, w).

Mass spectral data (EI, m/z, ^{79}Br): 483 $[M]^+$, 412 $[M-CH_2CMe_3]^+$.

^1H NMR data (400MHz, d_6-benzene, 298K): 1.12 (s, 9, CH_2CMe_3), 1.30, 1.31 (d, 12, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 1.34, 2.54 (d, 2, $^2J_{HH}$ = 11.6 Hz, CH_2CMe_3), 4.06 (sept., 2, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 5.76 (s, 5, C_5H_5), 6.96 (t, 1, $^3J_{HH}$ = 7.6 Hz, *p*-C_6H_3), 7.06 (d, 2, $^3J_{HH}$ = 7.6 Hz, *m*-C_6H_3).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 23.73, 24.63 (q, J_{CH} = 126 Hz, CH*Me_2*), 27.88 (d, J_{CH} = 125 Hz, *C*HMe$_2$), 33.20 (q, J_{CH} = 125 Hz, CH$_2$C*Me_3*), 36.66 (s, CH$_2$*C*Me$_3$), 92.05 (br, $\upsilon^{1}/_{2}$ = 63 Hz, J_{CH} = 123 Hz*, *C*H$_2$CMe$_3$), 110.30 (d, J_{CH} = 126 Hz, *C*$_5$H$_5$), 123.15 (d, J_{CH} = 156 Hz, *m*-C$_6$H$_3$), 125.45 (d, J_{CH} = 160 Hz, *p*-C$_6$H$_3$), 145.23 (s, *o*-C$_6$H$_3$), 151.61 (s, *ipso* -C$_6$H$_3$).

*- Coupling constants obtained from ^{13}C satellites in ^{1}H NMR spectra.

5.2.12 Reaction of CpNb(NAr)Cl$_2$ with an Excess of Me$_3$CCH$_2$MgCl: *Preparation of CpNb(NAr)(CH$_2$CMe$_3$)$_2$ (11) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).*

To a stirring solution of (C$_5$H$_5$)Nb(NAr)Cl$_2$, (0.98g, 2.48mmol) in diethylether (50 mL) at *ca.* -78°C, was added Me$_3$CCH$_2$MgCl as a 2.2M solution in diethylether (4.51 mL, 9.92 mmol). The solution allowed to warm to RT and stirred for 4 hrs to afford an orange suspension. The solution was filtered from the MgCl$_2$ residue and the solvent removed under reduced pressure to give an brown solid. The solid was washed with cold n-pentane (2 x 5 mL) and the yellow residue extracted into n-pentane. Two further recrystallisations gave well formed yellow-orange crystals. Yield, 0.62g, 53%.

Elemental analysis for C$_{27}$H$_{44}$NNb Found (Required): %C, 68.1 (68.2); %H, 9.6 (9.3); %N, 2.6 (2.9).

Infrared data (Nujol, CsI, cm^{-1}): 3060(w), 2910(s), 2850(s), 2700(br), 1460(s), 1430(m), 1380(m), 1360(m), 1330(m), 1280(m), 1100(w), 1020(m), 980(m), 800(s), 750(s).

Mass spectral data (EI, m/z): 330 [M-2CH$_2$CMe$_3$]$^+$.

^{1}<u>*H NMR data*</u> (250MHz, d_6-benzene, 298K): 1.12 (s, 18, $CH_2C\mathit{Me_3}$), 1.12, 1.88 (d, 4, $^2J_{HH}$ = 11.8 Hz, $C\mathit{H_2}CMe_3$), 1.32 (d, 12, $^3J_{HH}$ = 7.5 Hz, $CH\mathit{Me_2}$), 4.08 (sept., 2, $^3J_{HH}$ = 7.5 Hz, $C\mathit{H}Me_2$), 5.86 (s, 5, $C_5\mathit{H_5}$), 6.98 (t, 1, $^3J_{HH}$ = 5.0 Hz, *p*-C_6H_3), 7.10 (d, 2, $^3J_{HH}$ = 5.0 Hz, *m*-C_6H_3).

^{13}<u>*C NMR data*</u> (100MHz, d_6-benzene, 298K): 24.53 (q, J_{CH} = 125 Hz, $CH\mathit{Me_2}$), 27.91 (d, J_{CH} = 128 Hz, $\mathit{C}HMe_2$), 34.25 (q, J_{CH} = 125 Hz, $CH_2C\mathit{Me_3}$), 36.44 (s, $CH_2\mathit{C}Me_3$), 85.68 (br, $\upsilon^1/_2$ = 41 Hz, J_{CH} = 113 Hz*, $\mathit{C}H_2CMe_3$), 107.41 (d, J_{CH} = 174 Hz, $\mathit{C_5}H_5$), 123.02 (d, J_{CH} = 155 Hz, *m*-C_6H_3), 123.93 (d, J_{CH} = 159 Hz, *p*-C_6H_3), 145.10 (s, *o*-C_6H_3), 152.20 (s, *ipso* -C_6H_3).

*- Coupling constants obtained from ^{13}C satellites in ^1H NMR spectra.

5.2.13 Reaction of $CpNb(NAr)Cl_2$ with an Excess of $Me_3CCHDMgBr$: *Preparation of $CpNb(NAr)(CHDCMe_3)_2$ (d_2-11) (Ar = 2,6-$^iPr_2C_6H_3$).*

The preparation of $CpNb(NAr)(CHDCMe_3)_2$ is undertaken by an analogous procedure to that described above for $CpNb(NAr)(CH_2CMe_3)_2$ (**11**).

^{1}<u>*H NMR data*</u> (400MHz, d_6-benzene, 298K): 1.11 (s, 18, $CHDC\mathit{Me_3}$), 1.12, 1.77 (br, 1, $C\mathit{H}DCMe_3$)*, 1.32 (d, 12, $^3J_{HH}$ = 7.5 Hz, $CH\mathit{Me_2}$), 4.02 (sept., 2, $^3J_{HH}$ = 7.5 Hz, $C\mathit{H}Me_2$), 5.87 (s, 5, $C_5\mathit{H_5}$), 6.98 (t, 1, $^3J_{HH}$ = 5.0 Hz, *p*-C_6H_3), 7.10 (d, 2, $^3J_{HH}$ = 5.0 Hz, *m*-C_6H_3).

*- The 2 other methylene hydrogen resonances are obscured by other signals.

5.2.14 Reaction of CpNb(NAr)Cl_2 with KCH_2Ph:

Preparation of CpNb(NAr)(CH_2Ph)Cl (13) (Ar = 2,6-$^iPr_2C_6H_3$).

Onto a mixture of CpNb(NAr)Cl_2, (1.20g, 2.97 mmol) and KCH_2Ph (0.41g, 3.12 mmol) in an ampoule at -196°C was condensed diethylether (50 mL). The mixture was allowed to warm over 2 hrs to RT and stirred for a further 6 hrs to afford a red-brown suspension. The supernatant solution was filtered from the KCl residue and the solvent removed under reduced pressure to give an oily red solid. The solid was extracted into n-pentane (15 mL) and prolonged cooling to *ca.* -30°C afforded pale yellow crystals. Yield, 0.3g, 22%.

Elemental analysis for $C_{24}H_{29}NClNb$ Found (Required): %C, 62.7 (62.7); %H, 6.5 (6.4); %N, 2.9 (3.1).

Infrared data (Nujol, CsI, cm^{-1}): 3040(w), 2910(s), 2840(s), 1590(w),1515(w), 1455(s), 1375(s), 1365(m), 1330(m), 1280(m), 1175(w), 1095(br, m), 1055(br, m), 1015(s), 810(s), 800(s), 755(s), 750(s), 685(m), 450(w), 370(br, w).

Mass spectral data (EI, m/z, ^{35}Cl): 459 $[M]^+$, 421 $[M\text{-}Cl]^+$, 368.$[M\text{-}C_7H_8]^+$.

^1H NMR data (250MHz, d_6-benzene, 298K): 1.28, 1.30 (d, 12, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$), 2.85, 3.29 (d, 2, $^2J_{HH}$ = 7.5 Hz, C*H*$_2$Ph), 4.01 (sept., 2, $^3J_{HH}$ = 7.0 Hz, C*H*Me$_2$), 5.64 (s, 5, C_5H_5), 6.72 (d, 2, $^3J_{HH}$ = 7.4 Hz, *o*-C_6H_5), 6.95 (t, 1, $^3J_{HH}$ = 7.5 Hz, *p*-C_6H_3), 6.98 (t, 2, $^3J_{HH}$ = 7.4 Hz, *m*-C_6H_5), 7.05 (d, 2, $^3J_{HH}$ = 7.5 Hz, *m*-C_6H_3), 7.37(t, 1, $^3J_{HH}$ = 7.4 Hz, *p*-C_6H_5).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 24.14, 24.66 (q, J_{CH} = 131 Hz, CH*Me*$_2$), 27.83 (d, J_{CH} = 129 Hz, *C*HMe$_2$), 50.90 (t, J_{CH} = 134 Hz, *C*$H_2C_6H_5$),

108.21 (d, J_{CH} = 176 Hz, C_5H_5), 122.82 (d, J_{CH} = 156 Hz, *m*-C_6H_3), 124.52 (s, *ipso*-C_6H_5), 125.19 (d, J_{CH} = 160 Hz, *p*-C_6H_3), 131.00 (d, J_{CH} = 160 Hz, *m*-C_6H_5), 131.38 (d, J_{CH} = 161 Hz, *p*-C_6H_5), 132.68 (d, J_{CH} = 159 Hz, *o*-C_6H_5), 144.69 (s, *o*-C_6H_3), 152.79 (s, *ipso* -C_6H_3).

5.2.15 Reaction of Cp°Ta(NAr)Cl_2 with KCH_2Ph:

Preparation of Cp°Ta(NAr)(CH_2Ph)$_2$ (14) (Ar = 2,6-$^iPr_2C_6H_3$).

Diethylether (50 mL) was condensed onto a mixture of Cp°Ta(NAr)Cl_2, (0.75g, 1.33 mmol) and KCH_2Ph (0.38g, 2.93 mmol) in an ampoule at -196°C. The mixture was allowed to warm over 1 hrs to RT and stirred for a further 2 hrs to afford an orange suspension. Subsequent filteration of the supernatant solution from the residues and removal of the solvent under reduced pressure gave an oily orange solid. Extraction of the solid into n-pentane (20 mL) and cooling at *ca*. -78°C afforded moisture-sensitive orange crystals. Yield, 0.65g, 73%.

Elemental analysis for $C_{36}H_{46}NTa$ Found (Required): %C, 63.6 (64.2); %H, 6.9 (6.9); %N, 1.9 (2.1).

Infrared data (Nujol, CsI, cm^{-1}): 3060(m), 3010(s), 2940(br, s), 2850(s), 2720(w), 1595(s), 1485(s), 1460(br, s), 1430(s), 1380(s), 1360(m), 1335(s), 1290(s), 1255(w), 1210(m), 1195(m), 1185(w), 1105(br, m), 1060(m), 1050(m), 1030(m), 1000(w), 980(m), 935(w), 895(w), 820(m), 800(m), 790(s), 755(s), 740(s), 730(sh, m), 690(s), 495(w), 435(br, w).

Mass spectral data (EI, m/z, ^{181}Ta): 584 $[M-C_7H_8]^+$, 490 $[M-C_{14}H_{15}]^+$.

^1H NMR data (400MHz, d_6-benzene, 298K): 1.30 (d, 12, $^3J_{HH}$ = 6.8 Hz, CHMe_2), 1.65 (s, 15, C_5Me_5), 2.12, 2.39 (d, 4, $^2J_{HH}$ = 13.6 Hz, CH_2Ph), 3.73 (sept., 2,

$^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 6.82-6.86, 7.02-7.11 (*o, m, p*-C_6H_5), 6.95 (t, 1, $^3J_{HH}$ = 8.0 Hz, *p*-C_6H_3), 7.19 (d, 2, $^3J_{HH}$ = 8.0 Hz, *m*-C_6H_3).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 10.70 (q, J_{CH} = 127 Hz, C_5Me_5), 25.13 (q, J_{CH} = 126 Hz, CH*Me*$_2$), 27.47 (d, J_{CH} = 128 Hz, *C*HMe$_2$), 73.35 (t, J_{CH} = 120 Hz, *C*H$_2$C$_6$H$_5$), 116.56 (s, *C*$_5$Me$_5$), 123.43 (d, J_{CH} = 191 Hz, *p*-C_6H_3), 145.18 (s, *ipso*-C_6H_5), 146.50 (s, *o*-C_6H_3), 150.63 (s, *ipso* -C_6H_3), not assigned (*m*-C_6H_3), not assigned (*o, m, p*-C_6H_5).

5.2.16 Reaction of Cp*Nb(NAr)(CH$_2$Ph)$_2$ with Trimethylphosphine: *Preparation of Cp*Nb(NAr)(η^1-CHPh(PMe$_3$) (15) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).*

Trimethylphosphine (0.08g, 0.99 mmol), was condensed onto a frozen solution of Cp*Nb(NAr)(CH$_2$Ph)$_2$ (0.39g, 0.66 mmol) in n-heptane (30 mL). On warming to 65°C the solution adopted a yellow colouration, and after stirring for a further 14 days the solution was concentrated to 10 mL to afford a red solution. Subsequent recrystallation of the solution at *ca.* -40°C gave orange needles which were collected and dried *in vacuo*. Yield, 0.10g, 28%.

Elemental analysis for $C_{32}H_{47}NNbP$ Found (Required): %C, 68.1 (67.5); %H, 8.3 (8.3); %N, 2.2 (2.5).

Infrared data (Nujol, CsI, cm^{-1}): 3040(w), 2930(s), 2840(s), 1585(w),1515(w), 1460(s), 1425(m), 1380(m), 1335(m), 1285(m), 1215(sh, m), 1120(m), 1025(w), 955(br, w), 815(m), 795(m), 770(w), 750(s), 735(w), 695(m), 380(br,m).

Mass spectral data (EI, m/z): 569 [M]$^+$, 493 [M-PMe$_3$]$^+$.

^{1}H NMR data (250MHz, d_6-benzene, 298K): 0.85 (d, 9, $^2J_{PH}$ = 7.6 Hz, P*Me$_3$*), 1.21, 1.32 (d, 12, $^3J_{HH}$ = 6.7 Hz, CH*Me$_2$*), 1.96 (s, 15, C$_5$*Me$_5$*), 4.21 (sept., 2, $^3J_{HH}$ = 6.7 Hz, C*H*Me$_2$), 6.91 (t, 1, $^3J_{HH}$ = 7.2 Hz, *p*-C_6H_3), 6.95-7.18 (*m*-C_6H_3, *m*-C_6H_5, *p*-C_6H_5), 7.75 (d, 2, $^3J_{HH}$ = 8.3 Hz, *o*-C_6H_5), 11.23 (d, 1, $^3J_{PH}$ = 5.4 Hz, C*H*Ph).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 11.52 (q, J_{CH} = 126 Hz, C$_5$*Me$_5$*), 16.75 (dq J_{CH} = 129 Hz, J_{CP} = 24 Hz, P*Me$_3$*), 24.76 (q, J_{CH} = 128 Hz, CH*Me$_2$*), 26.93 (d, J_{CH} = 127 Hz, *C*HMe$_2$), 112.38 (s, *C$_5$*Me$_5$), 121.58 (d, J_{CH} = 159 Hz, *m*-C_6H_3), 122.69, 127.54, 127.80 (*o, m, p*-C_6H_5), 124.24 (d, J_{CH} = 158 Hz, *p*-C_6H_3), 143.20 (s, *o*-C_6H_3), 148.20 (s, *ipso*-C_6H_5), 150.50 (s, *ipso* -C_6H_3), 268.60 (br, $\upsilon^1/_2$ = 35 Hz, *C*HC_6H_5).

^{31}P NMR data (101MHz, d_6-benzene, 298K): -1.56.

5.3 Experimental Details to Chapter 3.

5.3.1 Reaction of CpNb(NAr)Cl$_2$ with C_2H_5MgCl in the Presence of Trimethylphosphine:

Preparation of CpNb(NAr)(η^2-C_2H_4)(PMe$_3$) (1) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).

Trimethylphosphine (0.70g, 9.21 mmol), was condensed onto a frozen solution of CpNb(NAr)Cl$_2$ (0.75g, 1.86 mmol) in diethylether (100 mL). One atmosphere of nitrogen was then introduced and a 2M diethylether solution of C_2H_5MgCl (1.90 mL, 3.80 mmol) added *via* syringe. The mixture was allowed to cautiously warm to RT to afford an orange suspension. After stirring for a further 12 hrs the supernatant solution was filtered off the residue and the volatile components removed under reduced pressure to leave an oily orange solid. The solid was dissolved in n-pentane (70 mL), and cooled to *ca.* -78°C to yield orange crystals. Yield, 0.49g, 61%.

Elemental analysis for $C_{22}H_{35}NNbP$ Found (Required): %C, 60.3 (60.5); %H, 8.2 (8.1); %N, 2.9 (3.2).

Infrared data (Nujol, CsI, cm^{-1}): 3030(m), 2900(br, s), 2840(s), 1580(w), 1460(s), 1425(s), 1380(m), 1360(m), 1335(s), 1285(s), 1260(w), 1180(br, w), 1130(s), 1100(m), 1010(w), 970(sh, m), 955(s), 935(sh, m), 840(w), 800(m), 755(s), 745(m), 720(m), 670(w), 450(br, w), 370(w).

Mass spectral data (EI, m/z): 438 $[M+H]^+$, 409 $[M-C_2H_4]^+$.

^{1}H NMR data (400MHz, d_6-benzene, 298K): 0.51, 1.32, 1.63 (m, 4, C_2H_4), 0.91 (d, 9, $^2J_{PH}$ = 7.6 Hz, PMe_3), 1.19, 1.26 (d, 12, $^3J_{HH}$ = 7.2 Hz, $CHMe_2$), 3.64 (sept., 2, $^3J_{HH}$ = 7.2 Hz, $CHMe_2$), 5.40 (s, 5, C_5H_5), 6.90 (t, 1, $^3J_{HH}$ = 7.2 Hz, *p*-C_6H_3), 6.99 (d, 2, $^3J_{HH}$ = 7.2 Hz, *m*-C_6H_3).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 17.03 (qd, J_{CH} = 129 Hz, J_{CP} = 24 Hz, PMe_3), 23.98 (q, J_{CH} = 125 Hz, $CHMe_2$), 24.50 (br, $\upsilon^1/_2$ = 52 Hz, C_2H_4), 27.47 (d, J_{CH} = 131 Hz, $CHMe_2$), 28.21 (br, d, $\upsilon^1/_2$ = 48 Hz, $^2J_{CP}$ = 12 Hz, C_2H_4), 100.56 (d, J_{CH} = 171 Hz, C_5H_5), 121.71 (d, J_{CH} = 158 Hz, *p*-C_6H_3), 122.42 (d, J_{CH} = 140 Hz, *m*-C_6H_3), 143.49 (s, *o*-C_6H_3), 152.23 (s, *ipso* -C_6H_3).

^{31}P NMR data (101MHz, d_6-benzene, 298K): 18 (br, $\upsilon^1/_2$ = 2.02 kHz).

5.3.2 Reaction of Cp°Ta(NAr)Cl$_2$ with C_2H_5MgCl in the Presence of Trimethylphosphine :

Preparation of Cp°Ta(NAr)(η^2-C_2H_4)(PMe_3) (2) (Ar = 2,6-$^iPr_2C_6H_3$).

Onto a frozen solution of Cp°Ta(NAr)Cl$_2$ (0.53g, 0.95 mmol) in diethylether (40 mL) was condensed trimethylphosphine (0.14g, 1.90 mmol). One atmosphere of nitrogen was then introduced and a 2M diethylether solution of C_2H_5MgCl (0.95 mL, 1.90 mmol) added *via* syringe. The mixture was allowed to cautiously warm to RT to afford a lemon-yellow suspension. After stirring for a further 12 hrs the supernatant solution was filtered off the residue and the volatile components removed under reduced pressure to leave an oily yellow solid. The solid was dissolved in n-pentane (30 mL), and cooled to *ca.* -30°C to yield lemon-yellow crystals. Yield, 0.25g, 46%.

Elemental analysis for $C_{27}H_{45}NTaP$ Found (Required): %C, 54.2 (54.5); %H, 7.6 (7.6); %N, 2.2 (2.4).

Infrared data (Nujol, CsI, cm^{-1}): 3025(w), 2920(br, s), 2850(s), 2720(w), 1590(w), 1460(s), 1430(s), 1380(s), 1360(m), 1345(s), 1305(w), 1295(s), 1285(m), 1260(w), 1150(br, w), 1105(s), 1025(br, w), 970(m), 955(s), 935(m), 845(w), 800(w), 755(s), 735(w), 720(m), 520(w), 340(w).

Mass spectral data (EI, m/z, ^{181}Ta): 567 [M-C_2H_4]$^+$, 519 [M-PMe_3]$^+$.

^1H NMR data (400MHz, d$_6$-benzene, 298K): -0.14, 0.95, 1.60 (m, 4, C_2H_4), 1.08 (d, 9, $^2J_{PH}$ = 7.2 Hz, P*Me$_3$*), 1.29, 1.31 (d, 12, $^3J_{HH}$ = 6.8 Hz, CH*Me$_2$*), 1.78 (s, 15, C_5Me_5), 3.94 (sept., 2, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 6.96 (t, 1, $^3J_{HH}$ = 6.8 Hz, *p*-C_6H_3), 7.09 (d, 2, $^3J_{HH}$ = 6.8 Hz, *m*-C_6H_3).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 11.14 (q, J_{CH} = 126 Hz, C_5Me_5), 16.87 (qd, J_{CH} = 129 Hz, J_{CP} = 26 Hz, PMe_3), 24.79 (q, J_{CH} = 120 Hz, $CHMe_2$), 26.59 (d, J_{CH} = 130 Hz, $CHMe_2$), 29.61 (td, J_{CH} = 147 Hz, $^2J_{CP}$ = 2 Hz, C_2H_4), 35.66 (td, J_{CH} = 149 Hz, $^2J_{CP}$ = 11 Hz, C_2H_4), 108.65 (s, C_5Me_5), 120.74 (d, J_{CH} = 159 Hz, *p*-C_6H_3), 122.57 (d, J_{CH} = 153 Hz, *m*-C_6H_3), 142.70 (s, *o*-C_6H_3), 153.00 (s, *ipso* -C_6H_3).

^{31}P NMR data (202MHz, d_6-benzene, 298K): -5.08.

5.3.3 Reaction of $CpNb(NAr)Cl_2$ with n-C_3H_7MgCl in the Presence of Trimethylphosphine :

Preparation of $CpNb(NAr)(\eta^2$-$C_3H_6)(PMe_3)$ (3) (Ar = 2,6-$^iPr_2C_6H_3$).

Trimethylphosphine (0.08g, 0.99 mmol), was condensed onto a frozen solution of $CpNb(NAr)Cl_2$ (0.20g, 0.50 mmol) in diethylether (15 mL). One atmosphere of nitrogen was then introduced and a 2M diethylether solution of n-C_3H_7MgCl (0.50 mL, 0.99 mmol) was added *via* syringe. The mixture was allowed to cautiously warm to RT to afford an orange suspension. After stirring for a further 3 hrs the supernatant solution was filtered off the residue and the volatile components removed under reduced pressure to leave an oily orange solid. The solid was dissolved in n-pentane (10 mL), and cooled to *ca*. -78°C to yield orange crystals. Yield, 0.12g, 51%.

Elemental analysis for $C_{23}H_{37}NNbP$ Found (Required): %C, 60.9 (61.2); %H, 8.4 (8.3); %N, 2.8 (3.1).

Infrared data (Nujol, CsI, cm^{-1}): 3040(w), 2950(s), 2920(s), 2850(s), 1590(w), 1460(s), 1440(sh, m), 1425(m), 1380(m), 1360(br, m), 1330(m), 1285(m), 1260(sh, w), 1180(br, w), 1150(br, w), 1100(w), 1015(w), 950(s), 935(m), 860(w), 805(m), 670(w), 450(br, w).

Mass spectral data (EI, m/z): 451 $[\mathrm{M}]^+$, 409 $[\mathrm{M{-}C_3H_6}]^+$, 375 $[\mathrm{M{-}PMe_3}]^+$.

^{1}H NMR data (400MHz, $\mathrm{d_6}$-benzene, 298K): (a) 0.90 (d, 9, $^2J_{\mathrm{PH}}$ = 7.2 Hz, $\mathrm{P}\mathit{Me}_3$), 1.20, 1.26 (d, 12, $^3J_{\mathrm{HH}}$ = 6.8 Hz, $\mathrm{CH}\mathit{Me}_2$), 2.02 (d, $^3J_{\mathrm{HH}}$ = 6.4 Hz, $\mathrm{C_2H_3}\mathit{Me}$), 3.68 (sept., 2, $^3J_{\mathrm{HH}}$ = 6.8 Hz, $\mathrm{C}\mathit{H}\mathrm{Me_2}$), 5.43 (d, 5, $^3J_{\mathrm{PH}}$ = 1.2 Hz, $\mathrm{C_5}\mathit{H}_5$), 6.91 (t, 1, $^3J_{\mathrm{HH}}$ = 7.2 Hz, *p*-$\mathrm{C_6H_3}$), 7.00 (d, 2, $^3J_{\mathrm{HH}}$ = 7.2 Hz, *m*-$\mathrm{C_6H_3}$). (b) 0.96 (d, 9, $^2J_{\mathrm{PH}}$ = 7.2 Hz, $\mathrm{P}\mathit{Me}_3$), 1.16, 1.22 (d, 12, $^3J_{\mathrm{HH}}$ = 7.2 Hz, $\mathrm{CH}\mathit{Me}_2$), 1.53 (d, $^3J_{\mathrm{HH}}$ = 6.4 Hz, $\mathrm{C_2H_3}\mathit{Me}$), 3.51 (sept., 2, $^3J_{\mathrm{HH}}$ = 7.2 Hz, $\mathrm{C}\mathit{H}\mathrm{Me_2}$), 5.48 (d, 5, $^3J_{\mathrm{PH}}$ = 1.2 Hz, $\mathrm{C_5}\mathit{H}_5$), not assigned (*m*, *p*- $\mathrm{C_6}\mathit{H}_3$). (c) 0.95 (d, 9, $^2J_{\mathrm{PH}}$ = 7.2 Hz, $\mathrm{P}\mathit{Me}_3$), 1.17, 1.23 (d, 12, $^3J_{\mathrm{HH}}$ = 6.8 Hz, $\mathrm{CH}\mathit{Me}_2$), 2.24 (d, $^3J_{\mathrm{HH}}$ = 6.4 Hz, $\mathrm{C_2H_3}\mathit{Me}$), 3.90 (sept., 2, $^3J_{\mathrm{HH}}$ = 6.8 Hz, $\mathrm{C}\mathit{H}\mathrm{Me_2}$), 5.40 (d, 5, $^3J_{\mathrm{PH}}$ = 1.2 Hz, $\mathrm{C_5}\mathit{H}_5$), not assigned (*m*, *p*-$\mathrm{C_6}\mathit{H}_3$). (d) 1.01 (d, 9, $^2J_{\mathrm{PH}}$ = 7.2 Hz, $\mathrm{P}\mathit{Me}_3$), 1.23, 1.29 (d, 12, $^3J_{\mathrm{HH}}$ = 6.8 Hz, $\mathrm{CH}\mathit{Me}_2$), 2.06 (d, $^3J_{\mathrm{HH}}$ = 6.4 Hz, $\mathrm{C_2H_3}\mathit{Me}$), 4.02 (sept., 2, $^3J_{\mathrm{HH}}$ = 6.8 Hz, $\mathrm{C}\mathit{H}\mathrm{Me_2}$), 5.35 (d, 5, $^3J_{\mathrm{PH}}$ = 1.2 Hz, $\mathrm{C_5}\mathit{H}_5$), not assigned (*m*, *p*- $\mathrm{C_6}\mathit{H}_3$).

^{13}C NMR data (100MHz, ^{1}H decoupled, $\mathrm{d_6}$-benzene, 298K): (a) 16.96 (J_{CP} = 24 Hz, $\mathrm{P}\mathit{Me}_3$), 25.98 ($\mathrm{C_2H_3}\mathit{Me}$), not assigned ($\mathrm{CH}\mathit{Me}_2$), 27.46 ($\mathit{C}\mathrm{HMe_2}$), 101.37 ($\mathit{C}_5\mathrm{H_5}$), 121.72 (*m*-$\mathrm{C_6H_3}$), 122.52 (*p*-$\mathrm{C_6H_3}$), 143.66 (*o*-$\mathrm{C_6H_3}$), 152.32 (br, $\upsilon^{1}/_{2}$ = 26 Hz, *ipso* -$\mathrm{C_6H_3}$). (b) 18.06 (J_{CP} = 22 Hz, $\mathrm{P}\mathit{Me}_3$), 25.20 ($\mathrm{C_2H_3}\mathit{Me}$), not assigned ($\mathrm{CH}\mathit{Me}_2$), 27.30 ($\mathit{C}\mathrm{HMe_2}$), 101.58 ($\mathit{C}_5\mathrm{H_5}$), 122.60 (*p*-$\mathrm{C_6H_3}$), 122.81 (*m*-$\mathrm{C_6H_3}$), 143.73 (*o*-$\mathrm{C_6H_3}$), not assigned (*ipso* -$\mathrm{C_6H_3}$). (c) 17.40 (J_{CP} = 23 Hz, $\mathrm{P}\mathit{Me}_3$), 25.95 ($\mathrm{C_2H_3}\mathit{Me}$), not assigned ($\mathrm{CH}\mathit{Me}_2$), 26.94 ($\mathit{C}\mathrm{HMe_2}$), 100.74 ($\mathit{C}_5\mathrm{H_5}$), 121.48 (*m*-$\mathrm{C_6H_3}$), 122.58 (*p*-$\mathrm{C_6H_3}$), 142.98 (*o*-$\mathrm{C_6H_3}$), 152.32 (br, $\upsilon^{1}/_{2}$ = 26 Hz, *ipso* -$\mathrm{C_6H_3}$). (d) 17.79 (J_{CP} = 22 Hz, $\mathrm{P}\mathit{Me}_3$), 24.35 ($\mathrm{C_2H_3}\mathit{Me}$), not assigned ($\mathrm{CH}\mathit{Me}_2$), 27.32 ($\mathit{C}\mathrm{HMe_2}$), 101.14 ($\mathit{C}_5\mathrm{H_5}$), 121.84 (*m*-$\mathrm{C_6H_3}$), 122.80 (*p*-$\mathrm{C_6H_3}$), 143.11 (*o*-$\mathrm{C_6H_3}$), not assigned (*ipso* -$\mathrm{C_6H_3}$),.

Both methine and methylene ^1H and ^{13}C NMR resonances the for propene ligand are not assigned.

5.3.4 Reaction of $Cp^*Ta(NAr)Cl_2$ with $n-C_3H_7MgCl$ in the Presence of Trimethylphosphine :

Preparation of $Cp^*Ta(NAr)(\eta^2-C_3H_6)(PMe_3)$ (4) (Ar = 2,6-$^iPr_2C_6H_3$).

Trimethylphosphine (0.07g, 0.89 mmol), was condensed onto a frozen solution of $Cp^*Ta(NAr)Cl_2$ (0.25g, 0.44 mmol) in diethylether (30 mL). One atmosphere of nitrogen was then introduced and a 2M diethylether solution of $n-C_3H_7MgCl$ (0.44 mL, 0.89 mmol) was added dropwise. The mixture was allowed to cautiously warm to RT to afford a lemon-yellow suspension. After stirring for a further 12 hrs the supernatant solution was filtered off the residue and the volatile components removed under reduced pressure to leave a orange solid. The solid was dissolved in n-pentane (5 mL), and cooled to *ca.* -30°C to yield orange crystals, which were collected and dried *in vacuo*. Yield, 0.11g, 41%.

Elemental analysis for $C_{28}H_{47}NPTa$ Found (Required): %C, 54.8 (55.2); %H, 7.8 (7.8); %N, 2.0 (2.3).

Infrared data (Nujol, CsI, cm^{-1}): 3.50(m), 2920(s), 2850(s), 2720(w), 1580(w), 1460(s), 1430(sh, m), 1380(s), 1360(m), 1340(br, s), 1290(m), 1260(m), 1160(w), 1100(br, m), 1020(br, m), 950(m), 885(w), 800(m), 750(s), 720(m), 350(br,w).

Mass spectral data (EI, m/z, ^{181}Ta): 567 $[M-C_3H_6]^+$, 533 $[M-PMe_3]^+$, 488 $[M-PMe_3-C_3H_6-3H]^+$.

^1H NMR data (400MHz, d_6-benzene, 298K): (a) 1.28 (d, 12, $^3J_{HH}$ = 6.8 Hz, $CH\mathit{Me}_2$), 1.41 (d, 9, $^2J_{PH}$ = 7.2 Hz, $P\mathit{Me}_3$), 1.76 (s, 15, $C_5\mathit{Me}_5$), 2.38 (dd, $^3J_{HH}$ = 6.4 Hz, $^4J_{PH}$ = 1.6 Hz, $C_2H_3\mathit{Me}$), 4.17 (sept., 2, $^3J_{HH}$ = 6.8 Hz, $C\mathit{H}Me_2$). (b) 1.16 (d, 9, $^2J_{PH}$ = 7.2 Hz, $P\mathit{Me}_3$), 1.28 (d, 12, $^3J_{HH}$ = 6.8 Hz, $CH\mathit{Me}_2$), 1.75 (s, 15, $C_5\mathit{Me}_5$), 2.30 (dd, $^3J_{HH}$ = 6.4 Hz, $^4J_{PH}$ = 1.6 Hz, $C_2H_3\mathit{Me}$), 4.05 (sept., 2, $^3J_{HH}$ = 6.8 Hz, $C\mathit{H}Me_2$). (c) 1.19 (d, 9, $^2J_{PH}$ = 7.2 Hz, $P\mathit{Me}_3$), 1.26 (d, 12, $^3J_{HH}$ = 6.8 Hz, $CH\mathit{Me}_2$), 1.81 (s, 15, $C_5\mathit{Me}_5$), 2.49 (dd, $^3J_{HH}$ = 6.4 Hz, $^4J_{PH}$ = 1.6 Hz, $C_2H_3\mathit{Me}$), 3.83 (sept., 2, $^3J_{HH}$ = 6.8 Hz, $C\mathit{H}Me_2$). (d) 1.11 (d, 9, $^2J_{PH}$ = 7.2 Hz, $P\mathit{Me}_3$), 1.32 (d, 12, $^3J_{HH}$ = 6.8 Hz, $CH\mathit{Me}_2$), 1.35 (dd, $^3J_{HH}$ = 6.4 Hz, $^4J_{PH}$ = 1.6 Hz, $C_2H_3\mathit{Me}$), 1.85 (s, 15, $C_5\mathit{Me}_5$), 4.28 (sept., 2, $^3J_{HH}$ = 6.8 Hz, $C\mathit{H}Me_2$).

Aryl ring hydrogens have not been assigned.

^{13}C NMR data (100MHz, ^1H decoupled, d_6-benzene, 298K): (a) 11.30 ($C_5\mathit{Me}_5$), 18.46 (J_{CP} = 24 Hz, $P\mathit{Me}_3$), 108.91 (C_5Me_5), 120.57 (p-C_6H_3), 122.33 (m-C_6H_3), 142.60 (o-C_6H_3), 152.34 (*ipso* -C_6H_3). (b) 10.78 ($C_5\mathit{Me}_5$), 16.79 (J_{CP} = 26 Hz, $P\mathit{Me}_3$), 108.58 (C_5Me_5), 120.60 (p-C_6H_3), 122.26 (m-C_6H_3), 141.41 (o-C_6H_3), 152.34 (*ipso* -C_6H_3). (c) 10.89 ($C_5\mathit{Me}_5$), 17.60 (J_{CP} = 24 Hz, $P\mathit{Me}_3$), 108.42 (C_5Me_5), 120.26 (p-C_6H_3), 122.70 (m-C_6H_3), 143.42 (o-C_6H_3), 152.34 (*ipso* -C_6H_3). (d) 11.65 ($C_5\mathit{Me}_5$), not assigned ($P\mathit{Me}_3$), 109.45 (C_5Me_5), not assigned (p-C_6H_3), 122.61 (m-C_6H_3), not assigned (o-C_6H_3), 152.34 (*ipso* -C_6H_3).

Both isopropyl and propene resonances are not assigned.

^{31}P NMR data (202MHz, d_6-benzene, 298K): (a) -4.89, (b) -4.70, (c) -5.32, (d) -15.46.

5.3.5 Reaction of CpNb(NAr)(η^2-C_3H_6)(PMe_3) with an Excess of Carbon Monoxide.

Preparation of CpNb(NAr)(CO)(PMe_3) (8) (Ar = 2,6-^{i}Pr$_2$$C_6H_3$).

One atmosphere of carbon monoxide was introduced into an ampoule containing a frozen solution of CpNb(NAr)(η^2-C_3H_6)(PMe_3) (0.30g, 0.65 mmol) in n-pentane (20 mL) cooled at -196°C. On allowing the solution to warm to RT, an immediate reaction ensued, resulting in the formation of a purple solution. The solution was filtered and then subsequently concentrated to afford a saturated solution. Recrystallisation from the n-pentane solution (10 mL) at *ca.* -30°C afforded cubic moisture sensitive crystals. Yield, 0.19g, 64%.

Elemental analysis for $C_{21}H_{29}NNbOP$ Found (Required): %C, 57.5 (57.7); %H, 7.3 (7.2); %N, 3.1 (3.2).

Infrared data (Nujol, CsI, cm^{-1}): 3040(m), 2920(s), 2850(s), 2720(w), 1870(s), 1825(m), 1585(w), 1460(s), 1425(s), 1380(s), 1360(m), 1340(s), 1325(sh, m), 1290(s), 1260(w), 1160(w), 1115(w), 1110(w), 1060(m), 1010(m), 1000(m), 960(sh, m), 950(s), 935(sh, m), 845(w), 810(s), 795(s), 775(s), 760(s), 735(m), 725(m), 670(m), 495(w), 365(w), 340(w), 300(br, w).

Mass spectral data (EI, m/z): 361 [M-PMe$_3$]$^+$, 332 [M-PMe$_3$-CO]$^+$, 275 [M- Ar]$^+$.

^{1}H NMR data (400MHz, d$_6$-benzene, 298K): 0.85 (d, 9, $^2J_{PH}$ = 7.2 Hz, P*Me$_3$*), 1.32 (d, 12, $^3J_{HH}$ = 6.8 Hz, CH*Me$_2$*), 4.06 (sept., 2, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 5.22 (s, 5, C$_5$*H$_5$*), 7.01 (t, 1, $^3J_{HH}$ = 7.2 Hz, *p*-C$_6$H$_3$), 7.11 (d, 2, $^3J_{HH}$ = 7.2 Hz, *m*-C$_6$H$_3$).

^{13}C NMR data (100MHz, d$_6$-benzene, 298K): 20.64 (qd, J_{CH} = 129 Hz, J_{CP} = 24 Hz, P*Me$_3$*), 23.58 (q, J_{CH} = 136 Hz, CH*Me$_2$*), 28.12 (d, J_{CH} = 128 Hz, *C*HMe$_2$), not

resolved (*CO*), 95.63 (d, J_{CH} = 173 Hz, C_5H_5), 122.03 (d, J_{CH} = 159 Hz, *p*-C_6H_3), 122.35 (d, J_{CH} = 154 Hz, *m*-C_6H_3), 141.53 (s, *o*-C_6H_3), 152.16 (br, $\upsilon^1/_2$ = 25 Hz, *ipso* -C_6H_3).

^{31}P NMR data (202MHz, d_6-benzene, 298K): 12.0 (br, $\upsilon^1/_2$ = 5.6 kHz).

5.3.6 Reaction of $Cp^{*}Ta(NAr)Cl_2$ with C_2H_5MgCl in the Presence of Ethylene :

Preparation of $Cp^{*}Ta(NAr)(\eta^2\text{-}C_2H_4)_2$ (12) (Ar = 2,6-$^iPr_2C_6H_3$).

A diethylether solution of $Cp^{*}Ta(NAr)Cl_2$ (1.00g, 1.78 mmol, in 50 mL diethylether) was frozen in an ampoule at -196^{o}C. A 2M diethylether solution of C_2H_5MgCl (1.78 mL, 3.56 mmol) was then added *via* syringe and the ampoule evacuated and sealed. The solution warmed to *ca.* -78^{o}C, one atmosphere of ethylene introduced and subsequently allowed to warm to RT to afford an orange suspension. After stirring for a further 12 hrs, the supernatant solution was filtered off the $MgCl_2$ residue, concentrated to half volume and cooled to *ca.* -78^{o}C to afford orange crystals. Yield, 0.61g, 63%.

Elemental analysis for $C_{26}H_{40}NTa$ Found (Required): %C, 56.8 (57.1); %H, 7.7 (7.4); %N, 2.4 (2.6).

Infrared data (Nujol, CsI, cm^{-1}): 3050(w), 2940(s), 2850(s), 2720(w), 1590(w), 1460(s), 1430(s), 1380(s), 1360(s), 1350(s), 1300(m), 1265(m), 1100(br, m), 1020(br, m), 985(w), 935(w), 795(m), 770(s), 750(s), 720(w), 530(w), 460(br, w), 360(m).

Mass spectral data (CI, isobutane carrier gas, m/z, ^{181}Ta): 548 $[M+H]^+$, 519 $[M+H-C_2H_4]^+$, 491 $[M-C_4H_8]^+$.

^1H NMR data (400MHz, d_6-benzene, 298K): 0.96, 1.68, 2.22, 2.48 (m, 8, C_4H_8), 1.39 (d, 12, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 1.73 (s, 15, C_5Me_5), 3.74 (sept., 2, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 7.00 (t, 1, $^3J_{HH}$ = 7.5 Hz, p-C_6H_3), 7.25 (d, 2, $^3J_{HH}$ = 7.5 Hz, m-C_6H_3).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 10.63 (q, J_{CH} = 127 Hz, C_5Me_5), 16.20 (t, J_{CH} = 129 Hz,C_4H_8), 24.46 (q, J_{CH} = 126 Hz, $CHMe_2$), 28.20 (d, J_{CH} = 124 Hz, $CHMe_2$), 53.54 (t, J_{CH} = 131 Hz,C_4H_8), 115.92 (s, C_5Me_5), 122.19 (d, J_{CH} = 152 Hz, m-C_6H_3), 122.91 (d, J_{CH} = 153 Hz, p-C_6H_3), 144.01 (s, o-C_6H_3), 157.70 (s, *ipso* -C_6H_3).

5.3.7 Reaction of $Cp^{\circ}Ta(NAr)(\eta^2\text{-}C_2H_4)_2$ with an Excess of Carbon Monoxide.

Preparation of $Cp^{\circ}\overline{Ta(NAr)[C(O)C_4H_8C}(O)]$ *(13) (Ar = 2,6-$^iPr_2C_6H_3$).*

One atmosphere of carbon monoxide was introduced into an ampoule containing a frozen solution of $Cp^{\circ}Ta(NAr)(\eta^2\text{-}C_2H_4)_2$ (0.25g, 0.46 mmol) in diethylether (40 mL), cooled at -196°C. On allowing the solution to warm to RT, an immediate reaction ensued, resulting in the formation of an orange solution. The solution was filtered and then subsequently concentrated to afford a saturated deep-red solution. Recrystallisation from the diethylether solution (10 mL) at *ca.* -30°C afforded orange crystals. Yield, 0.09g, 31%.

Elemental analysis for $C_{28}H_{40}NO_2Ta$ Found (Required): %C, 55.7 (55.8); %H, 6.8 (6.7); %N, 2.2 (2.3).

Infrared data (Nujol, CsI, cm^{-1}): 3025(w), 2920(s), 2850(s), 1630(w), 1590(w), 1540(w), 1460(s), 1435(s), 1380(s), 1350(s), 1300(m), 1265(br, w), 1215(br, w), 1190(w), 1105(m), 980(m), 935(w), 905(m), 800(br, w), 750(s), 720(br, m), 660(w), 605(m), 370(br, m).

Mass spectral data (EI, m/z, ^{181}Ta): 603 $[M]^+$, 428 $[M-Ar]^+$.

^{1}H NMR data (250MHz, d_6-benzene, 298K): 1.29 (d, 12, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$), 1.40, 1.65, 2.35, 2.65 (m, 8, [C(O)C_4H_8C(O)]), 1.96 (s, 15, C_5Me_5), 3.52 (sept., 2, $^3J_{HH}$ = 6.9 Hz, *C*HMe$_2$), 6.66 (t, 1, $^3J_{HH}$ = 7.8 Hz, *p*-C_6H_3), 7.13 (d, 2, $^3J_{HH}$ = 7.8 Hz, *m*-C_6H_3).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 10.44 (q, J_{CH} = 128 Hz, C_5Me_5), 23.03 (t, J_{CH} = 128 Hz, [C(O)C_4H$_8$C(O)]), 24.30 (q, J_{CH} = 126 Hz, CH*Me*$_2$), 27.40 (d, J_{CH} = 125 Hz, *C*HMe$_2$), 28.94 (t, J_{CH} = 131 Hz, [C(O)C_4H$_8$C(O)]), 118.79 (s, C_5Me$_5$), 121.03 (d, J_{CH} = 157 Hz, *p*-C_6H_3), 122.11 (d, J_{CH} = 153 Hz, *m*-C_6H_3), 133.74 (s, [*C*(O)C_4H_8*C*(O)]), 141.11 (s, *o*-C_6H_3), 150.86 (s, *ipso* -C_6H_3).

5.3.8 Reaction of Cp*Ta(NAr)(η^2-C_2H_4)(PMe$_3$) with an Excess of Carbon Monoxide.

*Preparation of Cp*Ta(NAr)(CO)(PMe$_3$) (15) (Ar = 2,6-$^iPr_2C_6H_3$).*

One atmosphere of carbon monoxide was introduced into an ampoule containing a frozen solution of Cp*Ta(NAr)(η^2-C_2H_4)(PMe$_3$) (0.26g, 0.43 mmol) in n-pentane (20 mL), cooled at -196°C. On allowing the solution to warm to RT, an immediate reaction ensued, resulting in the formation of an orange-brown solution. The solution was filtered and then subsequently concentrated to half volume. Recrystallisation from the n-pentane solution at *ca.* -30°C afforded very air-sensitive orange-brown crystals. Spectroscopic analysis by NMR showed the crystals to be a mixture of Cp*Ta(NAr)(η^2-C_2H_4)(PMe$_3$) and Cp*Ta(NAr)(CO)(PMe$_3$).

^{1}*H NMR data* (400MHz, d$_6$-benzene, 298K): 1.04 (d, 9, $^{2}J_{PH}$ = 7.2 Hz, P*Me$_3$*), 1.35, 1.37 (d, 12, $^{3}J_{HH}$ = 6.8 Hz, CH*Me$_2$*), 1.92 (s, 15, C$_5$*Me$_5$*), 4.07 (sept., 2, $^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 7.04 (t, 1, $^{3}J_{HH}$ = 8.4 Hz, *p*-C$_6$H$_3$), 7.13 (d, 2, $^{3}J_{HH}$ = 8.4 Hz, *m*-C$_6$H$_3$).

^{13}*C NMR data* (100MHz, ^{1}H decoupled, d$_6$-benzene, 298K): 11.38 (C$_5$Me$_5$), 20.99 (J_{CP} = 27 Hz, P*Me$_3$*), 23.81, 24.07 (CH*Me$_2$*), 27.65 (*C*HMe$_2$), 45.49 (*C*O), 105.78 (*C$_5$*Me$_5$), 121.32 (*p*-C$_6$H$_3$), 122.20 (*m*-C$_6$H$_3$), 141.32 (*o*-C$_6$H$_3$), 153.95 (*ipso* - C$_6$H$_3$).

^{31}*P NMR data* (202MHz, d$_6$-benzene, 298K): -6.15.

5.3.9 Reaction of CpNb(NAr)Cl$_2$ with Magnesium in the Presence of Trimethylphosphine:

Preparation of CpNb(NAr)(PMe$_3$)$_2$ (16) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).

Trimethylphosphine (0.56g, 7.40 mmol), was condensed onto a solution of CpNb(NAr)Cl$_2$, (0.75g, 1.86 mmol), and activated magnesium turnings (0.05g, 2.08 mmol), in THF (100 mL) cooled at -196°C. Upon warming to RT a yellow suspension characteristic of CpNb(NAr)(PMe$_3$)Cl$_2$ was formed. The yellow suspension darkened over a period of 6 hrs until a black colouration was afforded. The supernatant solution was subsequently filtered from the residues and the volatile components removed under reduced pressure to afford an extremely air-sensitive oily black solid which was dried briefly *in vacuo*. Yield, 0.43g, 48%.

Infrared data (Nujol, CsI, cm^{-1}): 2970(s), 2940(s), 2880(sh, s), 2870(s), 1625(br, m), 1460(s), 1440(sh, m), 1425(m), 1380(m), 1370(w), 1345(m), 1285(w), 1265(w), 1100(br, w), 1020(w), 950(m), 940(m), 800(s), 755(m), 745(m), 720(m), 660(w).

Mass spectral data (CI, isobutane carrier gas, m/z): 177 $[ArNH_2]^+$, 162 $[Ar+H]^+$, 77 $[PMe_3+H]^+$.

^1H NMR data (250MHz, d_6-benzene, 298K): 0.96 (br, $\upsilon^1/_2$ = 15 Hz, P*Me₃*), 0.99 (d, 12, $^3J_{HH}$ = 7.3 Hz, $CHMe_2$), 4.20 (sept., 2, $^3J_{HH}$ = 7.3 Hz, $CHMe_2$), 5.00 (s, 5, C_5H_5), 6.88 (t, 1, $^3J_{HH}$ = 7.1 Hz, *p*-C_6H_3), 7.02 (d, 2, $^3J_{HH}$ = 7.1 Hz, *m*-C_6H_3).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 24.26 (br, $\upsilon^1/_2$ = 6 Hz, PMe_3), 24.10 (q, J_{CH} = 125 Hz, $CHMe_2$), 27.25 (d, J_{CH} = 128 Hz, $CHMe_2$), 92.79 (d, J_{CH} = 172 Hz, C_5H_5), 120.01 (d, J_{CH} = 159 Hz, *p*-C_6H_3), 122.47 (d, J_{CH} = 153 Hz, *m*-C_6H_3), 140.94 (s, *o*-C_6H_3), 153.52 (br, $\upsilon^1/_2$ = 46 Hz, *ipso* -C_6H_3).

5.3.10 Reaction of $CpNb(NAr)Cl_2$ with PhMgCl in the Presence of Trimethylphosphine:

Preparation of $CpNb(NAr)Ph_2(PMe_3)$ (18) (Ar = 2,6-$^iPr_2C_6H_3$).

Trimethylphosphine (0.23g, 3.0 mmol), was condensed onto a solution of $CpNb(NAr)Cl_2$, (0.60g, 1.5 mmol), and PhMgCl (0.41g, 3.0mmol), in diethylether (30 mL) cooled at -196°C. Upon warming to RT an orange suspension was formed. After stirring for a further 4 hrs the supernatant solution was filtered off the $MgCl_2$ residue and concentrated. Recrystallisation from the diethylether solution (20 mL) at *ca.* -30°C afforded cubic orange crystals. Yield, 0.25g, 30%.

Elemental analysis for $C_{32}H_{41}NNbP$ Found (Required): %C, 68.3 (68.3); %H, 7.7 (7.3); %N, 2.3 (2.5).

Infrared data (Nujol, CsI, cm^{-1}): 2940(br, s), 2850(s), 2720(br, w), 1565(w), 1465(s), 1430(sh, m), 1380(s), 1370(sh, m), 1330(w), 1270(m), 1155(br, w), 1100(br, w), 1010(w), 805(m), 760(m), 755(sh, w), 725(s), 705(m), 330(w), 310(w).

Mass spectral data (EI, m/z): 485 $[M-C_6H_6]^+$, 409 $[M-C_6H_6-PMe_3]^+$.

^1H NMR data (400MHz, d_6-benzene, 298K): 0.60 (d, 9, $^2J_{PH}$ = 5.9 Hz, PMe_3), 1.32 (d, 12, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 4.19 (sept., 2, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 5.72 (s, 5, C_5H_5), 6.97 (t, 1, $^3J_{HH}$ = 7.2 Hz, *p*-C_6H_3), 7.08 (t, 2, $^3J_{HH}$ = 6.0 Hz, *p*-C_6H_5), 7.09 (d, 2, $^3J_{HH}$ = 7.2 Hz, *m*-C_6H_3), 7.21 (t, 4, $^3J_{HH}$ = 7.2 Hz, *m*-C_6H_5), 7.56 (br, $\upsilon^1/_2$ = 16.0 Hz, 4, *o*-C_6H_5).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 14.78 (qd, J_{CH} = 129 Hz, J_{CP} = 17 Hz, PMe_3), 25.07 (q, J_{CH} = 125 Hz, $CHMe_2$), 27.15 (d, J_{CH} = 129 Hz, $CHMe_2$), 108.90 (d, J_{CH} = 175 Hz, C_5H_5), 123.52 (d, J_{CH} = 156 Hz, *m*-C_6H_3), 124.01 (d, J_{CH} = 160 Hz, *p*-C_6H_3), 124.46 (d, J_{CH} = 159 Hz, *p*-C_6H_5), 126.95 (d, J_{CH} = 157 Hz, *m*-C_6H_5), 137.86 (d, J_{CH} = 154 Hz, *o*-C_6H_5), 142.44 (br, $\upsilon^1/_2$ = 30 Hz, *o*-C_6H_3), 154.17 (br, $\upsilon^1/_2$ = 50 Hz, *ipso* -C_6H_3), 177.62 (br, $\upsilon^1/_2$ = 80 Hz, *ipso*-C_6H_5).

^{31}P NMR data (101MHz, d_6-benzene, 298K): -18.30 (br, $\upsilon^1/_2$ = *ca.* 500 Hz).

5.3.11 Reaction of $Cp^*Ta(NAr)Cl_2$ with PhMgCl:

Preparation of $Cp^*Ta(NAr)(Ph)Cl$ (19) (Ar = $2,6\text{-}^iPr_2C_6H_3$).

Diethylether (40 mL) was condensed onto a mixture of $Cp^*Ta(NAr)Cl_2$, (0.75g, 1.33 mmol) and PhMgCl (0.18g, 1.33 mmol) in an ampoule at -196°C. The mixture was allowed to warm to RT and stirred for a further 12 hrs to afford a yellow suspension. The supernatant solution was filtered from the $MgCl_2$ residue and the solvent removed under reduced pressure to give an orange solid which was dried *in* *vacuo* for 48 hrs. The solid was extracted into n-pentane (10 mL) and prolonged cooling at *ca.* -78°C afforded orange crystals.Yield, 0.50g, 62%.

Elemental analysis for $C_{28}H_{37}NClTa$ Found (Required): %C, 55.5 (55.7); %H, 6.6 (6.2); %N, 2.3 (2.3).

Infrared data (Nujol, CsI, cm^{-1}): 3060(m), 2900(br, s), 2720(w), 1590(w), 1460(s), 1440(sh, m), 1360(s), 1340(sh, m), 1340(s), 1305(sh, m), 1295(m), 1265(m), 1160(br, w), 1100(br, w), 1065(m), 1025(m), 1025(br, w), 485(w), 800(m), 765(s), 730(s), 700(s), 455(w), 365(m).

Mass spectral data (EI, m/z, ^{35}Cl, ^{181}Ta): 603 $[M]^+$, 566 $[M\text{-}Cl]^+$, 526 $[M\text{-}C_6H_5]^+$.

^1H NMR data (200MHz, d_6-benzene, 298K): 1.77 (s, 15, C_5Me_5), 1.30, 1.38 (d, 12, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 3.84 (sept., 2, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 6.90 (t, 1, $^3J_{HH}$ = 7.4 Hz, *p*-C_6H_3), 7.07 (t, 1, $^3J_{HH}$ = 7.3 Hz, *p*-C_6H_5) 7.21 (d, 2, $^3J_{HH}$ = 7.4 Hz, *m*-C_6H_3), 7.25 (t, 2, $^3J_{HH}$ = 8.0 Hz, *m*-C_6H_5), 7.72 (d, 2, $^3J_{HH}$ = 8.0 Hz, *o*-C_6H_5).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 11.22 (q, J_{CH} = 127 Hz, C_5Me_5), 22.64, 24.92 (q, J_{CH} = 126 Hz, $CHMe_2$), 28.10 (d, J_{CH} = 128 Hz, $CHMe_2$), 119.65 (s, C_5Me_5), 122.49 (d, J_{CH} = 154 Hz, *m*-C_6H_3), 124.15 (d, J_{CH} = 158 Hz, *p*-C_6H_3), 127.08 (d, J_{CH} = 158 Hz, *m*-C_6H_5), 127.43 (d, J_{CH} = 156 Hz, *p*-C_6H_5), 137.28 (d, J_{CH} = 158 Hz, *o*-C_6H_5), 145.20 (s, *o*-C_6H_3), 149.85 (s, *ipso* -C_6H_3), 194.83 (s, *ipso*-C_6H_5).

5.3.12 Reaction of Cp*Ta(NAr)Cl$_2$ with an Excess of PhMgCl:

Preparation of Cp*Ta(NAr)Ph$_2$ (20) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).

To a mixture of Cp*Ta(NAr)Cl$_2$, (0.75g, 1.33 mmol) and PhMgCl (0.72g, 5.32 mmol) in an ampoule at -196°C was condensed diethylether (40 mL). The mixture was allowed to warm to RT and stirred for a further 36 hrs to afford a orange-red suspension. The supernatant solution was filtered from the MgCl$_2$ residue and the solvent removed under reduced pressure to give a red solid which was dried *in vacuo* for 2 days. The solid was extracted into n-pentane (20 mL) and prolonged cooling at *ca.* -35°C afforded red needle-like crystals. Yield, 0.33g, 38%.

Elemental analysis for C$_{34}$H$_{42}$NTa Found (Required): %C, 62.9 (63.3); %H, 6.6 (6.6); %N, 2.1 (2.2).

Infrared data (Nujol, CsI, cm^{-1}): 3010(m), 2900(s), 2840(s), 1455(s), 1430(sh, s), 1375(s), 1340(sh, s), 1335(s), 1290(m), 1255(m), 1090(br, m), 1060(m), 1045(m), 1015(br, m), 985(w), 975(w), 790(s), 745(s), 715(s), 690(s), 450(br, w), 355(w).

Mass spectral data (EI, m/z, ^{181}Ta): 645 [M]$^{+\cdot}$ 567 [M-C$_6$H$_6$]$^+$, 510 [M-C$_5$Me$_5$]$^+$.

^{1}H NMR data (250MHz, d$_6$-benzene, 298K): 1.20 (d, 12, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$), 1.82 (s, 15, C$_5$*Me*$_5$), 3.94 (sept., 2, $^3J_{HH}$ = 6.9 Hz, *CH*Me$_2$), 6.95 (t, 1, $^3J_{HH}$ = 7.6 Hz, *p*-C$_6$H$_3$), 7.04 (t, 2, $^3J_{HH}$ = 7.3 Hz, *p*-C$_6$H$_5$), 7.06 (d, 2, $^3J_{HH}$ = 7.6 Hz, *m*-C$_6$H$_3$), 7.21 (t, 4, $^3J_{HH}$ = 7.4 Hz, *m*-C$_6$H$_5$), 7.76 (d, 4, $^3J_{HH}$ = 7.9 Hz, *o*-C$_6$H$_5$).

^{13}C NMR data (100MHz, d$_6$-benzene, 298K): 11.49 (q, J_{CH} = 127 Hz, C$_5$*Me*$_5$), 24.80 (q, J_{CH} = 125 Hz, CH*Me*$_2$), 27.74 (d, J_{CH} = 128 Hz, *C*HMe$_2$), 118.44 (s, *C*$_5$Me$_5$), 122.60 (d, J_{CH} = 153 Hz, *m*-C$_6$H$_3$), 123.24 (d, J_{CH} = 157 Hz, *p*-C$_6$H$_3$), 127.44 (d, J_{CH} = 167 Hz, *p*-C$_6$H$_5$), 128.29 (d, J_{CH} = 158 Hz, *m*-C$_6$H$_5$), 136.42 (d,

J_{CH} = 156 Hz, *o*-C_6H_5), 145.24 (s, *o*-C_6H_3), 150.79 (s, *ipso* -C_6H_3), 197.98 (s, *ipso*-C_6H_5).

5.3.13 Thermolysis of CpNb(NAr)Ph_2(PMe_3) in n-Heptane :

Preparation of CpNb(NAr)(η^2-C_6H_4)(PMe_3) (21) (Ar = 2,6-$^iPr_2C_6H_3$).

A n-heptane solution of CpNb(NAr)Ph_2(PMe_3) (0.40g, 0.71 mmol, in 20 mL n-heptane), was stirred at 60°C for 3 days to afford a brown solution. The solution was subsequently filtered and the volatile components removed under reduced pressure to give a yellow-black powder. Extraction with diethylether (15 mL) and prolonged cooling at *ca.* -40°C afforded green cubic crystals. Yield, 0.27g, 78%.

Elemental analysis for $C_{26}H_{35}NNbP$ Found (Required): %C, 64.0 (64.4); %H, 7.3 (7.3); %N, 2.7 (2.9).

Infrared data (Nujol, CsI, cm^{-1}): 3020(m), 2920(s), 2850(s), 1565(m), 1460(s), 1450(sh, m), 1425(m), 1415(sh, m), 1380(m), 1360(w), 1345(m), 1335(s), 1310(w), 1285(s), 1245(w), 1150(m), 1100(br, w), 1015(br, w), 980(w), 970(m), 955(m), 940(sh, w), 795(s), 760(740(s), 730(w), 395(w), 295(w).

Mass spectral data (EI, m/z): 485 $[M]^+$, 409 $[M-C_6H_4]^+$, 158 [M-NAr-PMe_3-$C_6H_4]^+$.

^1H NMR data (400MHz, d_6-benzene, 298K): 0.97, 1.16 (d, 12, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$), 1.13 (d, 9, $^2J_{PH}$ = 8.0 Hz, P*Me*$_3$), 3.56 (sept., 2, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 5.67 (d, 5, $^3J_{PH}$ = 1.2 Hz, C_5H_5), 6.89 (t, 1, $^3J_{HH}$ = 7.2 Hz, *p*-C_6H_3), 6.99 (d, 2, $^3J_{HH}$ = 7.2 Hz, *m*-C_6H_3), 7.53, 7.60, 7.71, 8.30 (m, 4, C_6H_4).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 17.93 (qd, J_{CH} = 130 Hz, J_{CP} = 25 Hz, P*Me*$_3$), 23.52, 24.00 (q, J_{CH} = 125 Hz, CH*Me*$_2$), 27.35 (d, J_{CH} = 130 Hz, *C*HMe$_2$), 103.37 (d, J_{CH} = 173 Hz, *C*$_5$H$_5$), 122.21 (d, J_{CH} = 154 Hz, *m*-C$_6$H$_3$), 122.87 (d, J_{CH} = 159 Hz, *p*-C$_6$H$_3$), 130.16, 130.63, 130.83, 132.10, 162.67 (*C*$_6$H$_4$), 143.74 (s, *o*-C$_6$H$_3$), 152.05 (br, $\upsilon^{1}/_{2}$ = 33 Hz, *ipso* -C$_6$H$_3$).

^{31}P NMR data (101MHz, d_6-benzene, 298K): 7.52 (br, $\upsilon^{1}/_{2}$ = 600 Hz).

5.4 Experimental Details to Chapter 4.

5.4.1 Reaction of Cp*Ta(NAr)Me$_2$ with Dihydrogen in the Presence of Trimethylphosphine :

Preparation of Cp*Ta(NAr)(H)$_2$(PMe$_3$) (6) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).

Trimethylphosphine (0.08g, 1.15 mmol), was condensed onto a frozen solution of Cp*Ta(NAr)Me$_2$ (0.40g, 0.77 mmol) in toluene (20 mL) in an ampoule, cooled at -196°C. One atmosphere of dihydrogen was added and the ampoule was slowly warmed to 100°C to afford a yellow solution. The solution was stirred for a further 20 days until a pale colouration was adopted, the solution was then filtered and the volatile components removed under reduced pressure to afford a pale solid. Extraction with n-pentane (15 mL) gave colourless crystals upon prolonged cooling at *ca.* -78°C. Yield, 0.25g, 57%.

Elemental analysis for $C_{25}H_{43}NPTa$ Found (Required): %C, 52.8 (52.7); %H, 7.8 (7.6); %N, 2.2 (2.5).

Infrared data (Nujol, CsI, cm^{-1}): 3050(w), 2960(s), 2920(s), 2855(s), 1710(m), 1650(br, m), 1590(w), 1460(s), 1430(m), 1380(m), 1360(sh, m), 1355(s), 1300(m), 1285(m), 1100(br, m), 1025(br, m), 980(m), 960(m), 915(w), 860(w), 800(s), 755(s), 735(m), 670(w), 370(w), 340(w).

Mass spectral data (EI, m/z, ^{181}Ta): 569 [M]$^+$, 567 [M-2H]$^+$, 491 [M-2H-PMe$_3$]$^+$.

^{1}H NMR data (400MHz, d$_6$-benzene, 298K): (a) 1.16 (d, 9, $^2J_{PH}$ = 7.6 Hz, P*Me*$_3$), 1.42 (d, 12, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$), 2.10 (d, 15, $^4J_{PH}$ = 0.4 Hz, C$_5$*Me*$_5$), 4.40 (sept., 2, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 6.99 (t, 1, $^3J_{HH}$ = 7.6 Hz, *p*-C$_6$H$_3$), 7.16 (d, 2, $^3J_{HH}$ = 7.6 Hz, *m*-C$_6$H$_3$), 7.18 (d, 2, $^2J_{PH}$ = 60.0 Hz, Ta*H*). (b) 1.11 (d, 9, $^2J_{PH}$ = 8.0 Hz, P*Me*$_3$), 1.36, 1.38 (d, 12, $^3J_{HH}$ = 7.2 Hz, CH*Me*$_2$), 2.06 (s, 15, C$_5$*Me*$_5$), 4.29 (sept., 2, $^3J_{HH}$ = 7.2 Hz, C*H*Me$_2$), 8.77 (dd, 1, $^2J_{PH}$ = 114 Hz, $^2J_{HH}$ = 17.2 Hz, Ta*H*), 8.87 (dd, 1, $^2J_{PH}$ = 35.6 Hz, $^2J_{HH}$ = 17.2 Hz, Ta*H*).

Aryl ring hydrogens have not been assigned for (b).

^{13}C NMR data (100MHz, d$_6$-benzene, 298K): (a) 11.97 (q, J_{CH} = 127 Hz, C$_5$*Me*$_5$), 20.28 (qd, J_{CH} = 120 Hz, J_{CP} = 25 Hz, P*Me*$_3$), 24.02 (q, J_{CH} = 125 Hz, CH*Me*$_2$), 27.19 (d, J_{CH} = 131 Hz, *C*HMe$_2$), 110.98 (s, *C*$_5$Me$_5$), 121.88 (d, J_{CH} = 159 Hz, *m*-C$_6$H$_3$), 121.92 (d, J_{CH} = 159 Hz, *p*-C$_6$H$_3$), 143.00 (s, *o*-C$_6$H$_3$), 151.90 (s, *ipso* -C$_6$H$_3$). (b) (^{1}H decoupled) 11.90 (s, C$_5$*Me*$_5$), 18.69 (d, J_{CP} = 28 Hz, P*Me*$_3$), 24.06, 24.93 (s, CH*Me*$_2$), 27.01 (s, *C*HMe$_2$), 110.57 (s, *C*$_5$Me$_5$), 122.20 (s, *m*-C$_6$H$_3$), not resolved (*ipso*-, *o*-, *p*- C$_6$H$_3$).

^{31}P NMR data (202MHz, d$_6$-benzene, 298K): (a) -13.98, (b) -5.26.

5.4.2 Reaction of $Cp^*Ta(NAr)(H)_2(PMe_3)$ with Methyl Iodide :

Preparation of $Cp^*Ta(NAr)(PMe_3)(H)(I)$ (13) (Ar = 2,6-${}^iPr_2C_6H_3$).

Methyl iodide (0.03g, 0.19 mmol), was added *via* syringe to a solution of $Cp^*Ta(NAr)(H)_2(PMe_3)$ (0.11g, 0.19 mmol) in n-pentane (15 mL) at RT in a nitrogen filled dry box. The resulting yellow solution was stirred for 48 hrs, filtered, concentrated (*ca.* 5 mL), and cooled to *ca.* -78°C to afford yellow crystals. Yield, 0.05g, 38%.

Elemental analysis for $C_{25}H_{42}NIPTa$ Found (Required): %C, 43.4 (43.1); %H, 6.5 (6.1); %N, 2.0 (2.0).

Infrared data (Nujol, CsI, cm^{-1}): 2910(s), 2850(s), 2780(br, w), 1750(br, m), 1520(sh,w), 1460(s), 1440(sh, m), 1380(s), 1360(m), 1345(m), 1295(m), 1260(w), 1100(br, w),1025(w), 975(w), 950(m), 940(w), 815(sh, w), 795(m), 755(s), 720(w), 355(w).

Mass spectral data (EI, m/z, ${}^{181}Ta$): 619 $[M-PMe_3]^+$, 569 $[M-I-PMe_3]^+$.

${}^1H$ NMR data (250MHz, d_6-benzene, 298K): 1.27 (d, 9, ${}^3J_{HH}$ = 7.6 Hz, P*Me*$_3$), 1.31, 1.38 (d, 12, ${}^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$), 2.01 (s, 15, C$_5$*Me*$_5$), 4.27 (sept., 2, ${}^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 6.97 (t, 1, ${}^3J_{HH}$ = 7.7 Hz, *p*-C_6H_3), 7.12 (d, 2, ${}^3J_{HH}$ = 7.7 Hz, *m*-C_6H_3), 7.99 (d, 1, ${}^3J_{HH}$ = 73.1 Hz, Ta-*H*).

${}^{13}C$ NMR data (100MHz, d_6-benzene, 298K): 12.59 (q, J_{CH} = 127 Hz, C$_5$*Me*$_5$), 18.70 (qd, J_{CH} = 127 Hz, J_{CP} = 27 Hz, P*Me*$_3$), 24.16 (q, J_{CH} = 132 Hz, CH*Me*$_2$), 26.97 (d, J_{CH} = 127 Hz, *C*HMe$_2$), 113.29 (s, *C*$_5$Me$_5$), 122.30 (d, J_{CH} = 154 Hz, *m*-

C_6H_3), 123.17 (d, J_{CH} = 159 Hz, *p*-C_6H_3), 143.32 (s, *o*-C_6H_3), 151.11 (s, *ipso* -C_6H_3).

5.4.3 Reaction of Cp*Ta(NAr)(PMe$_3$)(H)(I) with Ethylene :

Preparation of Cp*Ta(NAr)(Et)(I) (14) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).

One atmosphere of ethylene was introduced into an ampoule containing a solution of Cp*Ta(NAr)(PMe$_3$(H)(I) (0.20g, 0.29 mmol) in n-pentane (20 mL), cooled at -78°C. On allowing the solution to warm to RT and stirring for a further 48 hours an orange solution was afforded, which when filtered and the volatile components removed under reduced pressure to gave an orange crystalline solid. Yield, 0.11g, 59%.

Elemental analysis for $C_{24}H_{37}NITa$ Found (Required): %C, 46.3 (44.6); %H, 6.3 (5.7); %N, 2.1 (2.2).

Infrared data (Nujol, CsI, cm^{-1}): 3040(w), 2915(s), 2850(s), 2350(br, w), 1660(w), 1460(s), 1430(sh, m), 1380(s), 1360(m), 1345(s), 1295(m), 1285(sh, w), 1265(m), 1100(br, m), 1020(br, m), 980(w), 950(w), 820(sh, w), 800(s), 770(w), 755(m), 720(w), 360(br, w).

Mass spectral data (EI, m/z, ^{181}Ta): 647 [M]$^+$, 6.8 [M-Et]$^+$, 512 [M-Cp*]$^+$.

^{1}H NMR data (250MHz, d$_6$-benzene, 298K): 0.85 (m, 2, C*H*$_2$Me), 1.33, 1.36 (d, 12, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$), 1.78 (s, 15, C$_5$*Me*$_5$), 1.92 (t, 3, $^3J_{HH}$ = 7.7 Hz, CH$_2$*Me*), 3.64 (sept., 2, $^3J_{HH}$ = 6.7 Hz, C*H*Me$_2$), 6.96 (t, 1, $^3J_{HH}$ = 7.5 Hz, *p*-C_6H_3), 7.19 (d, 2, $^3J_{HH}$ = 7.5 Hz, *m*-C_6H_3).

^{13}C NMR data (100MHz, d_6-benzene, 298K): 11.70 (q, J_{CH} = 128 Hz, C_5*Me*$_5$), 15.41 (q, J_{CH} = 126 Hz, CH_2*Me*), 24.47, 25.70 (q, J_{CH} = 124 Hz, CH*Me*$_2$), 27.69 (d, J_{CH} = 128 Hz, *C*HMe$_2$), 67.61 (t, J_{CH} = 124 Hz, *C*H$_2$Me), 118.23 (s, *C*$_5$Me$_5$), 122.55 (d, J_{CH} = 156 Hz, *m*-C_6H_3), 123.71 (d, J_{CH} = 157 Hz, *p*-C_6H_3), 144.31 (s, *o*-C_6H_3), 149.96 (s, *ipso* -C_6H_3).

5.4.4 General Procedure for Work Undertaken Whilst on Industrial Placement with B.P. Chemicals Ltd..

The following described procedure is for the reaction of CpNb(NMe)Cl_2, $[Et_2AlCl]_2$ and ethylene, in isobutane solvent, but is generally applicable for all the proposed reactions outlined in 4.6.

CpNb(NMe)Cl_2 (*ca.* 0.3g), was transferred in a nitrogen filled drybox, to a preweighed catalyst dispenser, fitted with a screw-clip. The catalyst dispenser, containing CpNb(NMe)Cl_2 was subsequently removed from the drybox in order to be added to the polymerisation bench reactor.

The investigation of potential oligomerisation / polymerisation activity was carried out in a bench reactor consisting of a stirred (400 rpm) 2.3 litre stainless steel autoclave, which when not in use was maintained at 110^{o}C, under a nitrogen atmosphere (90 psi) to retain anhydrous conditions.

Before commencing a reactor run the autoclave was set at the desired reaction temperature (30 - 120^{o}C) *via* a water / steam heat exchange system, and the bench reactor purged of air by pressuring up with nitrogen to 90 psi, and venting down through a Worcester ball valve on the top of the reactor, to expel traces of moisture.

After purging the reactor, the reactor valve was left fully open and a slow nitrogen flow was passed through the system. A catalyst delivery tube was inserted into the open valve and was purged of air by the slow nitrogen flow.

At this point a hexane solution of $[Et_2AlCl]_2$ was added *via* syringe, under a slow flow of dinitrogen, to an isobutane measuring vessel, isobutane diluent (1 litre) being added to it immediately afterwards. The vessel containing the co-catalyst / isobutane was then pressurised up to 400 psi with dry dinitrogen.

The catalyst dispenser containing CpNb(NMe)Cl_2 was weighed and the latter charged to the reactor by connecting a dinitrogen purged rubber hose between the delivery tube and the dispenser. The screw-clip on the dispenser was opened and the CpNb(NMe)Cl_2 tipped into the the reactor. The delivery tube was removed from the Worcester valve which was then closed. The isobutane and $[Et_2AlCl]_2$ solution was subseqently added slowly (*ca.* 5 minutes) *via* the manifold to the reactor, the stirrer started and the autoclave temperature returned to the reaction temperature.

Upon re-attainment of the reaction temperature, ethylene was added cautiously to the autoclave via the reactor manifold, until a final pressure of 600 psi was reached. Ethylene was then subsequently supplied on demand at 600 psi.

Typically, the autoclave was allowed to stir for a period of one hour after which the ethylene supply was disconnected from the autoclave. To investigate the possibility of the formation of ethylene dimers, bomb samples were cautiously taken from the vapour phase of the reaction mixture, *via* a sampling line connected to the autoclave. The remaining highly volatile material in the autoclave was then slowly vented through the Worcester valve, after which the stirrer was switched off and the reactor opened to allow inspection for evidence of ethylene oligomers or polymer.

5.5 References.

1. R. B. King, F. G. A. Stone, *Inorg. Synth.*, 1963, 7, 99.
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5. R. R. Schrock, J. S. Murdzek, G. Bazan, M. DiMare, M. O'Regan, *J. Am. Chem. Soc.*, 1990, 112, 3875.

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11. S. C. Watson, J. F. Eastham, *J. Organomet. Chem.*, 1967, 9, 165.

Appendices.

Appendix 1A: Crystal Data for $CpNb(NAr)(CH_2CMe_3)_2$.

$C_{27}H_{43}NNb$: 474.6

Crystal System: Monoclinic

Space Group: $P2_1/n$

Cell Dimensions: a = 9.272(1) Å

b = 17.237(2) Å

c = 17.020(2) Å

$\beta = 95.02^{\circ}$

$V = 2709.7$ Å^3

Z = 4

$D_c = 1.163$ g cm^{-3}

Final R-value: 0.030 ($R_w = 0.037$)

Appendix 1B: Crystal Data for $Cp^*Nb(NAr)(\eta^1\text{-}CHPh)(PMe_3)$.

$C_{32}H_{47}NNbP$: 569.6

Crystal System: Triclinic

Space Group: $P\bar{1}$

Cell Dimensions: a = 11.975(2) Å

b = 113.870(2) Å

c = 9.976(1) Å

$\alpha = 97.65(1)^{\circ}$

$\beta = 103.87(1)^{\circ}$

$\gamma = 92.98(1)^{\circ}$

$V = 1588.2(4)$ Å^3

Z = 2

$D_c = 1.191$ g cm^{-3}

Final R-value: 0.0475 ($R_w = 0.0577$)

Appendix 1C: Crystal Data for CpNb(NAr)(η^2-C_3H_6)(PMe$_3$).

$C_{23}H_{37}NNbP$:	451.4
Crystal System:	Monoclinic
Space Group:	$P2_1/m$
Cell Dimensions:	a = 8.543(4)
	b = 16.069(4)
	c = 8.551(3)
	V = 1170.5 Å^3
	Z = 2
	D_c = 1.281 g cm^{-3}
Final R-value:	0.0660 (R_w = 0.0472)

Appendix 1D: Crystal Data for CpNb(NAr)(η^2-C_6H_4)(PMe$_3$).

$C_{26}H_{35}NNbP$:	485.4
Crystal System:	Orthorhombic
Space Group:	Pbca
Cell Dimensions:	a = 16.140(2) Å
	b = 16.919(2) Å
	c = 18.511(4) Å
	V = 5054.51(14) Å^3
	Z = 8
	D_c = 1.276 g cm^{-3}
Final R-value:	0.0567 (R_w = 0.0578)

Appendix 2

First Year Induction Courses: October 1989

The course consists of a series of one hour lectures on the services available in the department.

1. Departmental Organisation
2. Safety Matters
3. Electrical appliances and infrared spectroscopy
4. Chromatography and Microanalysis
5. Atomic absorption and inorganic analysis
6. Library facilities
7. Mass spectroscopy
8. Nuclear Magnetic Resonance
9. Glass blowing techniques

Examined Lecture Course: October - November 1989

The course consisted of 6 one hour lectures followed by a written examination.

" Modern NMR Techniques " Prof. R. K. Harris.

Research Colloquia, Seminars and Lectures Organised By the Department of Chemistry.

* - Indicates Colloquia attended by the author

During the Period 1989-1990

BADYAL, Dr J.P.S. (Durham University) Breakthroughs in Heterogeneous Catalysis.	1st November 1989
BECHER, Dr.J. (Odense University) Synthesis of New Macrocyclic Systems using Heterocyclic Building Blocks.	13th November 1989

*BERCAW, Prof. J.E. (California Institute of Technology) Synthetic and Mechanistic Approaches to Zieger-Natta Polymerisation of Olefins.	10th November 1989
BLEASDALE, Dr. C. (Newcastle University) The Mode of Action of some Anti-tumour Agents.	21st February 1990
BOWMAN, Prof. J.M. (Emory University) Fitting Experiment with Theory in Ar-OH.	23rd March 1990
BUTLER, Dr. A. (St. Andrews University) The Discovery of Penicillin: Facts anf Fancies.	7th December 1989
CHEETHAM, Dr.A.K. (Oxford University) Chemistry of Zeolite Cages.	8th March 1990
CLARK, Prof. D.T. (ICI Wilton) Spatially Resolved Chemistry (using Nature's Paradigm in the Advanced Materials Arena).	22nd February 1990
* COLE-HAMILTON, Prof. D.J. (St. Andrews University) New Polymers from Homogeneous Catalysis.	29th November 1989
CROMBIE, Prof. L. (Nottingham University) The Chemistry of Cannabis and Khat.	15th February 1990
DYER, Dr. U. (Glaxo) Synthesis and Conformation of C-Glycosides.	31st January 1990
* FLORIANI, Prof. C. (Lausanne Univ., Switzerland) Molecular Aggregates- A Bridge Between Homogeneous and Heterogeneous Systems.	25th October 1989
GERMAN, Prof. L.S. (USSR Academy of Sciences, -Moscow) New Syntheses in Fluoroaliphatic Chemistry: Recent Advances in the Chemistry of Fluorinated Oxiranes.	9th July 1990

GRAHAM, Dr.D. (B.P. Research Centre) How Proteins Absorb to Interfaces.	4th December 1989
* GREENWOOD, Prof. N.N. (University of Leeds) Novel Cluster Geometries in Metalloborane Chemistry.	9th November 1989
HOLLOWAY, Prof. J.H. (University of Leicester) Noble Gas Chemistry.	1st February 1990
HUGHES, Dr.M.N. (King's College, London) A Bug's Eye View of the Periodic Table.	30th November 1989
HUISGEN, Prof. R. (Universität München) Recent Mechanistic Studies of [2+2] Additions.	15th December 1989
KLINOWSKI, Dr.J. (Cambridge University) Solid State NMR Studies of Zeolite Catalysts.	13th December 1989
LANCASTER, Rev. R. (Kimbolton Fireworks) Fireworks - Principles and Practice.	8th February 1990
LUNAZZI, Prof. L. (University of Bologna) Application of Dynamic NMR to the Study of Conformational Enantiomerism.	12th February 1990
* PALMER, Dr. F. (Nottingham University) Thunder and Lightning.	17th October 1989
PARKER, Dr. D. (Durham University) Macrocycles, Drugs and Rock'N'Roll.	16th November 1989
* PERUTZ, Dr. R.N. (York University) Plotting the Course of C-H Activations with Organometallics.	24th January 1990

PLATONOV, Prof. V.E. (USSR Academy of Sciences - Novosibirsk) 9th July 1990
Polyfluoroindanes: Synthesis and Transformation.

POWELL, Dr.R.L. (ICI) 6th December 1989
The Development of CFC Replacements.

POWIS, Dr. I. (Nottingham University) 21st March 1990
Spinning off in a Huff: Photodissociation
of Methyl Iodide.

ROZHKOV, Prof. I.N. (USSR Academy of Sciences, -Moscow) 9th July 1990
Reactivity of Perfluoroalkyl Bromides.

* STODDART, Dr.J.F. (Sheffield University) 1st March 1990
Molecular Lego.

* SUTTON, Prof. D. (Simon Fraser Univ., Vancouver B.C.) 14th February 1990
Synthesis and Applications of Dinitrogen and Diazo
Compounds of Rhenium and Iridium.

THOMAS, Dr.R.K. (Oxford University) 28th February 1990
Neutron Reflectometry from Surfaces.

THOMPSON, Dr. D.P. (Newcastle University) 7th February 1990
The Role of Nitrogen in Extending Silicate
Crystal Chemistry.

During the Period 1990-1991

ALDER, Dr. B. J. (Lawerence Livermore Labs., California) 15th January 1991
Hydrogen in all its Glory.

BELL, Prof. T. (SUNY, Stoney Brook, U.S.A.) 14th November 1990
Functional Molecular Architecture and Molecular Recognition.

* BOCHMANN, Dr. M. (University of East Anglia) Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls.	24th October 1990
BRIMBLE, Dr. M. A. (Massey University, New Zealand) Synthetic Studies Towards the Antibiotic Griseusin-A.	29th July 1991
* BROOKHART, Prof. M. S. (University of N. Carolina) Olefin Polymerisation, Oligomerisation and Dimerization Using Electrophilic Late Transition Metal Catalysts.	20th June 1991
* BROWN, Dr. J. (Oxford University) Can Chemistry Provide Catalyts Superior to Enzymes?	28th February 1991
BUSHBY, Dr. R. (Leeds University) Biradicals and Organic Magnets.	6th February 1991
* COWLEY, Prof. A. H. (University of Texas) New Organometallic Routes to Electronic Materials.	13th December 1990
CROUT, Prof. D. (Warick University) Enzymes in Organic Synthesis.	29th November 1990
DOBSON, Dr. C. M. (Oxford University) NMR Studies of Dynamics in Molecular Crystals.	6th March 1991
GERRARD, Dr. D. (British Petroleum) Raman Spectroscopy for Industrial Analysis.	7th November 1990
HUDLICKY, Prof. T. (Virginia Polytechnic Institute) Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products.	25th April 1991
JACKSON, Dr. R. (Newcastle University) New Synthetic Methods: α-Amino Acids and Small Rings.	31st October 1990

* KOCOVSKY, Dr. P. (Uppsala University) Stereo-Controlled Reactions Mediated by Transition and Non-Transition Metals.	6th November 1990
LACEY, Dr, D, (Hull University) Liquid Crystals.	31st January 1991
LOGAN, Dr. N. (Nottingham University) Rocket Propellants.	1st November 1990
MACDONALD, Dr. W. A. (ICI Wilton) Materials for the Space Age.	11th October 1990
MARKAM, Dr. J. (ICI Pharmaceuticals) DNA Fingerprinting.	7th March 1991
PETTY, Dr. M. C. (Durham University) Molecular Electronics.	14th February 1991
* PRINGLE, P. G. (Bristol University) Metal Complexes with Functionalised Phosphines.	5th December 1990
* PRICHARD, Prof. J. (Queen Mary & Westfield College- London University) Copper Surfaces and Catalysts.	21st November 1990
SADLER, Dr. P. (Nottingham University) Comet Chemistry.	17th January 1991
* SCHROCK, Prof. R. R. (M. I.T) Metal-Ligand Multiple Bonds and Metathesis Initiators.	24th April 1991
SCOTT, Dr. S. K. (Leeds University) Clocks, Oscillations and Chaos.	8th November 1990
* SHAW, Prof. B. L. (Leeds University) Synthesis with Coordinated, Unsaturated Phosphine Ligands.	20th February 1991

SINN, Prof. E. (Hull University) Coupling of Little Electrons in Big Molecules.Implications for the Active Sites of (Metalloproteins and other) Macromolecules	30th January 1991
* SOULEN, Prof. R. (South Western University, Texas) Preparation and Reactions of Bicycloalkenes.	26th October 1990
WHITAKER, Dr. B. J. (Leeds University) Two-Dimensional Velocity Imaging of State-Selected Reaction Products.	28th November 1990

During the Period 1991-1992

ANDERSON, Dr. M. (Shell Research) Recent Advances in the Safe and Selective Chemical Control of Insect Pests.	30th January 1992
* BILLINGHAM, Dr. N. C. (University of Sussex) Degradable Plastic - Myth or Magic?	5th March 1992
BUTLER, Dr. A. R. (St. Andrews University) Traditional Chinese Herbal Drugs: a Different Way of Treating Disease.	7th November 1991
COOPER, Dr. W. D. (Shell Research) Colliod Science, Theory and Practice.	5th December 1991
* FENTON, Prof. D. E.(Sheffield University) Polynuclear Complexes of Molecular Clefts as Models for Copper Biosites.	12th February 1992
* FISCHER, Prof. R. D. (University of Hamburg) From Organo-f-Element Systems to Organo-Main-Group Polymers.	17th September 1992

GANI, Prof. D. (St Andrews University) 13th November 1991
The Chemistry of PLP Dependant Enzymes.

GEHRET, Dr. J.- C.(Ciba Geigy, Basel) 13th May 1992
Some Apects of Industrial Agrochemical Research.

* GRIGG, Prof. R. (Leeds University) 4th December 1991
Palladium Catalysed Cyclisation and Ion Capture Processes.

HANN, Dr. R. A. (ICI Imagedata) 12th March 1992
Electronic Photography - An Image of the Future

HARRIS, Dr. K. D. M. (St. Andrews University) 22nd January 1992
Understanding the Properties of Solid Inclusion Compounds.

HITCHMAN, Prof. M. L. (Strathclyde University) 26th February 1992
Chemical Vapour Deposition.

HOLMES, Dr. A. (Cambridge University) 29th January 1992
Cycloaddition Reactions in the Service of the Synthesis
of Piperdine and Indolizidine Natural Products.

* JOHNSON, Prof. B. F. G. (Edinburgh University) 6th November 1991
Cluster-Surface Analogies.

KEELEY, Dr. R, (Metropolitan Police Forensic Science) 31st October 1991
Modern Forensic Science.

KNIGHT, Prof. D. M. (Philosophy Department - University of Durham) 7th April 1992.
Interpreting Experiments: the Beginning of Electrochemistry.

* MARDER, Prof. T. (University of Waterloo) 6th May 1992
Metal Catalysed Alkene Hydroboration.

MASKILL, Dr. H. (Newcastle University) 18th March 1992
Concerted or Stepwise Fragmentation in a Deamination-Type Reaction.

* MORE O'FERRALL, Dr. R (University College, Dublin) 20th November 1991
Some Acid-Catalysed Rearrangements in Organic Chemistry.

NIXON, Prof. J. F. (University of Sussex) 25th February 1992
The Tilden Lecture: Phosphaalkynes, New Building Blocks
in Inorganic and Organometallic Chemistry.

SALTHOUSE, Dr. J. A. (University of Manchester) 17th October 1991
Son et Luminere - a Demonstration Lecture.

SAUNDERS, Dr. J. (Glaxo Group Research Ltd.) 13th February 1992
Molecular Modelling in Drug Discovery.

SMITH, Prof. A. L. (ex Unilever) 5th December 1991
Soap, Detergents and Black Puddings.

* THOMAS, Prof. E. J. (Manchester University) 19th February 1992
Applications of Organostannanes to Organic Synthesis.

* THOMAS, Dr. S. E. (Imperial College) 11th March 1992
Recent Advances in Organoiron Chemistry.

VOGEL, Prof. E. (University of Cologne) 20th February 1992
The Mugrave Lecture: Porphyrins, Molecules of
Interdisciplinary Interest.

WARD, Prof. I. M. (IRC in Polymer Science,-
University of Leeds) 28th November 1991
The SCI Lecture: The Science and Technology of
Orientated Polymers.

Conferences and Symposia Attended.
(*denotes paper presentation)

1. *"North East Graduate Symposium"*,
   University of Newcastle-upon-Tyne, 2nd April 1990.

2. *"Symposium in Honour of Professor Peter L. Pauson - Organometallic Chemistry of the Transition Metals"*,
   University of Strathclyde, Glasgow, 19th October 1990.

3.* *"Waddington Graduate Symposium on Inorganic Chemistry"*,
   University of Durham, 17th December 1990.

4. *"Autumn Meeting of the Royal Society of Chemistry"*,
   University of York, 29th September 1991.

5. *"North East Graduate Symposium"*,
   University of Durham, 3rd April 1992.

Publications

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