

Uranium, Zirconium and Hafnium η^8 -permethylpentalene chemistry

By

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The work described in this thesis was carried out in the Chemistry Research Laboratory, Mansfield Road, Oxford between October 2009 and August 2013 under the supervision of Professor Dermot O'Hare. All the work is my own unless stated to the contrary, and has not been submitted for any degree at this or any other university.

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ABSTRACT

Zirconium, hafnium and uranium η^8 -permethylpentalenechemistry

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The purpose of this project has been to expand the η^8 binding mode of the permethylpentalene ligand into uranium, zirconium and hafnium chemistry. All three of these elements have shown intriguing, high-hapticity carbocyclic chemistry and, because of their relatively large size, are excellent candidates for the development of organometallic permethylpentalene chemistry. **Chapter one** of this thesis will review previous work on η^n carbocyclic ring chemistry of these elements, where $n = 6 - 8$. This introduction will include the unsaturated rings systems where all the carbons are bonded to the metal centre, specifically η^6 arene systems, η^7 cycloheptatriene systems, and η^8 cyclooctatetraene and pentalene systems. Species of lower hapticity (e.g. the η^6 binding mode of cycloheptatriene) will not be covered but reviews, where available, will be referenced.

Chapter two documents the successful synthesis and characterisation of η^8 permethylpentalene uranium (IV) species. Initially, the uranocene equivalent, UPn^*_2 was synthesised and characterised structurally, magnetically and electrochemically. From here, a half-sandwich synthon $[\text{UPn}^*\text{Cl}_4][\text{Li}(\text{TMEDA})]_2$ was synthesised which was used for further salt metathesis chemistry in order to make a number of mixed sandwich complexes.

Chapter three is an account of the synthesis and characterisation of zirconium and hafnium η^8 permethylpentalene species. Initial work focused on the synthesis of a suitable synthon analogous to that used for the previously synthesised titanium species. However, this route was unsuccessful and an alternative species was formed, $[\text{MPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2[\text{Li}(\text{THF})_x(\text{Et}_2\text{O})_y]$. This species could be made on a multi-gram scale and proved to be a suitable synthon for further synthesis. Salt metathesis reactions were undertaken and a number of new species were synthesised and characterised including mixed-sandwich, alkyl, aryl and allyl species.

Chapter four reports the results of polymerisation testing that was undertaken for selected synthesised compounds. All compounds catalysed the formation of poly(ethylene), with the group 4 mixed sandwich species being particularly active catalysts. Two of the zirconium species, ZrPn^*CpCl and ZrPn^*Cp_2 were therefore used for

further optimisation experiments which were somewhat limited due to the high activity of the compounds. These were useful in gaining insight into conditions that should be investigated on a larger reaction scale.

Chapter five gives the full experimental details for all the syntheses described in chapters two and three as well as details of instrumentation used for characterisation, and also gives the respective loadings of catalyst and co-catalyst employed in the polymerisation testing reported in chapter four. **Chapter six** presents the full characterisation data obtained for the compounds synthesised and the **electronic appendix** attached as a CD at the back of the thesis contains the crystal data .cif files and the DFT output files (.out).

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For Mum

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LIST OF ELECTRONIC APPENDICES

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2_3.cif	X-ray crystallographic data for 2.2
3_1Zr.cif	X-ray crystallographic data for 3.1_{Zr}
3_1aZr.cif	X-ray crystallographic data for 3.1a_{Zr}
3_3Zr.cif	X-ray crystallographic data for 3.2_{Zr}
3_4Zr.cif	X-ray crystallographic data for 3.3_{Zr}
3_5Zr.cif	X-ray crystallographic data for 3.4_{Zr}
3_6Zr.cif	X-ray crystallographic data for 3.5_{Zr}
3_7Zr.cif	X-ray crystallographic data for 3.6_{Zr}
3_8Zr.cif	X-ray crystallographic data for 3.7_{Zr}
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3_1Hf.cif	X-ray crystallographic data for 3.1_{Hf}
3_1HfTMEDA.cif	X-ray crystallographic data for TMEDA adduct of 3.1_{Hf}
3_2Hf.cif	X-ray crystallographic data for 3.2_{Hf}
3_3Hf.cif	X-ray crystallographic data for 3.3_{Hf}
3_4Hf.cif	X-ray crystallographic data for 3.4_{Hf}
3_5Hf.cif	X-ray crystallographic data for 3.5_{Hf}
3_6Hf.cif	X-ray crystallographic data for 3.6_{Hf}
3_9aHf.cif	X-ray crystallographic data for 3.9a_{Hf}
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3_4Zr.out	DFT output file for 3.4_{Zr}
3_5Zr.out	DFT output file for 3.5_{Zr}
3_6Zr.out	DFT output file for 3.6_{Zr}
3_7Zr.out	DFT output file for 3.7_{Zr}
3_9Zr.out	DFT output file for 3.8_{Zr}

LIST OF ABBREVIATIONS

°C	Degrees celsius
Å	Ångström
Acac	Acetylacetone ($\text{CH}_3\text{COCHCOCH}_3$)
Ar^{F}	Pentafluorophenyl (C_6F_5)
Ax.	Axial
br	Broad
^nBu	<i>n</i> -butyl
^tBu	<i>tert</i> -butyl
$^{13}\text{C}\{^1\text{H}\}$ NMR	Proton decoupled ^{13}C nuclear magnetic resonance
cent.	Centroid
CHT	Cycloheptatrienyl ($\eta^7\text{-C}_7\text{H}_7$, unless other hapticity defined)
cm^{-1}	Wavenumber
COT	Cyclooctatetraene ($\eta^8\text{-C}_8\text{H}_8$, unless other hapticity defined)
Cp	Cyclopentadienyl ($\eta^5\text{-C}_5\text{H}_5$)
Cp^*	Pentamethylcyclopentadienyl ($\eta^5\text{-C}_5\text{Me}_5$)
d	Doublet
<i>d</i>	Deuterated
δ	Chemical shift
Dipp	2,6-di- <i>iso</i> -propylphenyl ($2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$)
DME	Dimethoxyethane, $\text{MeOCH}_2\text{CH}_2\text{OMe}$
e^-	Electron
EI-MS	Electron ionisation mass spectrometry
Et	Ethyl
Eq.	Equatorial
Fc	Ferrocene
FI-MS	Field ionisation mass spectrometry
FT	Fourier transform
h	Hour
HBBN	9-Borabicyclo[3.3.1]nonane
HOMO	Highest occupied molecular orbital
IR	Infra-red

λ_{max}	Wavelength of maximum absorption
Ln	Lanthanide
LUMO	Lowest unoccupied molecular orbital
m	Medium intensity (IR); multiplet (NMR)
M	mol dm^{-1}
MAO	Methylaluminoxane
Me	Methyl
Mes	Mesityl (2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$)
$\nu_{\frac{1}{2}}$	Peak width at half height
NHC	N-heterocyclic carbene
NMR	Nuclear magnetic resonance
Np	Neopentyl ($\text{CH}_2\text{C}(\text{CH}_3)_3$)
NWT	Non-wingtip
Ph	Phenyl
Pn	Pentalene ($\eta^8\text{-C}_8\text{H}_6$, unless other hapticity defined)
Pn*	Permethylpentalene ($\eta^8\text{-C}_8\text{Me}_6$, unless other hapticity defined)
PPM	Parts per million
^iPr	<i>iso</i> -propyl
quint.	Quintet
s	Strong (IR), singlet (NMR)
SQUID	Super quantum interference device
T	Temperature
t	Time; triplet (NMR)
THF	Tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$)
TMEDA	Tetramethylethylenediamine [$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$]
TMS	Trimethylsilyl [$\text{Si}(\text{CH}_3)_3$]
TTB	Tris- <i>tert</i> -butylbenzene (1,3,5- $^t\text{Bu}_3\text{C}_6\text{H}_3$)
UV	Ultraviolet
VT-NMR	Variable temperature nuclear magnetic resonance
WT	Wing-tip
χ	Magnetic susceptibility

1. INTRODUCTION

1.1 *Organometallic chemistry of zirconium, hafnium and uranium*

Zirconium and uranium both display widely-developed organometallic chemistry, with hafnium somewhat less so. Zirconium and hafnium organometallic chemistry emerged through the work of Wilkinson and Edmond with the syntheses of the metallocene dichlorides (MCp_2Cl_2 ; $\text{Cp} = \text{C}_5\text{H}_5$).^{1;2} Since then a wealth of organometallic group 4 compounds has been made, the bulk of which are based on this metallocene motif. Zirconium has the advantages of being both the cheapest second row transition metal and not particularly toxic;³ hafnium, because of its higher price, has comparatively under-developed chemistry, though it appears to be analogous to zirconium in most of its compounds (but there are exceptions, for example the solid state structures of MCp_4 , $\text{M} = \text{Zr, Hf}$).⁴ Organozirconium compounds have a huge variety of applications ranging from small molecule activation and α -olefin polymerisation to organic synthesis and biomedical utility.⁵⁻⁹

Organouranium chemistry has seen a resurgence in recent years.¹⁰ However uranium itself has been described as having a “Jekyll and Hyde” reputation - given that it offers both a clean energy source, but has extremely destructive potential.¹¹ With the enrichment process affording depleted uranium as an unwanted by-product organometallic chemists have found themselves with a relatively cheap source of the metal. Organouranium chemistry was stimulated initially by Reynolds and Wilkinson with the preparation of cyclopentadienyl (Cp , C_5H_5) derivatives in the 1950s.¹² However, it wasn’t until Streitwieser’s discovery of uranocene [$\text{U}(\text{COT})_2$; $\text{COT} = \text{C}_8\text{H}_8$] that organouranium chemistry truly blossomed.¹³ Since then, uranium compounds have been shown to activate small molecules, catalyse organic reactions and promote polymerisation.^{11;14} By synthesising analogous uranium, zirconium and hafnium species and comparing their

physical and chemical properties one can obtain intriguing insights into the effects of d - and f -orbitals on their chemistry.

1.2 Carbocyclic rings

Carbocyclic molecules are defined as molecules of one or more rings containing only carbon atoms within the rings. These may be saturated or unsaturated hydrocarbons and may have all manner of substituents. In the case of unsaturated carbocyclic systems, the π framework affords molecular orbitals to which a metal can bind either *via* the π electrons of the carbocycle donating to the d - or f -orbitals of the metal (by σ or π bonding) or by the d - or f -electrons from the metal donating to the π^* anti-bonding orbitals of the carbocycle (*via* π or δ back-bonding). Furthermore, when combined with the electrostatic attraction that can occur between a positive metal cation and an anionic carbocycle this can lead to strong bonding between the metal atom and the carbon atoms of the ligand. When bound in this fashion the ring is said to be bound in a multi-haptic (η) manner.

The first-discovered and most common multi-haptic carbocyclic ligand in organometallic chemistry is the cyclopentadienyl anion (Cp^-). Seen initially in 1951 in ferrocene, this ligand has now been employed with most metals across the periodic table.^{15–19} Chemists interested in organometallic synthesis have since been challenged by the question as to how small, and how large, such ring systems can be. This introduction will review the work carried out on η^n -carbocyclic systems where $n = 6 - 8$ for the metals zirconium, hafnium and uranium.

1.3 η^6 bound carbocyclics: the binding of benzene

Arene rings acting as ligands bind to a metal centre in two ways, firstly by weak arene to metal σ and π donation and secondly by stronger metal to ligand π and δ back-donation. The e_{2g} orbital of the arene is closer in energy to the metal orbitals than in the analogous Cp system and thus stronger back-bonding is observed for the arene (figure 1.1).²⁰ In such a complex the arene remains aromatic with all the bond lengths

within the ligand being of equal length giving it D_{6h} symmetry (as opposed to D_{3d} if the double bonds were localised). The degree of back-bonding (and thus the strength of the metal-arene bond) can be seen in a lengthening of the ring C–C distances.

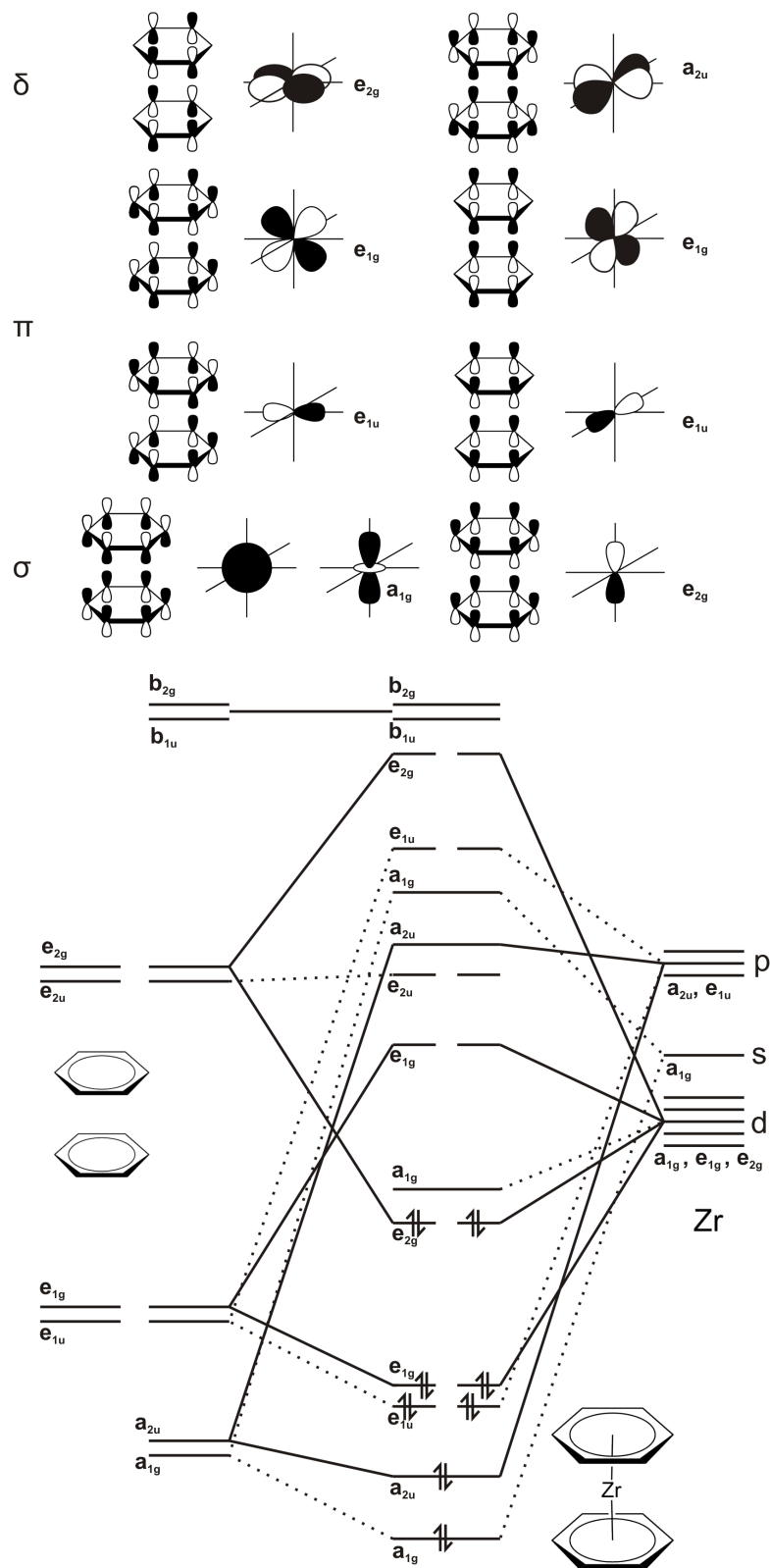


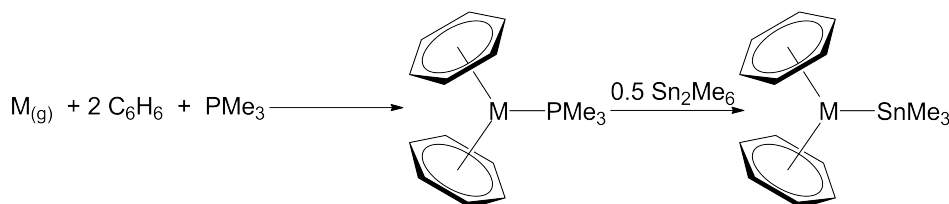
Figure 1.1: The molecular orbital diagram for $Zr(C_6H_6)_2$, adapted from *Organometallics: A Concise Introduction*.²⁰

The first bis(arene) metal complex was discovered in 1955 by Hafner and Fischer: $\text{Cr}(\text{C}_6\text{H}_6)_2$.^{21;22} This was formed by the reaction of CrCl_3 , aluminium and benzene in the presence of AlCl_3 , forming a bis(arene)chromium (I) salt, which when reduced with $\text{Na}_2\text{S}_2\text{O}_6$ formed a brown crystalline solid identified as $\text{Cr}(\text{C}_6\text{H}_6)_2$. Since this discovery, many attempts have been made to synthesise similar transition metal, lanthanide and actinide derivatives by this method (referred to as the Fischer-Hafner synthesis).

1.3.1 Zirconium and hafnium (0) arene complexes via metal vapour synthesis

The first mention of Zr arene complexes in the literature is a pair of patents by Fischer and Hafner. However the synthesis of $\text{Zr}(\text{C}_6\text{H}_6)_2$ cannot be achieved by their method, which instead results in a trinuclear Zr(II) arene complex, $[\text{Zr}(\text{C}_6\text{Me}_6)(\mu\text{-Cl})_2]_3[\text{Al}_2\text{Cl}_7]_2$ [*vide infra* for Zr and Hf(II)/(III) arene chemistry].^{23;24} However, with the development of metal-vapour synthesis by Cloke *et al.* new routes were accessible to novel compounds including the first group 4 zero valent arene compounds: $\text{M}(\text{arene})_2(\text{PMe}_3)$ ($\text{M} = \text{Zr}, \text{Hf}$; arene = C_6H_6 , $\text{C}_6\text{H}_5\text{Me}$).^{25–27} Synthesis was achieved by co-condensation of the metal, arene and phosphine (scheme 1.1). These compounds were found to have a bent structure and when stirred with Sn_2Me_6 the phosphine groups are readily replaced by SnMe_3 (with the solid state crystal structure of the Hf derivative having been determined).²⁸ Because of the size of the SnMe_3 substituents it was actually found that the arene rings showed a slight deviation from planarity. Although the $\text{M}(\text{arene})_2$ compounds were assumed to be present at low temperatures (because of a vivid colour change) they were not isolable, and when the reaction was conducted in the absence of PMe_3 warming the reaction mixture above -100°C resulted in the decomposition of the product to arene and pyrophoric metal.

By adapting this synthesis to allow the bis(arene) products to be made in the pres-

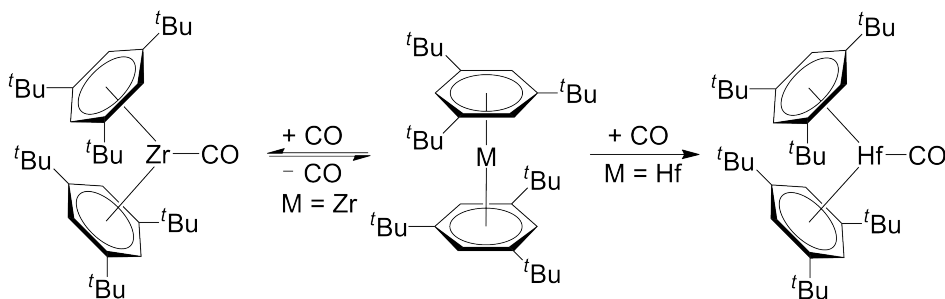


Scheme 1.1: The metal-vapour synthesis of group 4 arene complexes

ence of activated alumina the catalytic properties of these compounds with respect to the polymerisation of propylene were investigated.²⁹ Tullock reacted the co-condensate with activated alumina (*in situ*) at $-80\text{ }^{\circ}\text{C}$ for one hour before warming the mixture to room temperature and undertaking polymerisation experiments. The Zr and Hf arene species were found to be moderately active catalysts for the polymerisation giving high molecular weight polypropylene. Though the active catalyst was not determined Tullock argues that the bis(arene) species undergoes oxidative addition with the surface hydroxyl groups to form a metal (II) mono-arene catalytic species. To prove that an arene-metal species was the active catalyst (and not merely the metal alone binding to the alumina) the experiment was repeated with the arene being replaced with nonaromatic solvent: these displayed no catalytic activity.

It was by the introduction of more sterically demanding ligands into the metal complex that synthesis of a base-free bis(arene) complex $[\text{M}(\text{arene})_2]$ was achieved. The use of $[1,3,5\text{-}^t\text{Bu}_3(\text{C}_6\text{H}_3)]$ (tris-tertbutyl-benzene; TTB) in metal vapour synthesis gave $\text{M}(\text{TTB})_2$ in approximately 40 % yield ($\text{M} = \text{Zr}$ or Hf).³⁰ The TTB ligand stabilises the $\text{M}(0)$ centre not only by protecting it with its steric bulk but also through the combined inductive effect of the ^tBu groups strengthening the M-arene bond. The green and purple crystals ($\text{M} = \text{Zr}$ or Hf respectively) were found to be diamagnetic and thermally stable up to $120\text{ }^{\circ}\text{C}$, highly sensitive to air and moisture and were characterised by mass spectrometry, ^1H NMR and elemental analysis. An investigation was undertaken to see if these 16 e^- species would bind electron donors to form 18 e^- adducts like their less substituted cousins. Addition of PMe_3 to both gave no observable reaction due to the steric protection of the ligands, and addition of the smaller PF_3 led to decomposition. However, addition of CO led to a swift colour change in both solutions, with the zirconium's green colour becoming lighter and the Hf changing from purple to green. This was found to be irreversible for the Hf but reversible for the Zr (scheme 1.2)

In 1996, King *et al.* carried out thermochemical and quantum mechanical investigations into the strength of the metal-arene bond in these systems.³¹ These showed that the strongest bonding was the δ back-bonding from the metal to the ligand π^*



Scheme 1.2: The reaction of $M(\text{TTB})_2$ with CO ($M = \text{Zr}$ and Hf).

orbitals. This interaction is stronger for the Hf example, demonstrated by lengthening of the carbon-carbon bonds within the benzene ring (1.430 Å for Hf, 1.426 Å for Zr, 1.400 Å for free benzene). The same report excitingly indicated that uranium and thorium zerovalent arene complexes would, like their group 4 congeners, be thermodynamically stable with respect to the parent metal and arene. Further investigations utilising DFT and unsubstituted benzene rings as the ligands have been carried out and support King’s findings of increased back-bonding down the group.^{32;33}

Although they have not been isolated and characterised there is evidence for the possible existence of monobenzene adducts of Zr and Hf, $M(\text{C}_6\text{H}_6)$. These appear to be formed by laser-ablation of the metal atoms and benzene in solid argon giving the first experimental evidence for a “ $M(\text{C}_6\text{H}_6)$ ” moiety.³⁴ Interestingly, the data predict a $^3\text{A}_2$ ground state and non- C_{6v} symmetry, implying that there is deformation of the carbon skeleton. However no more work has been done on these substances.

1.3.2 Zirconium and hafnium (II/III) arene complexes

It has already been mentioned that use of the harsh Fischer-Hafner synthesis with ZrCl_4 did not yield a neutral bis(arene) but rather a trinuclear Zr(II) complex: $[\text{Zr}(\text{C}_6\text{Me}_6)(\mu\text{-Cl})_2]_3[\text{X}]_n$ [$n = 1$, $\text{X} = \text{PF}_6$, Al_2Cl_7 ; $n = 2$, $\text{X} = \text{Cl}$; (C) in figure 1.2; *vide infra*].^{23;24} However, it was noted that these products arose after hydrolytic treatment of the reaction mixture at low temperature and, in a manner similar to titanium, Pampaloni and co-workers found that by exclusion of the water step monomeric Zr arene complexes could be formed.³⁵ The formula was erroneously proposed to be $\text{Zr}(\text{arene})(\text{AlX}_4)_2$ [(D) in figure 1.2],³⁶ but later crystallographic analysis found the Zr to adopt a tetrahedral environment with two arene rings bound to the centre giving it

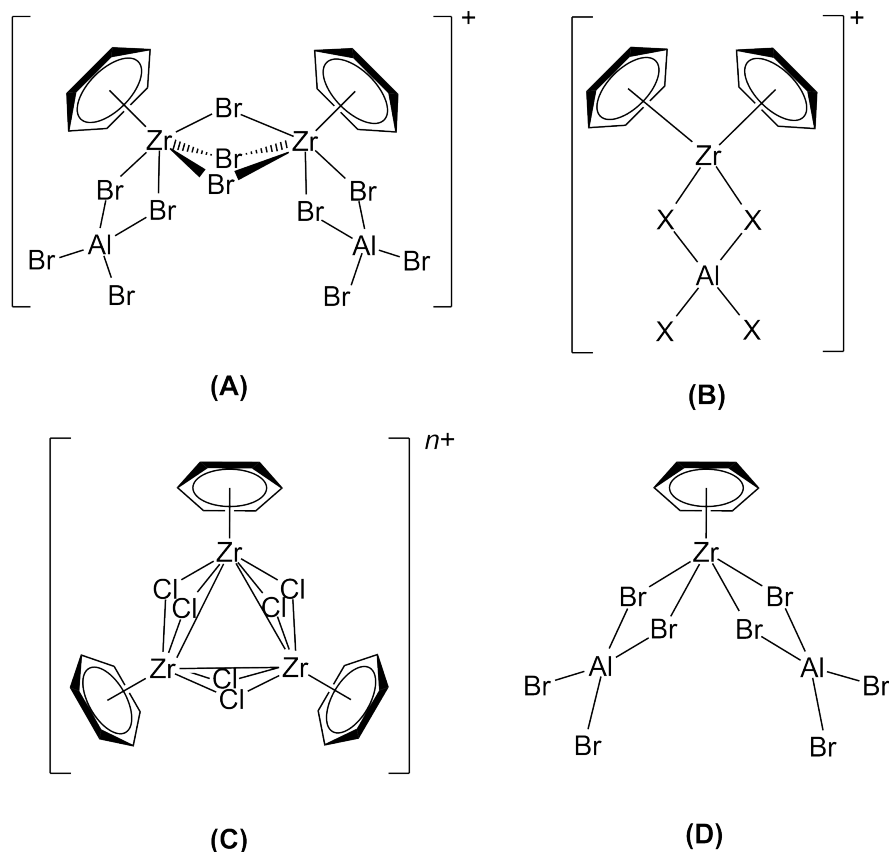
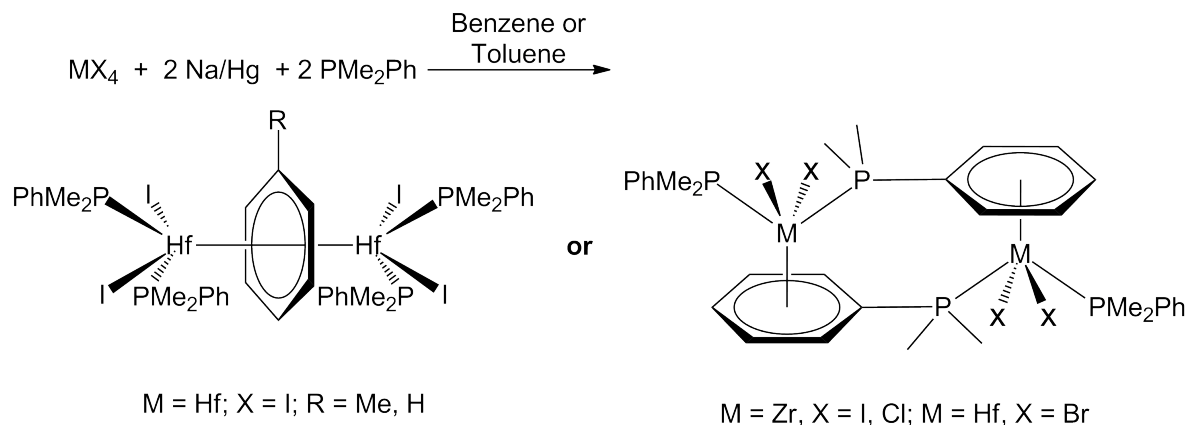


Figure 1.2: The four types of Zr structures formed *via* the Fischer-Hafner synthesis.

a full 18 e⁻: $\text{Zr}(\text{arene})_2(\text{AlX}_4)$ [(B) in figure 1.2].³⁷

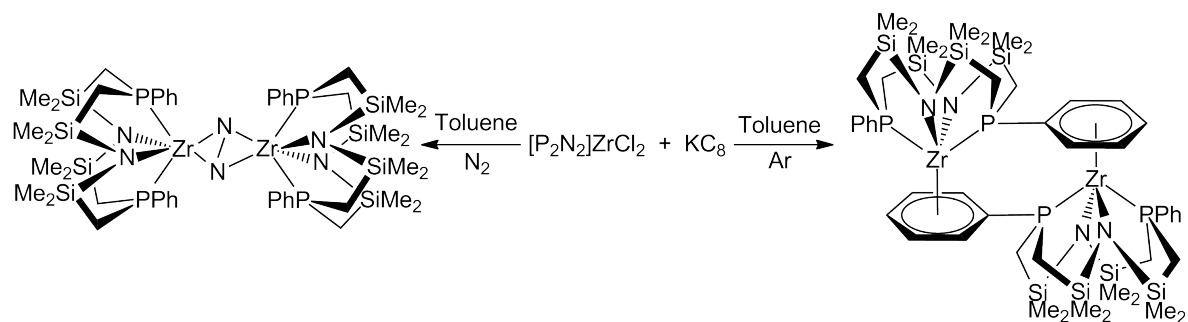
Cotton *et al.* showed that reducing agents other than those of the traditional Fischer-Hafner system could be employed to form group 4 arenes. Treatment of HfI_4 with two equivalents of Na/Hg in the presence of PMe_2Ph and benzene (or toluene) gave a species in which the arene was found to bridge two metal centres: $[\text{Hf}(\text{PMe}_2\text{Ph})_2\text{I}_2]_2[\mu\text{-}\eta^6\text{:}\eta^6\text{-arene}]$, the first group 4 bridging arene (left hand side of scheme 1.3).³⁸ Quantum mechanical calculations however showed that the electronic incentive for bridging was small and an $\text{MI}_2(\text{PR}_3)_2(\text{arene})$ complex was hypothesised. A slight chemical change (chlorine or bromine for iodine or Zr for Hf) resulted in the formation of similar complexes. In these, however, the metal centre binds to an arene from a neighbouring metal's PMe_2Ph ligand instead of incorporating a solvent arene (right hand side of scheme 1.3).^{39;40} Almost simultaneously with these reports, Diamond *et al.* established that treatment of ZrCl_4 with a Na/Hg amalgam in the presence of PMe_3 and toluene produced $[\text{Zr}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{PMe}_3)_2\text{Cl}_2]$ as green, air-sensitive crystals in poor yield, an example of the mono-arene system hypothesised, but not synthesised, by Cotton.^{41;42}



Scheme 1.3: Synthesis of group 4 arene complexes.

More recently, this intramolecular phenylphosphine arene system has been observed with a macrocycle. $\text{Zr}(\text{P}_2\text{N}_2)\text{Cl}_2$ [$\text{P}_2\text{N}_2 = \text{PhP}(\text{CH}_2\text{SiMe}_2\text{NSiMe}_2\text{CH}_2)_2\text{PPh}$] was found (when reduced with KC_8) to behave differently under Ar and N_2 (scheme 1.4). Initially the reduction created a Zr(III) product that bound N_2 (left hand side of scheme 1.4).⁴³ However, during the reaction a small amount of a yellow crystalline by-product was observed which was later identified (by X-ray diffraction) as $\{\text{Zr}[\mu\text{-(P}_2\text{N}_2)]\}_2$ where the arene bound to the phosphorus coordinates to a second metal, and it was found that this could be made in good yield if N_2 was excluded (right hand side of scheme 1.4).⁴⁴ Interestingly in this dimeric species the arene shows significant distortion from planarity with the ring adopting something closer to a boat geometry, in what may more accurately be described as $\eta^3:\eta^3$ binding of a bis(allyl) dianion.

In 1994 Sergei Troyanov undertook a review of arene complexes and brought to light a number of compounds that had been hidden behind the iron curtain.⁴⁵ Troyanov showed that the reaction conditions employed in the Fischer-Hafner system are an



Scheme 1.4: The reduction of the $[\text{P}_2\text{N}_2]\text{ZrCl}_2$ system with KC_8 : on the left under N_2 atmosphere and on the right under an Ar atmosphere.

important factor in deciding what complex stoichiometry eventually results; varying the halide, reductive metal, arene ligand, reaction time and reactant concentration can all give rise to different complexes. Indeed, it is often the case that a mixture of complexes is produced and this can lead to the formation of an oil and difficulty in extraction and purification. A summary of some of the Zr complexes so prepared (and the requisite conditions) is presented in table 1.1. Generally it was found that the Zr complexes formed cationic dimers of varying oxidation state in order to satisfy their electron deficiency.

Table 1.1: A summary of how varying conditions can result in different products with the Fischer-Hafner synthesis.

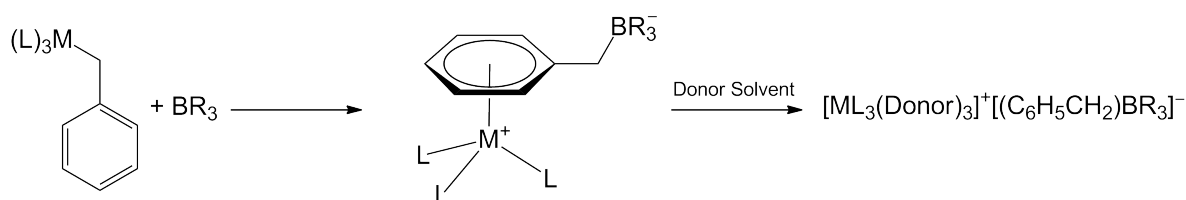
ZrX ₄ /AlX ₃ /Al/Benzene system		
X ⁻	Structure Type (in figure 1.2)	Reaction Speed
Cl ⁻	A	Slow reaction even if heated
Br ⁻	A	Fast reaction
I ⁻	B	Fast reaction
ZrCl ₄ /AlCl ₃ /Al/C ₆ H ₃ Me ₃ system		
	Structure Type (in figure 1.2)	Zr Oxidation State
Increasing reaction time ↓	C ($n = 3+$)	3
	C ($n = 2+$)	2.667
	B	2
	Structure Type (in figure 1.2)	Counter-ion
Decreasing AlX ₃ concentration ↓	B	Al ₃ X ₁₀ ⁻
	C ($n = 3+$)	Al ₂ X ₇ ⁻
	C ($n = 2+$)	Al ₂ X ₇ ⁻
	C ($n = 2+$)	AlX ₄ ⁻

1.3.3 Zirconium and hafnium (IV) arene complexes

Unlike the situation for the Zr and Hf(II)/(III) complexes already surveyed, there is only one example of neutral Zr/Hf(IV) arene complexes, which are generally less thermodynamically stable than the lower oxidation states. However, they are in fact extremely simple to make. Stirring ZrCl_4 in CH_2Cl_2 with the appropriate stoichiometry of durene (1,2,4,5- $\text{C}_6\text{Me}_4\text{H}_2$) resulted in the complex $[\text{Zr}(\eta^6\text{-durene})\text{Cl}_2](\mu\text{-Cl})_3(\text{ZrCl}_3)$.^{46;47} This was found to slowly catalyse both the Jacobsen rearrangement of the durene to other benzene derivatives and the trimerization of alkynes to benzene derivatives. This is the only example of a neutral Zr(IV) arene species, there are no equivalent Hf examples.

In contrast to the rarity of neutral Zr/Hf(IV) complexes, Zr/Hf(IV) cationic complexes featuring an η^6 -arene ring have been very widely studied owing to their potential as Ziegler-Natta catalysts for the polymerisation of α -olefins. It has been shown that a Zr/Hf(IV) benzyl complex may be reacted with a Lewis acid (often BAr^{F}_3 although Al based co-catalysts may also be used; $\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5$) forming a complex of formula $[\text{ML}_3]^+[\text{C}_6\text{H}_5\text{CH}_2\text{BR}_2]^-$, but the aromatic ring is still weakly bound to the metal centre (scheme 1.5). These are found to be extremely active species for the insertion, polymerisation and oligomerisation of alkenes, but addition of a donor solvent (e.g. THF) breaks apart the zwitterionic species and solvates the metal centre thereby seriously impeding catalytic ability.⁴⁸ This type of η^6 -arene has been incorporated into a wealth of systems including: $\text{Zr}(\text{CH}_2\text{Ph})_4$,⁴⁹ $\text{ZrCp}(\text{CH}_2\text{Ph})_3$ and substituted cyclopentadienes,⁵⁰ amides,^{51;52} aryloxides,^{53;54} dienes⁵⁵ and alkoxides.^{56;57} All these systems display good catalytic activity for the polymerisation of olefins and have been extensively reviewed.⁵⁸

A variant on this has been produced by Baird and co-workers who treated methyl Cp complexes (MCpMe_3) with BAr_3^{F} in the presence of excess arenes.^{59;60} It was found that the Lewis acid abstracted a methyl group from the metal complex to form $[\text{MCpMe}_2]^+$.



Scheme 1.5: The general route to Zr and Hf(IV) zwitterionic η^6 benzyl complexes

This cation, in order to satisfy its electronic demand, will bind arenes to form $[\text{MCpMe}_2(\eta^6\text{-arene})]^+[\text{MeBAr}_3^{\text{F}}]^-$ ($\text{M} = \text{Zr}$, arene = toluene, 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$, benzene, styrene, *p*-xylene, *m*-xylene; $\text{M} = \text{Hf}$, arene = toluene, *p*-xylene, *m*-xylene, anisole). A similar Hf complex has also been made with a bis- $(\text{SiMe}_3)\text{Cp}$ ligand.⁶¹

1.3.4 Uranium arene complexes

It is possible to prepare U mono-arene complexes with the Fischer-Hafner synthesis. U(IV) undergoes reduction to U(III) and the derivative $\text{U}(\eta^6\text{-C}_6\text{H}_6)(\text{AlCl}_4)_3$ may be isolated as black crystals in 70-80 % yield.⁶² X-ray analysis revealed the uranium to be disposed in a pentagonal-based bipyramidal geometry, with the arene and one chloride taking the axial positions (and the five other bridging chlorines taking up the equatorial positions) and the uranium being somewhat displaced towards the arene ring with a U-C_{ring} distance ranged from 2.91 to 2.93 Å. Cesari *et al.* therefore tentatively assigned a zero-bond order to the complex.

It was a further 14 years before another uranium arene complex was synthesised. Cotton *et al.* adapted the Fischer-Hafner synthesis separating the electrophilic addition and reduction steps, using a non-coordinating solvent for the former (in order to avoid chemical competition) and using a more polar solvent for the reduction step to overcome the insolubility of the intermediates.^{63;64} They allowed UCl_4 and excess AlCl_3 to react in the presence of C_6Me_6 in hexane, before replacing the solvent with CH_2Cl_2 and treating with Zn. After subsequent work-up, yellow crystals were isolated and were shown by X-ray diffraction to be $[\text{U}_2(\eta^6\text{-C}_6\text{Me}_6)_2\text{Cl}_4(\mu\text{-Cl})_3]^+(\text{AlCl}_4)^-$ [figure 1.3(a)]. If the zinc is left out of the reaction mixture and the quantity of AlCl_3 is reduced to stoichiometric amounts it is possible to isolate a trinuclear “U-arene” containing compound. This compound is related to the former *via* the insertion of a UCl_5^- subunit into the $(\mu\text{-Cl})_3$ bridge [figure 1.3(B)]. The average U-C_{ring} distances [2.92(4) Å and 2.94(2) Å] are comparable with the previously mentioned U(III) complex. The fact that the bond length does not change with oxidation state is intriguing as with the higher oxidation state one would expect weaker bonding due to worse orbital overlap. However the more electron rich arene is a better ligand and electrostatic considerations therefore have less

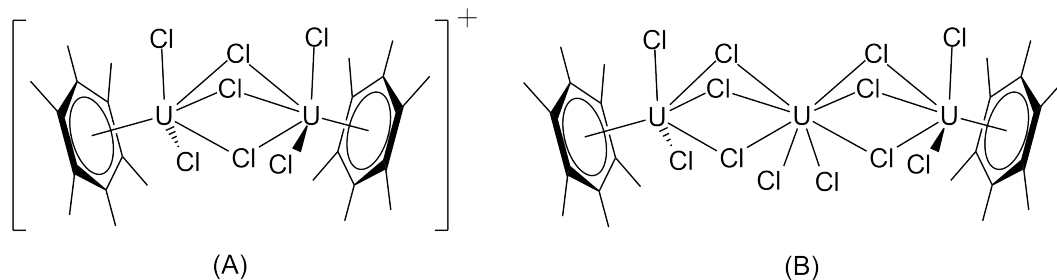


Figure 1.3: Two complexes containing the “U(C₆Me₆)” moiety.

influence with neutral ligands.

More recently, low valent U(III) compounds have been shown to satisfy their low coordination spheres by binding arene complexes. Although the bulk of the work on this has been on arenes bridging two uranium centres, there are a few reports of arenes binding to a single metal centre. For example, heating U(BH₄)₄ in 1,3,5-trimethylbenzene or hexamethyl benzene results in thermal decomposition to yield U(η⁶-arene)(BH₄)₃.^{65–67} Aryloxide species will spontaneously bind to the arene ring of an adjacent uranium centre’s ligands, and recently Meyer *et al.* synthesised a rigid aryloxide tripodal scaffold that holds an arene ring close to one side of the uranium centre in order to stabilise the U(III) centre.^{68;69}

1.3.5 Uranium bridging arene complexes

Arguably the most intriguing aspect of U(arene) chemistry is when two metal centres are bridged by an arene ring. This M₂(μ-η⁶:η⁶-arene) binding mode is relatively rare, with only 73 such complexes structurally characterised containing any two metals, but over a third of these contain two uranium atoms. The particularly fascinating thing about these complexes is that it is unclear what oxidation state the uranium centre is in. The first of these complexes was synthesised by Cummins and co-workers.⁷⁰ They found that reduction of U(N^tBuAr)₃I (Ar = 3,5-Me₂C₆H₃) with KC₈ in toluene gave (UN^tBuAr)₂(μ-η⁶:η⁶-C₇H₈). In this compound the uranium adopted a two legged piano stool geometry and was shown by X-ray diffraction to have a considerably smaller U-C_(ring) distance [2.59(1) Å] than those previously seen. Because of this, the question was raised as to the formal oxidation state of the metal centre - was it U(II) with a neutral bridging arene, U(III) with a dianionic anti-aromatic arene, or was it a U(IV)

species with a tetra-anionic arene. DFT results provided evidence for considerable covalent δ -backbonding from the d -orbitals to the LUMO of the arene and therefore a U(II) oxidation state was tentatively assigned. However, a more recent, in-depth, spectrometric analysis has corrected this to an assignment of U(III) with a formal dianionic bridging arene.⁷¹ Use of the ketimide ligand allowed the same group to form analogous species with a three-legged piano stool arrangement around the uranium centre whilst incorporating different arenes such as naphthalene.^{72;73}

Four years after this, Evans showed that reduction of the sterically encumbered UCp^*_3 resulted in the species $(\text{UCp}^*_2)(\mu:\eta^6:\eta^6\text{-C}_6\text{H}_6)$.^{74–76} Similarly to the previous example this species showed curious chemistry: it would react with either two equivalents of PhN=NPh or three equivalents of COT to form $\text{UCp}^*_2(\text{NPh})_2$ or $(\text{COT})\text{Cp}^*_2[\mu:\eta^8:\eta^8\text{-COT}]$ respectively. In both these reactions Evans’ bridging arene is acting as a six electron reductant. Furthermore the species itself shows a fascinating structural feature in that the bridging arene strongly deviates from planarity, adopting a shallow “boat” geometry (seen before as evidence of more precise formulation as $\eta^3:\eta^3$ bonding).

More recently uranium complexes containing bridging arenes have revealed some further, intriguing properties. For example, Patel and co-workers have shown that this binding mode is not limited to species of *pseudo*-U(II) oxidation state, instead synthesising a U(V) species with a toluene tetra-anion [assigned as this oxidation state based on magnetic data but therefore *pseudo*-U(III) with a neutral arene; (A) in figure 1.4]. The same group also synthesised a bridging arene species that acts as a single molecule magnet that does not rely upon a super exchange mechanism [(B) in figure 1.4].⁷⁷

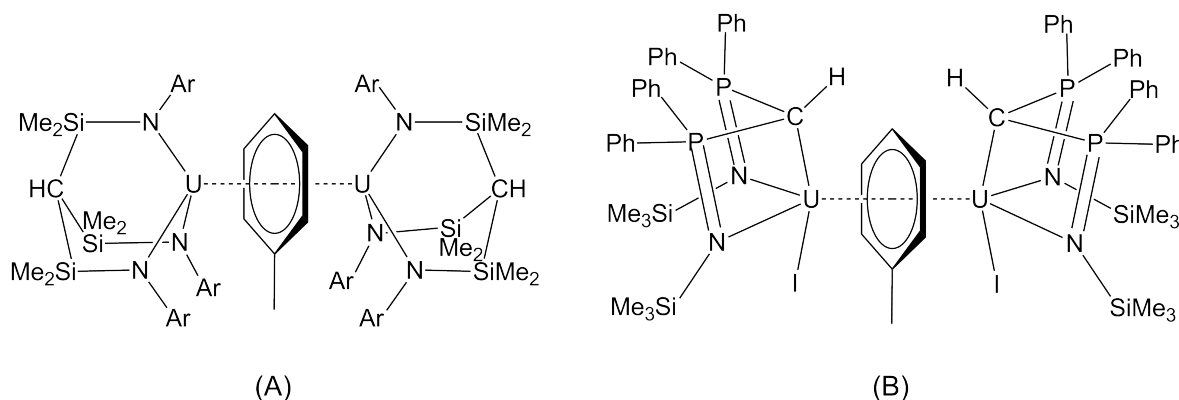
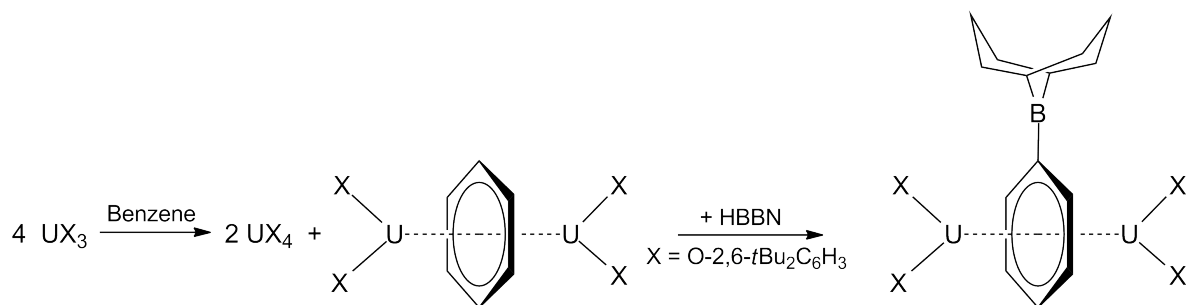


Figure 1.4: Two interesting U bridging arene species: (A) the first formally U(V) bridging arene, (B) the bridging arene species that is a single molecule magnet.

It turns out that the simple U(III) starting materials UX_3 [$X = N(SiMe_3)_2$ or $O-2,6-^tBu_2C_6H_3$] will spontaneously reduce benzene or toluene under prolonged heating (scheme 1.6).⁷⁸ This technique not only allowed the incorporation of arenes that would be incompatible with the previous reductive synthetic routes (e.g. Ph_3SiH) but also revealed that these species activated the trapped arenes towards borylation. In their report it is proposed that should this be followed by arene exchange a catalytic cycle for the borylation of arenes could be envisaged.



Scheme 1.6: The facile synthesis of bridging U arenes and the subsequent borylation of the arene.

1.4 η^7 bound carbocyclics: cycloheptatrienyl

The C_7 carbocyclic ring has two main binding modes. The first, in which it is a neutral six electron donor, is referred to as cycloheptatriene ($\eta^6-C_7H_8$). In this binding mode, one of the ring carbons is sp^3 hybridised with two hydrogens attached and does not bind to the metal. Since this introduction is concerned with wholly unsaturated carbocyclic rings, an in depth analysis of this binding mode is beyond the scope of this chapter

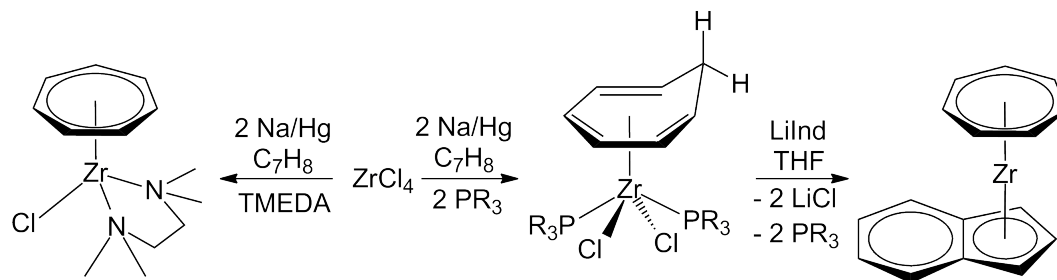
but the field has been reviewed by Green and Ng.⁷⁹ The other binding mode, where all seven of the ring carbons bind to the metal centre (referred to as cycloheptatrienyl; CHT = $\eta^7\text{-C}_7\text{H}_7$) will be discussed here.

The chemical nature of the CHT ligand has been the subject of much debate. Originally it was proposed formally to be the six π -electron aromatic tropylium ion: $(\eta^7\text{-C}_7\text{H}_7)^+$. However, this classification portrayed a misleading picture of the properties of the ligand. By assuming this representation it would seem that the CHT ligand would be more susceptible to nucleophilic attack than the other carbocyclic rings (e.g. Cp or arene), but this is not the case, with CHT being the least susceptible.⁸⁰ Further studies (X-ray PES, *ab initio* calculations, metallation experiments and ^{13}C NMR spectroscopy) have shown CHT^+ to be an inadequate description of the bonding.^{81–84} However, similar studies have shown that the other aromatic scenario [$\eta^7\text{-C}_7\text{H}_7^{3-}$; 10 π electrons] is also a poor description.⁸⁵ In truth, the bonding situation lies between these two extremes.

1.4.1 Zirconium and hafnium cycloheptatrienyl complexes

Compared to hafnium and uranium, considerably more research has been carried out on zirconium CHT compounds. The first zirconium and hafnium CHT complexes were synthesised by Cloke *et al.* using metal vapour condensation techniques.⁸⁶ In this technique the metal was condensed onto an excess of cycloheptatriene to form a red oil of approximate formulation $\text{M}(\text{C}_7\text{H}_8)_3$. Heating the sample and recrystallisation yielded $\text{M}(\text{CHT})(\eta^5\text{-C}_7\text{H}_9)$ in 20 % yield. Homoleptic sandwich compounds can also be made by reducing C_7H_8 with four equivalents of Na/Hg amalgam in the presence of ZrCl_4 to give $\text{Zr}(\eta^6\text{-C}_7\text{H}_8)_2$ (formally a zero valent compound).^{87;88} Further reaction with CO, Sn_2Me_6 , PMe_3 or TMEDA promotes hydrogen migration to form the stable $\text{Zr}(\text{CHT})(\eta^5\text{-C}_7\text{H}_9)$ in high yields (> 90 %), though the products of the reactions with phosphines give thermally unstable adducts.

A more convenient synthesis of mixed-sandwich species or half-sandwich species can be achieved using the metal chlorides. Reaction of ZrCl_4 with C_7H_8 and one equivalent of TMEDA and two equivalents of sodium amalgam yielded the half sandwich:

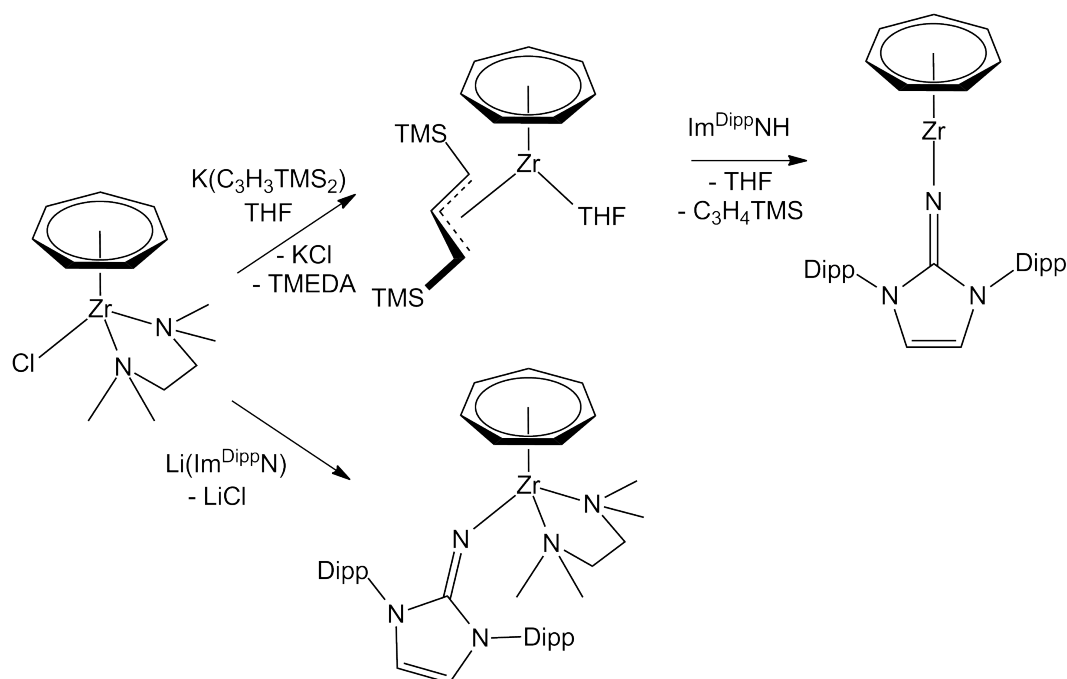


Scheme 1.7: The synthesis of ZrCHT containing half sandwiches by Green *et al.*

Zr(CHT)Cl(TMEDA) (left hand side of scheme 1.7).^{89;90} It is also possible to use other metal halide starting materials, but it was found that replacement of TMEDA for phosphines resulted in the formation of $\text{Zr}(\eta^6\text{-C}_7\text{H}_8)\text{Cl}_2(\text{PR}_3)_2$. This latter Zr species could react further with LiInd (Ind = C_9H_7) to form the mixed sandwich analogue $\text{Zr}(\text{CHT})(\eta^5\text{-Ind})$ (right hand side of scheme 1.7).^{91–93} This compound can bind donor ligands such as phosphines whilst keeping the same hapticity of both rings. No work on the Hf equivalents has been reported.

Mixed sandwich species can also be made directly from ZrCpCl_3 using reductive methods. Reaction of the Cp (or substituted Cp) starting material with an excess of $^i\text{PrMgBr}$ in the presence of C_7H_8 resulted in the formation of $\text{ZrCp}(\text{CHT})$ in moderate yields.^{94;95} In the last five years, Glöckner and co-workers have made a library of substituted $\text{ZrCp}(\text{CHT})$ compounds (coining the term “trozircene”).^{96;97} This work revealed two fascinating structural features. Firstly, the hydrogens of the CHT ligand tend to flex in towards the metal centre, presumably in order to align the p -orbitals of the π system more towards the metal centre. Secondly, for all species considerably shorter metal-ring centroid distances were seen for the CHT ligand than for the Cp ligands, reflecting the stronger electrostatic pull of the formally trianionic ligand. Because the metal centres are electron deficient they will still bind donors, so if one of the carbons of the Cp ring is replaced with a phosphorus this can donate its electrons to an adjacent metal centre, forming a dimer in both the Hf and Zr cases.^{98;99}

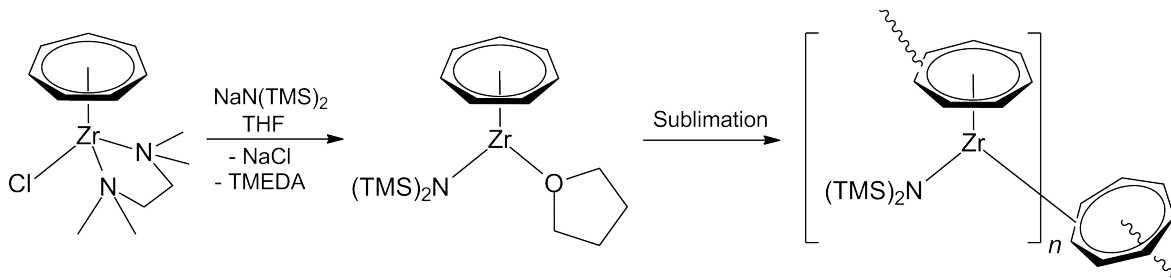
With a monochloride CHT starting material synthesised in acceptable yields (left hand side of scheme 1.7) further salt metathesis could be attempted. Indeed a library of substituted pentadiene, cyclopentadiene and allyl compounds has been made and recently reviewed by Glöckner and Tamm.¹⁰⁰ Generally, CHT Zr complexes require bulky



Scheme 1.8: The synthesis of a Zr piano stool structure

substituents, for example $\text{Zr}(\text{CHT})(\eta^3\text{-C}_3\text{H}_5)$ proved unobtainable, but using the bulkier substituted silyl-allyl allowed the isolation of $\text{Zr}(\text{CHT})(\eta^3\text{-C}_3\text{H}_3\text{TMS}_2)(\text{THF})$.¹⁰¹ It is possible to replace the THF with other two electron donors such as phosphines and NHCs. By exploiting the reactivity of the silylated allyl moiety Tamm and co-workers were able to attach a bulky imidazolin-2-iminato complex which following an intramolecular deprotonation resulted in the formation of a one-legged piano stool or “pogo stick” geometry (scheme 1.8).¹⁰²

Most recently $\text{Zr}(\text{CHT})$ containing amino and alkoxide complexes have been synthesised.¹⁰³ These, if sublimed to remove other binding ligands stabilise themselves by forming dimers or polymeric structures. Of particular note is the species $[\text{Zr}(\text{CHT})\text{N}(\text{TMS})_2]_n$, where the CHT ligand binds antifacially to the adjacent Zr centre making a one dimensional polymer (scheme 1.9).¹⁰³

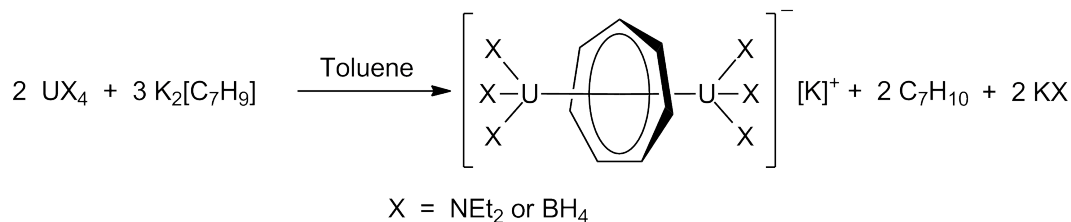


Scheme 1.9: The synthesis of amido CHT derivatives and the polymeric structure of the base-free analogue.

The recent isolation of $[\text{Zr}(\text{CHT})\text{N}(\text{TMS})_2]_n$ opens the possibility for further acid-base reactions, and also the exciting $\mu:\eta^7:\eta^2$ bridging mode poses the (synthetically challenging) possibility of multi-decker sandwich compounds. Notwithstanding the fascinating structural features observed with the CHT ligand, very little work has been done on developing the reactivity of these new compounds. The only application reported in the literature is the use of $\text{Zr}(\text{CHT})\text{Cp}$ as a precursor for atomic layer deposition.¹⁰⁴ Of particular interest to the present project would be whether $\text{Zr}(\text{CHT})$ containing complexes polymerise olefins - given the electron deficient nature of the metal centre it might be expected that these compounds could make potent catalysts.

1.4.2 Uranium cycloheptatrienyl complexes

Actinide CHT chemistry is exceedingly sparse, with only five papers on complexes containing the “ $\text{U}(\text{CHT})$ ” moiety. The first report was by Miller and Dekock, who treated UCl_4 with 3 equivalents of $\text{LiC}_7\text{H}_8\text{R}$ ($\text{R} = \text{H}, \text{Me}, {}^n\text{Bu}$).¹⁰⁵ Although no U products were characterised it was postulated, on the basis of the ${}^1\text{H}$ NMR data and chemical reactivity, that the $[\text{C}_7\text{H}_7]^{3-}$ ligand was present. It was not for another 13 years before further work was published on $\text{U}(\text{CHT})$ -containing complexes. Arliguie *et al.* altered Miller’s synthesis by using the potassium CHT salt and $\text{U}(\text{NEt}_2)_4$ or $\text{U}(\text{BH}_4)_4$ as the U synthons (these have the advantage over UCl_4 of being easily detectable by ${}^1\text{H}$ NMR).^{106;107} By addition of 18-crown-6 the former synthon yielded a complex that was isolable and characterisable: $[\text{K}(18\text{-crown-6})][(\text{NEt}_2)_3\text{U}(\mu\text{-}\eta^7:\eta^7\text{-C}_7\text{H}_7)\text{U}(\text{NEt}_2)_3]$ (scheme 1.10). However the latter synthon’s product, $[\text{K}][(\text{BH}_4)_3\text{U}(\mu\text{-}\eta^7:\eta^7\text{-C}_7\text{H}_7)\text{U}(\text{BH}_4)_3]$, had issues with purification from $[\text{U}(\text{BH}_4)_3(\text{THF})_3]$. Addition of dimethylphosphine ethane however allowed the competing complex to be removed and the product characterised. On



Scheme 1.10: Synthesis of U cycloheptatrienyl inverted sandwiches

one occasion the cation (usually solvated K^+) was replaced with a rare U(III) cation: $[\text{U}(\text{BH}_4)_2(\text{THF})_5]^+$ which was characterised by X-ray diffraction.

The crystal structure of $[\text{U}(\text{BH}_4)_3(\text{THF})_3][(\text{BH}_4)_3\text{U}(\mu\text{-}\eta^7\text{:}\eta^7\text{-C}_7\text{H}_7)\text{U}(\text{BH}_4)_3]$ shows the cation and anion as a discrete pair. The CHT ligand is treated as a trianion, and thus predicted to be aromatic by Hückel theory, which is corroborated by the planarity of the CHT ring in the complex. The average $\text{U-C}_{(\text{ring})}$ distance is $2.69(2) \text{ \AA}$, which is comparable to related Cp and COT structures [$2.68(2) \text{ \AA}$ for $\text{U}(\text{COT})(\text{BH}_4)_2(\text{OPPH}_3)$ and $2.66(3) \text{ \AA}$ for $\text{UCp}(\text{BH}_4)_3$].^{108;109} However, overall the formation of these complexes is extremely atomically inefficient (scheme 1.10), with the cycloheptadienyl starting material having to reduce itself to form the CHT ligand. This, combined with the aforementioned problems with purification, led to poor yields.

The only other U(CHT)-containing compound in the literature is the sandwich compound: $[\text{K}][\text{U}(\eta^7\text{-C}_7\text{H}_7)_2]$, which has been studied by X-ray crystallography and the 18-crown-6 solvate.¹¹⁰ This was made by the combination of UCl_4 with an excess of C_7H_8 in the presence of potassium in good yield (78 % as a green powder, or, if combined with 18-crown-6, 52 % as green crystals). This was the first η^7 -CHT sandwich compound. The crystal structure showed that the compound similarly consisted of discrete cation and anion pairs. The sandwich anion $[\text{U}(\text{C}_7\text{H}_7)_2]^-$ is of C_{2h} symmetry, with the regular heptagonal geometry of the planar C_7H_7 rings showing them to be aromatic. The average $\text{U-C}_{(\text{ring})}$ distance is $2.53(2) \text{ \AA}$, which is shorter than the other U(CHT)-containing compound (*vide supra*) and also other U(IV) Cp and cyclooctatetraene compounds. This has been seen with other CHT complexes of the early transition metal and is rationalised by proposed metal to ligand electron transfer giving an increase in formal oxidation state of the metal. An extensive theoretical investigation into the structure of $\text{U}(\text{C}_7\text{H}_7)_2$ and $[\text{U}(\text{C}_7\text{H}_7)_2]^-$ (among other actinides) was undertaken by Li and

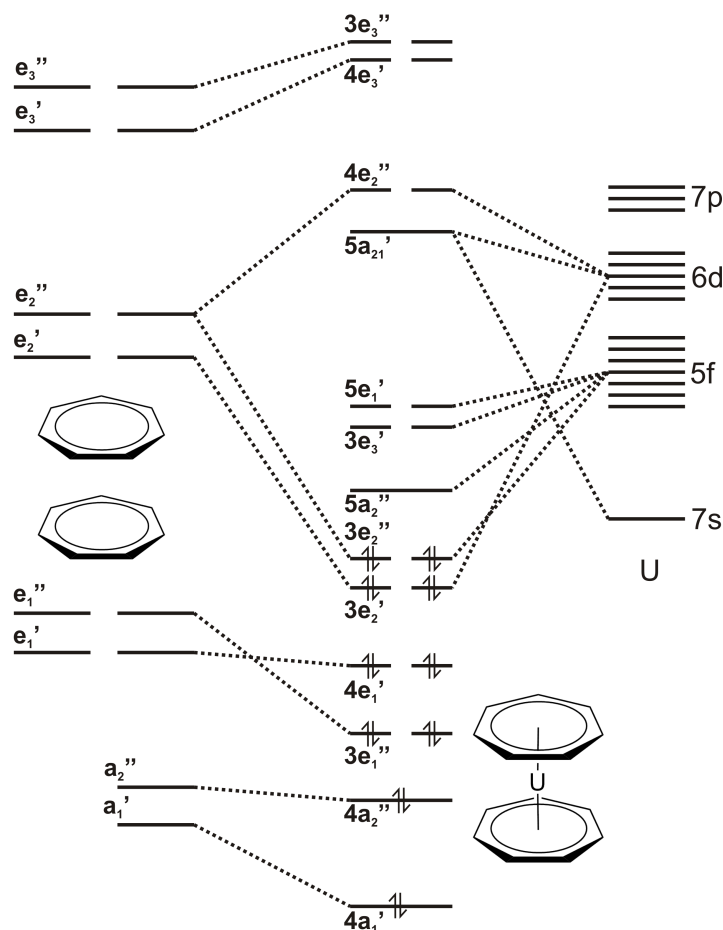


Figure 1.5: Schematic correlation diagram for the interaction of the orbitals of U and the two C_7H_7 ligands under D_{7h} symmetry. Electron occupations are for $U(C_7H_7)_2$.¹¹¹

Bursten.¹¹¹ It was shown that within these sandwich systems the $5f$ and $6d$ orbitals of the metal lie close in energy to the C_7H_7 π_2 orbitals (figure 1.5). In both $U(C_7H_7)_2$ and the $[U(C_7H_7)_2]^-$ cases the $3e_2''$ MO is nearly an equal mixture of $5f$ and π_2 and also contains four electrons. This leads to the reasonable conclusion that these electrons are equally split between these orbitals, thus making the best electronic description as $[C_7H_7]^{2-}$ and the metal either U(IV) (for the neutral complex) or U(III) for the anionic complex.

1.5 η^8 bound carbocyclics: cyclooctatetraene (COT) and pentalene

The η^8 coordination mode is the first coordination mode to have two possible carbocyclic rings that could bind: cyclooctatetraene (COT = C_8H_8) and pentalene (Pn = C_8H_6) (figure 1.6). Pn is related to COT *via* a 1,4-transannular ring pinching and is isoelectronic with COT and thus is predicted to be anti-aromatic as a neutral molecule ($4n$ π

Hückel definition).^{112;113} COT stabilises itself by adopting a tub geometry, Pn however can not adopt such a geometry (due to the transannular bond) and therefore stabilises itself by a $[2 + 2]$ cycloaddition (figure 1.6).¹¹⁴ However, both COT and Pn can be reduced to form a 10 π electron, aromatic dianion.^{115–117}

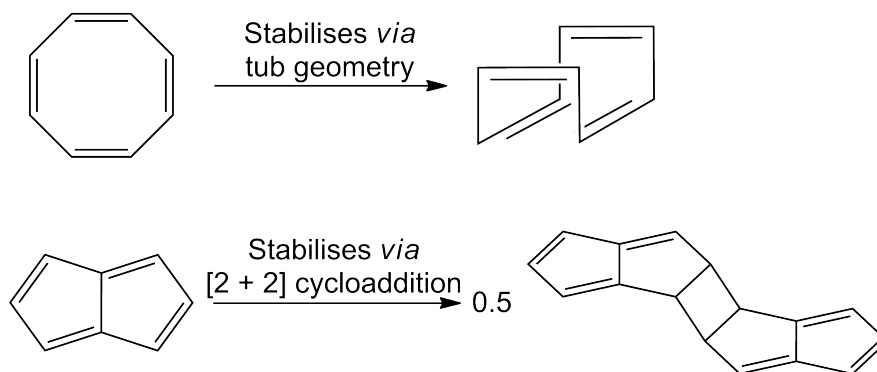


Figure 1.6: Rearrangements of the COT and Pn ligands.

Organometallic COT chemistry is considerably better developed than organometallic Pn chemistry due to the wider availability of suitable precursors. Generally, Pn syntheses are cursed with poor yield and purity or require specialised equipment, whereas COT is commercially available.^{118–120} This is in particular reflected in the number of structures in the Cambridge Structural Database (table 1.2).

Table 1.2: Number of structurally characterised η^8 -COT/Pn species in the Cambridge Structural Database (structures from this work excluded).

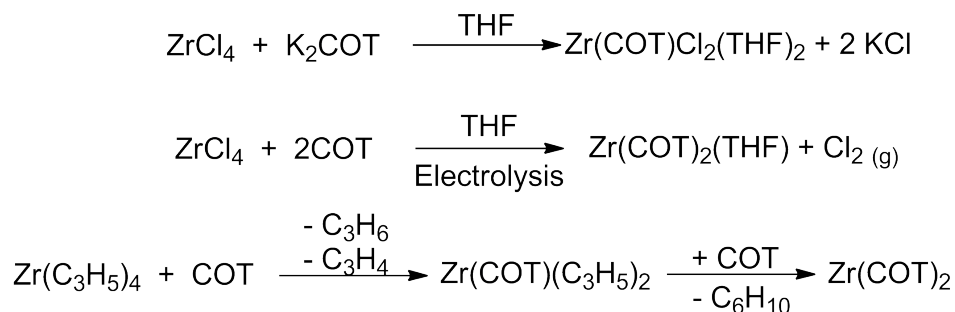
	Number of η^8 -COT structures	Number of η^8 -Pn structures
Zr	33	1
Hf	4	0
U	81	4

1.5.1 Zirconium and hafnium cyclooctatetraene complexes

The first report of group 4 COT complexes was in 1970, where it was found that the reaction of MCl_4 ($M = \text{Zr}$ or Hf) with C_8H_8 gave a species of assumed formula $M(\text{C}_8\text{H}_7)_2\text{MCl}_2$.¹²¹ This was characterised by elemental analysis and IR spectroscopy, and due to the similarities with the neutral C_8H_8 species it was assumed that the COT ligand was still in its D_{2d} ‘tub’ geometry. It was not until five years later when

a single crystal X-ray diffraction study was undertaken that the true formulation of $M(\text{COT})\text{Cl}_2 \cdot 2\text{THF}$ was revealed.¹²²

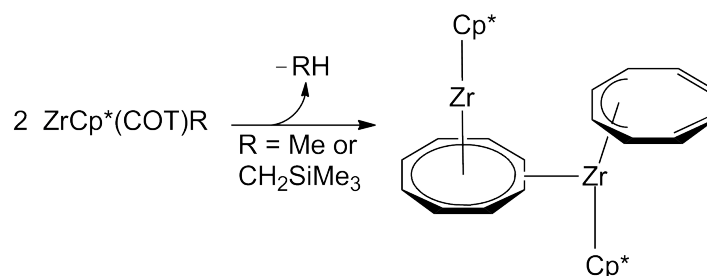
Around the same time, workers in the Max-Planck Institute were undertaking the same reaction but with electrolysis in order to reduce the COT *in situ*.¹²³ This reaction pathway gave the same dichloride THF adducts if the metal and COT were in a 1:1 ratio, but if two equivalents of COT were used the assumed homoleptic sandwiches $M(\text{COT})_2$ were formed. The Zr compound was soon thereafter studied by X-ray diffraction and found in fact to be a THF adduct of more accurate formulation: $\text{Zr}(\eta^4\text{-COT})(\eta^8\text{-COT})(\text{THF})$, formally an 18 electron complex.¹²⁴ It was not until nearly two decades later that the non-solvated sandwich was isolated and structurally characterised (along with the Hf congener and two other electron donor adducts).¹²⁵ Remarkably in the solid state the unsolvated sandwich remains in its $\eta^4:\eta^8$ binding mode. As would be expected, the two COT rings quickly interchange their binding modes and are indistinguishable by ^1H NMR. Almost simultaneously Kablitz and co-workers established an alternative pathway to the homoleptic sandwiches *via* the reaction of $\text{Zr}(\text{allyl})_4$ and COT.¹²⁶ This report also included the first attempts at the reduction of these sandwich compounds hinting that COT could be an ideal stabilising ligand for such systems. The syntheses of these early $\text{Zr}(\text{COT})$ precursors are summarised in scheme 1.11.



Scheme 1.11: The syntheses of appropriate $\text{Zr}(\text{COT})$ precursors.

It was not until 1982 that the first mixed sandwich species involving COT was formed. Woodward *et al.* found that combination of ZrCl_4 with $\text{K}_2\text{C}_8\text{H}_8$ and LiCp^* resulted in the formation of $\text{Zr}(\eta^8\text{-COT})(\text{Cp}^*)\text{Cl}$ in 80 % yield.¹²⁷ This was used in further salt metathesis reactions and yielded a variety of derivatives (including alkyl, aryl, vinyl and acetylide).¹²⁸ Of particular interest were the allyl derivatives - in the

unsubstituted compound the allyl moiety was found to bind in an η^3 fashion, pushing the COT to bind η^4 [giving a formula of $\text{Zr}(\eta^4\text{-COT})(\text{Cp}^*)(\eta^3\text{-C}_3\text{H}_5)$] though upon substitution of the allyl with a single methyl group the allyl was found to revert to an η^1 binding mode and the COT to η^8 . This varied hapticity demonstrates the curious ability of carbocyclic rings to respond to the electronic demands of the metal centre. Heating the methyl and CH_2SiMe_3 derivatives results in the elimination of an equivalent of RH and the dimerisation of the species to form a bridging COT species: $\text{Cp}^*\text{Zr}(\mu\text{:}\eta^8\text{:}\eta^2\text{-COT})\text{ZrCp}^*(\eta^4\text{-COT})$ (scheme 1.12).¹²⁹

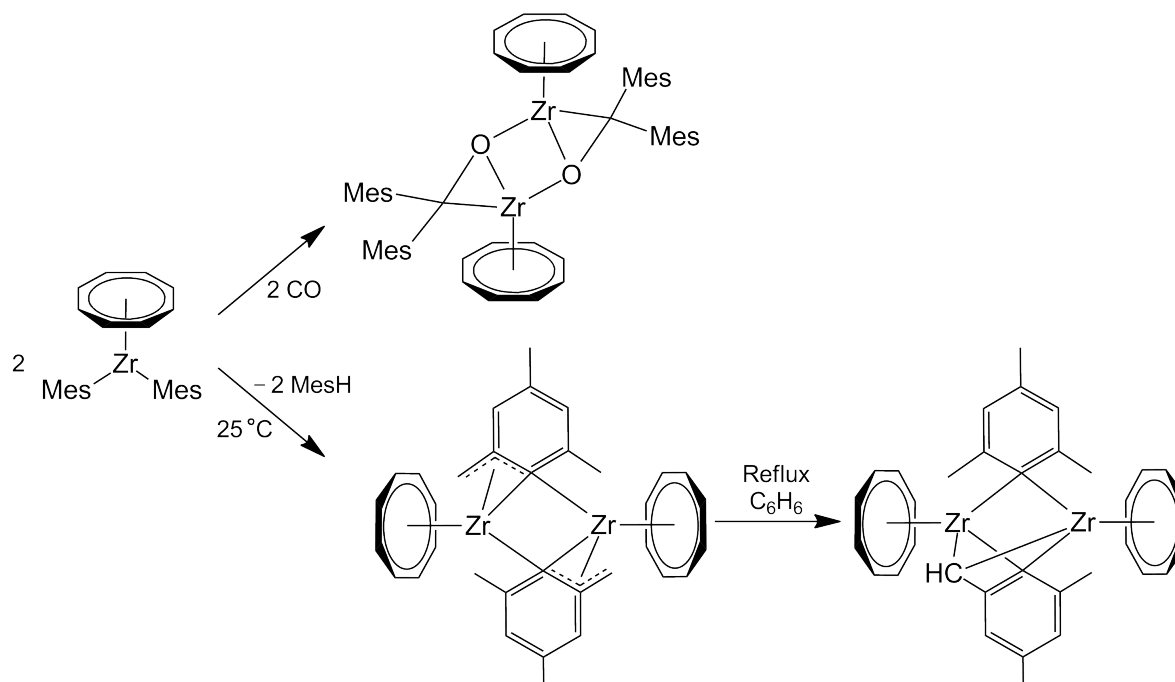


Scheme 1.12: The thermal decomposition of $\text{Zr}(\text{COT})\text{Cp}^*\text{R}$ ($\text{R} = \text{Me}, \text{CH}_2\text{SiMe}_3$).

Further to the above Zr(IV) studies with the mixed sandwich species it is possible to reduce $\text{Zr}(\eta^8\text{-COT})\text{Cp}^*\text{Cl}$ with a Na/Hg amalgam, or by reaction of ZrCp^*Cl_3 with COT in the presence of Mg.^{95;127} However, this species could only be studied with IR and ESR spectroscopy and it was not until 2010 that Cloke (with a substituted COT derivative) attained single crystal X-ray structures (*vide infra*).¹³⁰

The chemistry of half sandwich complexes of the type $\text{M}(\text{COT})\text{R}_2$ is somewhat limited. In one of the earlier papers, the ^1H NMR spectra of $\text{Zr}(\text{COT})\text{R}_2$ ($\text{R} = \text{Me}, \text{Et}$) were reported but the compounds were found to be thermally sensitive.¹²⁶ However in 1986 the synthesis of the thermally metastable mesityl derivate $\text{Zr}(\text{COT})(\text{Mes})_2$ [$\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$] was reported.¹³¹ This species was shown to undergo insertion with CO like the cyclopentadiene alkyl and aryl derivatives to form an epoxy dimer (top of scheme 1.13).¹³² However as stated earlier this bis-mesityl species was only semi-thermally stable, and if left at room temperature dimerises with the elimination of MesH to give two bridging $\mu\text{:}\eta^1\text{:}\eta^3$ mesityl groups, which undergo rearrangement to form a compound of formula $[\text{Zr}(\text{COT})]_2[\mu\text{:}\eta^1\text{:}\eta^1\text{-Mes}][\mu\text{:}\eta^3\text{:}\eta^3\text{-Mes}]$ (bottom of scheme 1.13).^{133;134}

Previously mentioned was Cloke's substituted COT ligand COT^{R} [$\text{R} = 1,4\text{-(SiMe}_3)_2$,



Scheme 1.13: CO insertion and the thermal degradation of $\text{Zr}(\text{COT})\text{Mes}_2$

Me may be exchanged for bulkier alkyl groups such as $i\text{Pr}$ or $t\text{Bu}$).¹³⁵ This bulky ligand was used to stabilise and crystallise the Zr(III) and Hf(III) compounds: $\text{MCp}^*(\text{COT})$. Interestingly these compounds displayed a rare difference between Zr and Hf chemistry with the former being a monomeric species, $\text{ZrCp}^*(\text{COT})$, and the latter dimerising through the COT rings to form a compound of formula $\text{Cp}^*\text{Hf}(\eta^7\text{-C}_8\text{H}_7\text{-}\eta^7\text{-C}_8\text{H}_7)\text{HfCp}^*$ where a C–C σ bond has formed between two COT rings (figure 1.7).¹³⁰

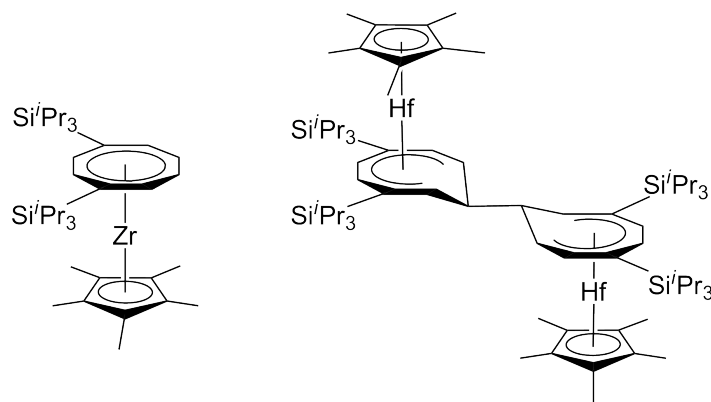


Figure 1.7: The results of the reduction of $(\text{COT}^{\text{R}})\text{MCp}^*\text{Cl}$ by KC_8 .¹³⁰

In an effort to form a “pogo stick” structure as had been seen in titanium COT imido chemistry Dunn and co-workers employed this ligand to form a half sandwich imido derivative: $[\text{Zr}(\text{COT}^{\text{R}})(\mu\text{-NAr})_2]$ [$\text{R} = 1,4\text{-(SiMe}_2t\text{Bu)}_2$, $\text{Ar} = 2,6\text{-C}_6\text{H}_4\text{Me}_2$] from the bridging imido dichloride starting material.¹³⁶ Wigley and co-workers had previ-

ously synthesised both Hf and Zr derivatives with unsubstituted COT but structural characterisation eluded them.¹³⁷ However the bulkier substituted silyl group in Dunn's compound enhanced the compound's crystallisability and it was shown conclusively to be a dimer.

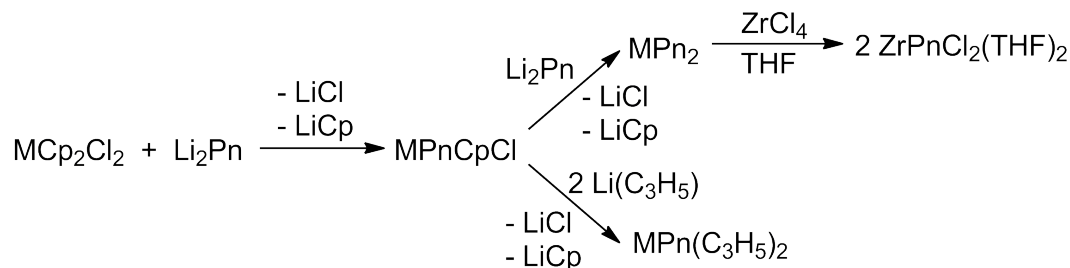
1.5.2 Zirconium and hafnium pentalene complexes

It was noted earlier that COT is isoelectronic with Pn but that Pn precursors are notoriously difficult to make and that this has restricted this area of organometallic chemistry. To date there are only four accounts of Zr compounds containing the Pn ligand in the literature, and only two crystal structures. Before the work described in this thesis there were no crystal structures of Hf compounds containing the Pn ligand.

The initial report of the η^8 -Pn binding mode contained four Pn compounds. It was found that combination of MCp_2Cl_2 with one equivalent of Li_2Pn led to the elimination of LiCl and LiCp to give the 18 electron complexes MPnCpCl ($\text{M} = \text{Zr}$ or Hf). The Zr congener was structurally characterised *via* single crystal X-ray diffraction, the structure differing from the previously synthesised COT species in that the Pn ligand folded around the metal centre increasing orbital overlap.¹³⁸ Addition of a further equivalent of Li_2Pn resulted in the formation of the homoleptic sandwich species MPn_2 . Disappointingly, the solid state structure of these species (nor the mono-methylated derivative that was synthesised in the same paper) were not reported - these would have made an interesting comparison with the $\text{M}(\eta^4\text{-COT})(\eta^8\text{-COT})$. Though the report did not contain any single crystal X-ray structures, the non methylated versions were the subject of a further photo-electron spectroscopic study which predicted their geometries having staggered Pn rings bound in the η^8 fashion.

Reaction of the Zr homoleptic sandwich with an equivalent of $\text{ZrCl}_4 \cdot 2\text{THF}$ at room temperature resulted in a redistribution reaction giving the ZrPn-containing half sandwich $\text{ZrPnCl}_2(\text{THF})_2$. This half sandwich compound seemed as if it would open the door to further salt metathesis but none has been attempted. In a review of the organometallic chemistry of pentalene Summerscales asserts that ZrPnIndCl was synthesised but no evidence of this is to be found elsewhere in the literature.¹³⁹ Reaction of ZrPnCpCl with

two equivalents of lithium allyl resulted in the formation of $\text{ZrPn}(\eta^3\text{-C}_3\text{H}_5)$.¹⁴⁰ Again this was not crystallised so geometric parameters could not be established. However it was the subject of detailed NMR analysis which established the energy requirements for interconversion of stereoisomers to be 64 kJ mol^{-1} at -40°C .



Scheme 1.14: A summary of the previously synthesised group 4 Pn compounds.

1.5.3 Uranium complexes of cyclooctatetraene

1.5.3.1 Sandwich compounds: uranocene

The symmetry of the HOMO of COT is such that it is complementary to the f -orbitals, similar to the way Cp is complementary to the d -orbitals. This can be illustrated by ferrocene, in which the ligand π molecular orbitals share a nodal plane with the appropriate d -orbital of the central Fe^{2+} [(A) in figure 1.8]. In order for a similar interaction to occur for COT an eight lobed orbital is required - i.e. an f -orbital [(B) in figure 1.8]. Because of this, there is comparatively more uranium COT chemistry than for zirconium or hafnium.

The isolation of uranocene itself, $\text{U}(\text{COT})_2$, in 1968 is arguably the most excit-

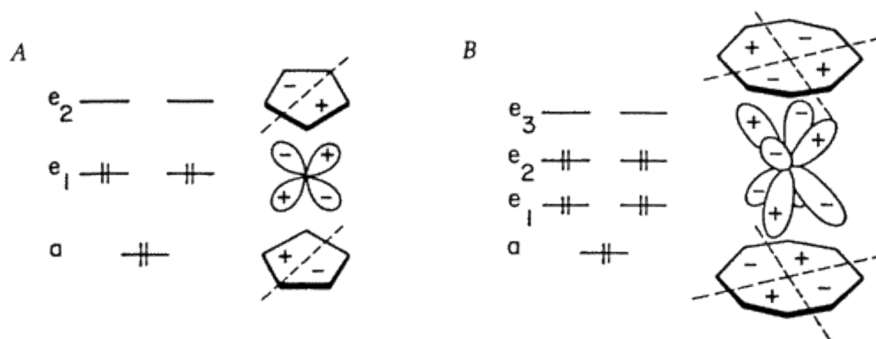


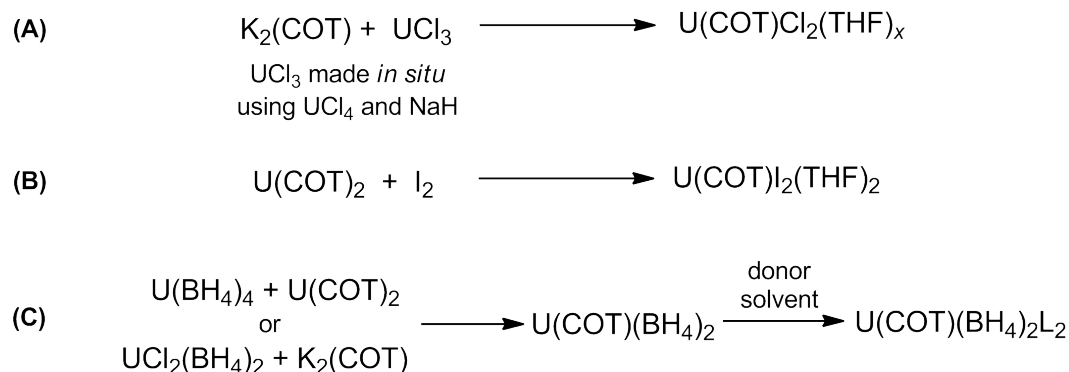
Figure 1.8: (A) The ligand π orbitals of two Cp^- and the appropriate Fe^{2+} d -orbitals. (B) the HO- π -MOs of two COT dianions and the $f_{\pm 2}$ of a central U^{4+} atom. Reproduced from Streitwieser, A., Jr. *A Lifetime of Synergy with Theory and Experiment, Profiles, Pathways and Dreams: Autobiographies of Eminent Chemists*; Seeman, J. I., Series Ed.; American Chemical Society: Washington, DC, 1996, p 183.

ing discovery in organoactinide chemistry.¹³ The synthesis was achieved by the combination of UCl_4 with K_2COT yielding uranocene as green pyrophoric crystals, although it can also be synthesised by direct reaction of COT with the metal.^{141;142} Uranocene had been hinted at in earlier theoretical papers, and its eventual synthesis by Streitweiser was a great (and exciting) step forward, in particular its D_{8h} structure and the degree of orbital interaction between the f -orbitals on the metal and the ligand.^{143;144} An enormous range of spectroscopic studies has been undertaken and these have generally supported the view that there is significant f -orbital involvement, but their contribution is less than that of the d -orbitals.^{145–156} A large number of uranocene derivatives with substituted COT rings has since been synthesised and characterised including alkyls,^{157–163} alkoxy,¹⁶⁴ amino,¹⁶⁴ aryl,¹⁶⁵ carboxy ethers,¹⁶⁶ benzo-,¹⁶⁷ ansa bridged and silylated.^{168–170} However in contrast to ferrocene, the reactivity of the uranocenes has proved disappointingly limited, with $\text{U}(\text{COT})_2$ itself being unreactive towards Friedel-Crafts acylating agents or organolithium reagents.¹⁷¹ Uranocene is, however, redox active. Electrochemical oxidation led to the formation of the expected $[\text{U}(\text{COT})_2]^+$ cation and then further oxidation to the dication resulted in decomposition through an assumed dimerisation process.^{172;173} More success has come from the reduction of uranocene, which could be chemically reduced with Li naphthalenide to an assumed $[\text{U}(\text{COT})_2]^-[\text{Li}(\text{THF})]^+$.¹⁷⁴ Although no crystal structure was determined this species was studied with visible spectroscopy, EPR and [somewhat surprisingly since it is U(III)] NMR spectroscopy. Attempts to repeat this synthesis by other groups, however, have failed however success was achieved in reducing substituted uranocenes with potassium metal in THF.¹⁷⁵ X-ray diffraction studies of the methyl substituted uranocene showed the metal centre to be displaced towards one of the rings with the potassium counter-ion bound on the other side of the more distant COT ring.¹⁷⁶ The only other reduced uranocene derivative to be characterised is the bis-silylated COT prepared developed by Cloke and co-workers, which showed essentially the same structure.¹⁷⁷ Further uranocene chemistry is limited. Very recently it was shown that extremely hard ions such as azide or cyanide will bind to the thorium centre in thorocene, but the only U derivative achievable was the cyanide:

$[\text{U}(\text{COT})_2(\text{CN})]^-[\text{Na}(18\text{-crown-6})]^+$. A recent theoretical report has also suggested the possibility of the synthesis of a double uranocene sandwich with the two uranocene monomers linked *via* C–C between the COT rings but no further synthetic work has been done on this.¹⁷⁸ A detailed account of the conception and synthesis of uranocene was published in a cover article of *Organometallics* in 2004.¹⁷⁹

1.5.3.2 Half-sandwich compounds

It was not until 20 years after the initial report of uranocene that $\text{U}(\text{COT})$ half sandwich chemistry was discovered whereupon a number of half sandwich synthons were discovered in quick succession. The first paper reported the synthesis of $\text{U}(\text{COT})[\text{N}(\text{TMS})_2]_2$.¹⁸⁰ This synthesis was achieved *via* $\text{U}(\text{COT})\text{Cl}_2(\text{THF})_2$, the preparation of which was not published until two years later.¹⁸¹ The direct combination of UCl_4 and K_2COT would only yield uranocene, but if reduction were to take place *in situ* by addition of NaH and then followed by addition of K_2COT the isolation of the dichloride half sandwich in good yield was possible [(A) in scheme 1.15]. This was shown to bind two THF molecules making the formula $[\text{U}(\text{COT})\text{Cl}_2(\text{THF})_2]$ and X-ray diffraction studies showed the THF molecules to adopt axial positions in a trigonal bipyramid structure. Within the same study it was shown that the THF could easily be displaced by other electron donors (e.g. pyridine) and the chlorides were shown to be suitable for metathesis [reaction with $\text{Na}(\text{acac})$ led to the isolation of $\text{U}(\text{COT})(\text{acac})_2$]. One year after this report, the di-iodide was reported *via* a different synthesis - a redistribution of uranocene with iodine in THF to form $\text{U}(\text{COT})\text{I}_2(\text{THF})_2$ [(B) in scheme 1.15].¹⁸² Simultaneously with the development of these di-halide precursors, Cloke (and Ephritikhine shortly after) reported the synthesis of the borohydride half sandwich $\text{U}(\text{COT})(\text{BH}_4)_2$ [(C) in scheme 1.15].^{109;183} Cloke's communication only mentioned the initial synthesis but Ephritikhine's report went into more depth, showing the species to bind donor solvents [giving the molecular structure of $\text{U}(\text{COT})(\text{BH}_4)_2(\text{OPPh}_3)$ - indeed $\text{U}(\text{COT})(\text{BH}_4)_2$ is soluble only in donor solvents] and, importantly, showing the borohydride ligands to be substitutionally labile [both with TiCl_4 and $\text{NaN}(\text{TMS})_2$].



Scheme 1.15: The three syntheses of U(COT)-containing half-sandwich starting materials.

With the development of three suitable starting materials, one would have expected U(COT) half sandwich chemistry to blossom, but the bulk of the work has been by Ephritikhine using U(COT)(BH₄)₂. The body of work carried out is summarised in figure 1.9. The borohydride starting material, U(COT)(BH₄)₂, is substitutionally active either by protonolysis or salt metathesis. The species in figure 1.9 (*vide supra*) have all been characterised, many with single crystal X-ray structures. Of particular interest is the ability of the half sandwich to stabilise the metal in curious oxidation states. For example the species [U(COT)(DDDT)₂][−][Na(18-crown-6)]⁺ (on the far-right of the figure above) contains a relatively rare U(V) centre. Most recently Cloke *et al.* have prepared a U(III) half sandwich. In a one pot procedure combination of the potassium tris(pyrazolyl)borate with UI₃ formed the U[tris(pyrazolyl)borate]I₂ *in situ* and subsequent addition of K₂COT^R [R = 1,4-(SiⁱPr₃)₂] led to the formation of U(COT^R)Tp [Tp = tris(pyrazolyl)borate].¹⁸⁴ This synthesis has not been repeated with other ligands but provides an exciting entry point into U(III) half sandwich chemistry especially when combined with the relatively recent discovery of the simple synthesis of UI₃.¹⁸⁵

1.5.3.3 Mixed-ring compounds

Some of the most exciting, recent, developments in organouranium chemistry have involved mixed sandwich COT/Cp (and their substituted derivatives) species. The first such compound was synthesised and (partially) characterised a decade after the discovery of uranocene. It was found that the reaction of Cp₃UCl with K₂COT^R (R = 1,4-Me₂) gave a novel compound.¹⁹³ This was characterised by ¹H NMR, mass spectrometry and IR spectroscopy, and because of the IR spectrum the structure of

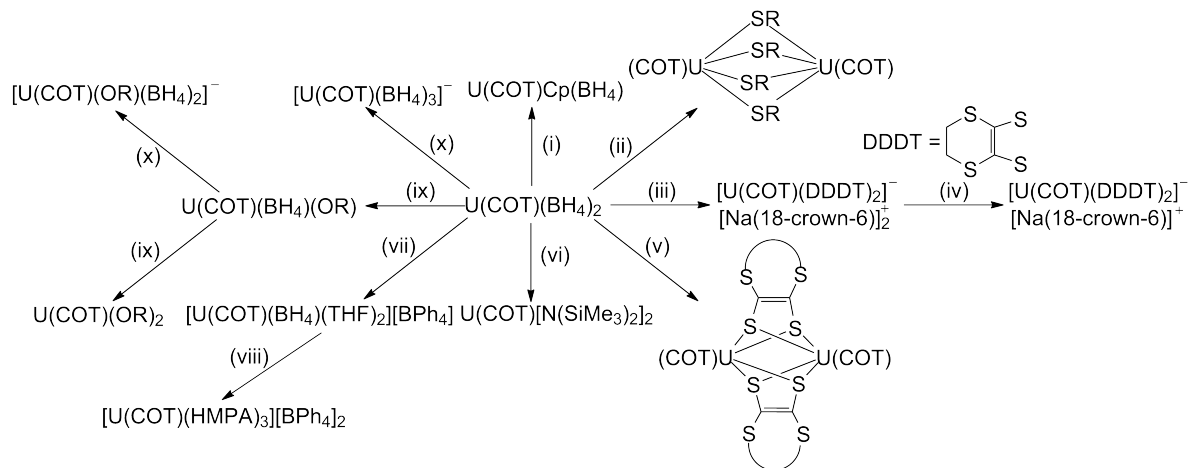


Figure 1.9: A summary of Ephritikhine's work. (i) TiCp ; ¹⁰⁹ (ii) RSH ($\text{R} = {}^i\text{Pr}, {}^n\text{Bu}, {}^t\text{Bu}$; ¹⁸⁶ (iii) NaDDDT ; ¹⁸⁷ (iv) AgBPh_4 or AgI ; ¹⁸⁷ (v) $\text{DDDT}(\text{CO})$; ¹⁸⁸; (vi) $\text{NaN}(\text{SiMe}_3)_2$; ¹⁰⁹ (vii) $(\text{NEt}_2\text{H})(\text{BPh}_4)$; ^{189;190} (viii) $(\text{NEt}_2\text{H})(\text{BPh}_4)$, HMPA ; ^{189;190} (ix) ROH ($\text{R} = \text{Et}, {}^i\text{Pr}, {}^t\text{Bu}$); ^{191;192} (x) BH_4^- . ^{191;192}

$(\text{UCp}_3)_2(\mu\text{-}\eta^3\text{-}\eta^3\text{-COT}^{\text{R}})$ was proposed, but this has never been confirmed by X-ray diffraction. For 15 years, no further work was reported on mixed sandwich species until Schake *et al.* developed a synthesis using a U(III) synthon.¹⁹⁴ The combination of $\text{Cp}^*\text{UI}_2(\text{THF})_3$ with K_2COT resulted in the formation of $\text{U}(\text{COT})\text{Cp}^*(\text{THF})$, which was characterised by ^1H NMR, IR and elemental analysis. Replacement of the THF by a bulkier, stronger donor (5,5'-dimethyl-2,2'-bipyridine) allowed the species to be crystallised giving the first structurally characterised $\text{U}(\text{COT})\text{Cp}$ -containing mixed sandwich complex.¹⁹⁴ Since these discoveries, a number of U(IV) $\text{U}(\text{COT})\text{CpR}$ species have been developed where $\text{R} = \text{Cl}^-$,¹⁹⁵ I^- ,¹⁹⁶ amide,^{196;197} borohydride and CH_2TMS .^{196;198}

However, the most interesting development in this area is small molecule activation using U(III) species. Tuning the steric demands around these metal centres has revealed some very exciting new reactivity. Cloke's seminal work on this has seen the formation of different species depending on the number of equivalents of CO added and the steric demand of the ligands (figure 1.10).^{199–202} For $\text{U}(\text{COT}^{\text{R}})\text{Cp}^{\text{R}'}$ [$\text{R} = 1,4\text{-(Si}^i\text{Pr}_3)_2$, $\text{R}' = \text{Me}_4$ or Me_5], one equivalent of CO will bind directly to the metal centre through the carbon, but this quickly isomerises to bind through the oxygen with subsequent coupling to form a bis(U) (IV) species bridged by an ynediolate. If the Cp ligand is tetramethylated and excess CO is admitted, four molecules couple to form the tetratate dianion $(\text{C}_4\text{O}_4)^{2-}$, but if the pentamethylated Cp^* ligand is used, only three molecules couple to form a deltate dianion $(\text{C}_3\text{O}_3)^{2-}$. If a mixture of gases is used different cou-

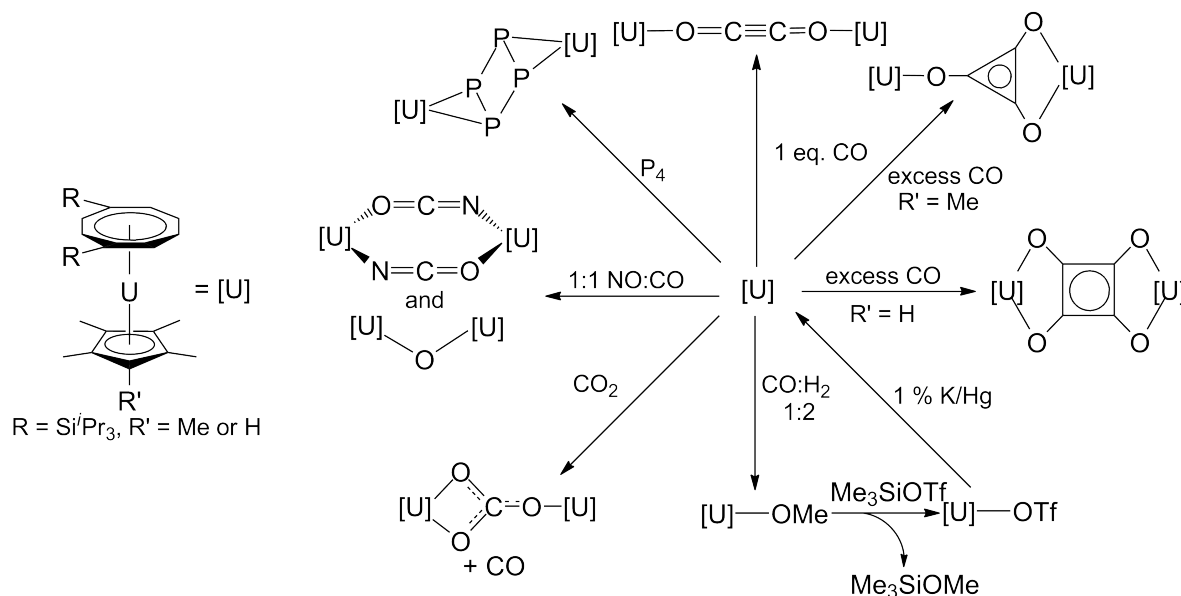


Figure 1.10: Examples of small molecule activation by Cloke's U(III) COT complex.

pling products can be made. For example, if a 1:1 mixture of NO and CO is used, two different U species are formed. One is an oxo-bridge dimer, $[U]-O-[U]$, the other a dimer bridged with two cyanate species, $[U]-(NCO)_2-[U]$ ($[U] = U[COT^R]Cp^*$).²⁰³ More excitingly, in the most recent report, if the $U(COT^R)Cp^*$ species is exposed to a 2:1 mixture of H_2 and CO a methoxide species is formed. This can be reacted with excess Me_3SiOTf to eject Me_3SiOMe and form $U(COT^R)Cp^*OTf$, which can be reduced back to the reactive species by a 1 % K/Hg amalgam.²⁰⁴ The same system has also revealed a new $\mu:\eta^2:\eta^2-P_4$ bonding mode when reacted with white phosphorous.²⁰⁵

Evans and co-workers have shown that, by exacting high steric demands on the U(III) centre, novel reactivity of the U centre results. Two equivalents of UCp^*_3 with three equivalents of COT give a formal three electron reduction to form a dimeric species with a bridging COT^{2-} ligand: $[U(COT)Cp^*]_2(\mu:\eta^3:\eta^3-COT)$.²⁰⁶ This is the same system that has been adapted as a reliable way to make bridging arenes (*vide supra*).^{74;207}

1.5.3.4 Pentalene uranium compounds

Due to the difficulty in the synthesis of Pn precursors there are only four reports of UPn-containing compounds. The earliest report concerned the synthesis of the substituted Pn uraniumocene equivalent $UPnR_2$ [$R = 1,4-(Si^iPr_3)_2$].²⁰⁸ This species was characterised

by ^1H NMR, mass spectrometry, elemental analysis and an in-depth photoelectron spectroscopy study (augmented with DFT). This predicted the geometry of the species but, due to the lack of a crystal structure, this could not be confirmed. Indeed it was not until this present work that a crystal structure of the permethylated Pn uranocene equivalent was achieved.²⁰⁹

Two further papers contain examples of U(III) Pn compounds. The first reports the synthesis of a tris(pyrazolyl)borate Pn species to the analogous COT species discussed earlier.¹⁸⁴ Finally there is a communication of the synthesis of a mixed sandwich $\text{Pn}^{\text{R}}/\text{Cp}^*$ species. Fascinatingly, this seems even more reactive than the COT congener mentioned above in that it will reversibly reduce dinitrogen to form $[\text{U}(\text{Pn}^{\text{R}})\text{Cp}^*]_2(\mu\text{:}\eta^2\text{:}\eta^2\text{-N}_2)$.^{210;211}

1.6 Aims of this thesis

With the relatively simple synthesis of permethylpentalene $[\text{Pn}^*; \text{C}_8\text{Me}_6]$ synthons: $\text{Li}_2\text{Pn}^*(\text{TMEDA})_x$ and $\text{Pn}^*(\text{SnMe}_3)_2$, the door has been opened to develop this exciting area of chemistry.^{212;213} Previous work within the group has focused on TiPn^* chemistry.²¹⁴ The purpose of this project is to extend the use of this ligand in its η^8 binding mode into the actinides and the other group 4 metals. Chapters two and three of this thesis will chart the synthesis and characterisation of the novel organometallic species created, and chapter four will give an account on the efficacy of the species as catalysts for the polymerisation of olefins.

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2. THE SYNTHESIS OF URANIUM PERMETHYLPENTALENE COMPLEXES

2.1 *Introduction*

The discovery of ferrocene in 1951¹ followed by the elucidation of its novel structure led to the proliferation of the cyclopentadienyl chemistry of the transition metals.² Extension of this chemistry to the *f*-block led to the isolation of a number of lanthanide compounds of the generic formula LnCp_3 .³ Their properties indicated ionic compounds; for example their absorption spectra in THF were similar to those of the aqueous ions and reaction with FeCl_2 yielded ferrocene.⁴ The fact that the *4f* elements gave such compounds suggested that the cyclopentadienyl derivatives of the *5f* elements might be accessible.

Early attempts to synthesise organoactinides were fraught with difficulty, cursed with poor yields of products often highly sensitive to air and heat. In 1956, Reynolds and Wilkinson reported the first of these cyclopentadienyl uranium species.⁵ They reacted anhydrous UCl_3 with NaCp in THF and subsequent work-up gave extremely air and temperature sensitive red crystals (albeit in low yield). Analysis demonstrated there was no Cl present and the compound to have the approximate formula $\text{UC}_{15}\text{H}_{15}$, however in view of the stability issues no further work was done on this compound at the time. On the other hand the reaction of UCl_4 with just under two equivalents of NaCp in THF gave UCp_3Cl as dark red crystals. This species, though air sensitive, was found to be thermally stable and therefore lent itself to further chemical analysis. The absorption spectrum of the uranium ion showed no similarity to that of the aqueous uranium ion and when the product was treated with FeCl_2 , no ferrocene was formed (a good counter-argument to the formation of ionic Cp^-). Neither was any reaction seen with maleic anhydride implying the bonding is not η^1 . As such an η^5 ‘sandwich-like’ bonding

situation was proposed. This gained support from a molecular orbital treatment which showed extensive $5f$ involvement in the bonding. It was also found that reaction of UCp_3Cl with AgClO_4 in THF gave silver chloride, implying the chloride was essentially ionically bound. It was not until 1965 that all this was confirmed *via* single crystal X-ray analysis.⁶

Synthesis of UCp_4 was achieved under the forcing conditions of refluxing UCl_4 with excess KCp in benzene.⁷ The resultant red crystals, formed in low yield (6%), were both air and thermally stable (although a solution in benzene proved to be highly air-sensitive). IR and solution phase dipole moment measurements indicated η^5 -bound Cp, which was later confirmed through crystallographic characterisation; this demonstrated the Cp ring centroids to be in a tetrahedral arrangement about the uranium centre.^{8;9} Mono- and bis-cyclopentadienyl uranium compounds have also been made, however UCp_2Cl_2 quickly disproportionates to UCpCl_3 and UCp_3Cl and the mono-cyclopentadienyl uranium trichloride can only be isolated as solvent adducts.^{10–13} Work on cyclopentadiene and pentamethylcyclopentadiene uranium derivatives has been vast, with many alkyl, aryl, hydride, alkoxide, amide and allyl compounds having been made.^{14–18} More recently, examples of catalytic processes mediated by uranium complexes have been discovered including dimerization, oligomerization, hydrosilation and hydroamination of terminal alkynes and the hydrogenation of alkenes.¹⁹ Furthermore uranium complexes have been shown to activate small molecules such as N_2 , CO and CO_2 .²⁰

The isolation of uranocene $[\text{U}(\text{COT})_2]$ ($\text{COT} = \text{C}_8\text{H}_8$) in 1968 is arguably the most exciting discovery in organoactinide chemistry.²¹ Uranocene had been hinted at in earlier theoretical papers, and its eventual synthesis by Streitwieser *et al.* was a great step forward. Of particular interest was its D_{8h} structure and the degree to which the ligand orbitals and the metal f -orbitals interacted. An enormous range of spectroscopic studies have been undertaken and these have generally supported the theory that though significant f -orbital involvement is observed, the contribution is less than that of the d -orbitals.^{22–29} A large number of substituted uranocene derivatives have since been synthesised. In comparison with ferrocene however, the reactivity of the

uranocenes has proved disappointingly limited, with $\text{U}(\text{COT})_2$ itself being unreactive towards Friedel-Crafts acylating agents or organolithium reagents.³⁰

As mentioned in chapter one pentalene is isoelectronic with COT, related *via* a transannular bond. However it was not until 1997 that the uranocene equivalent was synthesised by Cloke *et al.*: UPn_2^{R} [$\text{R} = 1,4\text{-(Si}^i\text{Pr}_3)_2$].³¹ This was shown *via* NMR to exist as a mixture of two isomers which did not interconvert (figure 2.1). Of particular interest in this molecule is the bonding situation which was investigated *via* photoelectron spectroscopy and DFT calculations, showing the presence of δ bonding between the π -orbitals of the ligand and the metal d - and f -orbitals.

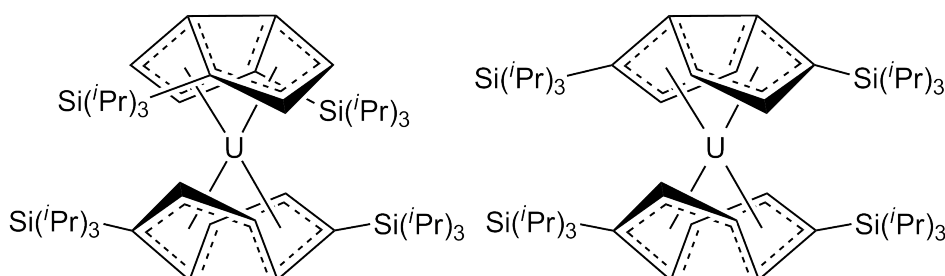


Figure 2.1: The two isomers of UPn_2^{R} [$\text{R} = 1,4\text{-(Si}^i\text{Pr}_3)_2$].

Cloke has also developed a pentalene U(III) compound: $\text{U}(\text{Pn}^{\text{R}})\text{Cp}^*$ [$\text{R} = 1,4\text{-(Si}^i\text{Pr}_3)_2$].³² This, like its COT cousins, has been shown to activate small molecules, in particular it has been shown to reversibly reduce dinitrogen to form a dinitrogen bridged dimer which has been characterised in the solid state (figure 2.2).

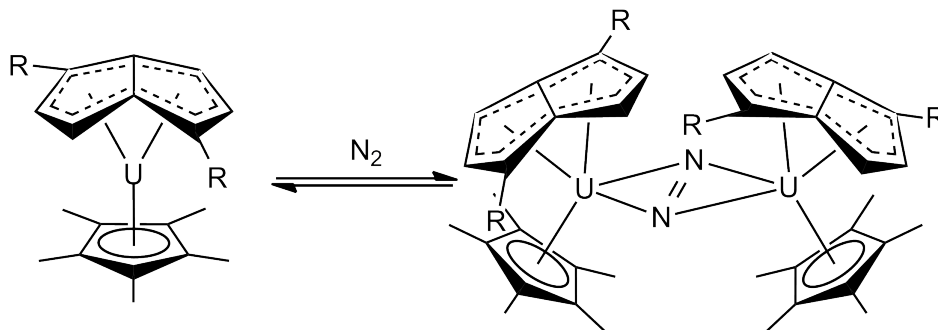


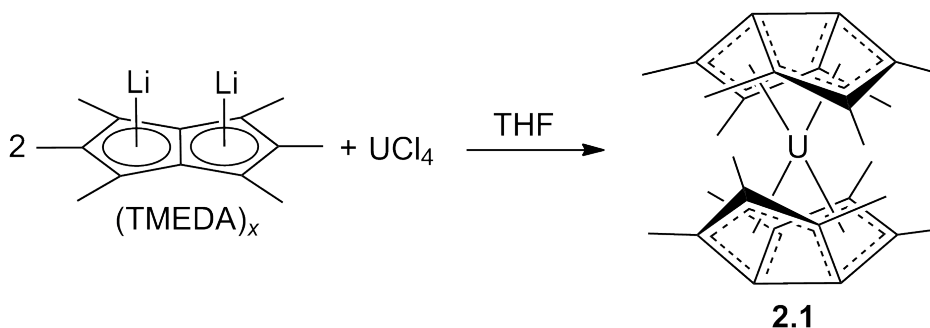
Figure 2.2: The reduction of dinitrogen by a U(III) pentalene complex [$\text{R} = 1,4\text{-(Si}^i\text{Pr}_3)_2$].

In this chapter the use of the permethylpentalene ligand is extended into the field of U(IV) chemistry. Its status as an isoelectronic ligand of COT is exploited and five new complexes are synthesised and characterised.

2.2 Bis(permethylpentalene)uranium (**2.1**)

2.2.1 Synthesis of **2.1**

It seemed appropriate to begin the investigation into permethylpentalene uranium chemistry with the synthesis and characterisation of the uranocene analogue. Initial attempts using $\text{UI}_4(\text{Et}_2\text{O})_2$ and $\text{Li}_2\text{Pn}^*(\text{TMEDA})_x$ in a variety of solvents generally yielded UPn^*_2 (**2.1**) in poor yields and purity. Efforts then moved on to using UCl_4 as the uranium synthon: reaction in THF gave a dark brown solution from which **2.1** was crystallised as black crystals in moderate yield (39 %) after extraction with toluene (scheme 2.1). **2.1** is very soluble in aromatic and ethereal solvents and sparingly soluble in pentane. To obtain crystals suitable for X-ray diffraction a saturated hot toluene solution was allowed to slowly cool to room temperature, and then cooled to $-38\text{ }^\circ\text{C}$ over three days (figure 2.3).



Scheme 2.1: The synthesis of **2.1**.

2.2.2 Characterisation of **2.1**

2.2.2.1 Single crystal X-ray diffraction characterisation

As found for the isostructural CePn^*_2 the pentalene ligands in **2.1** are disordered over three orientations, related to one another by 120° rotation about the c -axis.³³ However due to the larger relative size of the U atom *vs.* Ce this disorder presented more of an issue. In order to solve the structure, C–C bond lengths within the pentalene rings were fixed to $1.43(2)\text{ \AA}$ (the value found for the CePn^*_2 analogue). For a given orientation of one of the Pn^* ligands in a molecule there are three possible symmetry related orientations of the second (figure 2.4).

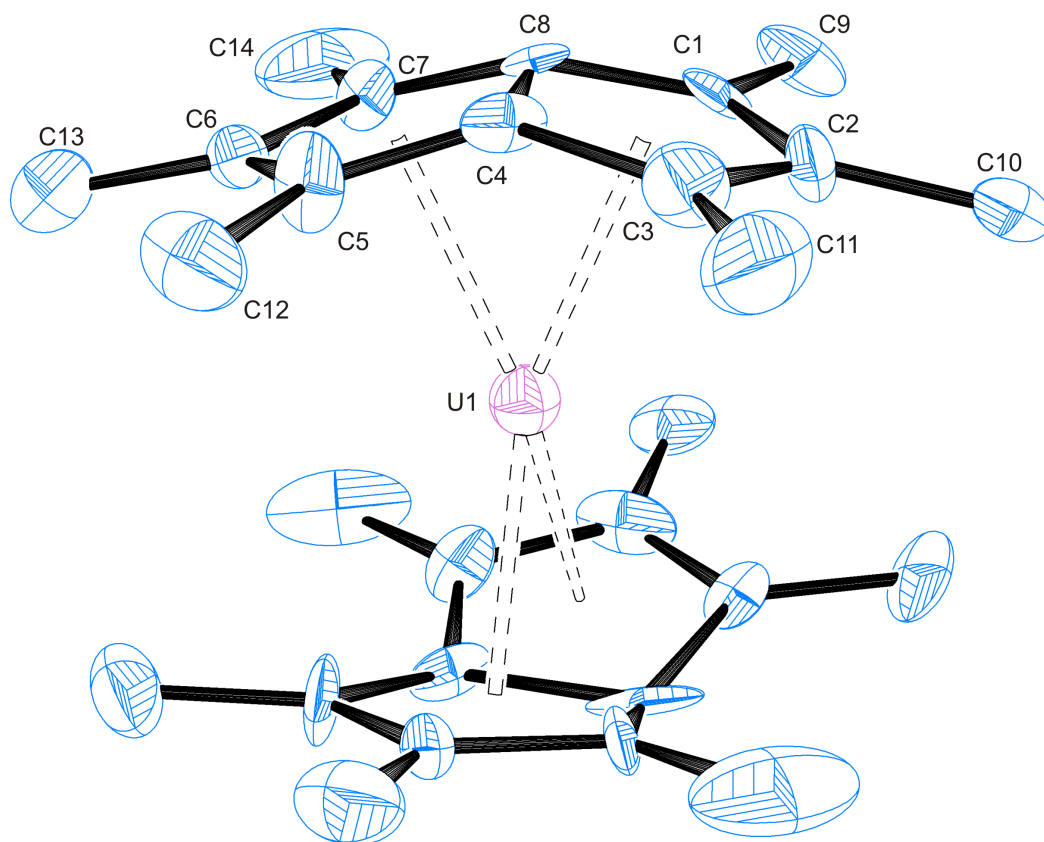


Figure 2.3: The X-ray single crystal structure of one of the stereoisomers of **2.1**. Thermal ellipsoids at 50 % probability and H-atoms omitted for clarity. Full crystallographic data for all species can be found in the electronic appendix.

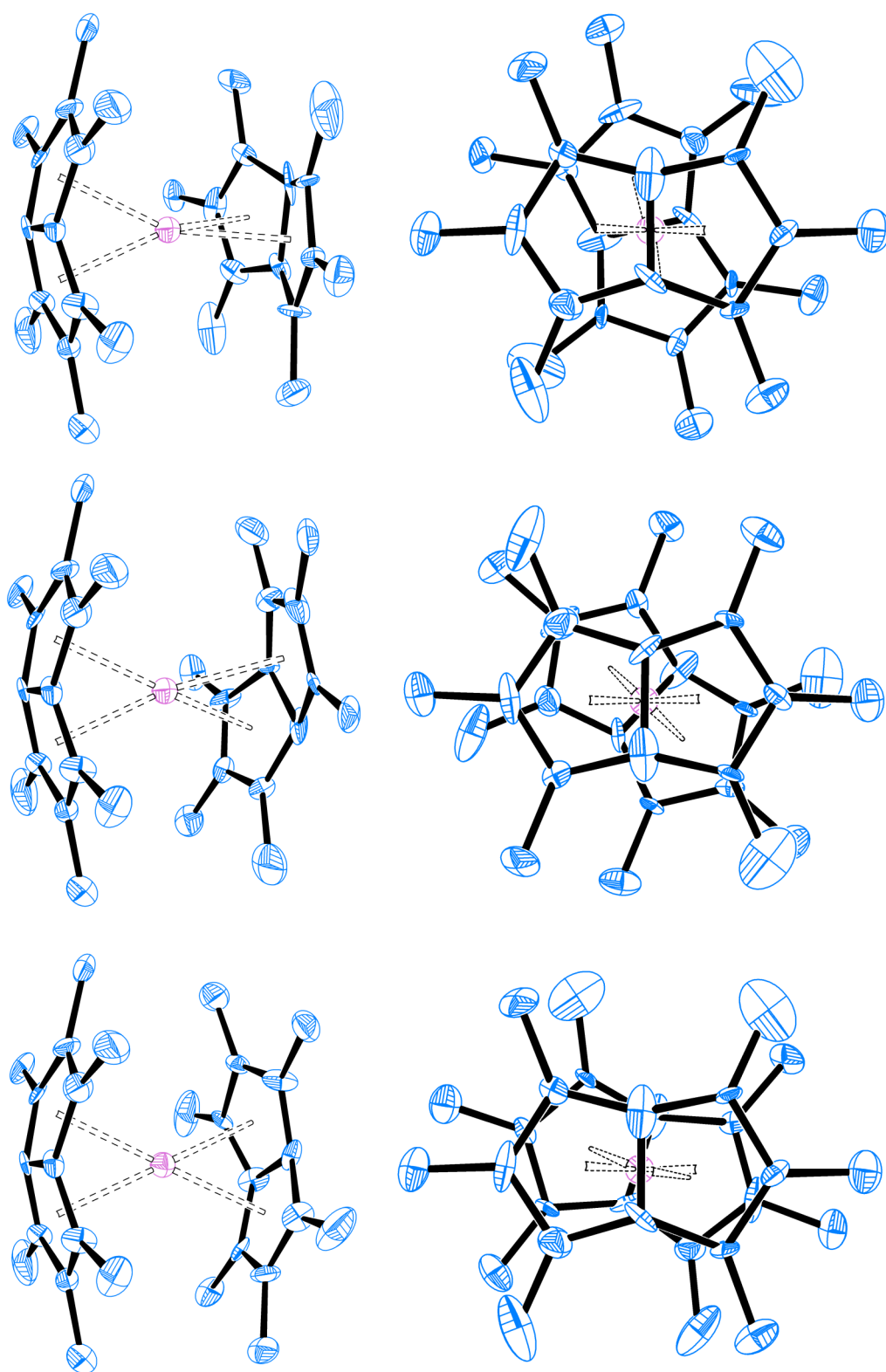


Figure 2.4: The three stereoisomers in the single crystal X-ray structure of **2.1** with interplanar angles (left to right): 15.6° , 44.6° and 75.4° .

Table 2.1: Selected structural parameters for **2.1**. The inter-planar angle is defined by the angle between the C2-U1-C6 plane and its symmetry counterparts. ESDs in parentheses.

Bond Lengths (Å)			
U–C(1)	2.74(2)	Av. C _{ring} –Me	1.459
U–C(2)	2.82(2)	U(1)–Pn* _{cent.}	2.325
U–C(3)	2.67(2)	U(1)–Pn* _{cent.}	2.340
U–C(4)	2.46(2)		
U–C(5)	2.70(2)		
U–C(6)	2.79(2)		
U–C(7)	2.68(3)		
U–C(8)	2.54(2)		
Bond Angles			
Fold Angle	25.7°		
Interplanar Angles	15.6°	44.6°	75.4°

It is impossible to tell if one stereoisomer dominates by diffraction alone, and examination of space-filling models suggests that none have unreasonably short contacts between non-bonded atoms. It is thus probable that either a static or dynamic equilibrium exists within the crystal; further experimentation (for example variable temperature single crystal X-ray diffraction or solid state MAS-NMR) to elucidate which is the case were not able to be carried out due to mechanical restrictions. The three conformations consist of two eclipsed arrangements with interplanar angles of 15.6° and 44.6° (defined as the angle between the two C2–U1–C6 planes) and an approximately staggered conformation with an interplanar angle of 75.4°, all of which are comparable to those found in CePn*₂.³³ Cloke *et al.* found in their investigation of the electronic structure of ThPn₂ that the eclipsed geometry (D_{2h}) of ThPn₂ would lie 0.21 eV higher in energy than the staggered (D_{2d}) structure due to the steric clash of the wing-tip hydrogens.³¹ Overall it was found for ThPn₂ that the energy surface of the ring rotation from staggered to eclipsed geometry was remarkably flat, and there was little electronic preference between the two conformations. On permethylation one would expect the

increase in steric bulk to raise the required energy for ring rotation; however the lack of the bulky Si^iPr_3 locking groups means that the presence of the three stereoisomers is not wholly unexpected.

The average $\text{U-Pn}^*_{\text{cent}}$ distance is 2.33 Å. This is considerably larger than the $\text{M-Pn}_{\text{cent}}$ distances found for d -block metals, but is comparable to the distances for the f -block metals (see table 2.2).³⁴ Generally the ordering of the $\text{M-Pn}_{\text{cent}}$ distances can be related to the relative atomic size of the central metal atom, which gets smaller across the periods. The only other uranium (IV) compound reported is the bridging dinitrogen complex: $[\text{U}(\text{Pn}^{\text{R}})\text{Cp}^*]_2[\mu\text{-N}_2]$ [$\text{R} = 1,4\text{-(Si}^i\text{Pr}_3)_2$], which has an average $\text{U-Pn}^{\text{R}}_{\text{cent}}$ distance of 2.28 Å. The slight increase in distance between this and **2.1** can be explained by the increased steric bulk of the Pn^* ligand compared to that of Pn^{R} where the Si^iPr_3 groups can orientate themselves to interlock and avoid steric clash.

The fold angle of 25.7° is comparable to other f -block compounds. It is somewhat greater than for the CePn^*_2 analogue (24.7°) which can be attributed to the increase in f -orbital overlap (due to the more diffuse $5f$ orbitals) compensating for the loss in aromaticity. Cloke's theoretical and photoelectron study of UPn_2 predicts a fold angle of 29.8° for UPn_2 , which is considerably larger than is found for **2.1**. This can be rationalised by the increased donor capability of Pn^* relative to Pn (as a result of permethylation). This increases the ligand orbital energies and as such gives better overlap with the metal orbitals. This, in turn, would mean the ligand has to fold less in order to stabilise the electron deficient metal. This electronic effect (combined with the increased steric bulk of the Pn^* ligand) results in this flattening of the ligand.

Table 2.2: Structural details for previously synthesised f -block η^8 -Pn compounds (R = SiⁱPr₃)

Compound	M-Pn _{cent.} (Å)	fold angle	M ⁺ ox. state	Ref.
YPn ^R I(THF)	unavailable	26.0°	+3	35
CePn [*] ₂	2.352/2.337	24.7°	+4	36
CePn ^R ₂	2.395	26.0°	+4	37
CePn ^R ₂ ⁺	2.495	22.0°	+3	37
Sm(η^8 -Pn ^R)(η^5 -Pn ^R H)	2.284	25.5°	+3	38
SmPn ^R Cp [*]	2.302	25.5°	+3	38
YbPn ^R (THF) ₃	unavailable	20.0°	+2	35
ThPn ^R ₂	2.426	24.0°	+4	39
(ThPn ^R Cl ₂) ₄	unavailable	24.7°	+4	40
UPn ₂ (calculated)	unavailable	25.0°	+4	31
UPn ^R Cp [*]	2.354	26.0°	+3	32
(UPn ^R Cp [*]) ₂ (μ -N ₂)	2.383/2.008	26.0°/22.5°	+4	32
UPn ^R tris(pyrazolyl)borate	2.406	23.5°	+3	41

2.2.2.2 NMR characterisation of **2.1**

The room temperature solution phase ¹H NMR of **2.1** exhibits two sharp singlets with a 2 : 1 intensity ratio at $\delta = 1.04$ and -27.89 ppm respectively. These sharp but shifted ¹H resonances are characteristic of U(IV) species.⁴² The large chemical shifts arise from a contact and pseudo-contact shift with the paramagnetic metal centre. The marked upfield shifted resonance at -27.89 ppm can be assigned to the C10 and C13 methyl protons [figure 2.4, the wingtip (WT) protons], with the other resonance assigned to the C9, C11, C12 and C14 methyl protons [the non-wingtip (NWT) protons]. The ¹³C NMR spectrum shows four resonances. HMBC 2-D NMR experiments indicated single bond coupling between the NWT protons (1.04 ppm) and a resonance at 968.6 ppm, and a single bond coupling between the WT proton resonance (-27.89 ppm) and a ¹³C resonance at around 875.0 ppm which was unobserved in the 1-D ¹³C NMR spectrum.

Variable temperature solution ¹H NMR (213 K to 373 K) studies show that the

NWT proton resonances vary between -45.45 ppm and -18.78 ppm and the WT proton resonances shift from -2.82 ppm to 2.16 ppm [figure 2.5(a)]. Figure 2.5(b) shows the linear dependence of these resonances versus T^{-1} , which is typical for uranocenes and indicative of a simple Curie paramagnet.⁴³

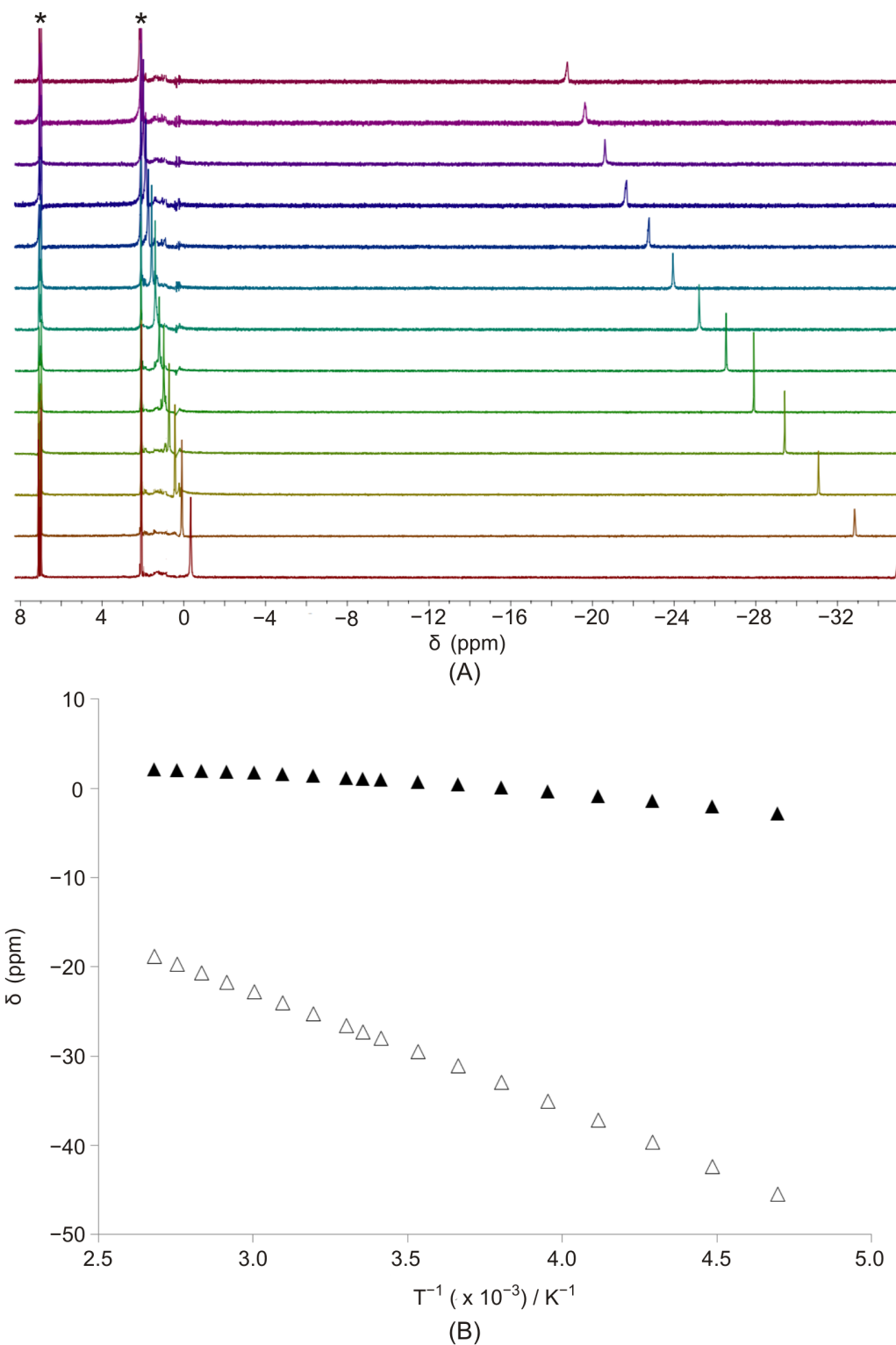


Figure 2.5: (A) A stack plot of the ^1H NMR of **2.1** from 253 K to 373 K (* indicates residual solvent resonance, temperature increases up the page); (B) the dependence of the chemical shift plotted against T^{-1} .

The solution phase magnetic moment of **2.1** was investigated *via* the Evans' method: the value was found to be $\mu_{\text{eff}} = 1.76 \mu_{\text{B}}$. This is slightly lower than that reported for uranocene ($\mu_{\text{eff}} = 2.40 \mu_{\text{B}}$).⁴⁴

2.2.2.3 Solid state magnetic measurements on **2.1**

Solid state magnetic measurements for **2.1** were obtained using a SQUID magnetometer, the results of which are plotted in figure 2.5. The molar magnetic susceptibility was fitted to the Langevin equation ($\chi_{\text{total}} = \chi_{\text{para}} + \chi_{\text{tip}}$) as the sample was found to have a temperature independent contribution to the molar susceptibility ($\chi_{\text{tip}} = 0.0031 \text{ cm}^3 \text{ mol}^{-1}$). The paramagnetic susceptibility was fitted to the Curie-Weiss law [$\chi_{\text{para}} = C / (T - \theta)$] between 5-300 K to give $C = 0.919 \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -4.9 \text{ K}$. This corresponds to an observed magnetic moment $\mu_{\text{eff}} = 2.90 \mu_{\text{B}}$, which is slightly higher than that of uranocene. It is also considerably lower than that of the $^3\text{H}_4$ ground state of a U^{4+} free ion ($3.58 \mu_{\text{B}}$), which may be explained by the perturbation of the free ion electric field by the Pn^* ligand. It should be noted that simple modeling of the electronic structure of Cloke's substituted pentalene derivative [$\text{U}(\text{Pn}^{1,5-\text{R}})_2$; $\text{R} = (\text{Si}^i\text{Pr}_3)$] proved inadequate, due to the f -orbitals lying close in energy to the HOMO, thus making it probable that the ground state in Cloke's compound (and by analogy in **2.1**) is multi-configurational.

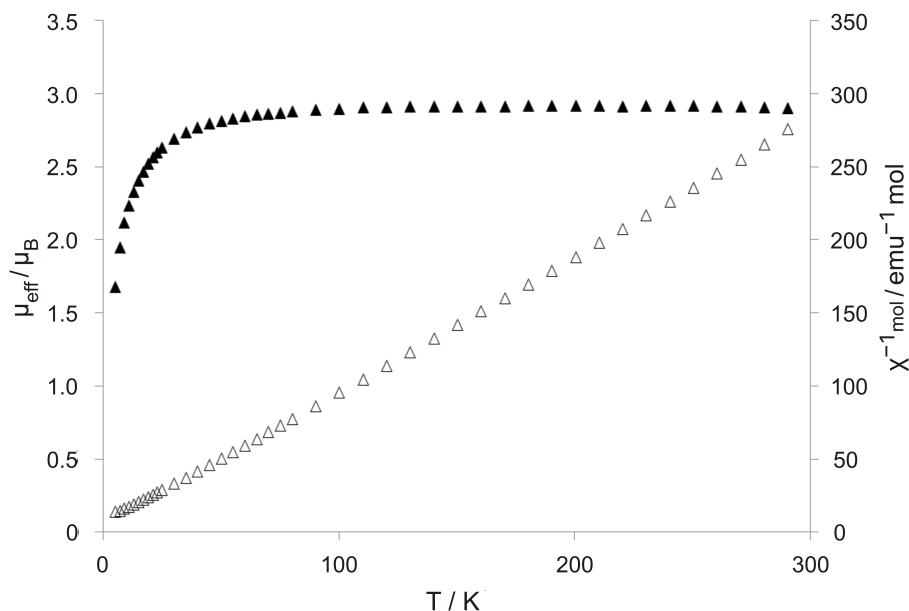


Figure 2.6: Temperature dependence of solid state μ_{eff} (▲) and $\chi^{-1} \text{ mol}$ (△) for **2.1**

2.2.2.4 Electrochemical measurements on **2.1** (carried out in collaboration with Gregory Wildgoose of UEA)

The electrochemistry of **2.1** was recorded using a sealed cell and proved to be non-trivial. The cyclic voltamograms were recorded under both N₂ and Ar, at varying scan rates. An example of such a scan is shown in figure 2.7 (recorded under N₂ at a scan rate of 100 mV s⁻¹).

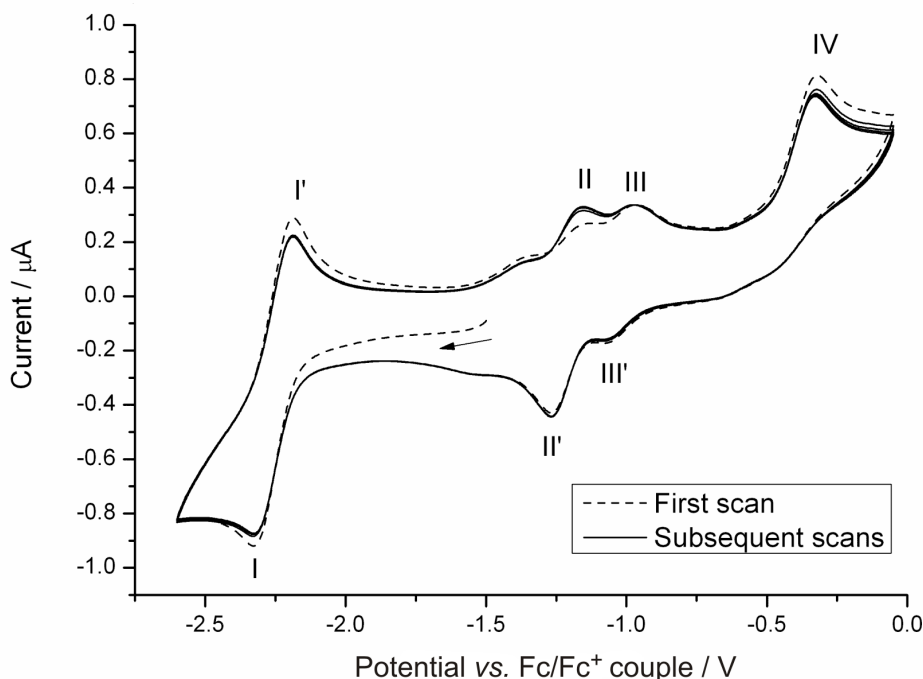


Figure 2.7: Five overlaid CV survey scans (scan rate = 100 mV s⁻¹) of 2.28 mM **2.1** in THF under N₂ containing 0.1 M tetrabutylammonium tetrafluoroborate. Initial reductive scan direction from -1.5 V *vs.* Fc/Fc⁺ couple.

Under these conditions a quasi-reversible redox couple is observed with a mid potential of -1.13 V relative to the Fc/Fc⁺ couple. Randles-Sevcik analysis of the reductive peaks,⁴⁵ I, returns a diffusion coefficient of 3×10^{-6} cm² s⁻¹ which is of the same order of magnitude as for the 1st row transition metal homoleptic permethylpentalene complexes, M₂Pn*₂, and is indicative of a single electron process, therefore suggesting a U(III)/U(IV) couple. Detailed analysis of peak I' proved impossible, due to the system lying on the limit of solvent breakdown. However, if the solution was thoroughly degassed with Ar, using freeze-thaw techniques, the I/I' couple becomes an irreversible reductive process. We therefore postulate that under an Ar atmosphere the unstable U(III) complex either undergoes an EC' process and regenerates U(IV) *via* an unknown

mechanism, or the reactive intermediate disproportionates to an unknown U(II) product, which is invisible within the potential window (figure 2.8). The latter mechanistic pathway is more likely as this not only regenerates the parent U(IV) complex, but also gives rise to the enhanced reduction current observed with respect to the N₂ case. This also may explain the broadening of the reduction wave observed under an Ar atmosphere since disproportionation reactions between U(II) and **2.1** are likely to be rapid. Such reactions would therefore occur on a similar timescale to the rates of coupled electron transfer and mass transport with the diffusion/depletion layer.

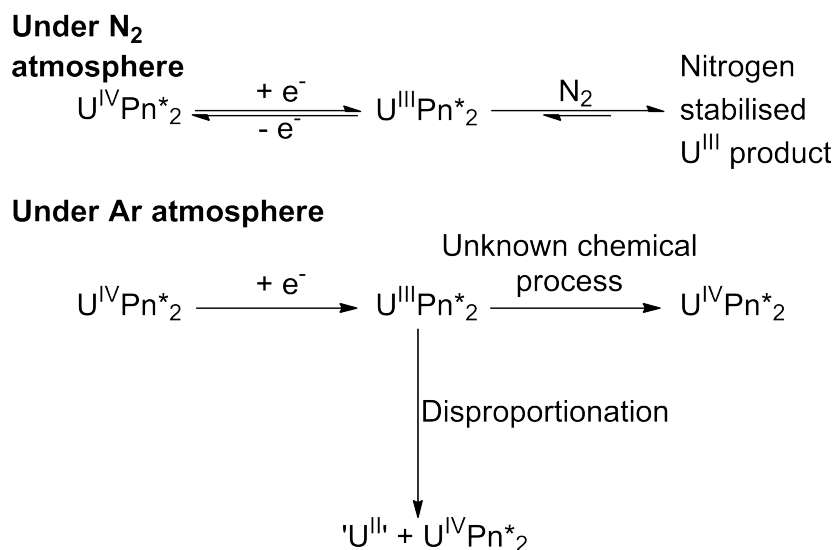


Figure 2.8: The two possible degradation pathways

An irreversible process occurs at +0.95 V relative to the Fc/Fc⁺ couple (under both N₂ and Ar atmospheres). Randles-Sevcik (irreversible form) analysis implies a single electron oxidation, and therefore a U(IV)/U(V) oxidation. However, an erroneous diffusion coefficient of $0.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ is calculated, which is indicative of a reversible system undergoing rapid follow-on chemistry; such an implication is substantiated by the subsequent growth of II after scanning through the couple IV.

2.2.2.5 Attempts at reduction of **2.1**

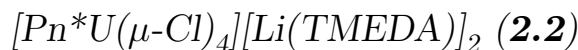
In light of the electrochemical measurements above attempts were made to chemically reduce **2.1**. Initial attempts were made using KC₈ as the reducing agent under both N₂ and Ar atmospheres, however no reaction occurred. Attempts then moved on to using a potassium mirror in an NMR tube. This led to the initial formation of a new

species with two broad ^1H NMR resonances at -10.15 ppm and -24.52 ppm. Over a period of a week the resonances at -10.15 ppm regress into the baseline, the signal at -24.52 ppm sharpens and two new resonances grow in at -4.97 ppm and -20.33 ppm. Mass spectrometry however showed a similar range of mass ion signals to **2.1** and all attempts at crystallisation failed.

2.2.2.6 Other characterisation of **2.1**

2.1 was also characterised *via* EI mass spectrometry, IR spectroscopy, UV-Visible spectroscopy and elemental analysis. Mass spectrometry gave a signal at $m/z = 610$, assigned to the molecular ion peak, and then the standard pentalene fragmentation pattern (a strong signal at $m/z = 186$ corresponding to $\text{C}_{14}\text{H}_{18}$, and then subsequent signals at intervals of 15 with the loss of methyl groups). IR spectroscopy (KBr plates) gave three strong bands at 2963 , 2907 and 2854 cm^{-1} associated with C–H stretching, and two bands at 1436 and 1379 cm^{-1} associated with C–H bending. UV-Visible spectroscopy (in THF) gave four peaks at $\lambda_{\text{max}} = 634$, 652^* , 675 and 686^* nm (* indicates these peaks are a shoulder in the preceding peak). Uranocene similarly gives four peaks in the UV-Visible spectrum (at wavelengths of 613 , 639 , 657 and 675 nm).⁴⁶ Elemental analysis gave results which corroborated a formula of $\text{UC}_{28}\text{H}_{36}$.

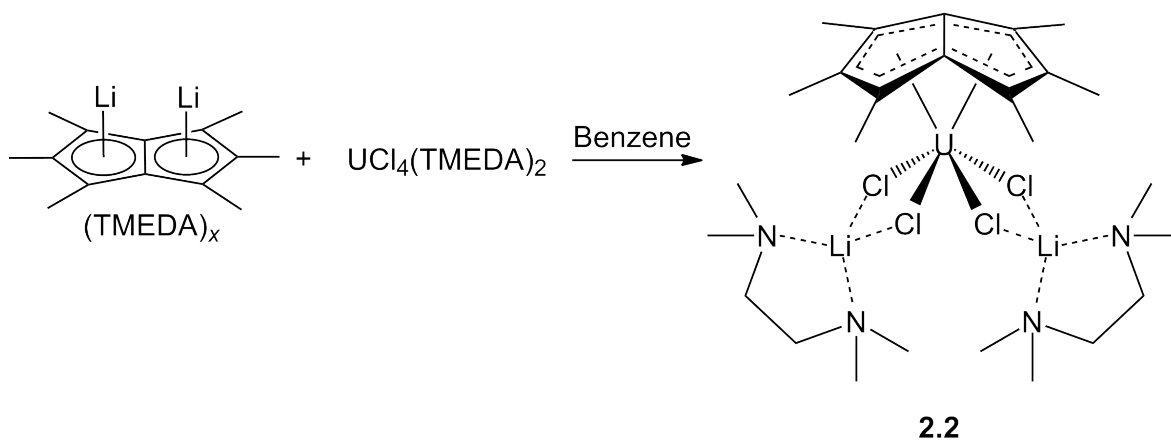
2.3 The uranium permethylpentalene half sandwich:



Having synthesised the permethylpentalene uranocene equivalent UPn^*_2 , it seemed appropriate to aim for the permethylpentalene uranium half sandwich compound, UPn^*Cl_2 , in order to access further permethylpentalene uranium chemistry. Uranocene half-sandwich chemistry is however extremely limited. $\text{U}(\text{COT})\text{Cl}_2$ can be formed as a 2:1 solvent adduct by the redistribution reaction of UCOT_2 with an equivalent of UCl_4 in THF to form $\text{U}(\text{COT})\text{Cl}_2 \cdot 2\text{THF}$.⁴⁷ This half sandwich adduct can easily have its solvent replaced with other strong donors (for example pyridine) however reaction with various alkyl/aryl lithiums and Grignard reagents resulted in no discernible products.⁴⁷

2.3.1 Synthesis of **2.2**

Attempts to synthesise a half-sandwich UPn^* species started with the addition of excess UCl_4 to UPn^*_2 in a redistribution reaction similar to the formation of the $\text{U}(\text{COT})$ half sandwich but in this case there was no reaction. Combining equal equivalents of UCl_4 and $\text{Li}_2\text{Pn}^*\cdot(\text{TMEDA})_x$ in benzene was tried, however this led only to formation of UPn^*_2 . The insolubility of UCl_4 was noted and in an attempt to solubilise the reactant two molar equivalents of TMEDA were added. This resulted in the formation of a solvent adduct that was not isolated but was further reacted with $\text{Li}_2\text{Pn}^*\cdot(\text{TMEDA})_x$ in benzene. This led to the formation of a novel species (identified *via* ^1H NMR spectroscopy) with bound TMEDA, which was later confirmed (by single crystal X-ray diffraction) as $[\text{UPn}^*(\mu\text{-Cl}_4)][\text{Li}(\text{TMEDA})]_2$, **2.2**. **2.2** is soluble in most aromatic and ethereal solvents, and is stable indefinitely at room temperature under a N_2 atmosphere. On application of vacuum no TMEDA appears to be lost, implying that it is bound strongly within the molecule.



Scheme 2.2: The synthesis of **2.2**.

2.3.2 Characterisation of **2.2**

2.3.2.1 Single Crystal X-ray characterisation of **2.2**

Single crystals of **2.2** were grown from a saturated toluene solution slow cooled to $-38\text{ }^\circ\text{C}$ over three days. **2.2** has a tendency (if crystallisation was rapid) to form either twinned crystals or, more often, an amorphous powder. The single crystal X-ray structure of **2.2** is shown in figure 2.9 (A). **2.2** crystallises in the $\text{P2}_1/n$ space group with

toluene co-crystallised within the structure. The crystal contains one molecule within the asymmetric unit. The uranium is in an approximately octahedral environment [figure 2.9 (B)], with the wingtip ring carbons and Cl(2) and Cl(4) making the equatorial plane, this bisects the Cl(1)–U(1)–Cl(3) angles of $144.9(1)^\circ$. The pertinent structural parameters are summarised in table 2.3.

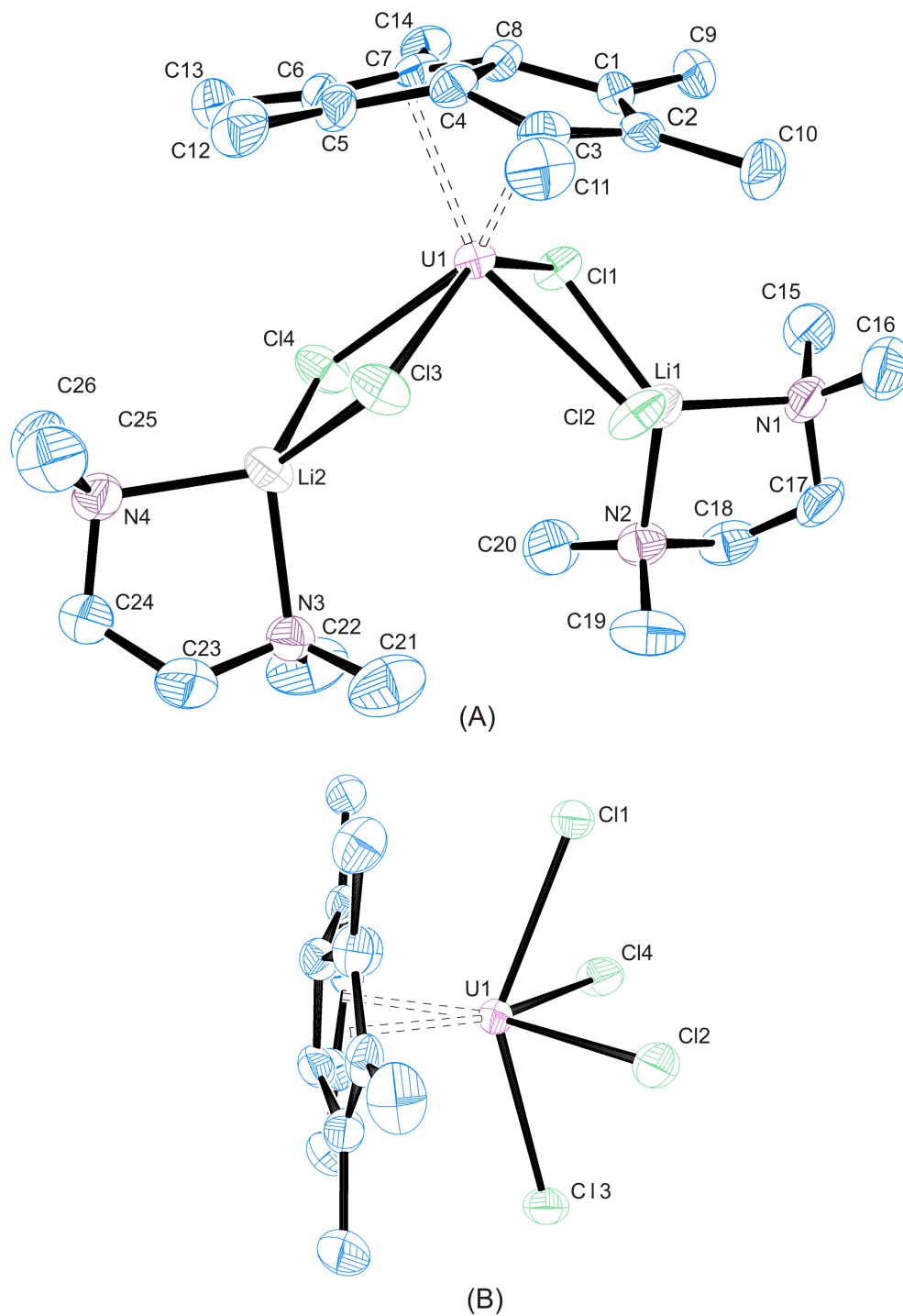


Figure 2.9: The X-ray single crystal structure of **2.2** both (A) the whole molecule and (B) the octahedral environment of the uranium centre. Thermal ellipsoids at 50% probability. H-atoms and co-crystallised toluene omitted for clarity.

Table 2.3: Selected structural parameters for **2.2**. ESDs in parentheses.

Bond lengths (Å)			
U–C(1)	2.74(2)	C(1)–C(2)	1.403(8)
U–C(2)	2.82(2)	C(2)–C(3)	1.408(8)
U–C(3)	2.67(2)	C(3)–C(4)	1.436(8)
U–C(4)	2.46(2)	C(4)–C(5)	1.432(8)
U–C(5)	2.70(2)	C(5)–C(6)	1.424(8)
U–C(6)	2.79(2)	C(6)–C(7)	1.412(8)
U–C(7)	2.68(3)	C(7)–C(8)	1.453(7)
U–C(8)	2.54(2)	C(8)–C(1)	1.450(7)
Av. C _{ring} –Me	1.459	C(4)–C(8)	1.448(7)
U(1)–Cl(1)	2.777(1)	U(1)–Cl(2)	2.745(2)
U(1)–Cl(3)	2.776(1)	U(1)–Cl(4)	2.748(2)
U(1)–Pn [*] _{cent.}	2.318(2)	U(1)–Pn [*] _{cent.}	2.318(2)
Bond angles			
Fold Angle		25.9(5)°	

The U–Pn^{*}_{cent.} distance in **2.2** and the fold angle are both comparable to those found for **2.1**. The distance is greater than those for the similar group four permethylpentalene dichloride dimers seen in chapter 3 as is expected due to the larger size of the uranium atom. There are only two other examples of uranium(IV) pentalene compounds in the literature, U(Pn^R)₂ (R = 1,4-(SiⁱPr₃)₂) and [U(Pn^R)Cp^{*}]₂[μ-N₂] (both synthesised by Cloke and co-workers), of which only the latter was structurally characterised.^{31;32} The structural parameters of this N₂ bridged dimer are mostly comparable to **2.2**, with the fold angles being 26° for one pentalene moiety and 22.5° for the other; Cloke justified the latter smaller angle by crystal packing forces. The U–C(1), U–C(3), U–C(5) and U–C(7) distances lie within the range 2.67(2)-2.74(2) Å, comparable both to Cloke’s uranium (IV) structure [range 2.688(11)-2.775(9) Å] and the parent U(III) compound, UPn^RCp^{*} [range 2.683(7)-2.733(7) Å], and indicative of δ-symmetry bonding interaction. The U–(μ-Cl)–Li moiety is relatively rare, with only 20 such structures registered in the

CSD.^{48–62} The U–Cl distance here [average of 2.762(4) Å] is however typical for such an environment. Presumably **2.2** exists as a solvate complex to alleviate somewhat the co-ordinately unsaturated and electron deficient uranium atom.

2.3.2.2 NMR characterisation of **2.2**

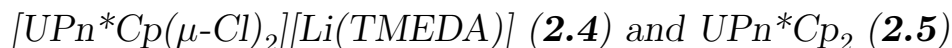
The ¹H NMR spectrum of **2.2** consists of 4 resonances: two sharp at $\delta = 10.61$ and 8.16 ppm and two broad centred at $\delta = 4.27$ and 2.48 ppm, of integral ratio 12:6:24:8 (like **2.1** the paramagnetism of the uranium metal centre causes the resonances to be severely shifted). These resonances can be assigned to the NWT methyl protons ($\delta = 10.61$ ppm; C9, C11, C12, C14; figure 2.9), WT methyl protons ($\delta = 8.16$ ppm; C13, C10; figure 2.9), the TMEDA methyl protons ($\delta = 4.27$ ppm; C15, C16, C19, C20, C21, C22, C25, C26; figure 2.9) and the TMEDA ethyl protons ($\delta = 2.48$ ppm; C17 C18, C23, C24; figure 2.9) respectively. In contrast to the other compounds within this chapter variable temperature ¹H NMR studies (203 K to 323 K) showed little change in line shape indicating that the TMEDA molecules are not labile and that the paramagnetism of the sample is not simple Curie behaviour. Evans' NMR method was employed to investigate this and it was found that the effective magnetic moment decreased with increasing temperature from 2.81 μ_B at 293 K to 2.74 μ_B at 353 K. This behaviour shows that, like **2.1**, **2.2** probably also exists in a multiconfigurational ground state and therefore its magnetism cannot be easily modelled. Due to time constraints investigations using SQUID were unable to be carried out.

The ¹³C{¹H} NMR of **2.2** shows 7 sharp resonances at $\delta = -456.7$, -78.38 , 11.1, 47.7, 57.7, 157.6 and 256.3 ppm. The TMEDA carbons can be assigned to the resonances at 47.7 ppm (Me) and 57.7 ppm. The WT methyls correspond to the 11.1 ppm resonance whilst the NWT methyls correspond to the -78.3 ppm resonance. HMBC experiments allow the resonance at 256.3 ppm to be assigned to the bridgehead bond however it is impossible to distinguish which of the WT or NWT quaternary ring carbons correspond to the -456.7 ppm resonance and the 157.6 ppm resonance. The ⁷Li NMR shows one single resonance at -2.01 ppm.

2.3.2.3 Other characterisation of **2.2**

2.2 was also characterised *via* EI-mass spectrometry, IR spectroscopy and elemental analysis. Mass spectrometry showed the presence of a strong signal at $m/z = 494$ (80 %) which corresponds to $[\text{UPn}^*\text{Cl}_2]^+$ together with the expected fragmentation patterns. The IR spectrum consists of a series of strong bands at 2958, 2838 and 2794 cm^{-1} corresponding to the C–H stretching, and bands at 1464, 1291, 1036 and 1019 cm^{-1} corresponding to the C–H bending vibrations. Elemental (CHN) analysis gave results which corroborated a formula of $[\text{UPn}^*\text{Cl}_4][\text{Li}(\text{TMEDA})]_2$.

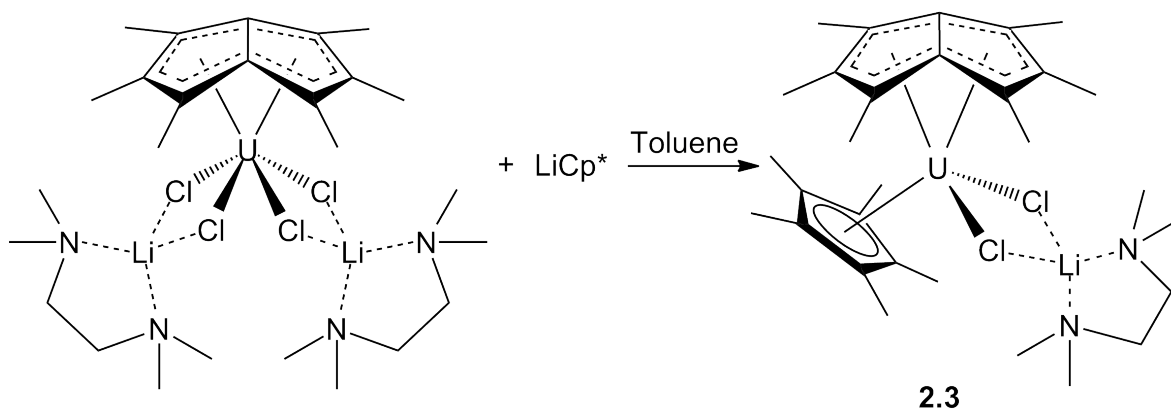
2.4 Synthesis of Mixed Sandwich species:



With the development of a high-yielding, multi-gram synthesis of the half sandwich equivalent, **2.2**, further salt metathesis chemistry became accessible. Echoing previous work in the area the cyclopentadienyl and pentamethylcyclopentadienyl ligands were employed.

2.4.1 Synthesis of **2.3**

Initially one equivalent of LiCp^* was combined with one equivalent of **2.2** in toluene and heated overnight. Following work up and extraction with pentane a black solid was obtained (in approximately 50 % yield) and identified (*via* ^1H NMR spectroscopy) as $[\text{UPn}^*\text{Cp}^*(\mu\text{-Cl})_2][\text{Li}(\text{TMEDA})]$.



Scheme 2.3: The synthesis of **2.3**.

2.4.2 Characterisation of **2.3**

2.4.2.1 Single Crystal X-ray characterisation of **2.3**

Crystallisation attempts were fraught with difficulty due to the tendency of **2.3** to either form amorphous powders or extremely small and twinned crystals. However a saturated heptane solution slow cooled to $-38\text{ }^\circ\text{C}$ over three days eventually yielded single crystals suitable for X-ray diffraction (figure 2.10). **2.3** crystallises in the $\text{P2}_1/c$ space group and contains three molecules in the asymmetric unit. The ligands around the uranium centre are in an approximately square-pyramidal arrangement with the two chlorides and the two Pn^* centroids taking up the four base positions and the Cp^* centroid taking the axial position. In a manner similar to **2.2**, **2.3** exists as a solvate complex with an incorporated LiCl . Due to the difficulty in crystallisation and the resultant weak data the R-factor for the model was 10.2 %.

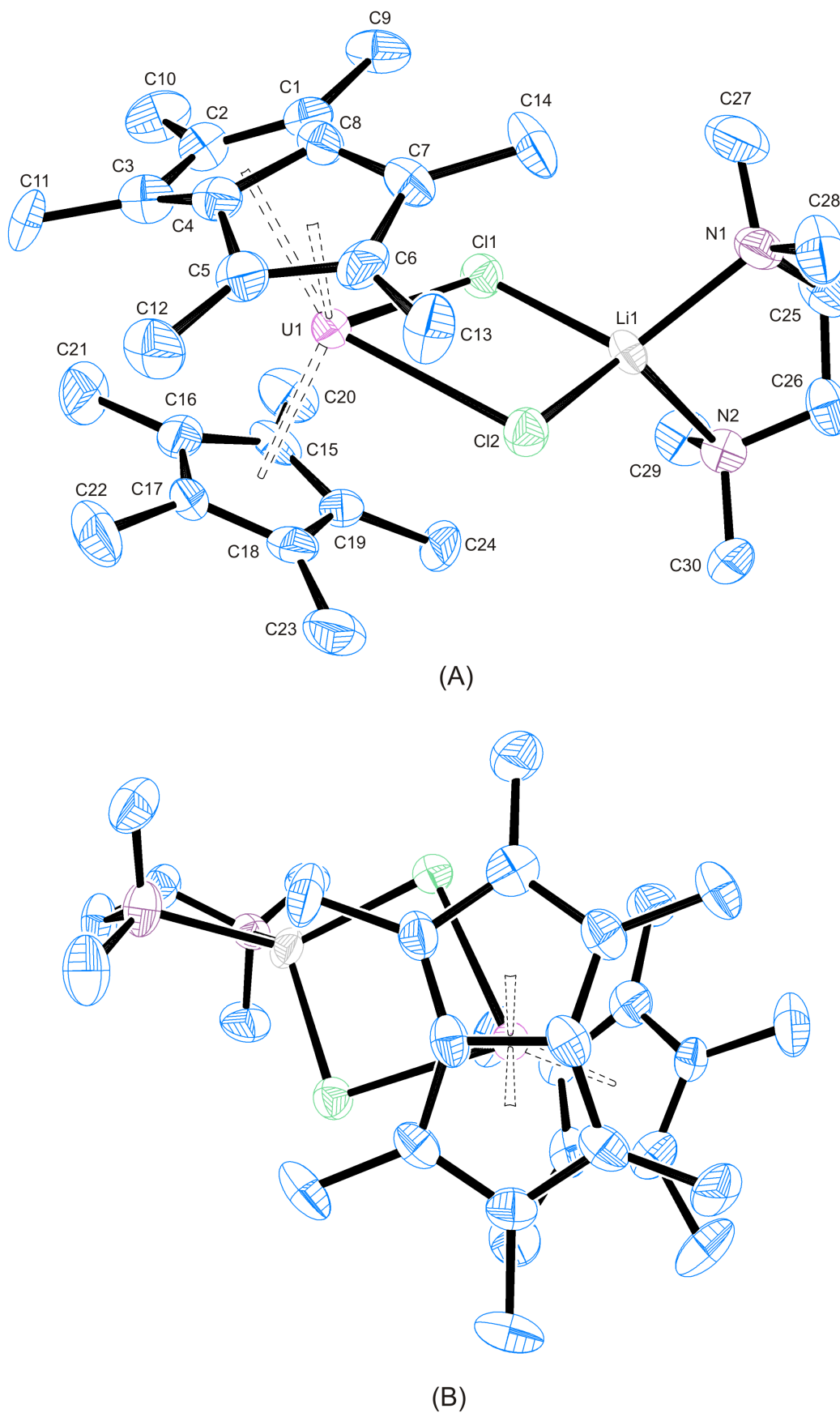


Figure 2.10: The X-ray single crystal structure of **2.3** both (A) a side view and (B) a top down view along the axis of the centroid of the bridgehead bond and the uranium centre. Thermal ellipsoids at 50% probability and H-atoms omitted for clarity

Table 2.4: Selected structural parameters for **2.3**. ESDs in parentheses.

Bond lengths (Å)			
U(1)–C(1)	2.74(2)	C(1)–C(2)	1.404(19)
U(1)–C(2)	2.82(2)	C(2)–C(3)	1.390(19)
U(1)–C(3)	2.67(2)	C(3)–C(4)	1.430(18)
U(1)–C(4)	2.46(2)	C(4)–C(5)	1.433(18)
U(1)–C(5)	2.70(2)	C(5)–C(6)	1.399(15)
U(1)–C(6)	2.79(2)	C(6)–C(7)	1.414(17)
U(1)–C(7)	2.68(3)	C(7)–C(8)	1.439(18)
U(1)–C(8)	2.54(2)	C(8)–C(1)	1.416(18)
U(1)–C(15)	2.80(2)	C(4)–C(8)	1.457(15)
U(1)–C(16)	2.81(1)	U(1)–Cl(1)	2.765(3)
U(1)–C(17)	2.79(1)	U(1)–Cl(2)	2.836(3)
U(1)–C(18)	2.78(1)		
U(1)–C(19)	2.78(1)		
Av. Pn* C _{ring} –Me	1.518	Av. Cp* C _{ring} –Me	1.513
U(1)–Pn* _{cent.}	2.359(5)	U(1)–Cp* _{cent.}	2.521(5)
U(1)–Pn* _{cent.}	2.370(5)		
Bond angles			
Fold Angle		25.3(5)°	

The U–Pn*_{cent.} distance in **2.3** is considerably longer than that found in both **2.1** and **2.2**. This combined with the lower fold angle of **2.3** demonstrates both the larger steric demand of the Cp* ligand and its greater electron donor ability, causing the Pn* ligand to be pushed out and subsequently flatten (due to lower orbital overlap giving less compensation for the loss in aromaticity of the ligand). This effect is reflected in the U–(μ–Cl) bond lengths, one of which is comparable to **2.2** [2.765(3) Å for **2.3** and an average of 2.762(4) Å for **2.2**], while the other is somewhat longer [2.836(3) Å]. The U–C(1), U–C(3), U–C(5) and U–C(7) [2.67(2) - 2.74(2) Å] bond lengths all still lie within the range of δ bonding.

The U-Cp* distance in **2.3** is effectively the same as that found for the only other uranium (IV) pentalene compound in the literature, [UPn^RCp*]₂[μ-N₂] [2.524 Å and 2.505 Å, *c.f.* 2.521(5) Å for **2.3**, R = 1,4-(SiⁱPr₃)₂]. Indeed it is close in distance to the U (III) compound: UPn^RCp* (2.486 Å). Cloke attributed the fact that the change in formal oxidation state here is not reflected in the structural parameters due to steric congestion of the metal centre - something that is clearly also a strong factor in **2.3**.

The U-Cp*_{cent.} distance in **2.3** is considerably shorter than the distances found for UCp*₃Cl [2.780(6) - 2.899(9) Å].⁶³ This is expected due to the considerably higher steric crowding in Evans' species when compared with **2.3**. Indeed, due to the extreme steric bulk in UCp*₃Cl, an exceptionally long (and essentially ionic) U-Cl bond is seen [2.90(1) Å].

2.4.2.2 NMR studies of **2.3**

The room temperature ¹H NMR spectrum of **2.3** is complex, consisting of four resonances: one sharp at δ = 9.31 ppm and three broader resonances at δ = -2.70, -3.91 and -14.04 ppm with an integral ratio of 15:12:4:6. These resonances can be assigned to the Cp* methyl protons for the sharp resonance, the WT methyl protons for the resonance at -14.04 ppm, the TMEDA methyl protons are at -2.70 ppm and the ethylene bridge protons for the resonances at -3.91 ppm. The resonance for the NWT methyl protons is not seen at room temperature due to being too broad because of a combination of fluxionality and paramagnetism within the molecule.

Variable temperature ¹H NMR studies further complicate the picture (figures 2.11 and 2.12), with a number of decoalescence phenomena seen. Firstly, upon cooling the sample to -10 °C a resonance at δ = 54.52 ppm begins to appear, which upon further cooling sharpens and moves downfield before splitting at -60 °C (left hand side of top spectra in figure 2.12). This resonance can be assigned to half of the NWT methyl protons. In the crystal structure there is no mirror plane along the plane of the bridgehead bond. This, combined with the lack of a C₂ rotation axis down the centroid of the bridgehead bond results in all four of the NWT methyl protons being inequivalent in the static model. This explanation is reinforced by the splitting of the WT resonances

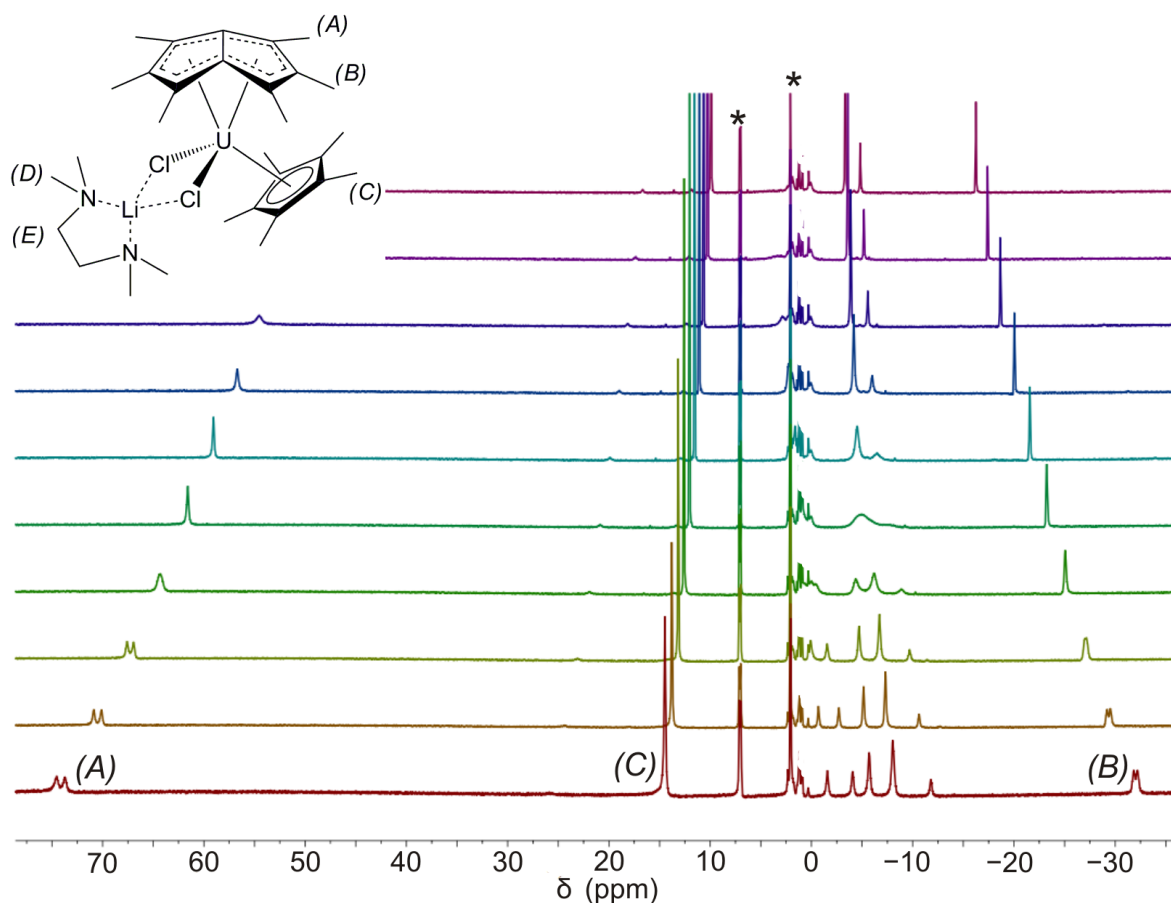


Figure 2.11: A stack plot of the ^1H NMR spectra of **2.3** from 183 K to 273 K. Temperature increases up the page. Resonances are labelled in reference to inset picture. * indicates residual solvent resonance.

at low temperatures [figure 2.12 (B)]. The other NWT methyl protons are assigned to the broad peak that appears at approximately $\delta = 3$ ppm before migrating upfield and splitting into two distinct peaks at -60 °C in a manner similar to the NWT resonance at higher ppm. The resonance at $\delta = -2.70$ ppm (corresponding to the TMEDA methyl resonances) splits into two distinct peaks at -54 °C, presumably as the fluxionality of the TMEDA reduces to being slower than the NMR time-scale.

On heating the sample, many of the peaks quickly broaden. However an extremely broad resonance does start to appear at approximately $\delta = 21$ ppm at approximately 303 K, which is presumed to be the coalesced resonance of all four NWT methyl protons. Further heating to 313 K led to extreme broadening and loss of spectral quality. Due to the complications within paramagnetic NMR spectroscopy 2-dimensional experiments were unable to unequivocally prove this assignment. Due to the pseudo-contact shift effect being an an r^{-3} relationship from the metal centre it is expected that the TMEDA

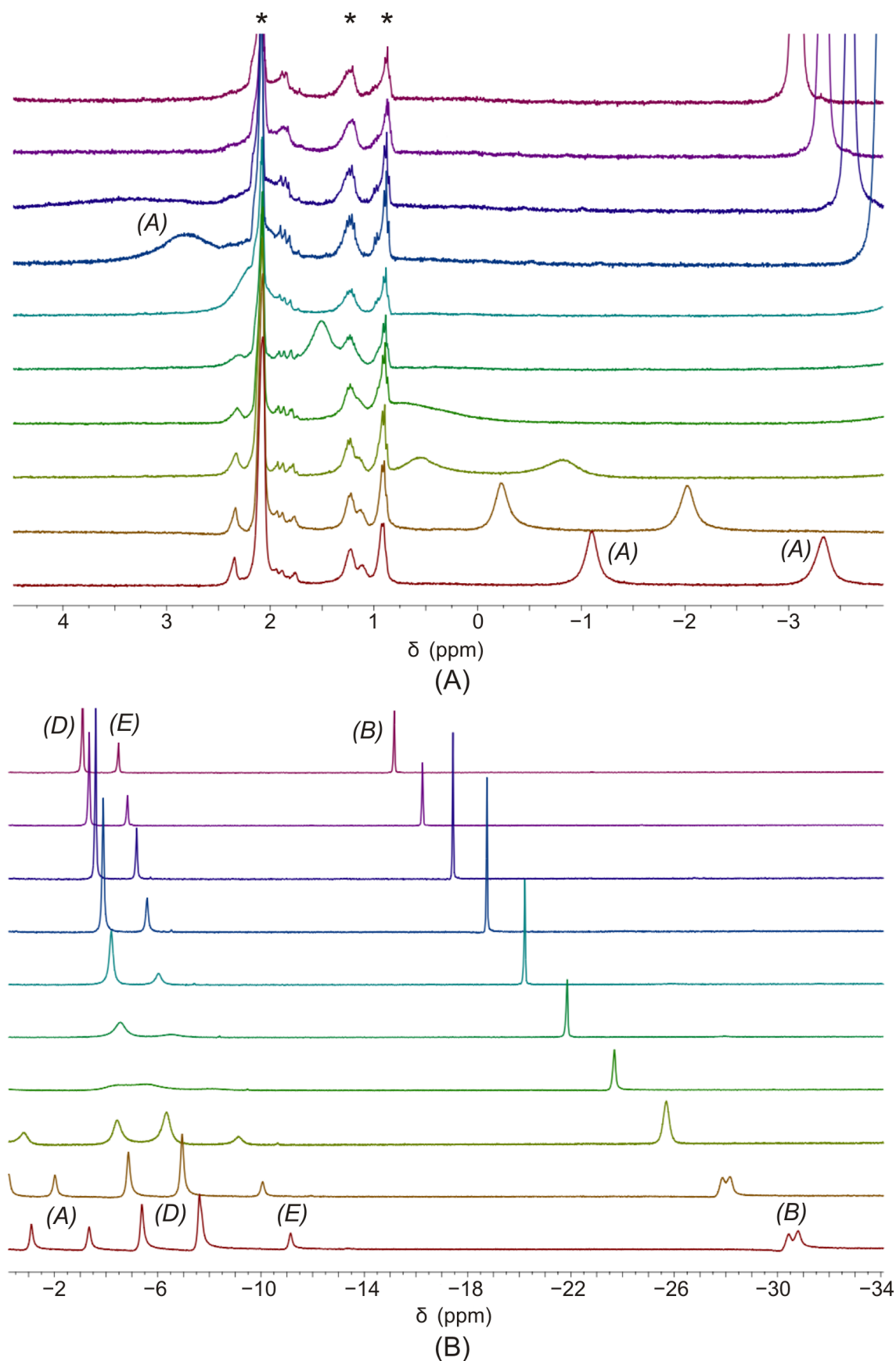
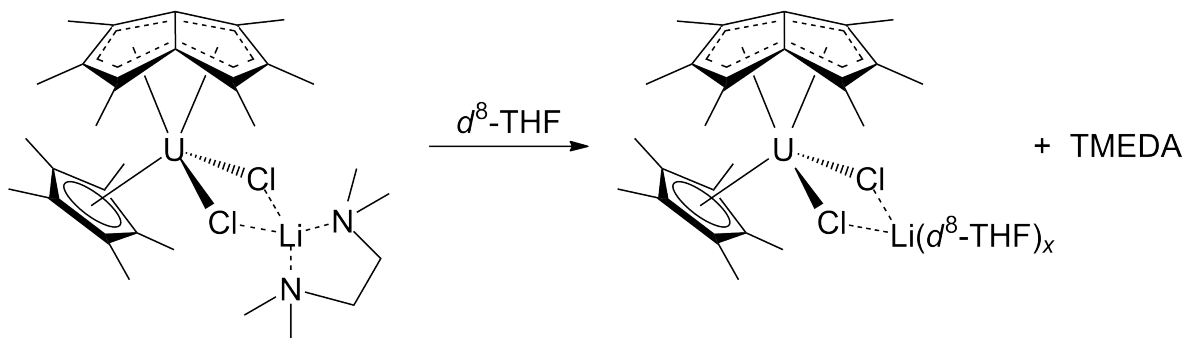


Figure 2.12: **(A)** detail of the splitting that occurs between $\delta = -4$ and 4 ppm, **(B)** detail of the splitting that occurs in the upfield region. For both spectra temperature increase up the page. Resonances labels refer to inset in figure 2.11 (*vide supra*). * indicates residual solvent from crystallisation.

resonance shifts will be less paramagnetically shifted than the Pn* methyl resonances.⁶⁴ Furthermore when a small amount (approximately three drops) of d^8 -THF is added the two paramagnetic resonances caused by bound TMEDA disappear, and resonances corresponding to uncoordinated TMEDA emerge.



Scheme 2.4: The displacement of TMEDA by d^8 -THF.

^{13}C NMR spectroscopy detected six resonances, which presumably correspond to the six non-quaternary environments, at $\delta = 177.8, 45.6, 35.6, 11.7, -23.4$ and -281.3 ppm. Due to the aforementioned fluxionality, paramagnetism and poor solubility recording two dimensional spectra proved impossible, and as a result the resonances cannot be assigned with confidence. The ^7Li NMR gave the expected sharp singlet (also paramagnetically displaced) at -43.50 ppm.

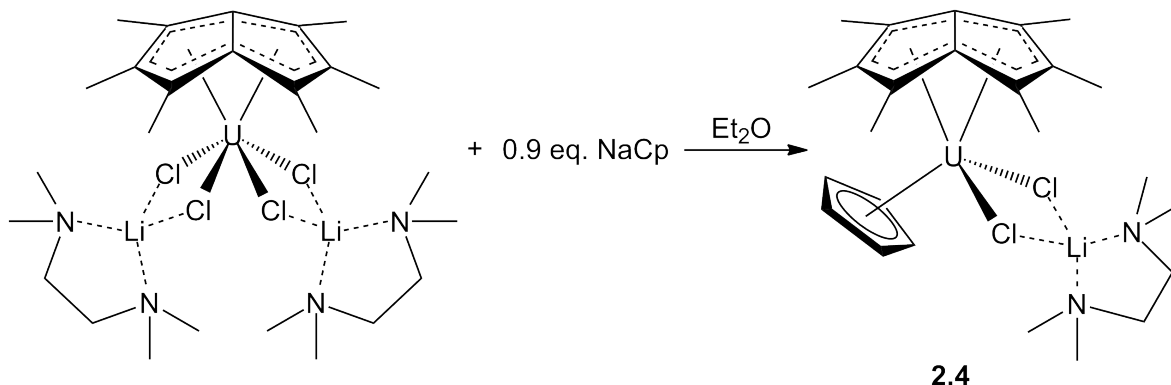
2.4.2.3 Other Characterisation of **2.3**

The mass spectrum of **2.3** gave a signal at $m/z = 594.3108$ corresponding to the $\text{UPn}^*\text{Cp}^*\text{Cl}^+$ molecular ion; fragmentation patterns of that ion were also observed. IR spectroscopy displayed a similar trio of strong bands to **2.1** and **2.2** at 2962, 2908 and 2853 cm^{-1} (due to C–H stretching) and C–H bending bands at 1646, 1461, 1370, 1261 and 1069 cm^{-1} .

2.4.3 Syntheses of **2.4** and **2.5**

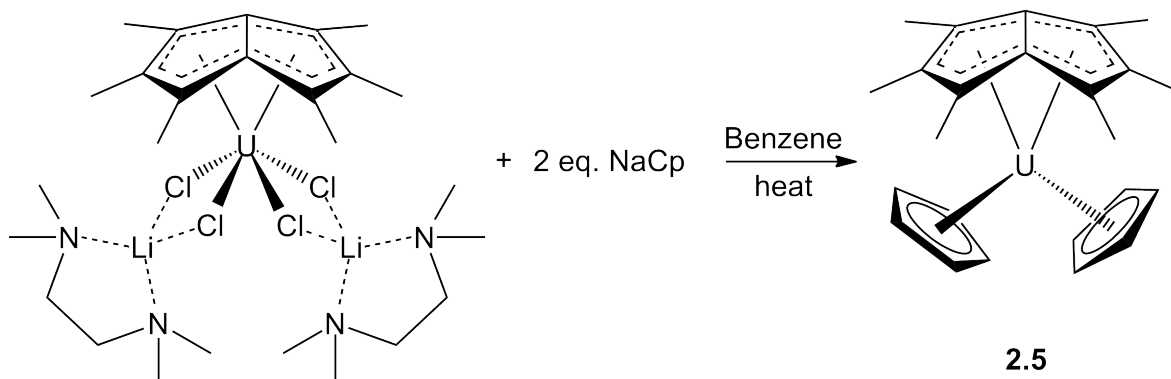
The non-permethylated cyclopentadienyl derivatives would afford an interesting comparison to **2.3**, both in terms of the lesser steric bulk of the Cp rings and also electronic factors of Cp versus Cp*.

$[\text{UPn}^*\text{Cp}(\mu\text{-Cl})_2][\text{Li}(\text{TMEDA})]$ (**2.4**) was synthesised by the addition of 0.9 equivalents of NaCp to **2.2** in Et_2O at room temperature. Fast addition was employed in order to avoid the formation of UPn^*Cp_2 . **2.4** was isolated as a black amorphous solid in moderate yield from a pentane extraction (42 %). ^1H NMR showed the presence of bound TMEDA which could not be removed upon application of a vacuum ($< 1 \times 10^{-2}$ mbar). From this observation the structural formula in scheme 2.5 is inferred.



*Scheme 2.5: The synthesis of **2.4**.*

UPn^*Cp_2 (**2.5**) may be formed either by reaction of **2.4** with a further equivalent of NaCp or by addition of an excess of NaCp to **2.2**, both with subsequent heating to ensure the reaction has reached completion (scheme 2.6). Both **2.4** and **2.5** are extremely soluble in aliphatic, aromatic and ethereal solvents and crystallisation attempts have yielded only amorphous powders which is unsurprising given the difficulty encountered crystallising **2.3** which has the added assistance of the permethylated cyclopentadienyl ligand (which should facilitate crystallisation).



*Scheme 2.6: The synthesis of **2.5**.*

2.4.4 Characterisation of **2.4** and **2.5**

2.4.4.1 NMR studies of **2.4**

Like **2.3**, the room temperature ^1H NMR of **2.4** is complex consisting of two sharp singlets at 3.69 and -16.52 ppm (integral ratio 5:6), and three broad peaks at 23.29, 1.10 and -0.52 ppm (integral ratio 12:12:4). Again, given the expectation that the pseudo-contact shift and contact shift effects would be less for the TMEDA protons than the NWT methyl protons (see **2.3**) a tentative assignment can be made that the peaks at 1.10 and -0.52 ppm correspond to a single bound TMEDA, and that the signals at 23.29, 3.69 and -16.52 ppm correspond to the NWT methyls, the Cp protons and the WT methyls respectively. Such an assignment was confirmed with the addition of a small amount of d^8 -THF upon which the two TMEDA resonances disappear.

Variable temperature ^1H NMR studies of **2.4** show the usual paramagnetic migration of the resonances (figure 2.13). Furthermore as the sample is cooled the low-field resonance at 23.29 ppm significantly broadens into the base line and on further cooling two more resonances appear, one significantly downfield (approximately 60 ppm) and the other initially underneath the solvent peak at around 7 ppm, which migrates further upfield. This decoalescence is attributed to the slowing of the rotation of the Pn^* ligand on the NMR timescale thus rendering the two sets of NWT methyl protons magnetically inequivalent (with the axis of rotation along the centroid of the bridgehead bond and the metal centre). Such a phenomenon is seen in **2.3**, however in that case the decoalescence occurs at a higher temperature (presumably due to the increased bulk of the Cp^* ligand making the energy barrier to rotation higher). Indeed in the Cp^* case further splitting is seen at extremely low temperatures. Due to solvent and mechanical limitations this further splitting point is not reached with **2.4**.

At high temperature it is possible to see four of the eight carbon resonances in the ^{13}C NMR spectrum, at $\delta = 243.2$, 84.6, 54.6 and 44.3 ppm although the strong paramagnetism and fluxionality within the molecule made recording a full ^{13}C spectrum impossible. These all have extremely low intensities and as such assignment is not possible. Furthermore due to the broadness of the resonances and solubility issues with the sample a low temperature spectrum was not accessible. ^7Li NMR gave a single

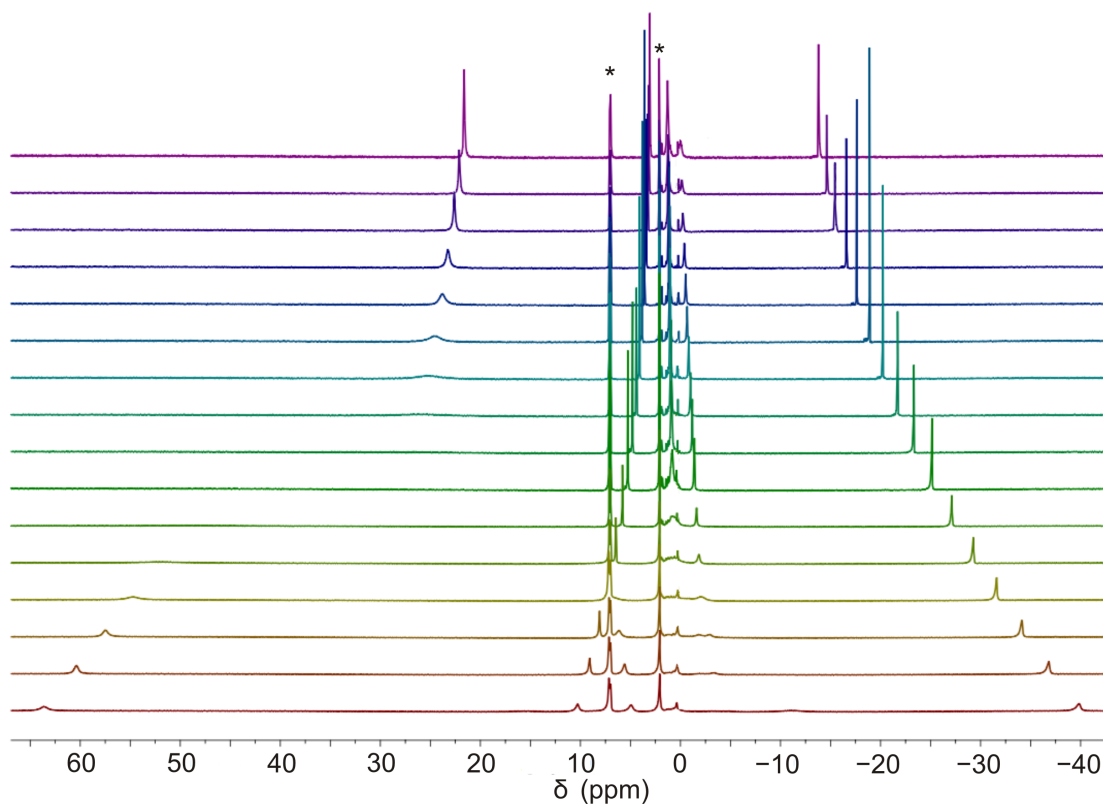


Figure 2.13: Stack plot of the ^1H NMR spectrum of **2.4** from 193 K to 353 K with temperature increasing in 10 K increments up the page. * indicates residual protio-solvent peaks.

sharp resonance at $\delta = -14.45$ ppm. The paramagnetism of **2.4** was investigated using Evans' method, and gave an effective magnetic moment of $2.32 \mu_{\text{B}}$. This remained constant with temperature showing that this sample, unlike **2.2**, is a Curie paramagnet at room temperature.

2.4.4.2 NMR characterisation of **2.5**

The ^1H NMR of **2.5** is simple by comparison consisting of three signals at $\delta = 42.05$, -0.48 and -41.09 ppm, corresponding to the NWT methyl, Cp and WT methyl protons respectively. The ^{13}C NMR consists of six resonances at $\delta = 545.4$, 259.3 , 61.4 , 45.6 , -4.8 and -95.2 ppm. These correspond to the NWT methyl carbons, the Cp ring carbons, the WT carbons, the bridge-head carbons, the NWT carbons and the WT methyl carbons. Variable temperature ^1H NMR studies on **2.5** show no evidence of any peak splitting, implying both Cp rings are bound in an η^5 fashion. The peaks do however migrate with a linear relationship to T^{-1} as is expected for the U^{IV} paramagnetic species (figure 2.14).

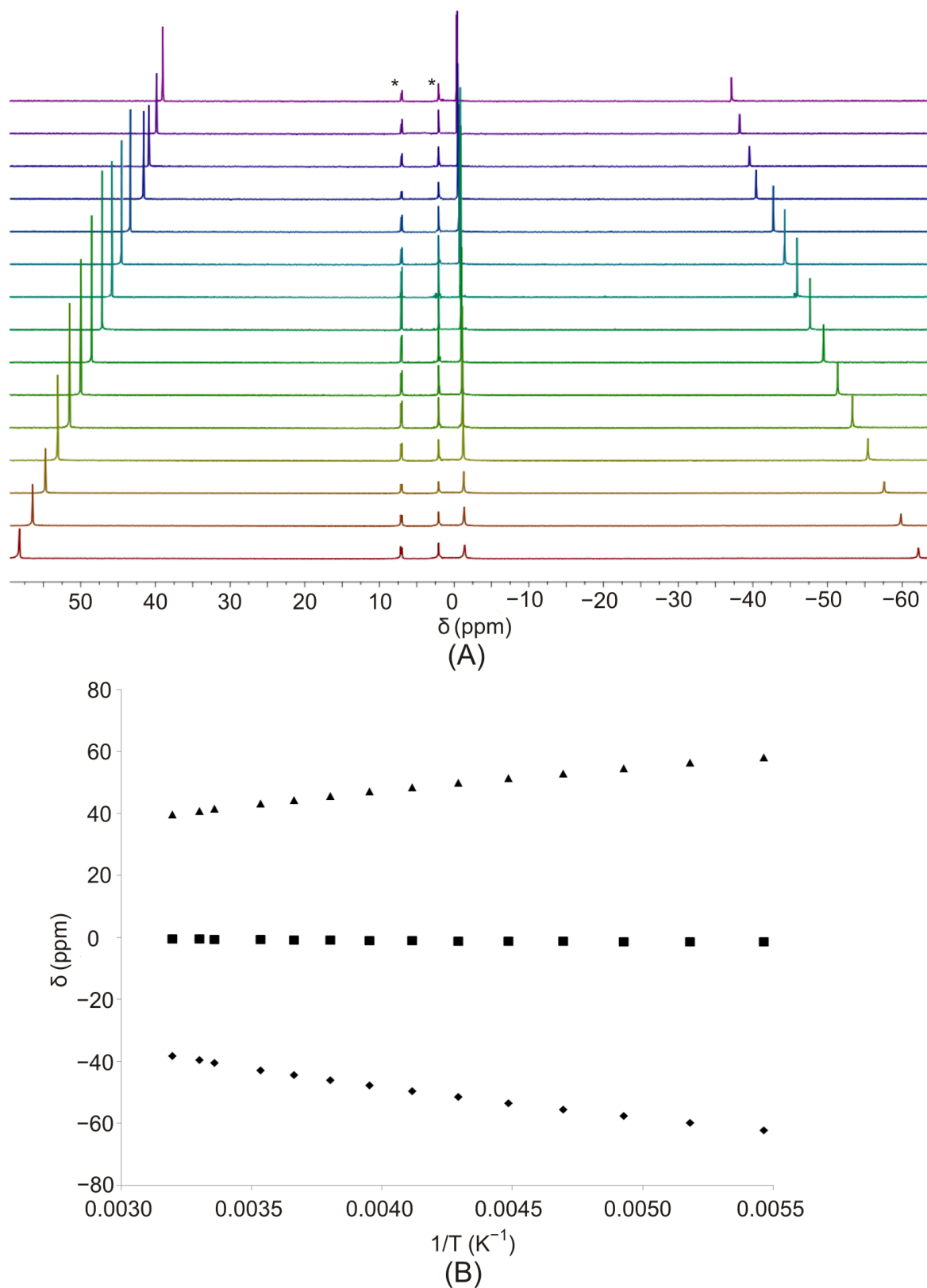


Figure 2.14: (A) Stack plot of the ^1H NMR of **2.5**. Temperature increases up the page in 10 K increments. * indicates residual protio-solvent.; (B) $1/T$ dependence of chemical shifts of **2.5**, $\blacktriangle$ = NWT-Me, $\blacksquare$ = Cp-H, $\blacklozenge$ = WT-Me.

2.4.4.3 Other Characterisation of **2.4** and **2.5**

2.4 and **2.5** were both also characterised *via* mass spectrometry and IR spectroscopy. For **2.4** a strong signal was seen for the molecular ion, $[\text{UPn}^*\text{CpCl}]^+$ ($m/z = 523.3129$), with expected fragmentation patterns. Furthermore a weak signal was seen at $m/z = 559.3169$ corresponding to $[\text{UPn}^*\text{CpCl}_2]^+$, giving further support to the proposed solvate formulation of $[\text{UPn}^*\text{CpCl}_2][\text{Li}(\text{TMEDA})]$. Mass spectrometry of **2.5** shows the presence of a signal at the expected molecular ion weight ($m/z = 554.3952$) and the anticipated fragmentations of such an ion.

IR spectroscopy of **2.4** (KBr plates) shows four strong bands at 2960, 2907, 2868 and 2837 cm^{-1} which can be attributed to C–H stretching, and two bands at 1464 and 1261 cm^{-1} due to C–H bending. A similar set of bands was seen in the IR spectrum of **2.5** (C–H stretching at 2958, 2838 and 2794 cm^{-1} ; C–H bending at 1464 and 1261 cm^{-1}) adding further evidence to the proposed bis- η^5 bonding situation (should a Cp ring be bound in the η^1 manner one would expect an sp^2 hybridised C–H stretch above 3000 cm^{-1} and a C=C stretch at around 1650 cm^{-1}).

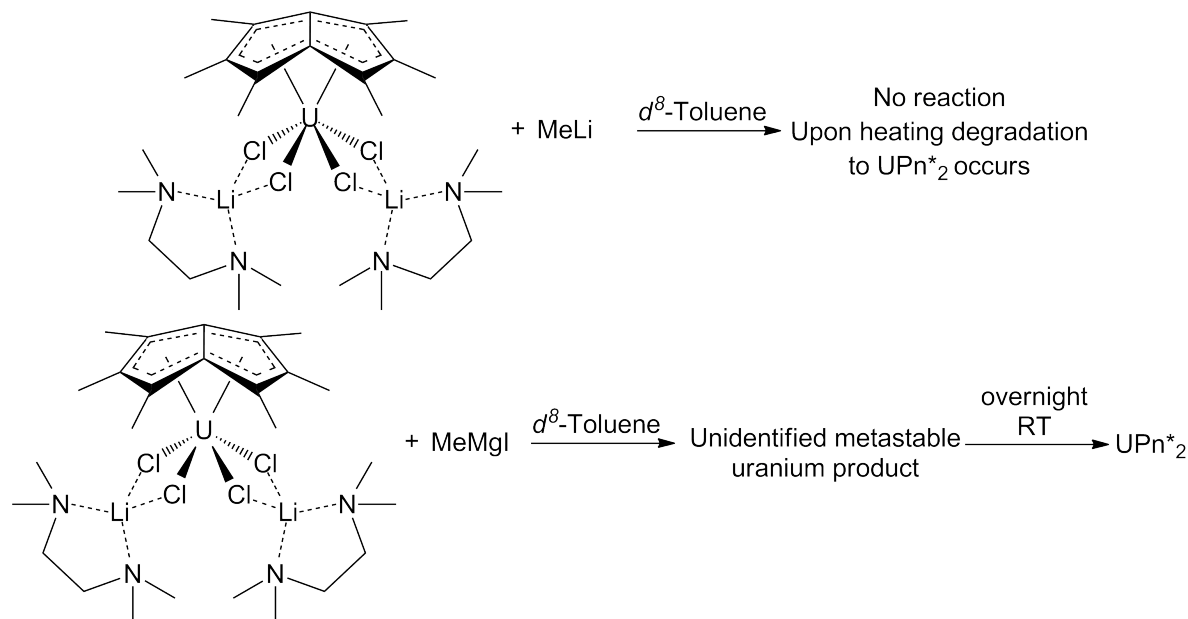
2.5 Attempted synthesis of alkyl derivatives of **2.2**

To date there are few examples of the U(COT) half sandwich with U–C σ -bonds. Therefore attempts were made to synthesise a number of σ -bound ligand derivatives of **2.2**. Generally these reactions were done on an NMR scale in an attempt to monitor the reaction. However with the issues of paramagnetic NMR products (if any were formed) could not be fully characterised.

2.5.1 Attempts at methylation

Attempted methylation reactions were carried out using both MeLi and MeMgI as the methyl transfer reagents. In the reaction of **2.2** and MeLi in d^8 -toluene, no reaction took place on initial addition. On subsequent heating and sonication degradation of **2.2** was observed and resonances due to **2.1** began to appear. In the mass spectrum only signals attributed to the UPn^*Cl_2 and UPn^*_2 molecular ions were seen. In reaction with MeMgI all resonances attributed to **2.2** quickly disappeared and two new,

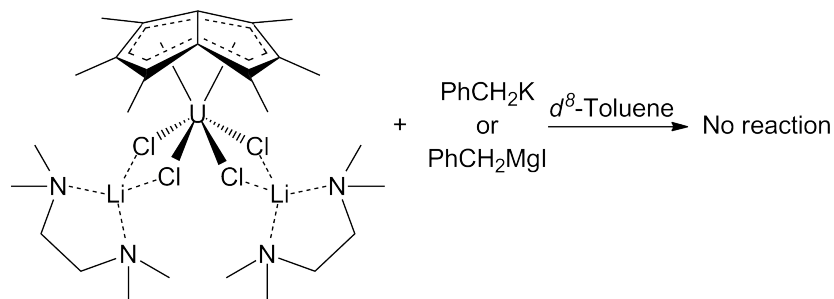
somewhat broad resonances emerge at 0.85 ppm and -0.51 ppm. Over time the intensity of these diminished and resonances due to **2.1** appeared (scheme 2.7). Mass spectrometry showed the presence of two previously unseen molecular ion peaks at 267.0222 and 551.2195, which may be attributed to the UMe_2^+ and U_2Me_5^+ molecular ions respectively.



Scheme 2.7: The attempted methylation of **2.2**.

2.5.2 Other alkylation attempts: benzyl, neopentyl and neosilyl

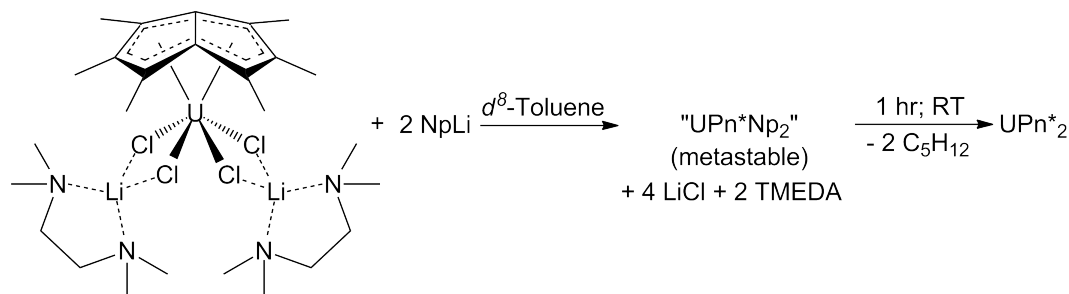
Attempts to make a $\text{UPn}^*\text{CH}_2\text{Ph}$ species were completely unsuccessful. Addition of CH_2PhK or PhCH_2MgI led to the immediate disappearance of the resonances attributed to **2.2** and no other resonances appeared. MS analysis of the sample showed no evidence for any uranium pentalene species (scheme 2.8).



Scheme 2.8: The attempted reaction of **2.2** with PhCH_2K and PhCH_2MgI .

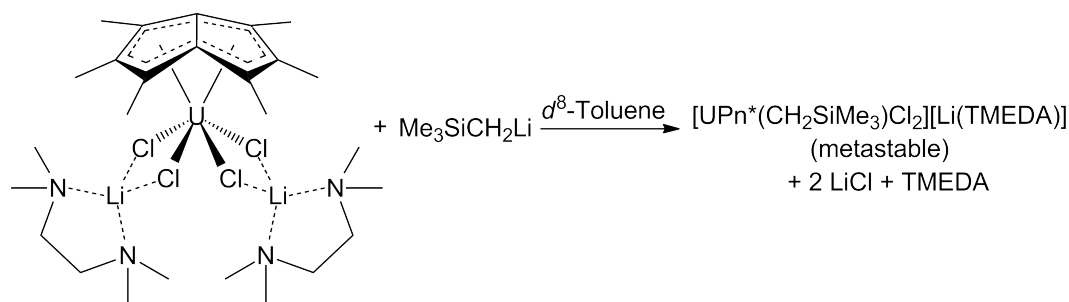
Reaction with LiNp ($\text{Np} = \text{CH}_2^t\text{Bu}$) led to the immediate disappearance of the resonances attributed to **2.2**, with three new resonances appearing in the ^1H NMR

spectrum: two attributed to a paramagnetic uranium species at 11.36 and -5.65 ppm, and one at 0.89 ppm attributed to neopentane. Monitoring the reaction over an hour shows the growth of the neopentane resonances as the uranium species degrades. After one hour the neopentane resonance has swamped the spectrum, and after removal *via* freeze-pump-thaw degassing of the sample the only paramagnetic resonances left are those belonging to **2.1**. Attempts to scale up this reaction led only to the isolation of **2.1**, implying that any $\text{U(IV)Pn}^*\text{Np}_2$ species formed is extremely unstable.



Scheme 2.9: The reaction of **2.2** with LiNp.

Similar to above, addition of $\text{LiCH}_2(\text{TMS})$ ($\text{TMS} = \text{SiMe}_3$) to **2.2** led to the growth of seven new paramagnetic ^1H NMR resonances (75.78 , 11.44 , 0.47 , -5.84 , -7.48 , -8.15 and -38.27 ppm) and the resonances attributed to **2.2** completely receding. Within a species of formula $[\text{UPn}^*(\text{CH}_2\text{TMS})\text{Cl}_2][\text{Li}(\text{TMEDA})]$ seven different environments would be expected (assuming a 6:6:6 splitting of the Pn^* resonances) and such a formula is tentatively proposed (scheme 2.10), however lack of a crystal structure means firm assignment of the resonances is not possible. Over the course of 24 hours a resonance attributed to SiMe_4 appears and swamps the spectrum, and on subsequent freeze-vacuum-thaw degassing no paramagnetic resonances remain. Attempts to scale up the reaction yielded nothing. The tendency of **2.2** to form unstable alkyl species was not wholly unexpected given the lack of such species for the isoelectronic $\text{U}(\text{COT})$ moiety.⁶⁵

Scheme 2.10: The reaction of **2.2** with LiNp.

2.6 Concluding remarks

The extension of the permethylpentalene ligand to organoactinide chemistry has been a success. Five new uranium species have been synthesised and fully characterised. **2.1** displays curious electrochemical behaviour and a fascinating solid state structure in which three stereoisomers are simultaneously seen within the crystal. A permethylpentalene half sandwich has been synthesised and can be made on a multi-gram scale making it a suitable entry point into further synthesis. Utilising **2.2** three mixed sandwich species have been synthesised. Their tendency to form solvate complex has limited their crystallisability but one structure was obtained (**2.3**). This species also showed complex NMR behaviour combining paramagnetism and fluxionality. In comparison **2.4** and **2.5** were more amenable to characterisation *via* NMR spectroscopy.

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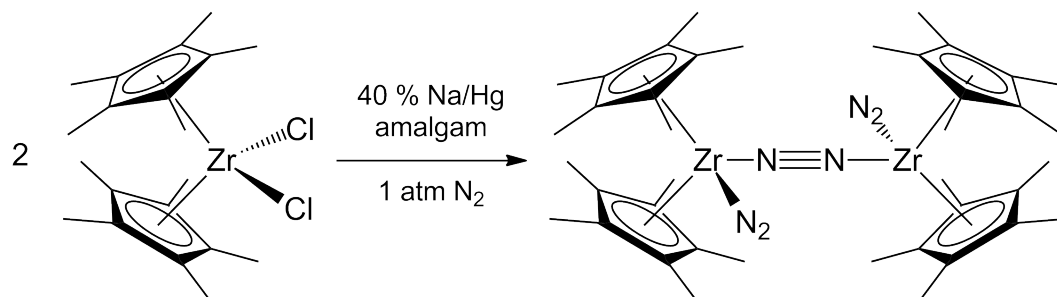
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3. THE SYNTHESIS OF ZIRCONIUM AND HAFNIUM PERMETHYLPENTALENE COMPLEXES

3.1 Introduction

Coordination compounds of group 4 constitute one of the most widely developed areas of organometallic chemistry, with applications ranging from industrial catalysis to anti-cancer agents and small molecule activation - and in all of these applications group 4 metallocenes have been a cornerstone.¹⁻⁴ Group 4 metallocenes have shown a rich variety of chemical and physical properties and have thus interested both practical and theoretical chemists. Bis(cyclopentadienyl)zirconiumdichloride, commonly called zirconocene dichloride (ZrCp_2Cl_2 , $\text{Cp} = \text{C}_5\text{H}_5$) was initially synthesised along with the titanium analogue by Birmingham and Wilkinson in 1954;⁵ it was not until 12 years later that the synthesis of hafnocene dichloride would be reported.⁶ The crystal structures found both to be monomeric and isostructural with the titanocene dichloride, with the metal adopting a tetrahedral geometry.^{7;8} Due to the propensity of zirconium and hafnium to favour the +4 oxidation state the zirconium analogue of ferrocene, though reported in 1996, was found to be non-isolable.⁹ It was quickly found that the chloride ligands of ZrCp_2Cl_2 could be replaced (*via* bond metathesis) by neutral and/or anionic ligands, leading to a broader definition of a group 4 bent metallocene as a d^0 *pseudo*-tetrahedral organometallic compound that contains two η^5 -bound cyclopentadienyl type ligands and two σ -ligands.

Following the discovery of the permethylated Cp^* ligand, Bercaw *et al.* quickly applied its use to the group 4 metals, synthesising permethylated bent metallocene analogues.¹⁰ The ability of Cp^* to stabilise a metal centre led to the formation of a dinitrogen compound by the reduction of $\text{ZrCp}^*_2\text{Cl}_2$ using a sodium amalgam (scheme 3.1). This compound, though not crystallographically characterised, was shown to react



Scheme 3.1: The reduction of $\text{ZrCp}^*_2\text{Cl}_2$ to form $[(\text{ZrCp}^*(\text{N}_2))_2](\mu\text{-N}_2)$

with mineral acids to form hydrazine.¹⁰

The idea that pentalene (Pn; C_8H_6) can be considered as two ring fused cyclopentadiene units but with two fewer electrons was introduced in chapter one. It can thus be envisaged that replacing the two Cp moieties of the group 4 bent metallocene with a Pn unit would form a more electron deficient bent “pentalocene” species which would show interesting reactivity. However, due to a lack of suitable starting materials only a handful of Zr and Hf Pn compounds have been reported. In the first pair of papers describing the η^8 -Pn binding mode, Jonas *et al.* reported the syntheses of the first set of group 4 η^8 -Pn compounds.¹¹ Reaction of ZrCp_2Cl_2 with one equivalent of $\text{Li}_2\text{Pn}^{\text{R}}$ ($\text{R} = \text{H}; 2\text{-Me}$) formed the 18 e^- complex $\text{ZrPn}^{\text{R}}\text{CpCl}$, this was one of the first structurally characterised Pn compounds and its structural parameters, along with other structurally characterised Zr and Hf η^8 -Pn compounds, are summarised in table 3.1. Addition of two equivalents of $\text{Li}_2\text{Pn}^{\text{R}}$ to the same starting material (or the Hf equivalent) resulted in the formation of the homoleptic sandwich compounds MPn^{R}_2 ($\text{M} = \text{Zr}, \text{Hf}$). Though neither of these compounds were crystallographically characterised they were the subject of a further study using photoelectron spectroscopy and stimulated much theoretical discussion.^{12–15} The PES study led Gleiter *et al.* to predict a torsion angle between the two Pn rings of 50.6° or 49.3° ($\text{M} = \text{Zr}$ or Hf respectively, $\text{R} = \text{H}$) and fold angles of 27.7° and 28.9° . The ZrPn_2 species was subsequently shown to react with an equivalent of $\text{ZrCl}_4 \cdot 2\text{THF}$ to form $\text{PnZrCl}_2 \cdot 2\text{THF}$, which is a *pseudo*-octahedral 18 e^- complex and contrasts to ZrCp_2Cl_2 , 16 e^- , which does not bind THF. The two chlorine atoms occupy the axial positions and the equatorial positions taken up by the oxygens of the two coordinated THF molecules and the two centroids of the Pn rings (figure 3.1).

There is only one other previously reported Zr (non-permethylated) Pn complex in the literature, $\text{ZrPn}(\text{C}_3\text{H}_5)_2$.¹⁶ Due to the fluxional nature of the allyl moiety this complex was the subject of an in-depth NMR study. The measured energy barrier for the rotation of the allyl ligands was found to be 64 KJ mol^{-1} at -40°C . It was also shown that the two allyl groups do not lie at a torsion angle of 90° to the Pn rings (as also predicted for the sandwich compounds MPn_2), though due to the lack of a single crystal X-ray structure the exact coordination could not be determined. The singular Pn^* -containing Zr species was synthesised by an analogous manner to Jonas' method by reaction of ZrCp_2Cl_2 with $\text{Li}_2\text{Pn}^*(\text{TMEDA})_x$ leading to the formation of ZrPn^*CpCl (albeit in low yield due to difficulties with purification from the LiCp by-product). A decrease in fold angle is seen with permethylation (30.7° for Pn^* 33° for Pn) and can be attributed to the increased donor capability of the Pn^* ligand versus the non-substituted Pn.¹⁷

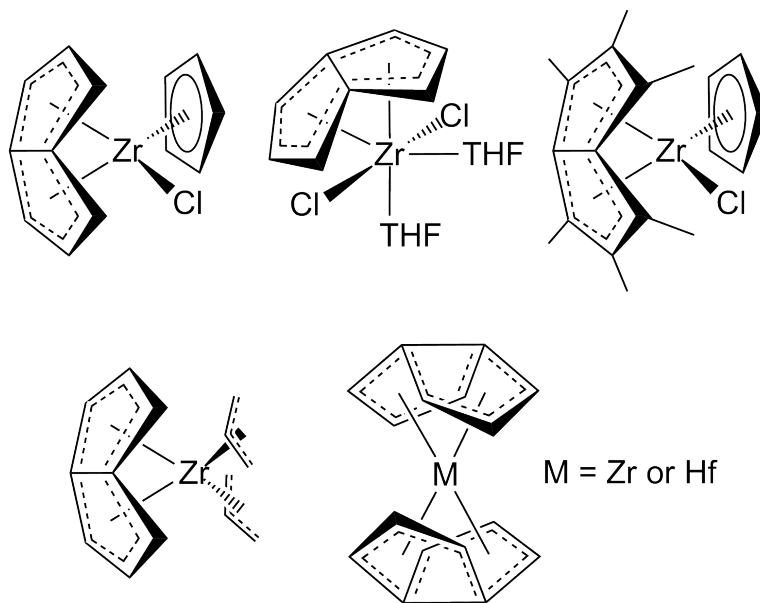


Figure 3.1: The six previously synthesised Zr and Hf η^8 -Pn compounds

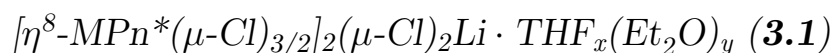
Table 3.1: A summary of selected structural parameters for the previously reported Zr and Hf Pn complexes ([†] indicates parameters calculated *via* photoelectron spectroscopy)

Compound	Fold Angle °	Av. M-Pn* _{cent.} Å	Torsion Angle °
ZrPnCpCl	33.0	2.096	n/a
ZrPnCl ₂ ·2THF	30.0	2.110	n/a
ZrPn* _{cent.} CpCl	30.7	2.110	n/a
ZrPn ₂	27.7 [†]	2.111 [†]	50.6 [†]
HfPn ₂	28.9 [†]	2.177 [†]	49.3 [†]

The purpose of this chapter is to expand upon the severely limited field of group 4 Pn chemistry. Previous work in this group has focused on TiPn* chemistry.¹⁸ Initially the suitable group 4 Pn* synthons were targeted, namely ‘MPn*Cl₂’, upon which it was hoped further ligand metathesis could occur. This chapter discusses the synthesis of these (and related) synthons and their further reactivity.

*Throughout this chapter Zr and Hf analogues will be discussed simultaneously. Zr compounds will be referred to as **3.X_{Zr}** and the Hf congener will be referred to as **3.X_{Hf}**.*

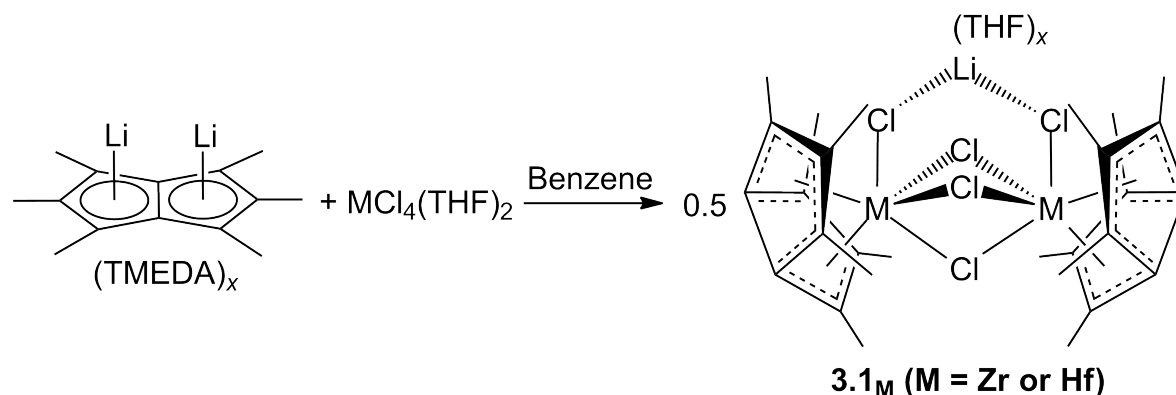
3.2 Zirconium and hafnium ‘dichloride’ starting materials:



3.2.1 Synthesis of **3.1**

It was found that direct combination of the Li₂Pn*(TMEDA)_x precursor with Ti(IV) reagents led to the decomposition of the ligand through oxidation and formation of Ti(III) salts.¹⁹ However combination of Li₂Pn*(TMEDA)_x with TiCl₃ · 3 THF and subsequent *in situ* oxidation using PbCl₂ did form the Ti synthon [TiPn*Cl(μ-Cl)]₂. However this was unreliable and suffered from poor yields (8 %) making this an unsuitable entry point to TiPn* chemistry. A process was therefore developed utilising isomeric control of the Pn* starting materials. The softer *cis*-(SnMe₃)₂Pn* synthon in direct combination with TiCl₄ · 2 THF {increasing the yield of [TiPn*Cl(μ-Cl)]₂ to 78 %}.²⁰ Initial efforts to form the remaining group 4 congeners focused on a parallel synthetic pathway. However all attempts failed to produce the desired products. It was posited

that the reducing power of $\text{Li}_2\text{Pn}^*(\text{TMEDA})_x$ should prove less problematic with the second and third row transition metals, due to their inherently lower susceptibility to reduction. Indeed it was found that the simple salt metathesis reaction between $\text{Li}_2\text{Pn}^*(\text{TMEDA})_x$ and $\text{MCl}_4 \cdot 2 \text{ THF}$ ($\text{M} = \text{Zr}$ or Hf) led to the formation of a novel Pn^* species with ^1H NMR spectroscopy revealing the presence of coordinated THF. On cooling a saturated THF solution to -35°C crystals suitable for single crystal X-ray diffraction were obtained in good yield (50 % for Zr, 76 % for Hf) which identified the compounds as $[\text{M}(\eta^8\text{-Pn}^*)(\mu\text{-Cl})_{3/2}]_2(\mu\text{-Cl})_2\text{Li} \cdot 2 \text{ THF}$ [$\text{M} = \text{Zr}$ or Hf (**3.1_{Zr/Hf}**), scheme 3.1]. Practically, it was found that crystallisation from an Et_2O solution proved more effective (due to the greater solubility gradient and lower solubility of the LiCl byproduct); however it resulted in the mixed coordination of THF and Et_2O . The partial removal of solvent was achieved by subjecting **3.1** to a dynamic vacuum, but attempts at the complete removal *via* high vacuum whilst heating (1×10^{-7} mbar/ 130°C) led to the decomposition of **3.1**. The overall formulation is thus $[\text{M}(\eta^8\text{-Pn}^*)(\mu\text{-Cl})_{3/2}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{THF})_x(\text{Et}_2\text{O})_y$ with the x and y values found *via* careful integration of ^1H NMR signals.



Scheme 3.2: The synthesis of **3.1_M** ($\text{M} = \text{Zr}$ or Hf).

3.2.2 Characterisation of **3.1**

3.2.2.1 Single Crystal X-ray Diffraction Characterisation

Both congeners of **3.1** crystallise as yellow blocks and are in the $\text{P } 1 \ 2_1 \ 1$ space group with a single asymmetric molecule in the unit cell (figure 3.2). **3.1_{Hf}** is the first Hf Pn compound to be characterized *via* single crystal X-ray diffraction. **3.1** alleviates

its coordinative unsaturation and electron deficiency by forming a dimer {in a manner similar to $[\text{TiPn}^*(\mu\text{-Cl})\text{Cl}]_2$ } and by incorporation of LiCl to form a solvate complex (a common occurrence when using lithium salts in metathesis reactions of the second and third row transition metals) making them formally 18 e^- species. Recrystallisation from other donor solvents allows for solvent exchange within **3.1**. The crystal structure of the TMEDA adduct of **3.1_{Hf}** is attached as an electronic appendix, however it is not extensively reported here as it is isostructural with the THF adduct.

Table 3.2: Selected structural parameters for **3.1**. ESDs in parentheses.

Bond lengths Å					
	3.1_{Zr}	3.1_{Hf}		3.1_{Zr}	3.1_{Hf}
M(1)-C(1)	2.524(5)	2.485(4)	M(2)-C(15)	2.508(5)	2.517(5)
M(1)-C(2)	2.630(5)	2.605(5)	M(2)-C(16)	2.635(5)	2.615(4)
M(1)-C(3)	2.479(5)	2.469(4)	M(2)-C(17)	2.489(5)	2.466(4)
M(1)-C(4)	2.256(5)	2.243(4)	M(2)-C(18)	2.271(5)	2.240(4)
M(1)-C(5)	2.482(5)	2.467(4)	M(2)-C(19)	2.506(5)	2.455(4)
M(1)-C(6)	2.632(5)	2.619(4)	M(2)-C(20)	2.627(5)	2.606(4)
M(1)-C(7)	2.518(5)	2.483(4)	M(2)-C(21)	2.513(5)	2.497(4)
M(1)-C(8)	2.275(5)	2.244(4)	M(2)-C(22)	2.266(5)	2.242(4)
M(1)-Pn* _{cent.}	2.108(2)	2.082(2)	M(2)-Pn* _{cent.}	2.109(2)	2.091(2)
M(1)-Pn* _{cent.}	2.105(2)	2.086(2)	M(2)-Pn* _{cent.}	2.113(2)	2.080(2)
Av. C _{ring} -Me	1.501	1.506	Av. M-($\mu\text{-Cl}$) _M	2.649	2.623
M(1)-M(2)	3.645(1)	3.616(1)	Av. M-($\mu\text{-Cl}$) _{Li}	2.581	2.554
Bond angles °					
Fold Angle	30.0(4)	30.6(3)	Cl(2)-M(1)-Cl(4)	141.03(4)	140.23(3)

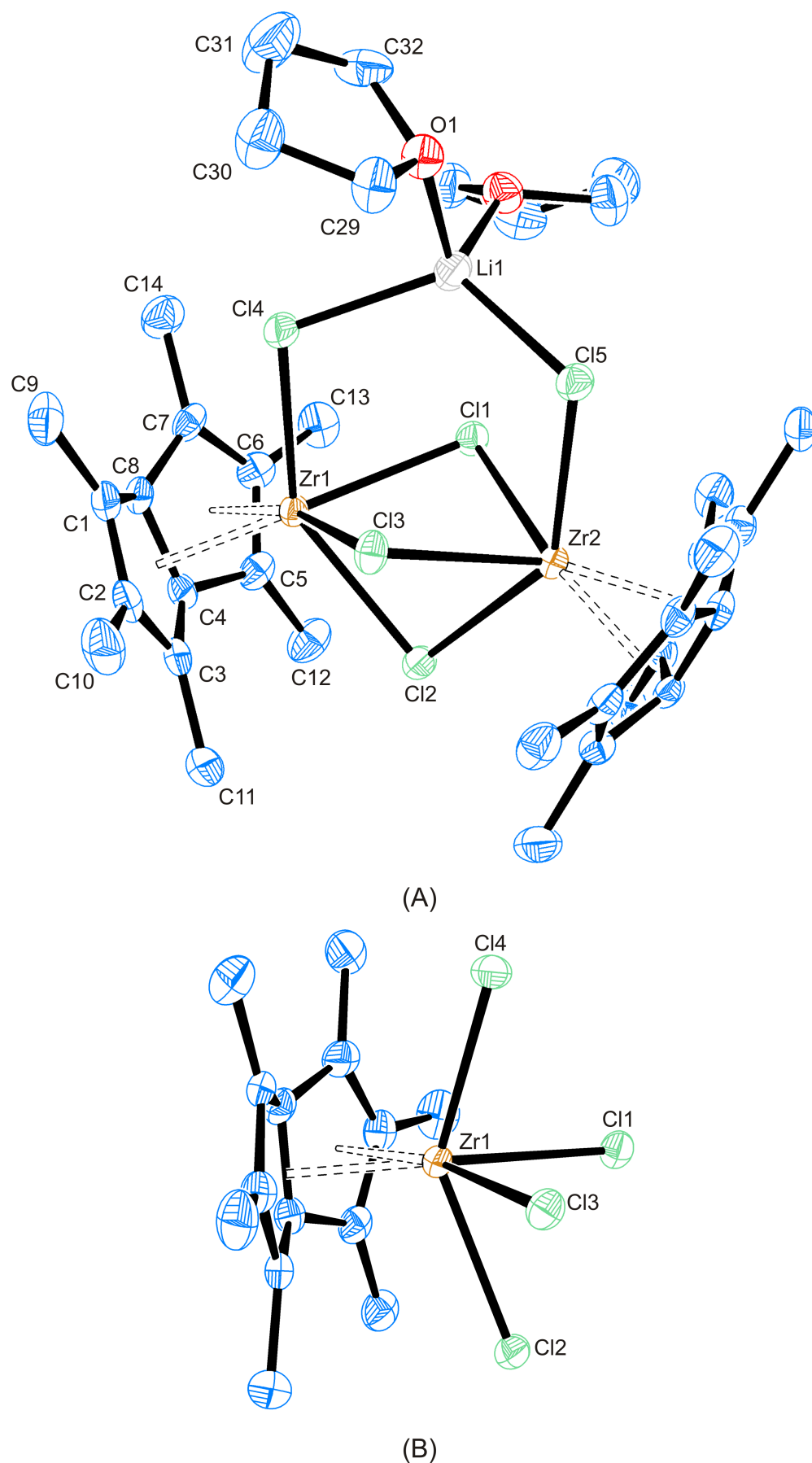


Figure 3.2: (A) The X-ray single crystal structure of **3.1_{Zr}** and (B) the *pseudo*-octahedral environment of the Zr atom. Thermal ellipsoids at 50% probability and H-atoms, labels of second THF and second Pn* ring omitted for clarity; **3.1_{Hf}** is isostructural.

The metal centres have a distorted *pseudo*-octahedral geometry with Cl(2) and Cl(4/5) adopting the axial positions while Cl(1), Cl(3) and the relevant Pn* centroids forming the equatorial planes [figure 3.2 (B)]. This is structurally analogous to the previously reported $(\eta^8\text{-Pn})\text{ZrCl}_2 \cdot 2\text{THF}$, in which the two chlorine atoms adopt the axial positions while the two Pn centroids and the two THF molecules make up the equatorial plane. The Cl(2)-Zr-Cl(4) angle is 143° which is comparable to the angle in **3.1_{Zr}** (141°) with a similar angle seen for **3.1_{Hf}** (140°). The average M-($\mu\text{-Cl}$)_M distances for **3.1_{Zr}** and **3.1_{Hf}** are 2.649 and 2.623 Å respectively and the former is in good agreement with other examples containing the $\text{Zr}_2(\mu\text{-Cl})_3$ fragment in the CSD (2.536-2.794 Å).²¹⁻²⁶ **3.1_{Hf}** is the first example of this bonding motif for a neutral Hf species and so comparisons can only tentatively be made with the $(\text{Hf}_2\text{Cl}_9)^-$ anion [the only other $\text{Hf}_2(\mu\text{-Cl})_3$ containing species in the CSD], which has expectedly shorter average Hf($\mu\text{-Cl}$) distances (2.576-2.611 Å).²⁷⁻²⁹ The average Zr-($\mu\text{-Cl}$)_{Li} distance for **3.1_{Zr}** is 2.581 Å, which is appreciably longer than that seen in the related dimeric compounds: $\{\text{Zr}[\eta^5\text{-}\sigma\text{-Me}_2\text{C}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Cl}(\mu\text{-Cl})_{3/2}\}_2\text{Li} \cdot 2\text{THF}$ (2.424 Å)²² [figure 3.3(A)] and $[\text{ZrCp}'\text{Cl}_2(\mu\text{-Cl})_{3/2}]_2\text{Li} \cdot \text{DME}$ (Cp' = $\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$) (2.476 Å) [figure 3.3 (B)].²¹ Indeed, the distance is closer to the average bond length observed for the terminal chlorides in $\text{ZrPnCl}_2 \cdot 2\text{THF}$ (2.580 Å).¹¹ The reason for this is that **3.1_{Zr}** is an 18 e⁻ species (as is Jonas' compound) whereas both the complexes in figure 3.3 are 16 e⁻. The corresponding distance in **3.1_{Hf}** (2.554 Å) is slightly shorter than **3.1_{Zr}** but compares reasonably well with the only two examples of Hf-($\mu\text{-Cl}$)_{Li} bonds in the literature: 2.525(5) and 2.507(3) Å, however both of these are found for monomeric species: $\text{Hf}[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Cl}_2(\mu\text{-Cl}) \cdot \text{Li}(\text{THF})_3$ and $\text{Hf}\{\text{CyNC}[\text{N}(\text{TMS})_2]\text{NCy}\}(\mu\text{-Cl}) \cdot \text{Li}(\text{THF})_3$ respectively.^{28;29}

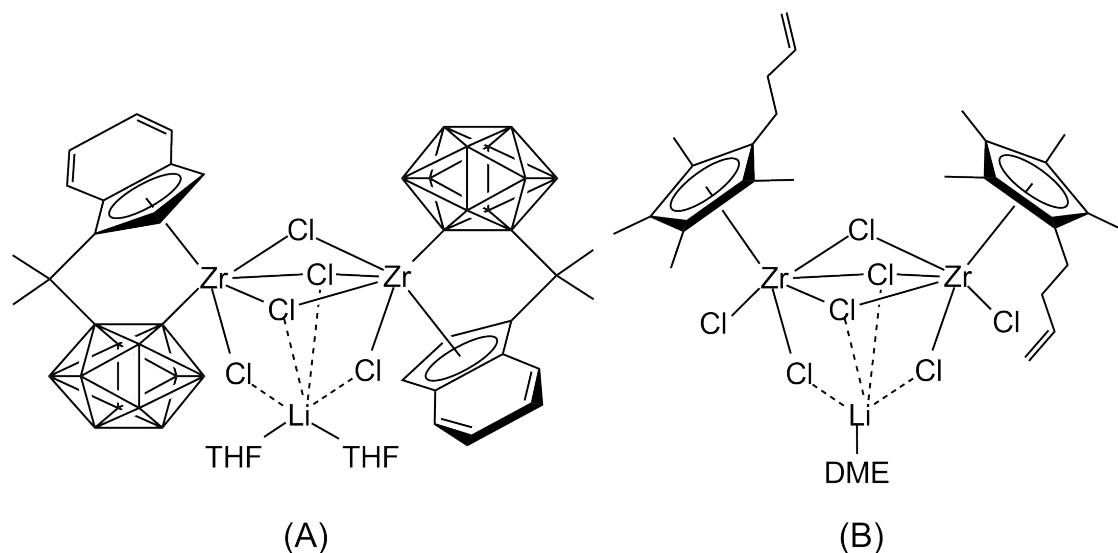


Figure 3.3: Two structures comparable to **3.1_{Zr}**.^{21;22}

In general, the bond lengths of **3.1_{Hf}** are marginally shorter than those of **3.1_{Zr}**, which is expected due to the stronger orbital overlap present for the Hf metal centre with its more radially extended $5d$ orbitals. This is well illustrated by the shorter average $\text{M-Pn}^*_{(\text{centroid})}$ distance [2.085 *vs.* 2.109 Å respectively] and the larger fold angle [30.6(3)° *vs.* 30.0(4)°]. As expected both **3.1_{Zr}** and **3.1_{Hf}** have considerably smaller fold angles than the Ti Pn^* dichloride analogue [$\text{Pn}^*\text{Ti}(\mu\text{-Cl})\text{Cl}_2$] [32.3(3)°].²⁰ This is attributed to a combination of the larger atomic radii of Zr and Hf and the increased electron density on the metal centres (18 e^- *vs.* 16 e^-) which has been shown to be a factor in decreasing fold angle of $\eta^8\text{-Pn}$ species.¹⁷ The $\text{M-Pn}^*_{\text{cent.}}$ distance and fold angle for **3.1_{Zr}** are in excellent agreement with that of the analogous isoelectronic species $\text{ZrPnCl}_2 \cdot 2\text{THF}$ (2.110 Å and 30.0° respectively).¹¹

2.2 and both congeners of **3.1** contain the same “ MPn^*Cl_4 ” octahedral fragment. A comparison of selected relevant structural parameters of these compounds are shown in table 3.3

Table 3.3: A comparison of selected structural parameters for **2.2** and **3.1**. ESDs in parentheses.

	2.2	3.1_{Zr}	3.1_{Hf}
Av. M–Pn* _{cent.}	2.318(2)	2.109(2)	2.085(2)
Av. M–Cl _{eq.}	2.747(2)	2.652(1)	2.626(1)
Av. M–Cl _{ax.}	2.777(1)	2.612(1)	2.584(1)
Cl _{ax.} –M–Cl _{ax.}	145.0(3)	141.0(1)	140.2(1)

In general we see a considerable increase in the structural parameters of **2.2**. This is probably due to both the larger ionic radius of U when compared to Zr and Hf and combined with the more diffuse orbitals allowing for longer bonds. For **2.2** we see the U–Cl bond lengths are slightly shorter for the *psuedo*-equatorial bonds compared with the *psuedo*-axial bonds. The opposite is seen in both congeners of **3.1**, however this is due to one of the axial chlorine atoms bridging between the group 4 metal and the lithium atom resulting in a much smaller M–Cl bond length for that example. The increase in Cl_{ax.}–M–Cl_{ax.} angle may be due to the fact that both examples of **3.1** are dimers, and therefore one of the axial chlorine atoms must bridge to the other metal centre and therefore more of a pinching effect is seen.

3.2.2.2 NMR characterisation

The room temperature ¹H NMR spectra of **3.1_{Zr}** and **3.1_{Hf}** are curiously different. **3.1_{Zr}** consists of five resonance signals, two triplets assigned to the coordinated THF and three resonance signals assigned to the Pn* Me protons of 6:6:6 intensity ratio [$\delta = 2.18$ and 2.12 ppm (NWT-Me) and $\delta = 1.86$ ppm (WT-Me)], showing the NWT-Me groups (C9, C11, C12, C14 in figure 3.2) are not equivalent. By contrast **3.1_{Hf}** consists of four resonances; again two triplets for the coordinated THF, and the remaining two assigned to the Pn Me groups (of 12:6 intensity) showing the NWT-Me in **3.1_{Hf}** to be equivalent on an NMR timescale. This phenomenon is also seen in the ¹³C NMR where **3.1_{Hf}** exhibits five Pn* resonances whereas **3.1_{Zr}** possesses eight Pn* resonances because of the reduced symmetry. An additional two resonances are seen in both ¹³C spectra of **3.1** due to coordinated THF. The two symmetrically inequivalent resonances of the

3.1_{Zr} NWT-Me groups were found to coalesce when heated giving a single resonance ($\delta = 2.11$ ppm) at temperatures above 315 K. The origins of this fluxional process are postulated to arise from the Pn* ligand ring-whizzing (a phenomenon readily observed for Cp and Cp* complexes), with rotation along the axis of the metal and mid-point of the bridge-head bond, rendering all NWT-Me groups equivalent on an NMR timescale. Attempts to freeze out the process in **3.1_{Hf}** proved futile, with cooling of the sample to 193 K not producing a decoalescence of the resonance. This phenomenon (of Zr congeners having a higher barrier to Pn* ring rotation than their Hf cousin) is seen in many of the compounds in this chapter.

3.2.2.3 Other characterisation

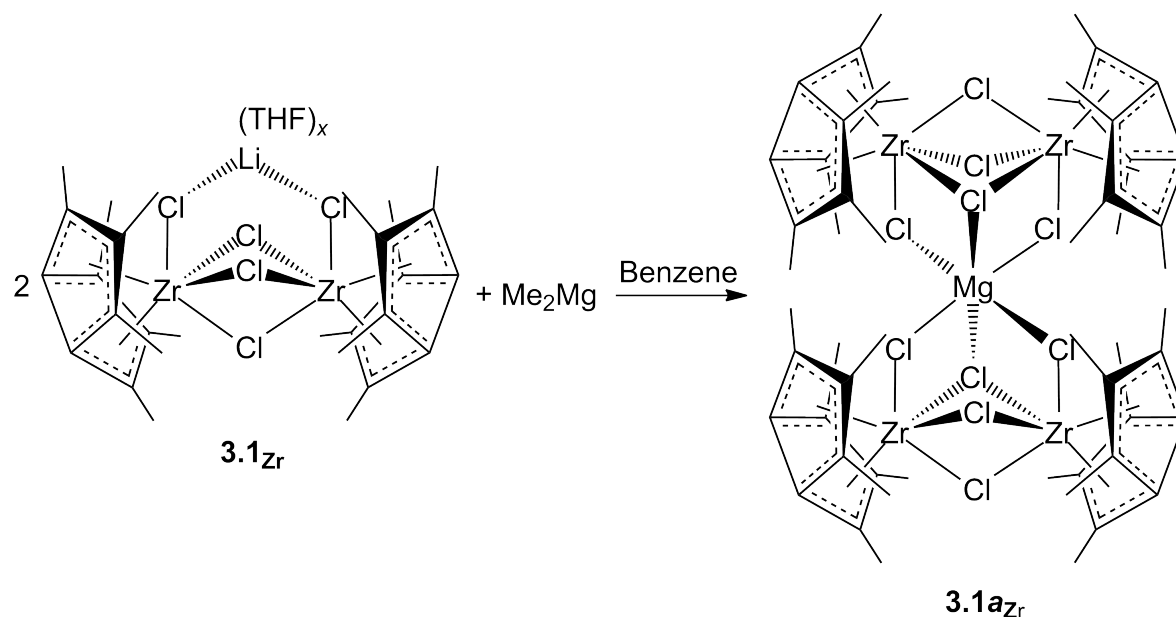
Both **3.1_{Zr}** and **3.1_{Hf}** were also characterised by IR spectroscopy, mass spectrometry and elemental analysis. IR spectroscopy showed the characteristic C–H stretching and bending bands (C–H stretching giving two broad bands at 2908 and 2726 cm^{-1} in **3.1_{Zr}** and a very broad band at 2969 cm^{-1} in **3.1_{Hf}**; C–H bending giving sharp bands at 1440, 1379 and 1224 cm^{-1} for **3.1_{Zr}** and at 1447, 1365, 1273 and 1216 cm^{-1} for **3.1_{Hf}**). High resolution MS gave a signal at $m/z = 345.9843$ and 436.0240 (the appropriate signal for the monomer unit $[\text{MPn}^*\text{Cl}_2]^+$, M = Zr or Hf). Due to the varying levels of THF/Et₂O remaining bound elemental analysis would give different results for different samples, however they would support the calculated solvent values calculated from the relevant integral ratios in the ¹H NMR.

3.2.3 Metal exchange in **3.1**

It is possible to exchange the Li atom integrated in **3.1** for a different metals. These species were serendipitously discovered and as a consequence were only partially characterised.

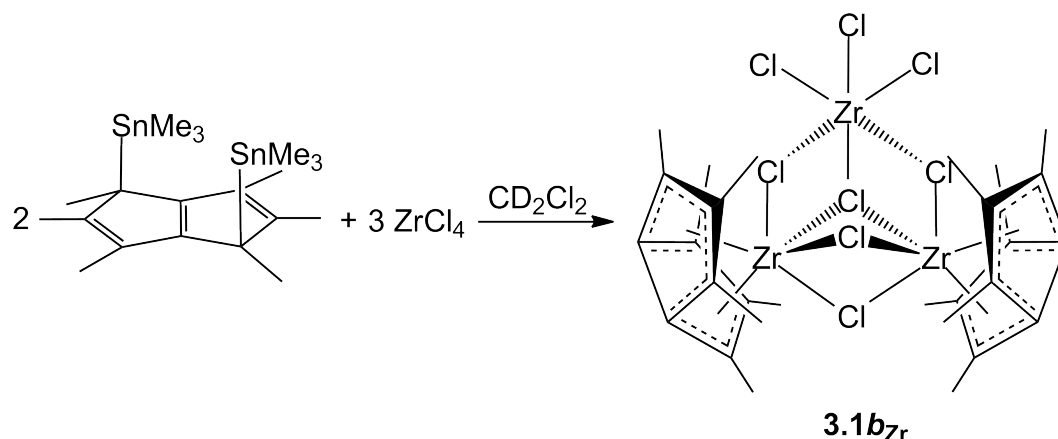
An NMR scale reaction of **3.1_{Zr}** with Me₂Mg showed that it is possible to exchange the alkali metal for magnesium. ¹H NMR spectroscopy still revealed a 6:6:6 splitting but at marginally higher upfield chemical shift and the THF and Et₂O could be removed under vacuum. Upon slow evaporation of the solvent in an inert atmosphere yellow

crystals suitable for single crystal X-ray diffraction were formed. This showed the structure to be $[\text{ZrPn}^*(\mu\text{-Cl})]_4[(\mu_3\text{-Cl})_2(\mu\text{-Cl})_2\text{Mg}]$ (**3.1a_{Zr}**, scheme 3.3).



Scheme 3.3: The synthesis of **3.1a_{Zr}**.

In an initial attempt to synthesise **3.1_{Zr}** it was found that combination of $\text{Pn}^*(\text{SnMe}_3)_2$ with ZrCl_4 in CD_2Cl_2 gave a product which was demonstrated by single crystal X-ray diffraction to be $[\text{ZrPn}^*(\mu\text{-Cl})]_2[(\mu_3\text{-Cl})(\mu\text{-Cl})_2\text{ZrCl}_3]$ (**3.1b_{Zr}**, scheme 3.4). This similarly showed a 6:6:6 splitting in the ^1H NMR at very similar chemical shifts to **3.1a_{Zr}** and **3.1_{Zr}**.³⁰



Scheme 3.4: The synthesis of **3.1b_{Zr}**.

3.1a_{Zr} crystallises in the $P \bar{1}$ space group and **3.1b_{Zr}** crystallised in the $P 2_1/n$ space group both with a single molecule in the asymmetric unit of the unit cell. Their molecular structures are shown in figure 3.4. The central Mg in **3.1a_{Zr}** and the Zr(3) in

3.1b_{Zr} are both in an approximately octahedral environment and the Zr atoms attached to the Pn* rings adopt the same octahedral environment seen in **3.1_{Zr}** [figure 3.2(B)]. The incorporated metal atoms in both are offset from the plane of Zr(1)-Cl(4)-Cl(5)-Zr(2), presumably in order to adopt the preferred octahedral geometry of both.

In order for the incorporated metal in **3.1a_{Zr}** and **3.1b_{Zr}** to adopt the octahedral environment a chlorine atom is forced to adopt a triply bridging bonding configuration [Cl(3) and Cl(8) in **3.1a_{Zr}** and Cl(3) in **3.1b_{Zr}**]. Such a binding motif incorporating two Zr centres is not common with only five reported in the CSD of which none are bridging to magnesium. Generally the average Zr-(μ_3 -Cl) distances (2.719 Å and 2.754 Å for **3.1a_{Zr}** and **3.1b_{Zr}** respectively) are somewhat shorter than the structures in the CSD (distances range from 2.768(2) to 2.886(1) Å).^{21;22;31;32} Other than this (μ_3 -Cl) motif, the structural parameters are generally similar to those seen in **3.1_{Zr}**, with a general lengthening of the Zr-(μ_M -Cl) depending both on the incorporated metal's electron deficiency and its size (see table 3.4), with any other slight differences attributed to the different crystal packing forces.

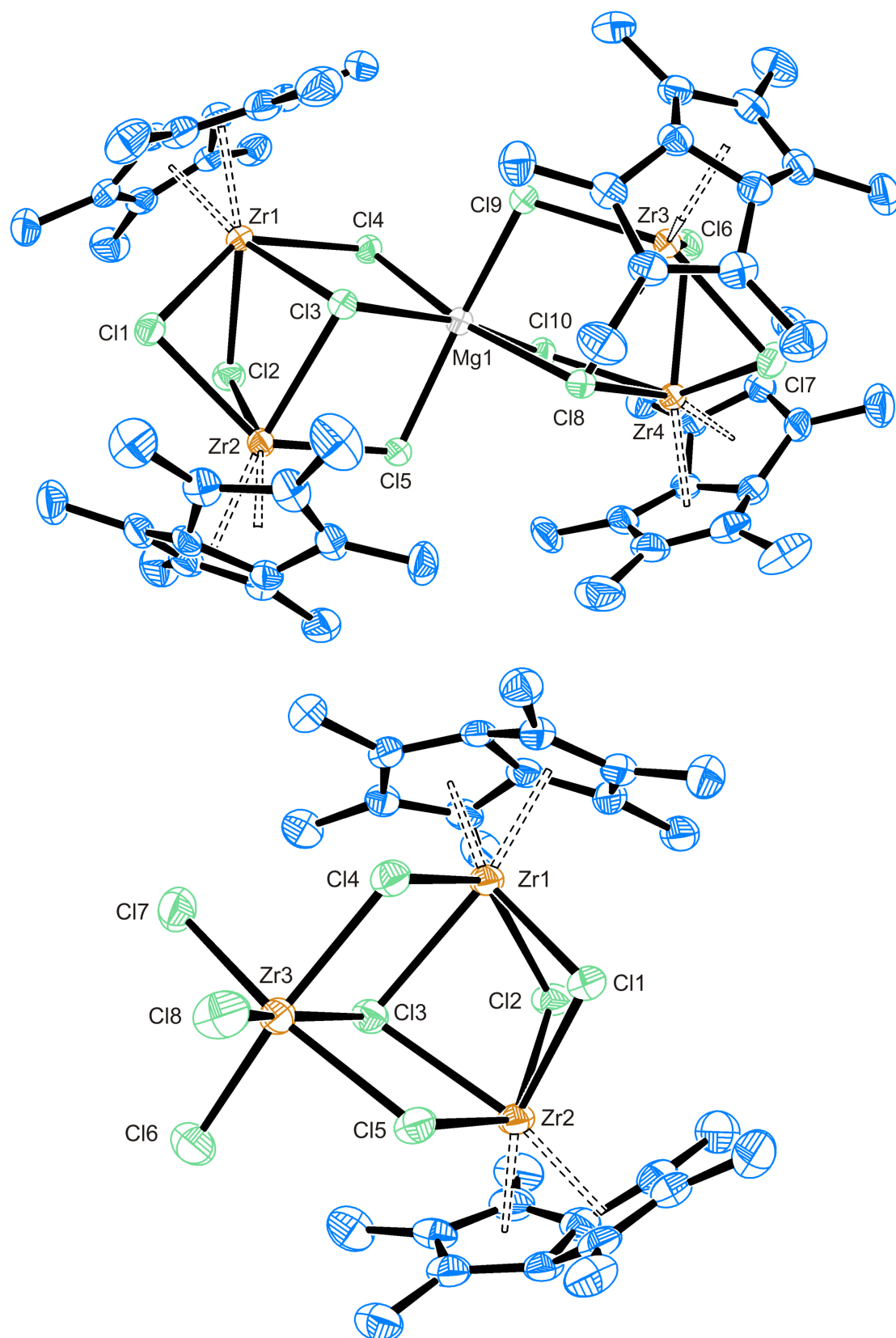


Figure 3.4: The solid state molecular structure of **3.1a_{Zr}** (top) and **3.1b_{Zr}** (bottom). Thermal ellipsoids at 50 % probability. H-atoms and Pn* labels omitted for clarity.

Table 3.4: Selected structural parameters for **3.1a_{Zr}** and **3.1b_{Zr}**

	3.1_{Zr}	3.1a_{Zr}	3.1b_{Zr}
Av. Zr-Pn* _{cent.}	2.109(5)	2.102(3)	2.085(2)
Av. Zr-(μ-Cl _{Zr})	2.649(1)	2.635(2)	2.627(2)
Av. Zr-(μ-Cl _M)	2.581(1)	2.616(2)	2.671(2)
Av. Zr-(μ ₃ -Cl)	n/a	2.720(2)	2.755(2)
Fold angles	30.0(4), 30.6(3)	28.7(6), 28.9(6) 29.7(6), 30.1(5)	29.0(3), 29.4(4)

Variable temperature ¹H NMR experiments were undertaken for **3.1a_{Zr}** and coalescence of the NWT-Me resonances was found to occur at 368 K. This is considerably higher than the temperature required for **3.1_{Zr}** and can be attributed to the increased steric bulk leading to a higher energy required for the rings to rotate.

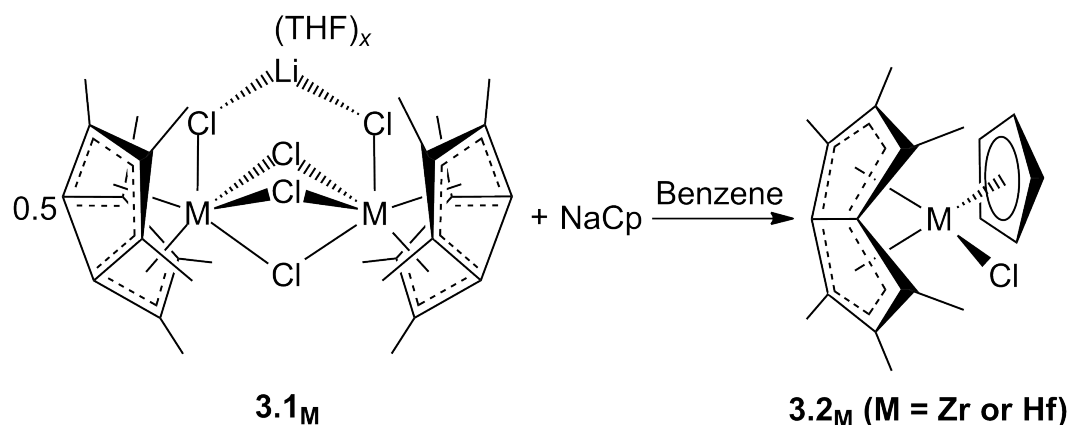
3.3 Mixed sandwich compounds: MPn*CpCl (**3.2**), MPn*Cp₂ (**3.3**) and MPn*Cp*Cl (**3.4**)

Having developed a reliable and high yielding synthesis of a suitable starting material further salt metathesis reactions were investigated to expand further group 4 Pn* chemistry. With the ubiquity of Cp and Cp* ligands in organometallic chemistry, and the previous successes discussed in chapter two, it seemed appropriate to initially target mixed sandwich species.

3.3.1 The improved synthesis of ZrPn*CpCl and the synthesis of HfPn*CpCl (**3.2**)

ZrPn*CpCl (**3.2_{Zr}**), had already been synthesised previously by this group, albeit in poor yield (12 %).¹⁹ Having synthesised an alternative starting material, it was envisaged that the simple salt metathesis reaction with a suitable transfer reagent should furnish the target material and drastically improve the yield, whilst also facilitating the synthesis of the as yet unknown Hf derivative. Indeed, reaction of **3.1** with one equivalent of NaCp in ethereal solvent yielded MPn*CpCl (**3.2**, scheme 3.5), which was crystallised in drastically improved yield by slow cooling of a hexane solution (83.4 %

for **3.2_{Zr}**, 83.3 % for **3.2_{Hf}**). This new synthetic methodology circumvented difficulties associated with previous work up methods (*i.e.* separation from LiCp by product).



Scheme 3.5: The synthesis of **3.2_M** (M = Zr or Hf).

3.3.2 Characterisation of **3.2**

3.3.2.1 Single crystal X-ray diffraction characterisation of **3.2**

Both **3.2_{Zr}** and **3.2_{Hf}** crystallise in the $P 2_1/c$ space group. The molecular structure of **3.2_{Hf}** is shown in figure 3.5. The Hf centre is approximately tetrahedral in geometry and though C_s symmetric in the solution phase it does not have a crystallographic mirror plane in the solid state. The bond lengths in **3.2_{Hf}** are extremely similar to **3.2_{Zr}**, with the trend being that **3.2_{Hf}** generally shows a slight shortening in M-X distances [e.g. M-Pn*_{cent.} is 2.090 Å for **3.2_{Hf}** whereas it is 2.110 Å for **3.2_{Zr}**, or M-Cl distance is 2.517(2) Å for **3.2_{Hf}** and is 2.548(1) Å for **3.2_{Zr}**] - this is the same trend seen in **3.1** (and in the rest of the compounds in this chapter).

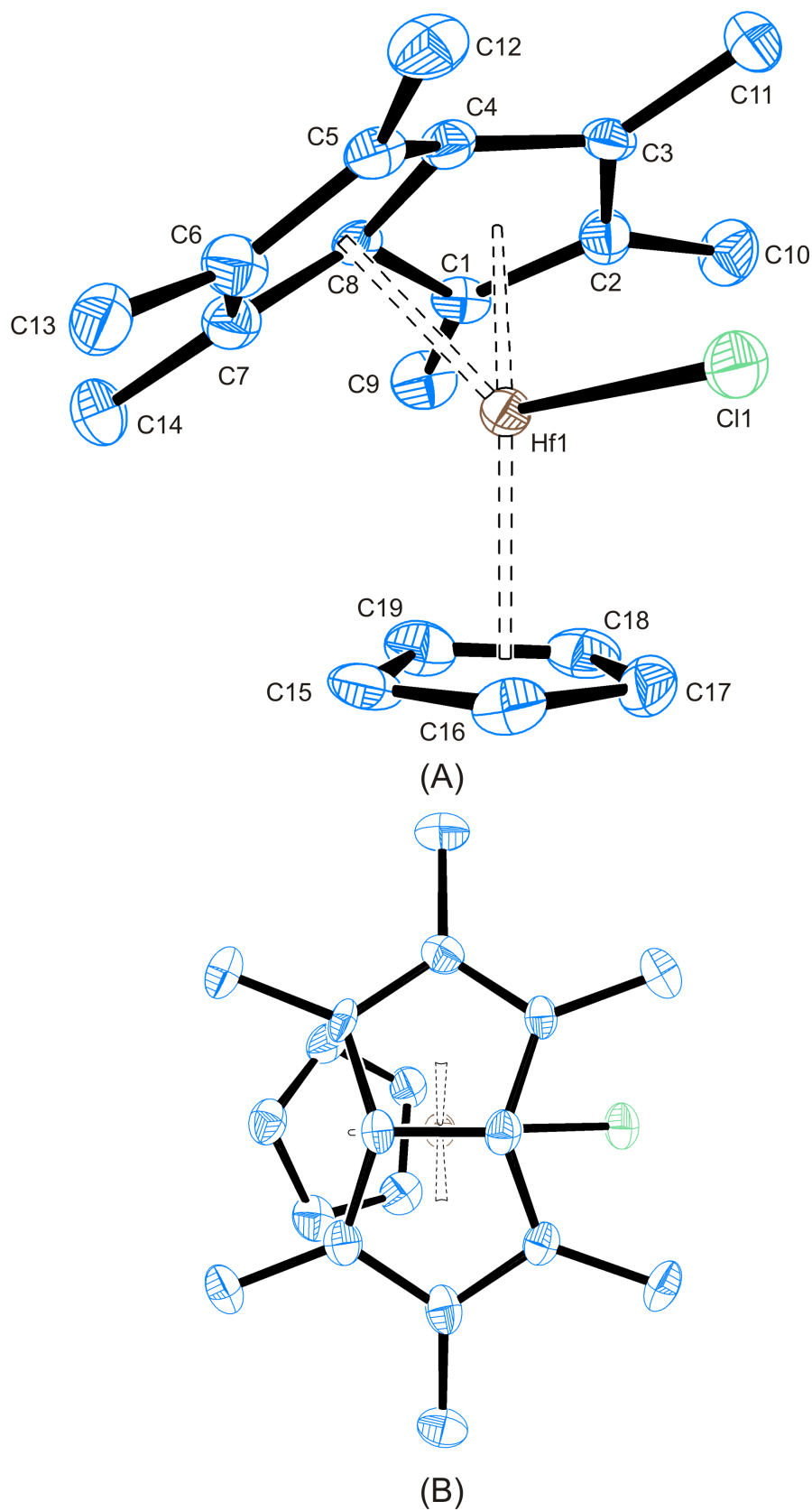


Figure 3.5: A side-on and top-down view of the solid state molecular structure of **3.2_{Hf}**. H-atoms omitted for clarity; thermal ellipsoids at 50 % probability. **3.2_{Zr}** is isostructural.

Table 3.5: Selected structural parameters for **3.2_{Hf}**

Bond lengths Å			
M-C(1)	2.417(5)	M-C(15)	2.509(6)
M-C(2)	2.605(6)	M-C(16)	2.494(6)
M-C(3)	2.557(6)	M-C(17)	2.512(6)
M-C(4)	2.267(6)	M-C(18)	2.511(6)
M-C(5)	2.534(6)	M-C(19)	2.470(6)
M-C(6)	2.621(7)	M-Cl(1)	2.517(2)
M-C(7)	2.430(6)	M-Pn* _{cent.}	2.089(3)
M-C(8)	2.229(5)	M-Pn* _{cent.}	2.090(3)
Av. C _{ring} -Me	1.503	M-Cp _{cent.}	2.190(3)
Bond angles °			
Fold angle		30.9(6)	

The fold angle in **3.2_{Hf}** is the same as those found in **3.1_{Hf}**, and the M-Pn*_{cent.} distances are also extremely similar. This is unsurprising bearing in mind that both complexes are 18 e⁻ and shows the relative steric demand of three bridging chlorides is approximately the same as a Cp ring within the coordination sphere. The M-Cp_{cent.} distance is comparable to other bis(cyclopentadiene)dichloride Hf compounds in the literature: HfCpCp*Cl₂, HfCp*₂Cl₂ · CaCp*₂ and HfCp₂Cl₂ [average 2.20 Å compared to 2.190(3) Å for **3.2_{Hf}**]^{8;33;34}. The average Hf-C distance for the Cp ring is the same as that seen for HfCp₄ (2.50 Å).³⁵ The Hf-Cl distance is however considerably longer than these compounds and more comparable to the known Zr Pn compounds: ZrPn*₂CpCl, ZrPnCpCl and ZrPnCl₂·2THF.^{11;19} This lengthening of the Hf-Cl bond is presumably a cooperative effect of both the higher electron count of the pentalene complexes compared to compounds containing the ‘HfCp₂’ moiety (18 e⁻ *vs.* 16 e⁻) causing the metal centre to be more electron rich and therefore not bind as strongly to the chlorine atom and also due to the higher steric demands of the Pn* ligand.

3.3.2.2 NMR characterisation of **3.2_{Hf}**

The solution phase ^1H NMR spectrum of **3.2_{Hf}** consists of four resonances of 5:6:6:6 intensity ($\delta = 5.56, 2.10, 1.94$ and 1.72 ppm respectively), indicative of the plane of symmetry along the bridgehead bond and metal centre making it C_s symmetric. The ^{13}C NMR spectrum shows the expected eight resonances: three Pn^* Me environments, four quaternary Pn^* environments and a single Cp environment; HMBC, HMQC and nOesy experiments allowed for the definitive assignment of all the resonances.

Variable temperature studies were undertaken in order to investigate whether coalescence of the two NWT-Me environments could be achieved (C11/C12 and C9/C14), and thus determine the energetics of such ring whizzing. However, although a slight broadening of the Pn^* NWT-Me resonances was observed full coalescence of the resonance was not reached at temperatures up to 373 K. A variable temperature study of **3.2_{Zr}** was also undertaken and similarly showed little change over all temperatures studied.

3.3.2.3 Other characterisation of **3.2_{Hf}**

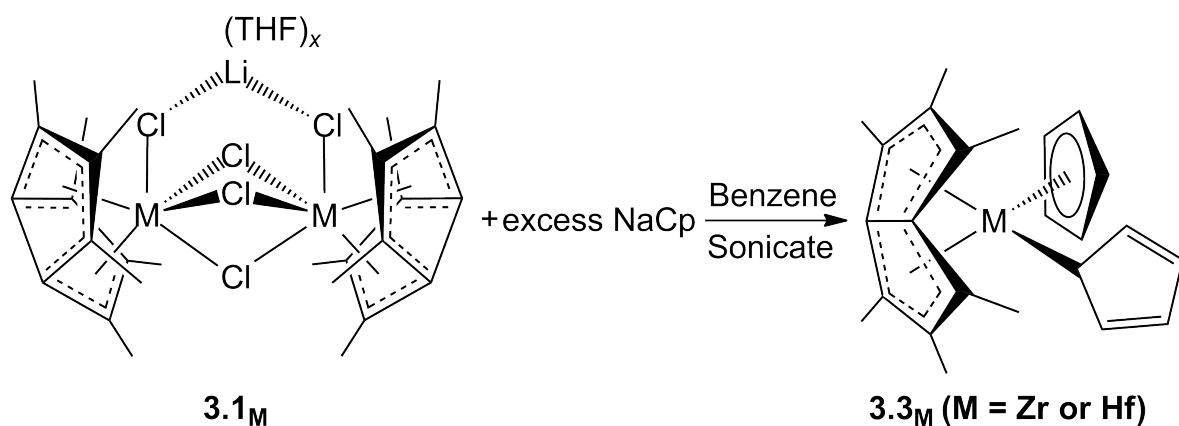
3.2_{Hf} has also been characterised by mass spectrometry, IR spectroscopy and elemental analysis. Within the high resolution mass spectrum a signal is seen at the expected molecular ion peak ($m/z = 466.0956$) and the expected fragmentation pattern of subsequent Cl and Cp loss is also observed. IR spectroscopy gave C–H stretching bands (at 2951, 2901 and 2872 cm^{-1}) and C–H bending bands (at 1621 and 1722 cm^{-1}). Some weak bands were seen at higher wavenumbers (over 3000 cm^{-1}) but it is assumed these were due to a small presence of the bis(cyclopentadienyl) species (**3.3**) (*vide infra*)

3.3.3 Synthesis of MPn^*Cp_2 (**3.3**)

Having synthesised the mono-cyclopentadienyl Pn^* derivatives of both Zr and Hf it seemed appropriate to attempt the synthesis of a bis-cyclopentadienyl Pn^* complex. Such a complex would be expected to be extremely sterically crowded and electronically saturated and this, in turn, may lead to interesting binding modes.

Initial efforts to synthesise MPn^*Cp_2 (**3.3**) focused on the direct combination of

3.1 with an excess of NaCp in a variety of solvents but this was found to lead only to the formation of **3.2**. Due to the extreme steric crowding of the potential product, forcing conditions were attempted. Heating the reaction mixture again failed to initiate a reaction, but success was achieved by prolonged sonication of a concentrated solution of **3.1** in benzene with a large excess of NaCp. Subsequent work-up and crystallisation from hexane identified the species as $\text{MPn}^*(\eta^1\text{-Cp})(\eta^5\text{-Cp})$ (**3.3**, scheme 3.6). The complete formation of **3.3_{Zr}** was found to occur (as judged by ^1H NMR spectroscopy) which was in contrast to **3.3_{Hf}** which would form in an approximate 1:6 ratio of **3.2_{Hf}** and **3.3_{Hf}**. Similar solubilities led to co-crystallisation of these species.



Scheme 3.6: The synthesis of **3.3_M** (M = Zr or Hf).

3.3.4 Characterisation of **3.3**

3.3.4.1 Single crystal X-Ray diffraction characterisation of **3.3**

Both analogues of **3.3** crystallise in the $P\bar{1}$ space group with a single asymmetric molecule in the unit cell. One Cp ring is bound in an η^5 -fashion and one in an η^1 -mode, affording 18 e^- complexes. **3.3_{Zr}** crystallises in 86 % yield and **3.3_{Hf}** crystallises in 64 % yield (though **3.3_{Hf}** co-crystallises with **3.2_{Hf}**). A diagram of the molecular structure of **3.3_{Zr}** is presented in figure 3.6.

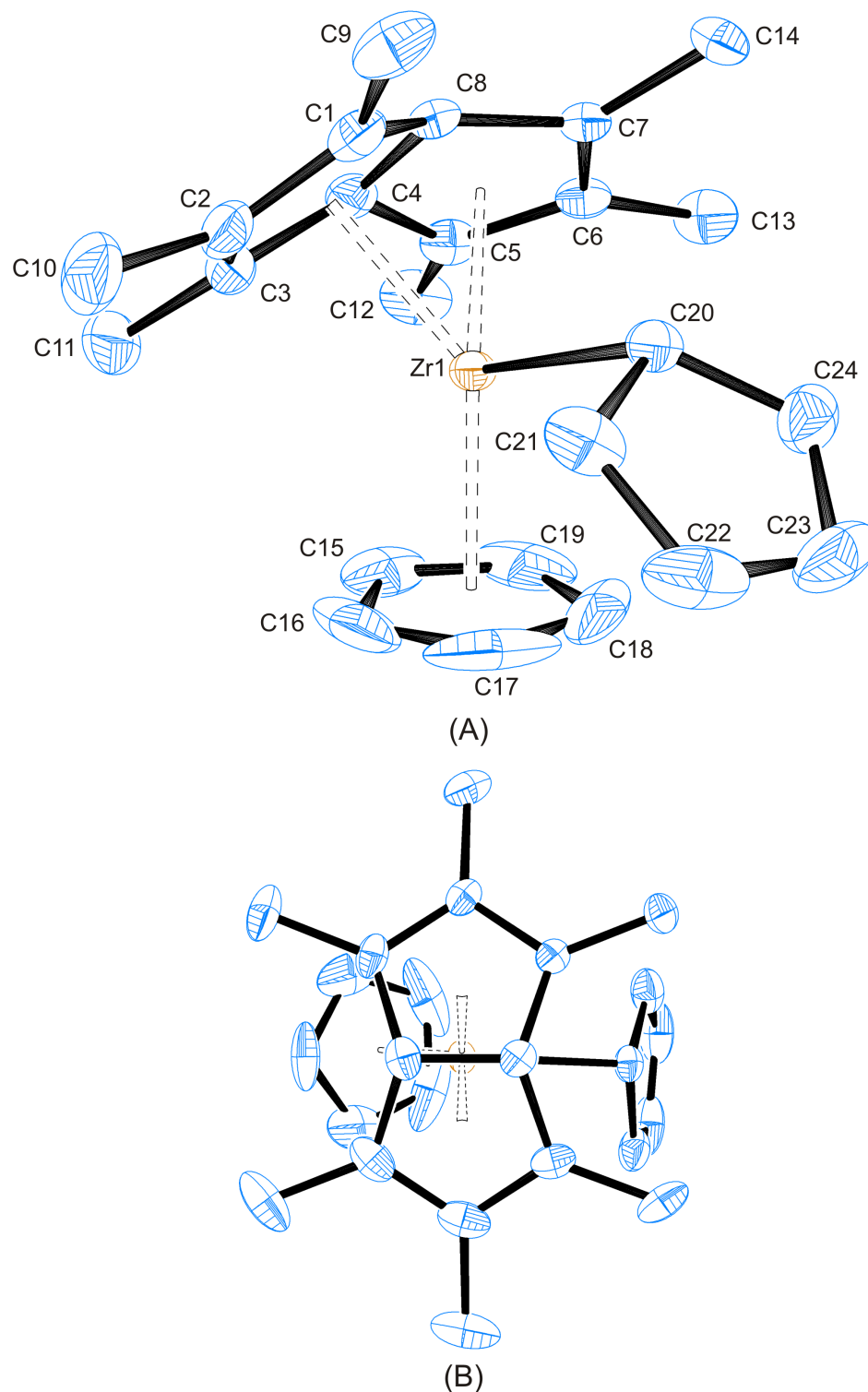


Figure 3.6: The molecular structure of **3.3_{Zr}**; (A) a side on view and (B) a top down view. Thermal ellipsoids at 50 % probability, H-atoms omitted for clarity. **3.3_{Hf}** is isostructural.

Similar to **3.2** there is not a crystallographic mirror plane in line with the bridgehead bond in the solid state. A list of structural parameters for **3.3_{Zr}** and **3.3_{Hf}** are presented in table 3.6. As expected **3.3_{Zr}** and **3.3_{Hf}** have extremely similar bond distances and

a slight increase in the fold angle seen between **3.3_{Hf}** and **3.3_{Zr}** is presumably due to the more diffuse 5*d* orbitals allowing better overlap (as seen in **3.1** and **3.2**) and compensating for the loss in aromaticity.

Table 3.6: Selected structural parameters for **3.3**. ESDs in parentheses.

Bond lengths Å					
	3.3_{Zr}	3.3_{Hf}		3.3_{Zr}	3.3_{Hf}
M-C(1)	2.577(2)	2.561(4)	M-C(15)	2.488(2)	2.465(5)
M-C(2)	2.639(2)	2.612(4)	M-C(16)	2.513(2)	2.487(5)
M-C(3)	2.440(2)	2.419(4)	M-C(17)	2.514(2)	2.484(5)
M-C(4)	2.258(2)	2.241(4)	M-C(18)	2.505(2)	2.477(5)
M-C(5)	2.462(2)	2.441(4)	M-C(19)	2.504(2)	2.478(5)
M-C(6)	2.608(2)	2.584(4)	M-C(20)	2.476(2)	2.441(4)
M-C(7)	2.536(2)	2.508(4)	C(20)-C(21)	1.443(3)	1.450(6)
M-C(8)	2.295(2)	2.279(4)	C(21)-C(22)	1.378(3)	1.357(8)
M-Pn* _{cent.}	2.119(1)	2.097(2)	C(22)-C(23)	1.413(4)	1.428(10)
M-Pn* _{cent.}	2.107(1)	2.081(2)	C(23)-C(24)	1.377(3)	1.360(8)
M-Cp _{cent.}	2.215(2)	2.186(3)	C(24)-C(20)	1.440(3)	1.439(6)
			Av. C _{ring} -Me	1.504	1.504
Bond angles °					
Fold Angle	30.9(2)	31.8(4)	M-C(20)-Cp _{cent.}	122.5(2)	124.5(2)

The crystal structure clearly shows the molecule contains two distinct Cp binding modes (η^1 and η^5), and gives a count of 18 e^- on the metal centre. Within the literature there are only two structurally characterised examples Zr(η^1 -Cp) and only one example of Hf(η^1 -Cp). The two Zr examples [Zr(η^1 -Cp)(η^5 -Cp)₃ and Zr(η^1 -Cp^R)(η^5 -Cp^R)₂Cl (R = SiMe₃)]^{36;37} have Zr-(η^1 -Cp) distances of 2.442 and 2.396 Å respectively [*vs.* 2.476 (2) Å for **3.3_{Zr}**], with the latter, considerably shorter distance, being due to the 16 e^- metal centre. However even the former 18 e^- complex ZrCp₄ has a slightly shorter Zr-(η^1 -Cp) distance than that found in **3.3_{Zr}** due to the larger steric bulk of the Pn* pushing the η^1 -Cp ring out. However intriguingly the η^5 -Cp distance in

3.3_{Zr} [2.215(2) Å] is shorter than the other 18 e⁻ example above (2.294, 2.349 and 2.348 Å) and more comparable to Zr(η^1 -Cp^R)(η^5 -Cp^R)₂Cl (R = SiMe₃) (2.203 and 2.226 Å), implying that factors other than steric ones also play a role.³⁷ Therefore DFT calculations were undertaken to investigate the observed bond lengths. These showed that the HOMO is primarily a bonding orbital between the metal centre, the Pn* π -orbitals and the η^5 -Cp ring and an anti-bonding interaction between the M-(η^1 -Cp) ring (figure 3.7). The population of this orbital explains the relative differences in these structural parameters.

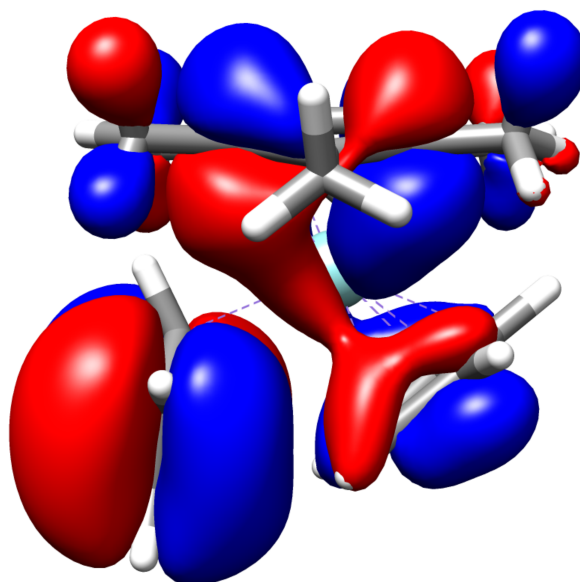


Figure 3.7: The HOMO of **3.3_{Zr}**. Zr atom is rendered in sky blue, C atoms are rendered in grey, H atoms are rendered in white. Molecular orbital occupancy: Zr d_{xy} 3.1 %; C(1) p_z 4.5 %; C(3) p_z 3.9 %; C(5) p_z 4.4 %; C(7) p_z 4.4 %; C(21) p_y 21.7 %; C(24) p_y 21.5 %. Isosurface limits: ± 0.014 .

The only example of a structurally characterised η^1 -Cp Hf complex is Hf(η^5 -Cp)₂(η^1 -Cp)₂.³⁸ The structural parameters of this 16 e⁻ complex [average Hf-(η^1 -Cp) = 2.387 Å and average Hf-(η^5 -Cp_{cent.}) = 2.199 Å] show a parallel trend as the Zr example above with **3.3_{Hf}**'s Hf-(η^1 -Cp) distance being longer [2.441(4) Å] but the Hf-(η^5 -Cp_{cent.}) distance being slightly shorter [2.186(3) Å]. It is thought the same argument regarding the nature of the HOMO stands for **3.3_{Hf}** but due to the complications arising from relativistic considerations DFT calculations were not undertaken.

3.3.4.2 NMR Characterisation of **3.3**

The room temperature ^1H NMR spectrum of **3.3_{Hf}** at room temperature consists of five singlets of 5:5:6:6:6 intensity at 5.88, 4.91, 2.16, 1.95 and 1.70 ppm. The two resonances of integral five are broad and are attributed to the two cyclopentadienyl units. The presence of two resonances show that at room temperature the η^5 ring and η^1 ring do not inter-convert their binding modes faster than the NMR timescale; however the η^1 resonance integral indicates this ring is undergoing a fluxional process with the M-C σ -bond moving from carbon to carbon. In the ^{13}C NMR spectrum there are nine sharp signals as expected. The room temperature ^1H NMR of **3.3_{Zr}** similarly shows five singlets of 5:5:6:6:6 intensity ratio at comparable chemical shifts however they are considerably broader at room temperature.

Variable temperature ^1H NMR studies were therefore undertaken to investigate the kinetics and mechanism of this fluxionality (figure 3.8). It was found that on warming both samples the NWT-Me resonances coalesced into a single broad peak at 314 K for **3.3_{Zr}** and at 356 K for **3.3_{Hf}** and the two Cp resonances broadening into the baseline of the spectrum. Upon further warming of **3.3_{Zr}** a new broad peak of integral 10 emerged at 5.39 ppm which was attributed to all the Cp protons (indicating all the Cp environments had become equivalent on the NMR timescale) and a resonance of integral 12 began to emerge at approximately 2 ppm (showing the NWT-Me groups were now equivalent on the NMR timescale). Due to the broadening occurring at a higher temperature for **3.3_{Hf}** it was not possible to reach the temperature where a similar scenario was apparent. On cooling the sample initially all four of the NWT and Cp resonances sharpened, however on further cooling the most downfield resonances (attributed to the η^1 -bound Cp ring) began to broaden and eventually flattened fully into the baseline. It is assumed that this is due to the η^1 -Cp ring-whizzing becoming slower than the NMR timescale. In the case of **3.3_{Zr}** it was not possible to fully freeze out the η^1 -Cp ring, however for **3.3_{Hf}**, two new peaks began to appear (at $\delta = 3.66$ and 6.35 ppm, integral ratio 1:2) and, by comparison with the previously synthesised Pn^*TiCp_2 , it is hypothesised that a third resonance of integral ratio two was under the solvent peak at approximately 7 ppm.¹⁸ Disappointingly due to mechanical limitations

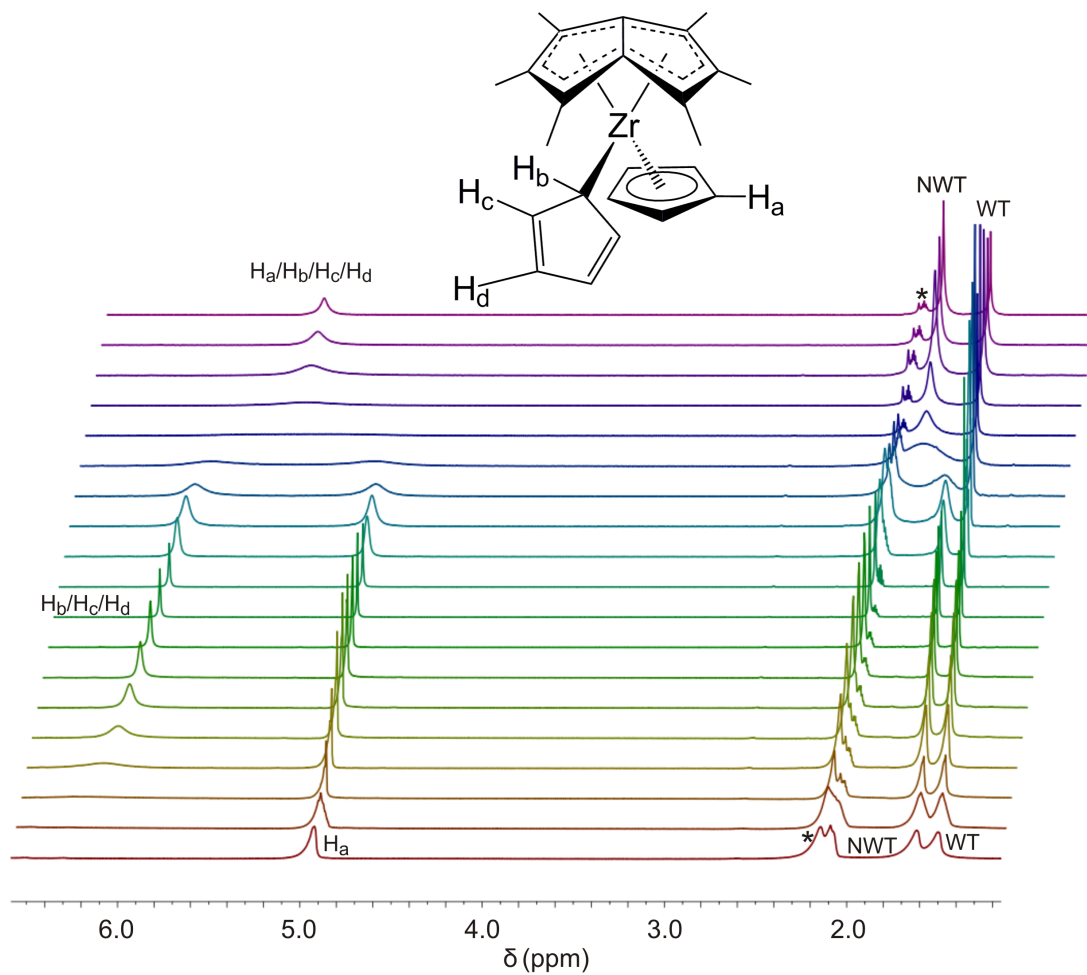


Figure 3.8: Variable temperature ^1H NMR studies of **3.3_{Zr}**. Temperature increases from 173 K to 353 K in 10 K increments up the page. NWT and WT refer to the respective methyl resonances, * indicates resonance attributed to residual solvent.

it was not possible to reach the slow exchange limit and as a consequence kinetic parameters for this process could not be determined.

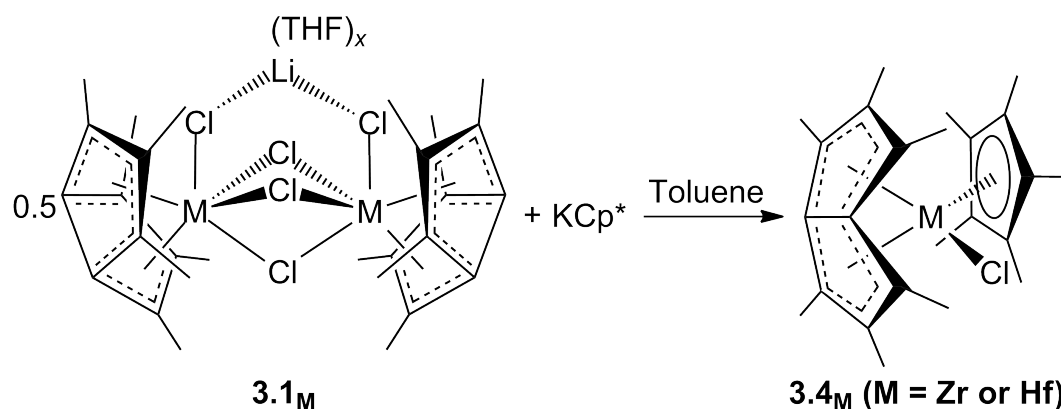
3.3.4.3 Other characterisation of **3.3**

The IR spectra of both congeners of **3.3** contain sharp peaks above 3000 cm^{-1} attributable to sp^2 hybridised C–H stretching. A number of broad peaks are seen around 2900 cm^{-1} which are due to C–H stretching, and then a signal at 1444 cm^{-1} or 1445 cm^{-1} (for **3.3_{Zr}** or **3.3_{Hf}** respectively) due to C=C stretching. There are also a number of signals at lower wavenumber assignable to C–H bending and the fingerprint of the molecule. Due to persistent co-crystallisation of **3.2** satisfactory elemental analyses were not obtained.

3.3.5 Synthesis of MPn^*Cp^*Cl (**3.4**)

Having achieved the synthesis and characterisation of the non-permethylated Cp derivatives **3.2** and **3.3** it seemed appropriate to attempt the synthesis of MPn^*Cp^*Cl (**3.4**). Attempts to synthesise $TiPn^*Cp^*Cl$ had proved unsuccessful and resulted in the presumed reduction of the $TiPn^*$ moiety with no products elucidated. However it was postulated that with: a) the higher stability of the lower group 4 metals with respect to oxidation and b) their greater atomic size it might be possible to form **3.4** with Zr and Hf.

Combination of **3.1** with two equivalents of $LiCp^*$ in toluene resulted in a lightening of the colour of the two solutions (scheme 3.7). Subsequent work-up and crystallisation from a saturated toluene solution cooled to $-38\text{ }^{\circ}C$ led to the formation of yellow or orange plates (for **3.4_{Zr}** and **3.4_{Hf}** respectively) in moderate yield.



Scheme 3.7: The synthesis of **3.4_M** ($M = \text{Zr or Hf}$).

3.3.6 Characterisation of **3.4**

3.3.6.1 Single crystal X-ray characterisation of **3.4**

Both **3.4_{Zr}** and **3.4_{Hf}** crystallise in the $P\ 2_1/n$ space group with a single molecule in the asymmetric unit of the unit cell, a model of which is shown in figure 3.9. Indeed, as seen before **3.4_{Zr}** and **3.4_{Hf}** have extremely similar unit cell dimensions and structural parameters. Like **3.2** and **3.3** there is not a crystallographic mirror plane down the C(4)-C(8)-M(1) plane within the crystal. A full discussion of the structural parameters of mixed sandwich compounds, with a comparison of **3.2**, **3.3** and their Ti counterparts will be addressed after the results of other characterisation methods for **3.4** are analysed.

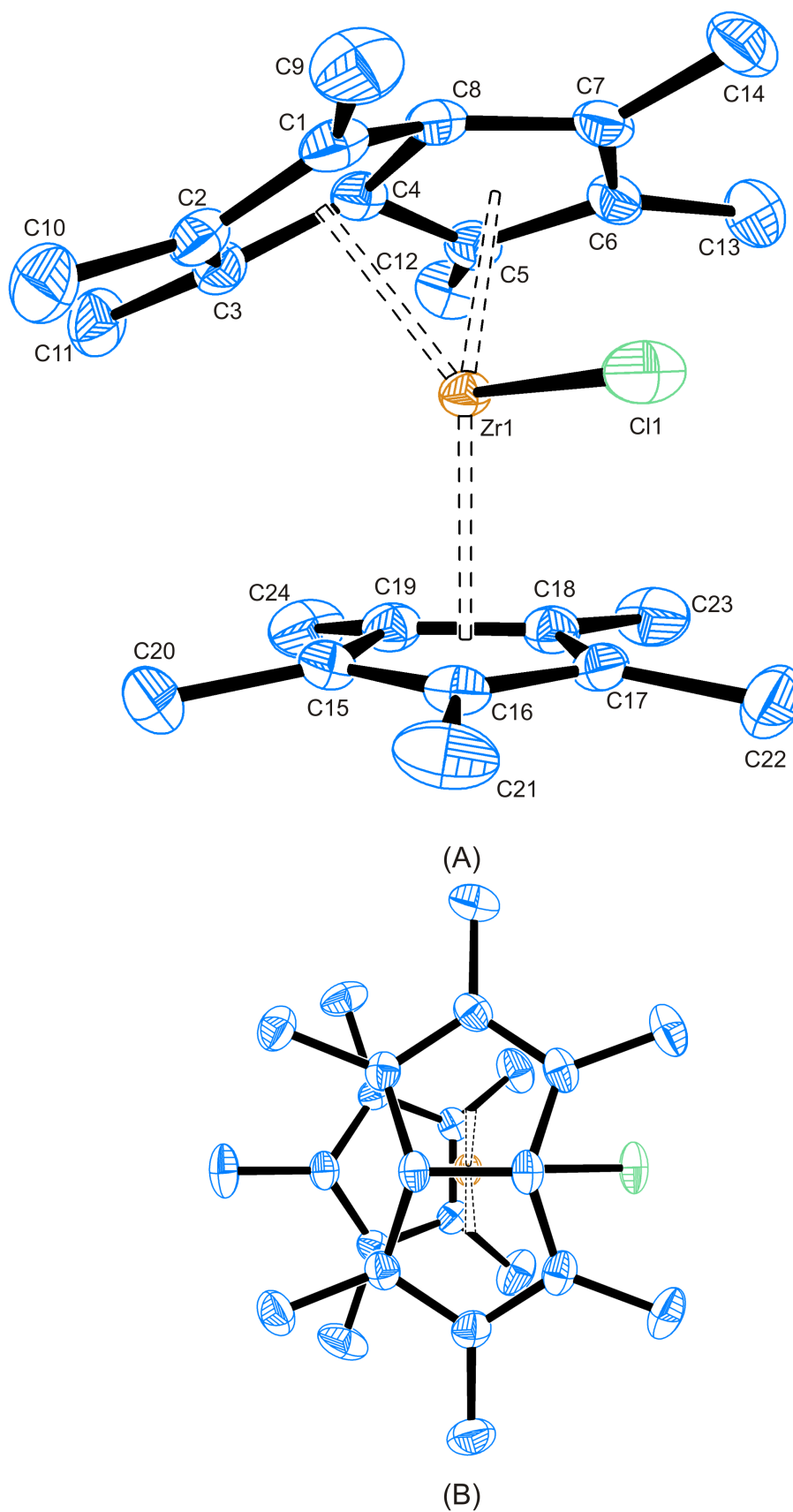


Figure 3.9: The solid state molecular structure of $\text{ZrPn}^*\text{Cp}^*\text{Cl}$ (**3.4_{Zr}**) both (A) a side on view and (B) a top down view. H-atoms omitted for clarity, thermal ellipsoids at 50 % probability. **3.4_{Hf}** is isostructural.

Table 3.7: Selected structural parameters for **3.4**. ESDs are in parentheses.

Bond lengths Å					
	3.4_{Zr}	3.4_{Hf}		3.4_{Zr}	3.4_{Hf}
M-C(1)	2.558(2)	2.569(4)	M-C(15)	2.562(2)	2.540(4)
M-C(2)	2.635(2)	2.645(3)	M-C(16)	2.562(2)	2.517(4)
M-C(3)	2.468(2)	2.456(4)	M-C(17)	2.559(2)	2.529(4)
M-C(4)	2.266(2)	2.251(4)	M-C(18)	2.550(4)	2.530(4)
M-C(5)	2.477(2)	2.447(4)	M-C(19)	2.545(2)	2.533(4)
M-C(6)	2.663(2)	2.613(4)	Av. C _{Pn*} ring-Me	1.501	1.502
M-C(7)	2.580(2)	2.535(4)	Av. C _{Cp*} ring-Me	1.502	1.504
M-C(8)	2.291(2)	2.286(4)	M-Cl(1)	2.526(1)	2.501(9)
M-Pn* _{cent.}	2.121(1)	2.101(2)	M-Cp* _{cent.}	2.253(1)	2.223(2)
M-Pn* _{cent.}	2.135(1)	2.117(2)			
Bond angles °					
Fold Angle	29.3(2)	30.3(3)			

3.3.6.2 NMR Characterisation of **3.4**

The ¹H NMR spectra of **3.4** consists of four resonances in a 6:6:15:6 intensity ratio ($\delta = 2.08, 1.95, 1.77$ and 1.67 ppm for **3.4_{Zr}** and $\delta = 2.20, 2.11, 1.80$ and 1.66 ppm for **3.4_{Hf}** respectively), demonstrating **3.4** to be C_s symmetric. The ¹³C NMR shows the expected 10 resonances, eight from the Pn* ring and two from the Cp* ring. This implies that (in a manner similar to **3.2**) there is a mirror plane along the metal atom and the bridgehead bond in solution, giving two NWT environments. When the sample is heated no change in peak shape is seen, showing the energetic barrier to rotation of the Pn* ring is higher than the NMR timescale at temperatures up to 100 °C. As expected, due to the increased steric bulk of the Cp* *vs.* Cp, the resonances of **3.4** do not begin to broaden unlike those in **3.2_{Hf}**, demonstrating **3.4** has a higher energetic barrier to ring rotation than **3.2**.

3.3.6.3 Other characterisation of **3.4**

The high resolution mass spectra of **3.4_{Zr}** and **3.4_{Hf}** gave signals at the appropriate molecular ion mass ($m/z = 446.1305$ for **3.4_{Zr}** and 536.1740 for **3.4_{Hf}**) and the expected subsequent fragmentation patterns corresponding to loss of the Cl and Cp* ligands. IR spectrometry showed expected bands due to C–H stretching and C–H bending and no bands due to C=C.

3.3.6.4 Comparison of the structures of **3.2**, **3.3** and **3.4**

The five complexes synthesised above, combined with those previously synthesised in the group (ZrPn*CpCl and TiPn*CpCl and TiPn*Cp₂) make a complete set of group 4 Pn* mixed sandwich compounds.^{18;19} By comparing and contrasting their structural parameters, the effect of permethylation of the Cp moiety and descending down group 4 will be displayed. A table of the pertinent bond lengths is presented below (table 3.8).

Table 3.8: Pertinent structural parameters of group 4 Pn* mixed sandwich compounds. ESDs are in parentheses.

	Fold Angle	M–Cl or M-(η^1 -Cp) Å	M-Pn* _{cent.} Å		M-Cp _{cent.} or M-Cp* _{cent.} Å
TiPn*CpCl ¹⁸	30.9(2)°	2.506(1)	1.997(2)	1.992(2)	2.063(2)
TiPn*Cp ₂ ¹⁸	31.6(2)°	2.439(3)	1.987(2)	2.009(2)	2.054(3)
ZrPn*CpCl ¹⁹	30.3(3)°	2.548(1)	2.109(2)	2.109(2)	2.219(2)
ZrPn*Cp ₂	30.9(2)°	2.476(2)	2.119(1)	2.107(1)	2.215(2)
ZrPn*Cp*Cl	29.3(2)°	2.526(1)	2.121(1)	2.135(1)	2.253(1)
HfPn*CpCl	30.9(6)°	2.517(2)	2.089(3)	2.090(3)	2.190(3)
HfPn*Cp ₂	31.8(4)°	2.441(4)	2.097(2)	2.081(2)	2.186(3)
HfPn*Cp*Cl	30.3(3)°	2.501(9)	2.101(2)	2.117(2)	2.186(3)

It is not possible to synthesise TiPn*Cp*Cl, with the reaction resulting in the reduction of the metal centre. This is something that has been previously seen in group 4 Pn* complexes. **3.1_{Zr/Hf}** could both be made from the Li₂Pn*(TMEDA)_x whereas to make

the suitable Ti starting material, $[\text{TiPn}^*\text{Cl}(\mu\text{-Cl})]_2$, the Pn^* synthon $[\text{Pn}^*(\text{SnMe}_3)_2]$ must be used, reflecting the relative ease of oxidation.²⁰

Looking at the table a couple of trends can be identified. Intriguingly, the Ti and Hf species have almost exactly the same fold angles. Ti^{4+} and Hf^{4+} have different ionic radii (0.68 Å for Ti and 0.78 Å for Hf) and as such one might expect Ti to have a greater fold than Hf. However, due to the more diffuse nature of the Hf atomic orbitals, it may be expected that there would be better orbital overlap to make up for the loss in aromaticity. It is down to this interplay of factors that Ti and Hf have the same fold angles. Zr represents the middle ground, being larger than Ti (ionic radius of Zr^{4+} is 0.79 Å), but having less diffuse orbitals than Hf (and therefore poorer orbital overlap) and this leads to smaller fold angles for the Zr congeners.

Comparing the mono- and bis-Cp complexes we see the structural parameters are, in general, extremely similar, with only a slight increase in fold angle for the bis-Cp derivatives of each metal (approximately 0.7°). This is not wholly unexpected with both **3.2** and **3.3** being 18 e^- complexes with the η^1 -Cp substituent pointing away from the metal centre and as such not causing too much of an increase in the steric demands of the ancillary ligands. This overcomes the fact that chloride is a more electron withdrawing ligand (which has been shown to be a factor in increasing the fold angle of a complex).¹⁷

Comparing the Cp and Cp^* complexes (**3.2** and **3.4**) generally reveals a flattening of the Pn^* ligand concomitant with a lengthening of both the $\text{M-Pn}^*_{\text{cent.}}$ and $\text{M-Cp/Cp}^*_{\text{cent.}}$ distances, and a slight shortening of the M-Cl bond. This may be due to the increased steric bulk of the Cp^* ligand forcing the bulky Pn^* ligand further out to minimise the steric interaction. This in turn results in a comparatively worse orbital overlap between the ligands and the metal centre resulting in a flattening of the Pn^* ring.

Having devised the moderate to high yielding syntheses of **3.2-3.4**, all of which have been fully characterised, they were elected as candidates for potential α -olefin polymerisation catalysts. The results from early catalytic testing of these species are reported in chapter four.

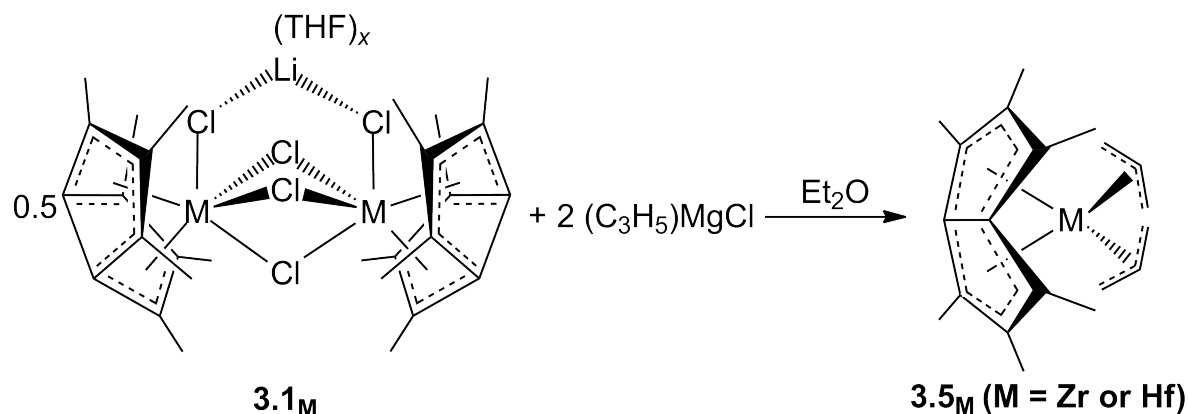
3.4 Synthesis and characterisation of $MPn^*(C_3H_5)_2$ (**3.5**)

The allyl moiety (C_3H_5) has many fascinating chemical features, from varied hapticity, to fluxional behaviour and rearrangements, to use in the polymerisation of olefins.^{39–41} Group 4 metal allyl complexes are however often thermally unstable, which has hampered their isolation and characterisation, especially in the solid state. $ZrCp_2(C_3H_5)_2$ was synthesised by the reaction of $ZrCp_2Cl_2$ with C_3H_5MgCl .⁴² It was found that the allyl ligands were fluxional at room temperature, with no decoalescence of the 1H NMR signals even when cooled to $-90\text{ }^\circ C$. IR spectroscopy indicated however that the structure contained mixed hapticity allyl ligands, and as such a formula of $ZrCp_2(\eta^3-C_3H_5)(\eta^1-C_3H_5)$ was assigned.

One of the earliest η^8 -Pn papers was a detailed NMR investigation into the solution phase structure of $ZrPn(C_3H_5)_2$ by Gabor *et al.*¹⁶ This compound was made by the combination of $ZrCpPnCl$ with two equivalents of LiC_3H_5 in good yields. The NMR investigation elucidated the solution phase structure (implying both to be bound in on η^3 fashion) but could not yield geometric details of the complex. Therefore, the Pn^* analogue was targeted, along with the Hf congener, in order to investigate the possible fluxional behaviour of the compounds (and comparing them to other allyl compounds) and owing to the Pn^* ligands' improved crystallisability (compared with Pn) potentially the geometric parameters could be elucidated. The Ti compound had been previously isolated but was found to be extremely thermally sensitive decomposing in minutes at room temperature in the solution phase and characterisation was therefore limited.¹⁸ The full synthesis and characterisation of the Zr and Hf species is reported below.

3.4.1 Synthesis of $MPn^*(\eta^3-C_3H_5)_2$ (**3.5**)

Due to the successful synthesis of the Ti compound $TiPn^*(C_3H_5)_2$ an analogous synthetic method was used: **3.1** was dissolved in Et_2O and combined with four equivalents of C_3H_5MgCl at room temperature (scheme 3.8). After subsequent work-up single crystals of $MPn^*(\eta^3-C_3H_5)_2$ (**3.5**) suitable for X-ray diffraction studies were obtained in good yield (59 % for **3.5_{Zr}**, 72.2 % for **3.5_{Hf}**) by slow cooling of a saturated Et_2O solution to $-38\text{ }^\circ C$.



Scheme 3.8: The synthesis of **3.5_M** (M = Zr or Hf).

3.4.2 Characterisation of **3.5**

3.4.2.1 Single crystal X-ray diffraction characterisation of **3.5**

Both **3.5_{Zr}** and **3.5_{Hf}** are isostructural, crystallising in the $P\bar{1}$ space group with extremely similar unit cells with both containing one molecule in the asymmetric unit (a model of **3.5_{Zr}** is shown in figure 3.10). Selected structural parameters are presented in table 3.9 and as seen with other compounds contained within this chapter the Hf analogue generally has slightly shorter bond lengths. The allyl units are bound in an η^3 -fashion, making **3.5** an 18 e⁻ complex. The allyl units tilt towards the metal centre presumably to optimise the overlap between the *d*-orbitals of the metals and the *p*-orbitals of the allyl carbons. The four centroids (two from the Pn*, one from each of the allyl moieties) arrange themselves as a distorted tetrahedron around the metal centre.

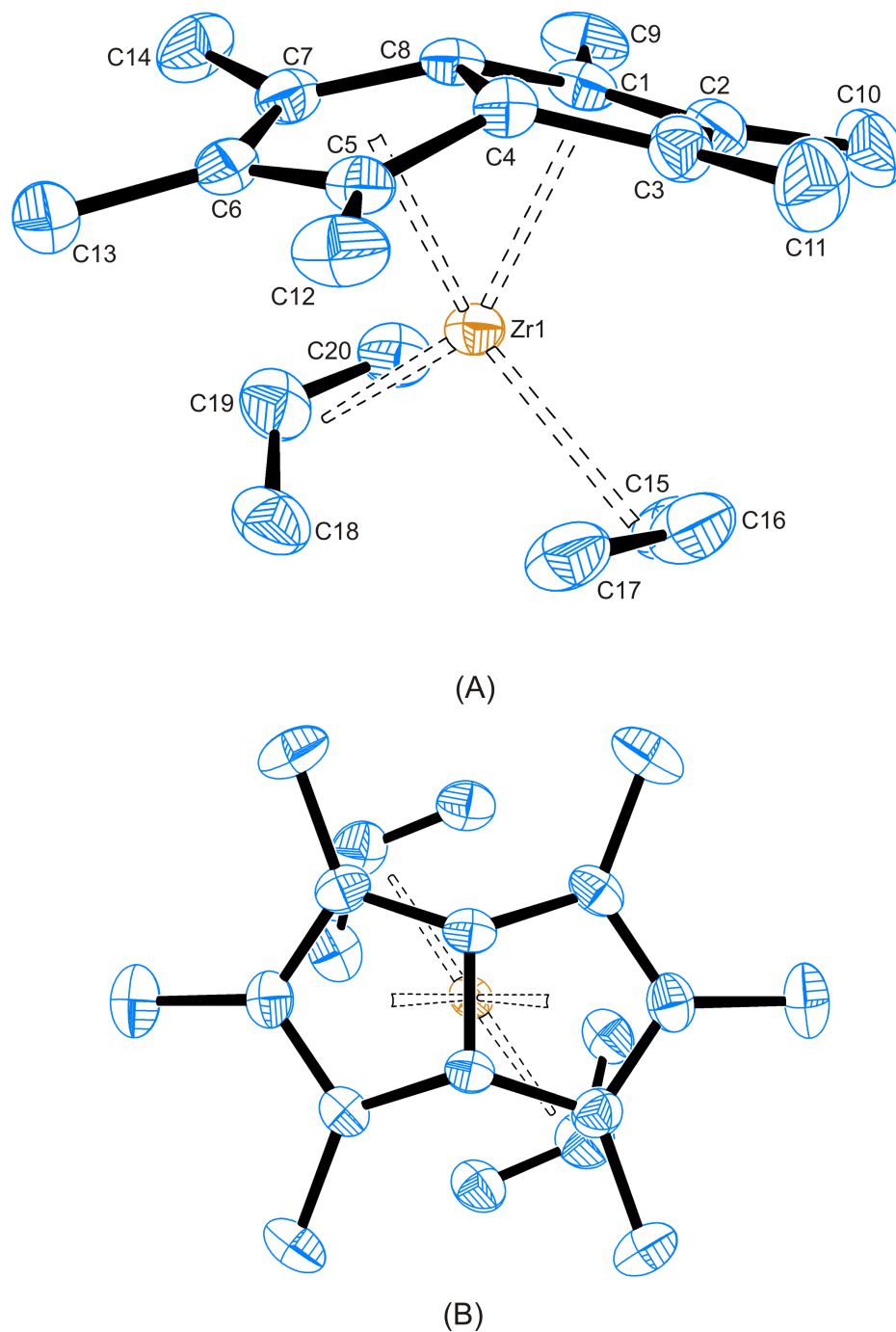


Figure 3.10: The solid state molecular structure of **3.5_{Zr}**; both (A) side view and (B) top down view. Thermal ellipsoids at 50 % probability and H-atoms are omitted for clarity. **3.5_{Hf}** is isostructural.

Table 3.9: Selected structural parameters for **3.5**. ESDs are in parentheses.

Bond lengths Å					
	3.5_{Zr}	3.5_{Hf}		3.5_{Zr}	3.5_{Hf}
M-C(1)	2.473(3)	2.545(6)	M-C(15)	2.516(4)	2.494(8)
M-C(2)	2.666(4)	2.651(6)	M-C(16)	2.514(4)	2.474(7)
M-C(3)	2.553(3)	2.446(5)	M-C(17)	2.503(4)	2.472(7)
M-C(4)	2.269(3)	2.256(5)	M-C(18)	2.509(4)	2.464(6)
M-C(5)	2.480(3)	2.542(5)	M-C(19)	2.507(4)	2.456(7)
M-C(6)	2.658(3)	2.640(6)	M-C(20)	2.477(3)	2.479(7)
M-C(7)	2.536(3)	2.444(5)	Av. C _{ring} -Me	1.503	1.502
M-C(8)	2.272(3)	2.246(6)			
M-Pn* _{cent.}	2.123(2)	2.104(3)	M-Pn* _{cent.}	2.128(2)	2.108(3)
M-(C ₃ H ₅) _{cent.}	2.282(3)	2.245(3)	M-(C ₃ H ₅) _{cent.}	2.270(3)	2.230(3)
Bond angles °					
Fold Angle	28.5(3)	27.1(4)			

Due to group 4 allyl compounds often being thermally unstable fully characterised examples in the solid state are somewhat rare, with only 12 examples of (unsubstituted) Zr allyls in the CSD and only four Hf examples.⁴³⁻⁵⁴ The majority of Zr examples contain a singly bound allyl unit, with only one example of a bis-allyl compound: ZrCp*(NP^tBu₃)(C₃H₅)₂.⁵³ This example differs from **3.5_{Zr}** however since only one of the allyl units is bound η^3 , with the other bound η^1 (however it should be noted these rapidly interconvert on the NMR timescale over all temperatures measured). The only example of a Zr compound containing two η^3 bound allyl units is ZrCp(η^3 -C₃H₅)₂(η^1 -C₃H₅).⁴⁶ The average Zr-(C₃H₅)_{cent.} distance of **3.5_{Zr}** (2.28 Å) agrees extremely well with the average of previously synthesised compounds (2.26 Å).

Even rarer are examples of structurally characterised Hf allyl compounds of which there are only four and all contain one allyl substituent.^{50;54} As such **3.5_{Hf}** represents the first structurally characterised bis-allyl Hf compound. The Hf-C_{allyl} distances of **3.5_{Hf}** are well within the range of those reported in the CSD [which range from 2.409(6) to

2.512(10) Å with an average value of 2.456 Å compared with an average 2.473 Å for **3.5_{Hf}**].

Comparing **3.5** to the previously synthesised mixed sandwich derivatives (**3.2-3.4**) and the ‘MPn*’ synthons (**3.1**) we see a considerable flattening of the Pn* ligand whilst retaining similar M-Pn*_{cent.} distances. The explanation for this may be that though **3.5** is an isoelectronic 18 e⁻ species the orbital overlap with the Pn* ring cannot be as good, thus energetically not making up for the greater loss in aromaticity.

3.4.2.2 NMR characterisation of **3.5**

As previously mentioned Gabor *et al.* undertook a detailed NMR analysis of ZrPn(η³-C₃H₅)₂,¹⁶ and therefore a similar investigation of **3.5** was undertaken. At room temperature the ¹H NMR spectrum of **3.5_{Hf}** consists of three resonances: a well-defined quintet at 5.16 ppm (J_{H-H} = 12.9 Hz, part of an AX₄ spin system), a sharp singlet at 1.59 ppm and an extremely broad hump centred at 1.92 ppm (ν_{1/2} = 91.1 Hz). In contrast the fluxionality of **3.5_{Zr}** is frozen out at room temperature with the Pn* ligand being resolved into three (slightly broadened) resonances of 6:6:6 intensity (δ = 2.07, 1.71 and 1.57 ppm), whilst the allyl units give five resonances of 2:2:2:2:2 intensity: a multiplet at δ = 5.15 ppm and four broad doublets at δ = 3.47, 2.45, 1.93 and 1.88 ppm. On further cooling of both congeners the spectra can be fully resolved and the multiplets and doublets reveal themselves to be AMNXY spin systems where coupling to all four of the terminal protons is different. Full assignment was made by inspection of the coupling constants between the terminal allylic protons and the central meso proton (J_{anti} = 15 Hz; J_{syn} = 9 Hz) in combination with NOESy NMR whereby the protons of C(20)/C(17) give a cross peak with the protons of the C(9)/C(12) Me groups respectively.

On warming either sample the NWT-Me proton resonances coalesce to a single resonance concomitant with the CH₂ allyl protons becoming equivalent and the multiplet of the central meso proton transforming into a well defined quintet coupling equally to all the terminal allylic protons (an AX₄ spin system). This is symptomatic of two possible scrambling mechanisms occurring (figure 3.11). Firstly the allyl ligands can spin at a

rate quicker than that of the ^1H NMR timescale, making the NWT-Me equivalent and the two sets of *anti*-/*syn*- protons equivalent (top scenario of figure 3.11). The second scrambling mechanism that could occur is the interchange of the *anti*- and *syn*- protons, which is hypothesised to go *via* an $\eta^1:\eta^3$ transition state.⁵⁵

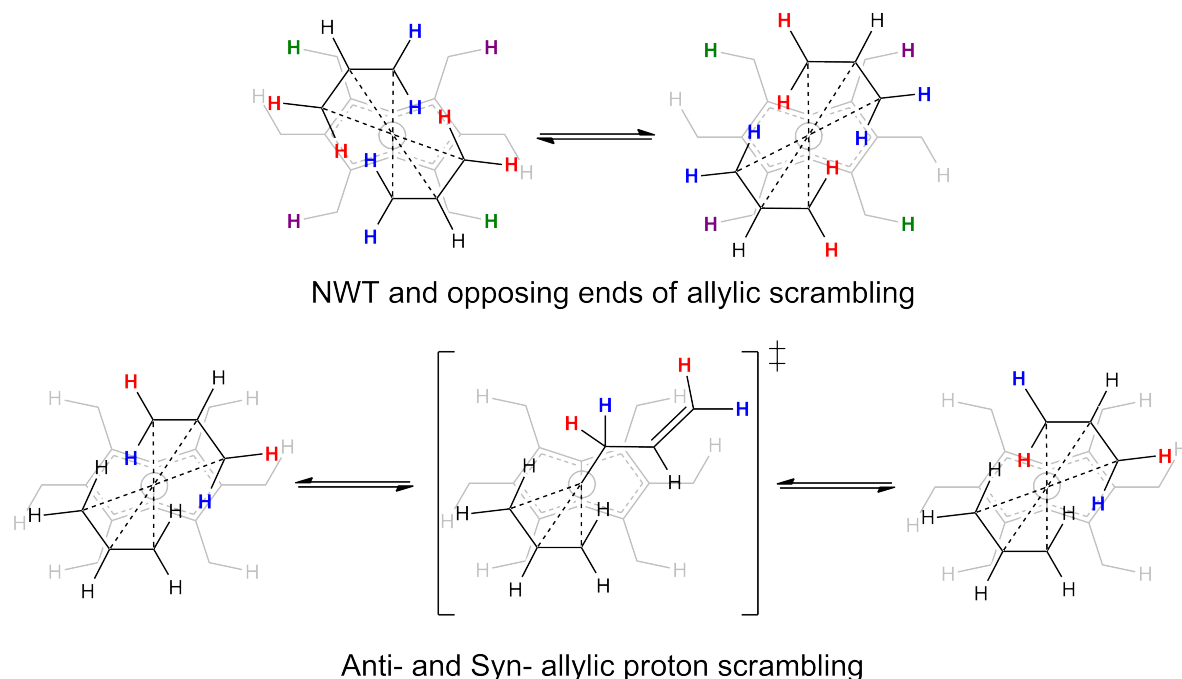


Figure 3.11: The two mechanisms of proton scrambling at work in **3.5**

By inspection of the line shape at the point of coalescence it is possible to calculate the energy required for the rotation along the metal and the bridge-head bond. This was found to be 58.4 kJ mol⁻¹ for **3.5_{Hf}** and 63.4 kJ mol⁻¹ for **3.5_{Zr}** at (15 °C and 43 °C respectively). These values are both comparable with that found for ZrPn(C₃H₅)₂ (64.0 kJ mol⁻¹).¹⁶

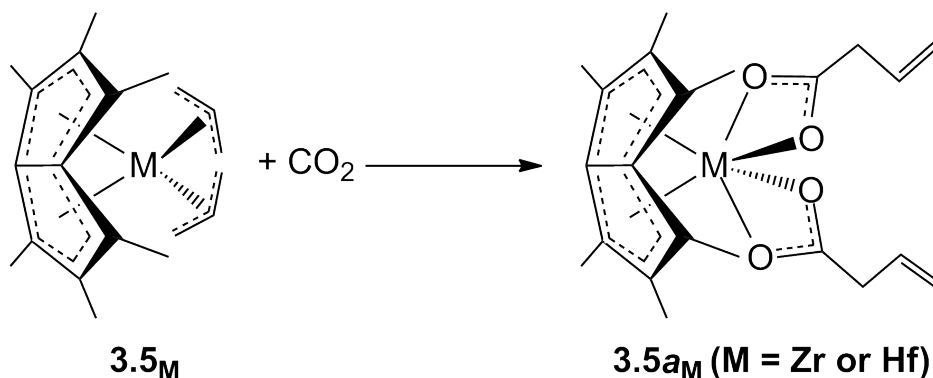
3.4.2.3 Other characterisation of **3.5**

IR spectroscopy would be able to detect the presence of a well-defined C=C in the η^1 transition state with a signal over 3000 cm⁻¹ corresponding to the sp^2 hybridised C-H stretching and a signal due to the C=C stretching around 1500 cm⁻¹. Indeed in the IR spectrum of both congeners of **3.5** a strong signal was detected both at 3065 cm⁻¹ and just above 1500 cm⁻¹. Therefore the proposed $\eta^1:\eta^3$ transition state is reinforced. **3.5_{Hf}** and **3.5_{Zr}** were both also characterised by mass spectrometry. The high resolution mass spectra showed signals at the relevant molecular ion peak ($m/z = 448.1652$ for **3.5_{Hf}**

and 358.1232 for **3.5_{Zr}**) and then subsequent fragmentation patterns of loss of allylic groups and then the breakdown of the Pn* ring.

3.4.2.4 Insertion of CO₂ into the η^1 transition state

Should the η^1 transition state mechanism be an accurate description of the scrambling seen in this species it was proposed that addition of CO₂ may result in trapping out this intermediate by the insertion of the molecule into the M-C σ -bond. An NMR sample of **3.5_M** (M = Zr or Hf) was charged with CO₂ which resulted in a swift lightening of the colour of the solution. The ¹H NMR spectrum consisted of seven resonances: three sharp singlets in the region expected for Pn* Me groups (integral ratio 6:6:6), a doublet positioned around $\delta = 3$ ppm (corresponding to the sp^3 hybridised CH₂ group, integral ratio 2), two overlapping doublet of multiplets at approximately $\delta = 5$ ppm (overall integral ratio 4) and a multiplet at just below $\delta = 6$ ppm (integral ratio 2). These data are consistent with the proposed CO₂ inserted species MPn*(κ -O₂CCH₂CHCH₂)₂ (**3.5a**; scheme 3.9). The ¹³C NMR data also showed the expected low field resonance for the κ^2 -O₂CR ($\delta = 191$ ppm).



Scheme 3.9: The insertion of CO₂ into **3.5_M** to form **3.5a_M** (M = Zr or Hf).

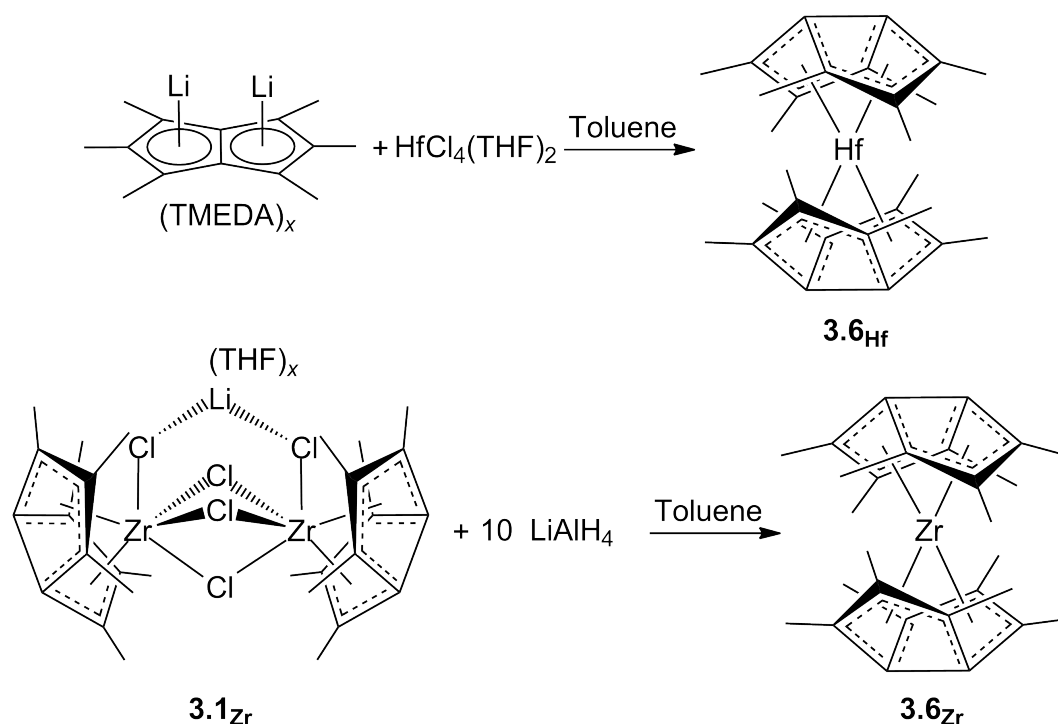
3.5 Homoleptic sandwiches of Group IV metals: MPn*₂ (**3.6**)

When the η^8 -binding mode of Pn was first reported NMR data for a series of homoleptic bis(pentalene) species were included (MPn^R₂, M = Ti, Zr, Hf, R = H, 2-Me). Disappointingly crystals suitable for X-ray diffraction could not be obtained, though the nature of the bonding, in particular the question of the total count of 20 electrons, caused a

stir amongst theoretical chemists, and sparked DFT, PES, geometry optimisation and symmetry studies on this curious species.^{12–15} However no further homoleptic species have been reported. The syntheses and structural elucidation of the bis(Pn*) Zr and Hf derivatives would therefore be of great interest, especially due to the high symmetry and high steric demand of the ligand. It was also hoped that permethylation of the rings would assist in the crystallisation of the species, a trend that has been seen before.⁵⁶

3.5.1 Synthesis of MPn^*_2 (**3.6**)

Simple combination of **3.1_{Zr}** and an excess of $Li_2Pn^*(TMEDA)_x$ in a variety of solvents gave no discernable reaction even with extended heating. As a result, it was initially thought the synthesis of $ZrPn^*_2$ (**3.6_{Zr}**) was unachievable due to the extreme steric crowding of $ZrPn^*_2$. However during attempts to reduce **3.1_{Zr}** mass spectrometry revealed a signal at the molecular weight of **3.6_{Zr}**. Indeed it was later found that reaction of **3.1** with $LiAlH_4$ yielded **3.6_{Zr}** in poor yield (scheme 3.8). In contrast, synthesis of $HfPn^*_2$ (**3.6_{Hf}**) was relatively simple, by direct combination of $HfCl_4 \cdot 2 THF$ with excess $Li_2Pn^*(TMEDA)_x$ and subsequent heating furnishing **3.6_{Hf}** as a red solid (scheme 3.10).



Scheme 3.10: The syntheses of **3.6_{Zr}** and **3.6_{Hf}**.

3.5.2 Characterisation of **3.6**3.5.2.1 Single crystal X-Ray characterisation of **3.6**

Single crystals of both congeners of **3.6** were grown by the slow evaporation of a toluene solution in an inert atmosphere yielding red crystals. Data collected for the crystals were somewhat weak, and this led to a slightly high R-factor with the model. **3.6_{Zr}** crystallises in the $P 2_1/n$ space group, with two molecules in the asymmetric unit of the unit cell. **3.6_{Hf}** crystallises in the C222 space group. A side-on and top-down view of **3.6_{Zr}** is shown in figure 3.12, and selected structural parameters for a single asymmetric unit are presented in table 3.10.

Table 3.10: Selected structural parameters for **3.6**. ESDs in parentheses.

Bond lengths Å					
	3.6_{Zr}	3.6_{Hf}		3.6_{Zr}	3.6_{Hf}
M-C(1)	2.484(12)	2.545(14)	M-C(15)	2.484(10)	2.567(11)
M-C(2)	2.711(11)	2.671(15)	M-C(16)	2.675(12)	2.666(11)
M-C(3)	2.559(10)	2.447(13)	M-C(17)	2.572(12)	2.448(15)
M-C(4)	2.306(11)	2.317(11)	M-C(18)	2.315(11)	2.285(12)
M-C(5)	2.462(13)	2.552(14)	M-C(19)	2.514(11)	2.594(12)
M-C(6)	2.701(11)	2.717(14)	M-C(20)	2.704(11)	2.690(14)
M-C(7)	2.538(11)	2.486(11)	M-C(21)	2.570(12)	2.466(14)
M-C(8)	2.302(11)	2.293(12)	M-C(22)	2.311(10)	2.244(11)
M-Pn* _{cent.}	2.161(5)	2.161(5)	M-Pn* _{cent.}	2.152(6)	2.153(6)
M-Pn* _{cent.}	2.153(6)	2.153(6)	M-Pn* _{cent.}	2.134(8)	2.165(5)
Av. C _{ring} -Me	1.512	1.492			
Bond angles °					
Fold Angle	27.3 (11)	26.3 (11)	Fold Angle	28.2 (11)	27.7 (11)
Dihedral Angle	43.2 (5)	45.3 (6)			

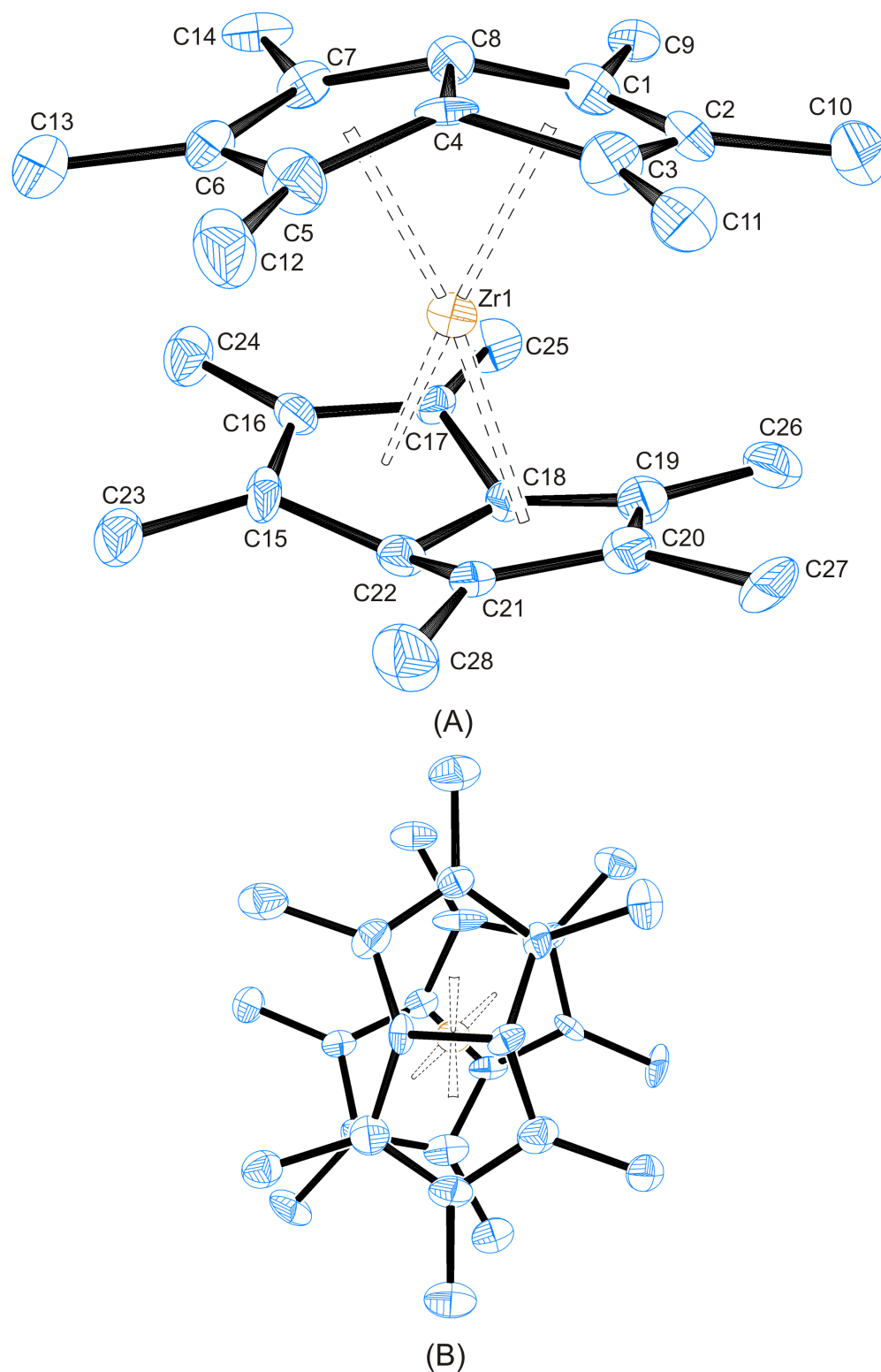


Figure 3.12: The solid state molecular structure of **3.6_{Zr}**; (A) a side on view and (B) a top down view. Thermal ellipsoids at 50 % probability and H-atoms excluded for clarity. **3.6_{Hf}** is isostructural.

Due to the poor data and difficulty in solving the crystal structures only tentative conclusions may be drawn. It is noteworthy that unlike **2.1** the Pn* rings are not disordered over three positions because the smaller size of the central metal atom locks

the conformations. The $M-Pn^*_{cent.}$ distances are greater than those already seen in this chapter [average 2.150 and 2.158 Å for **3.6_{Zr}** and **3.6_{Hf}** respectively, distances of previously synthesised compounds range from 2.080(2)-2.182(2) Å]. There is also a concomitant flattening of the Pn^* ring. This is thought to arise from the greater steric demand of two Pn^* ligands preventing close approach to the metal centre.

Of particular interest is the comparison of geometries found in the single crystal X-ray diffraction study and those predicted by DFT *ab initio* calculations carried out by Jonas and co-workers, a selection of bond lengths and angles are presented in table 3.11.¹²

Table 3.11: Comparison of calculated and found bond lengths and angles.

	3.6_{Zr}	ZrPn ₂ (calc.)	3.6_{Hf}	HfPn ₂ (calc.)
M-C(4)	2.31(1)	2.34	2.32(1)	2.32
M-C(8)	2.30(1)	2.34	2.29(1)	2.32
Average fold angle	27.8	27.7	27.0	28.9
Torsion Angles	43.2(5)	50.6	45.3(6)	49.3

The predicted distances within the carbon skeleton of ZrPn₂ agree extremely well with those found for **3.6_{Zr}**, as does the predicted degree of folding of the pentalene ligand. The Hf congener agrees less well, especially regarding the fold angle, where a flattening of the pentalene ring is seen (by approximately two degrees). The greatest difference is seen however in the torsional angle (defined as the angle between the planes made up between the WT carbons and the centroid of the bridgehead bond), where calculations predict the pentalene rings to be more staggered than they are. This can be justified by the extra steric bulk of the Pn^* ligand compared to the non-substituted analogue, in particular in the steric clash brought on by the methylation at the wing-tip position with the bridge head carbon on the other pentalene. It is expected this would move the energetic minimum of the HOMO to a lower torsion angle, thus explaining the difference. **3.6_M** is formally a 20 e⁻ complex. The two highest energy electrons would therefore be expected to be found in an anti-bonding orbital, however the previously mentioned DFT study found the HOMO of the MPn₂ species (M = Ti, Zr or Hf) to

be purely localised on the Pn framework. **3.6_M** would likely have a HOMO of similar make-up as MPn₂ and as such the slight lengthening in the M-Pn* distances compared to other species so far in this chapter is attributed to steric factors (though it could also be due to incomplete donation of electrons to the metal centre).

3.5.2.2 Other characterisation of **3.6**

Both **3.6_{Zr}** and **3.6_{Hf}** exhibit very simple room temperature ¹H NMRs which give two sharp resonances in a 12:6 ratio. This implies that the Pn* ligands can easily oscillate between the torsion angle minima and thus all the NWT-Me protons are equivalent at room temperature. Due to issues with the solubility of the compounds it was not possible to record a ¹³C NMR spectrum. **3.6_{Zr}** and **3.6_{Hf}** were also characterised by mass spectrometry. High resolution mass spectrometry gave signals $m/z = 462.1864$ (**3.6_{Zr}**) and 552.2288 (**3.6_{Hf}**), and the subsequent fragmentation of the loss of Pn*.

3.6 Methyl, benzyl and phenyl derivatives of “MPn*Cl₂”

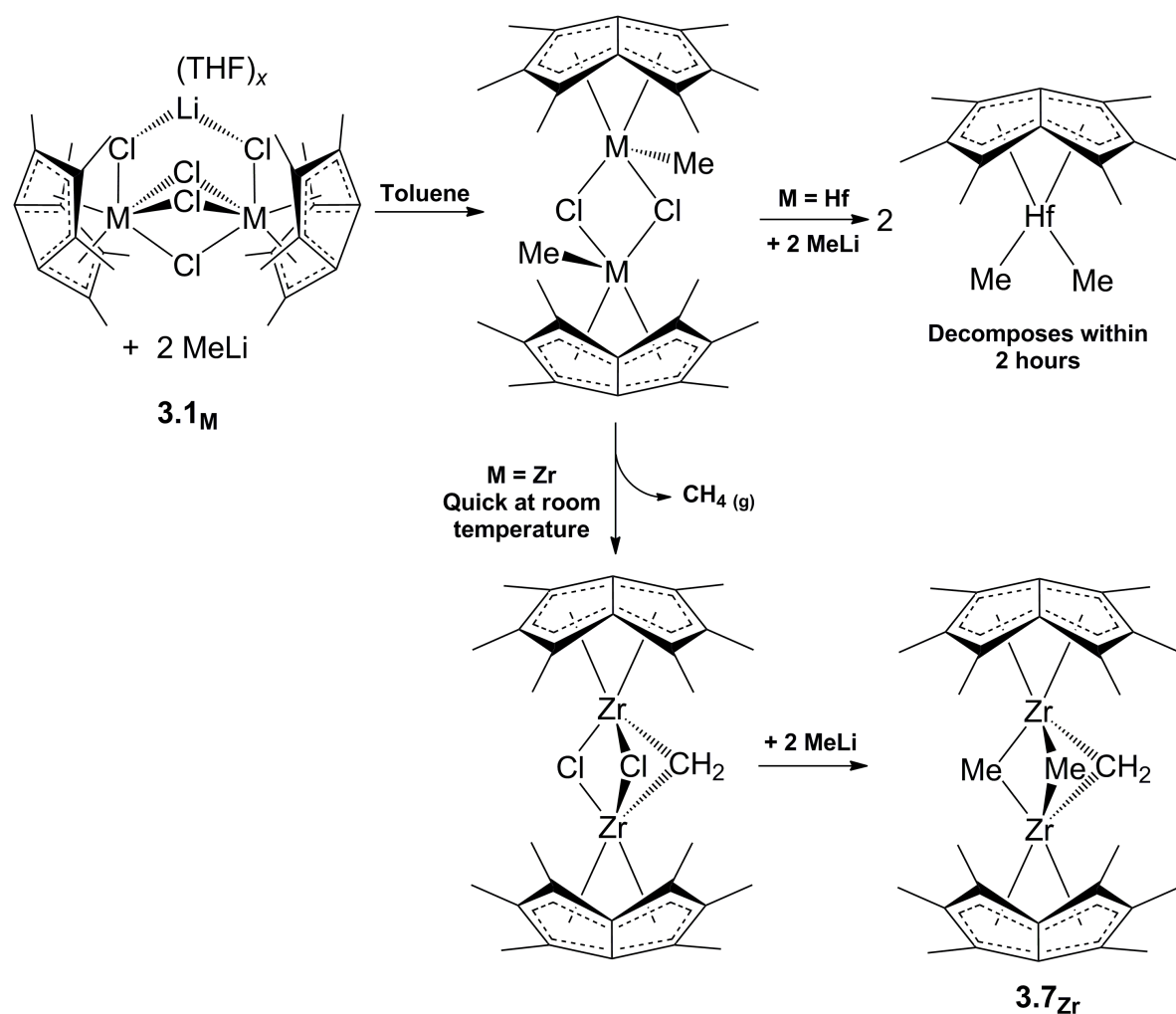
Alkyl and aryl group 4 complexes are of considerable interest due to the ease of removing one of the σ -bound ligands and forming highly reactive cationic species. These coordinatively unsaturated charged species currently form the corner-stone of Ziegler-Natta catalytic systems.⁵⁷ Species containing a M-C σ -bond were therefore targeted, namely methyl, phenyl and benzyl with differing results.

3.6.1 Synthesis of [MPn*]₂[μ -CH₃]₂[μ -CH₂] (**3.7**)

The simplest possible system to feature an M-C σ -bond is that involving the Me ligand, and as such this seemed the most appropriate system with which to begin. Addition of just over four equivalents of MeLi to **3.1_{Zr}** resulted in the solution changing from golden yellow in colour to a ruby red hue. Subsequent work-up yielded a red microcrystalline solid in moderate yield (63.6 %). ¹H NMR studies demonstrated there to be two different non-Pn* proton environments, and subsequent single crystal X-ray diffraction analysis revealed the structure to comprise of a dimer with three bridging groups, two methyl and one methylene unit.

To date it has not been possible to synthesise the Hf derivative of **3.7_{Zr}**. A parallel synthesis results in the formation of an orange solution which exhibits three proton environments in the ^1H NMR spectrum in a 12:6:6 intensity ratio. This compound was found to be thermally unstable, decomposing when heated or left overnight either in solution or in the solid state, and upon work-up resulted in an extremely pyrophoric yellow solid.

It is thus proposed that on addition of MeLi initially a compound of formula $[\text{MPn}^*\text{Me}(\mu\text{-Cl})]_2$ is formed (as has been isolated for the Ti derivative).¹⁸ For Zr this quickly undergoes elimination of methane to form $[\text{MPn}^*]_2(\mu\text{-CH}_2)(\mu\text{-Cl})_2$, which subsequently undergoes further metathesis with two further equivalents of MeLi (as is similarly observed with the Ti derivative) to form **3.7_{Zr}**. For the Hf congener it is thought that the metathesis occurs more quickly than the elimination of methane thus forming the species HfPn^*Me_2 (scheme 3.11).



Scheme 3.11: Proposed mechanism for the synthesis of **3.7_{Zr}**.

3.6.2 Characterisation of **3.7**

3.6.2.1 Single crystal X-Ray diffraction studies of **3.7_{Zr}**

Single crystals for **3.7_{Zr}** were grown from the slow evaporation of a toluene solution in an inert atmosphere, and revealed the structure to be dimeric. **3.7_{Zr}** crystallises in the P 2₁ space group with two molecules with the asymmetric unit of the unit cell. One molecule, and its corresponding structural parameters are shown in figure 3.13 and table 3.12. The second molecule does not deviate significantly in terms of structural parameters.

Due to the limitations of the single crystal X-ray diffraction data it was not possible to directly locate the hydrogens of the bridging groups on the electron density map. However, inspection of bond lengths reveals one carbon has a considerably shorter average Zr-C distance (C16), and as such it is proposed that that carbon is the μ -CH₂. Addition of the appropriate hydrogens to the model gives somewhat better agreement with the data (R = 5.3 % *vs.* 5.5 %), and a refinement of the position of the hydrogen atoms in the bridge puts them in sensible positions. The stronger interaction of the formally CH₂²⁻ group with the two metal centres results in a pinching of the two ‘ZrPn*’ fragments thus preventing them from being parallel [figure 3.13(B)]. The angle of the tilt (defined as the angle between the two planes consisting the metal and both WT carbons) is 29.5°.

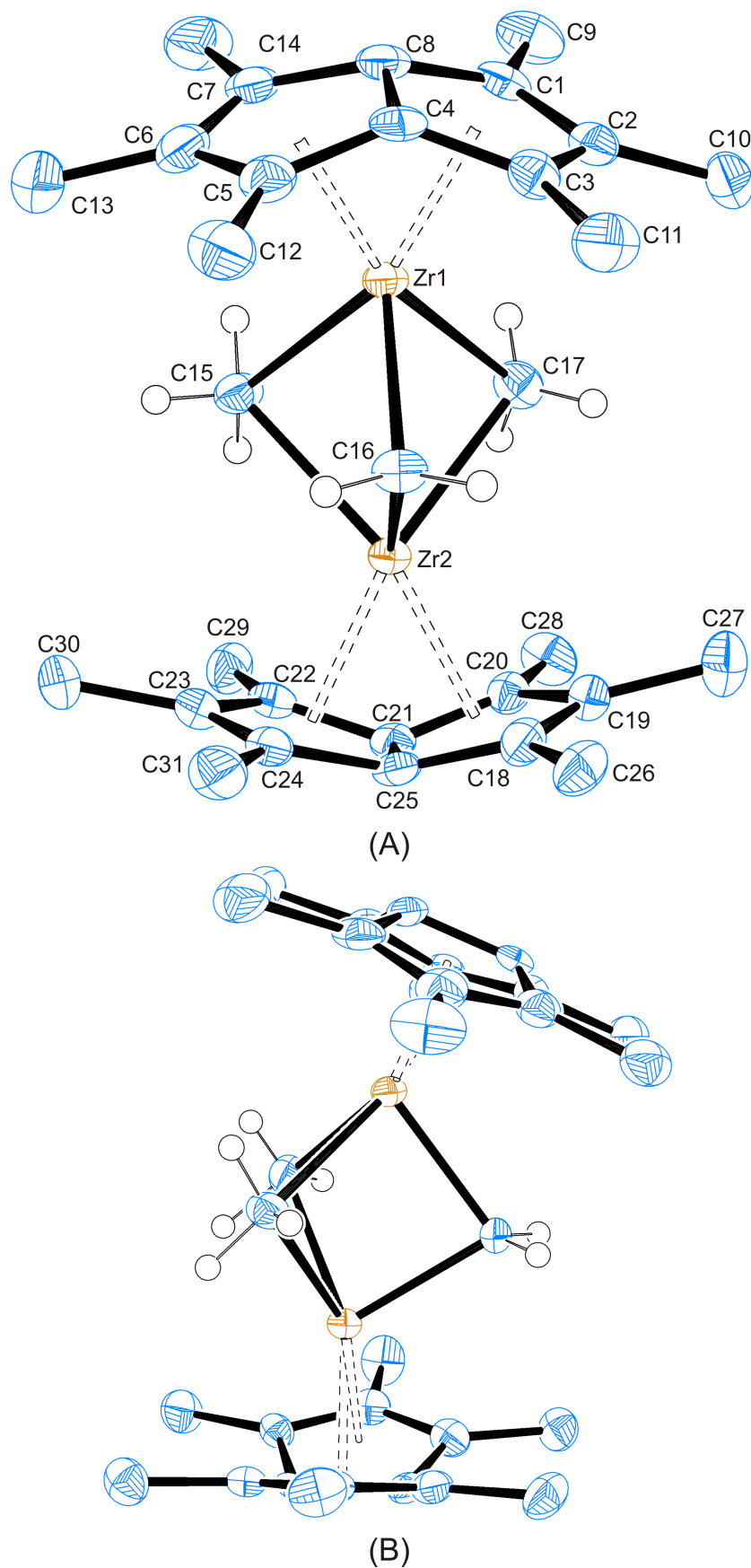


Figure 3.13: (A) The molecular structure of **3.7_{Zr}** in the solid state and (B) the side on view displaying the pinching of the metal centres; thermal ellipsoids at 50 % probability, H-atoms on Pn* rings omitted for clarity.

Table 3.12: Selected structural parameters for **3.7_{Zr}**. ESDs in parentheses.

Bond lengths Å			
M(1)-C(1)	2.447(5)	M(2)-C(18)	2.557(6)
M(1)-C(2)	2.611(6)	M(2)-C(19)	2.639(6)
M(1)-C(3)	2.516(5)	M(2)-C(20)	2.438(5)
M(1)-C(4)	2.287(5)	M(2)-C(21)	2.264(5)
M(1)-C(5)	2.531(6)	M(2)-C(22)	2.448(5)
M(1)-C(6)	2.637(6)	M(2)-C(23)	2.639(6)
M(1)-C(7)	2.454(6)	M(2)-C(24)	2.538(5)
M(1)-C(8)	2.263(4)	M(2)-C(25)	2.288(4)
M(1)-C(15)	2.442(5)	M(2)-C(15)	2.455(6)
M(1)-C(16)	2.283(5)	M(2)-C(16)	2.264(5)
M(1)-C(17)	2.479(6)	M(2)-C(17)	2.451(6)
M(1)-M(2)	3.052(1)	Av. C _{ring} -Me	1.503
M(1)-Pn* _{cent.}	2.096(3)	M(1)-Pn* _{cent.}	2.111(3)
M(2)-Pn* _{cent.}	2.115(3)	M(2)-Pn* _{cent.}	2.112(3)
Bond angles °			
Fold Angle	30.1(5)	Fold Angle	31.2(5)

The Zr centres are in an approximately square based pyramidal arrangement, with the two μ -Me groups and the Pn*_{cent.} forming the base. By forming the dimer **3.7_{Zr}** is a 16 e⁻ complex. Interestingly the fold angle of **3.7_{Zr}** is comparable to the cyclopentadienyl derivatives already seen in this chapter (**3.2_{Zr}**, **3.3_{Zr}** and **3.4_{Zr}**) and the M-Pn* centroid distance is also comparable.

Crystallographically characterised bridging Me and CH₂ groups between two Zr atoms are not particularly common, with only 10 such examples (only four of which are for neutral complexes and these usually have other bridging moieties assisting).^{58–67} There are no structurally characterised examples of a system involving three bridging Me/CH₂ groups between two Zr centres. Indeed there is only one structurally characterised compound involving three σ -bound carbon atoms between two Zr centres (and

that is a tetra-Zr cluster synthesised by Stephan *et al.*).⁵³

The average Zr-(μ -CH₂) distance (2.274 Å) is slightly longer than examples found in the CSD. For instance [(ZrCpMe)₂(μ -CH₂)₂]⁺[B(C₆F₅)₄]⁻ [(i) in figure 3.14] has an average distance of 2.234 Å, and for [ZrCp*(C₂B₉H₁₁)]₂[μ -CH₂] [(ii) in figure 3.14] the average distance is 2.182 Å.^{58;61} The average Zr-(μ -Me) distance (2.457 Å) is comparable to the literature examples, even for those systems which are cationic. For example this cationic ansa-bridge bis Cp complex ([Zr(C₅H₄SiMe₂NSiMe₂C₅H₄)₂[μ -CH₃]]) [(iii) in figure 3.14] an average distance of 2.44 Å is seen, or for this Zr amidinate dication({ZrCp*[N(^tBu)C(Me)N(Et)]})₂[μ -CH₃]₂)²⁺ [(iv) in figure 3.14] an average distance of 2.45 Å is reported.^{66;67}

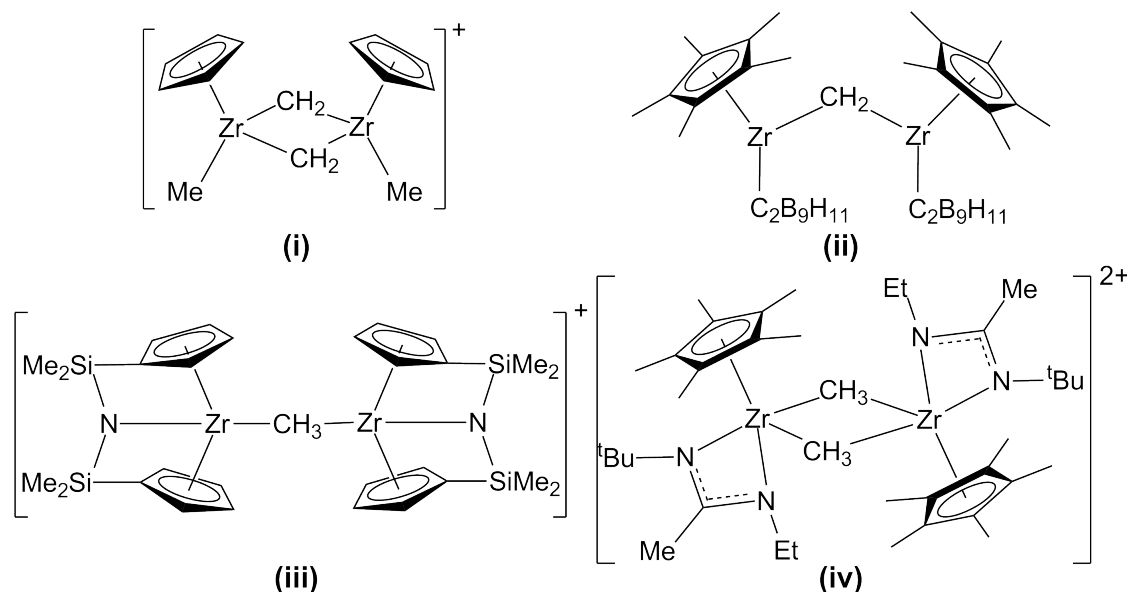


Figure 3.14: The four structures compared with **3.7_{Zr}**

3.6.2.2 NMR characterisation of **3.7**

The room temperature ¹H NMR spectrum of **3.7_{Zr}** consists of four resonances of integral ratio 2:24:12:6 at δ = 2.71, 1.96, 1.92 and -0.38 ppm respectively. On cooling **3.7_{Zr}** no evidence was seen of any decoalescence phenomenon and it can therefore be assumed that the Pn* rings are quickly rotating about the metal/bridgehead centroid axis. The CH₂ resonance comes somewhat upfield of other examples of this bridging mode showing this CH₂ to be more shielded.^{58;68}

The ¹³C of **3.7_{Zr}** shows the five expected Pn* resonances and two further resonances at δ = 38.9 and 127.9 ppm [corresponding to the (μ -Me) and (μ -CH₂) resonances re-

spectively). Similar to the ^1H NMR spectrum the CH_2 resonance is shifted considerably upfield, however the coupling constant seen in the decoupled spectrum is typical of a bridging methylene ($^1J_{\text{C-H}} = 115.4$ Hz). The previously mentioned reaction using Hf gave a ^1H NMR spectrum consisting of three resonances at $\delta = -0.44$, 1.96 and 2.10 ppm, in a 6:6:12 integral ratio. The considerable upfield shift is typical for terminal Me groups on a Hf (e.g. HfCp^*Me_2 $\delta_{\text{Me}} = 0.07$ ppm) and therefore the formulation depicted in scheme 3.11 is proposed.⁶⁹

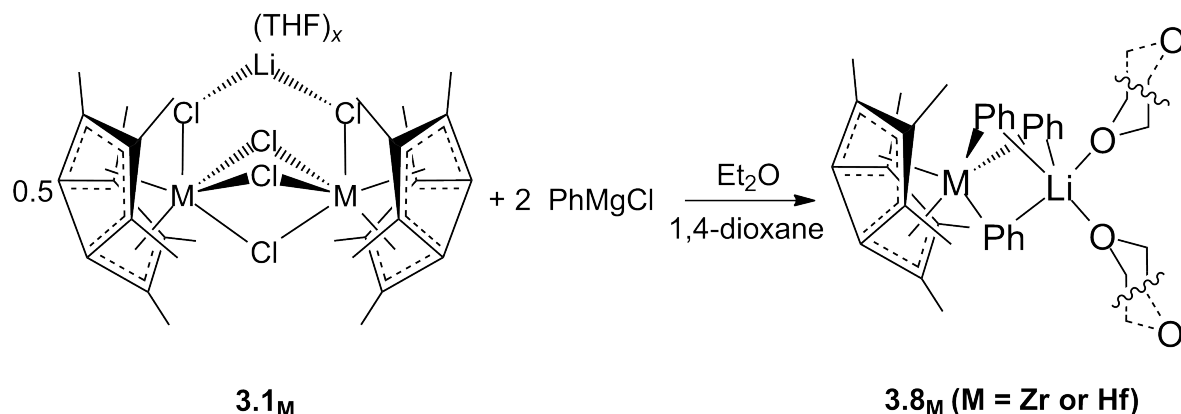
3.6.2.3 Other characterisation of **3.7_{Zr}**

Mass spectral analysis of **3.7** only gave a signal for Pn^* and its subsequent fragmentation. It was found that EI-MS would not give a signal for the Ti analogue, and as such it is unsurprising that no signal was seen for the Zr derivatives.

3.6.3 Synthesis of $\text{MPn}^*\text{Ph}(\mu\text{-Ph})_2\text{Li}(\text{dioxane})$ (**3.8**)

Another σ -bound ligand that is often used in organometallic chemistry is the phenyl (Ph; C_6H_5) ligand. If the Me derivative is the simplest possible σ -alkyl derivative then the Ph ligand is the simplest σ -aryl derivative, and therefore the Ph derivative of **3.1** was targeted.

Both congeners of **3.8** are synthesised by rapid addition of slightly over four equivalents of PhMgBr (3.0 M in Et_2O) to **3.1**. Having been allowed to stir overnight at room temperature 1,4-dioxane was added in order to precipitate the magnesium salts. Subsequent filtration and work-up revealed (by ^1H NMR) that the ' MPn^* ' fragment had been triply arylated and therefore an initial formulation of $\text{MPn}^*\text{Ph}_3 \cdot \text{Li}$ was proposed. Crystallisation revealed that 1,4-dioxane had been incorporated into the structure and single crystal X-ray diffraction studies elucidated the compound as $[\text{ZrPn}^*\text{Ph}(\mu\text{-Ph})_2\text{Li}(\mu\text{-1,4-dioxane})]_n$ (scheme 3.12). To date it has not been possible to grow single crystals of **3.8_{Hf}**



Scheme 3.12: The synthesis of **3.8_M** (M = Zr or Hf).

3.6.4 Characterisation of **3.8**

3.6.4.1 Single crystal X-ray diffraction studies of **3.8_{Zr}**

Single crystals of **3.8_{Zr}** suitable for X-ray diffraction were grown from a saturated hexane solution slow cooled to $-38\text{ }^{\circ}\text{C}$. **3.8_{Zr}** crystallises in the $P\bar{1}$ space group with a single molecule in the asymmetric unit of the unit cell. A diagram of the structure of a monomer unit is shown in figure 3.15 (A). This reveals the metal centre in **3.8_{Zr}** is surrounded by three Ph groups with a lithium cation bound in order to charge balance. **3.8_{Zr}** binds three Ph moieties in order to satisfy the coordinative and electronic unsaturation. This occurrence has already been seen in the dimerisation of **3.1** and its incorporation of LiCl. The geometry of the metal centre is best described as a distorted trigonal bipyramid, with the axial positions taken by one side of the Pn^* ring and one of the bridging Ph rings [centroid of ring C(4)-C(8) and C(27)], and the equatorial positions taken up by the remaining Pn^* centroid, a bridging Ph and the non-bridging Ph. Two of the Ph rings bridge to a lithium through the *ipso* carbon with the third solely bound to the Zr centre. The Li is solvated by two molecules of 1,4-dioxane. These solvent molecules bridge to another lithium cation in an adjacent monomer unit and thus form a 1-dimensional polymer extending across the (1 1 0) Miller Index figure 3.15 (B).

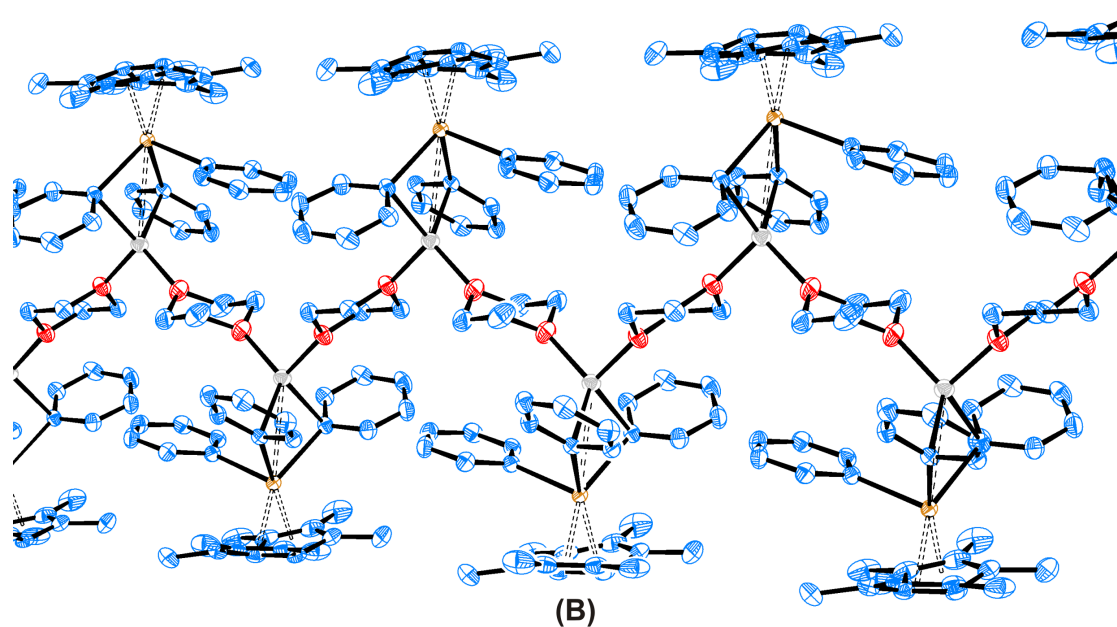
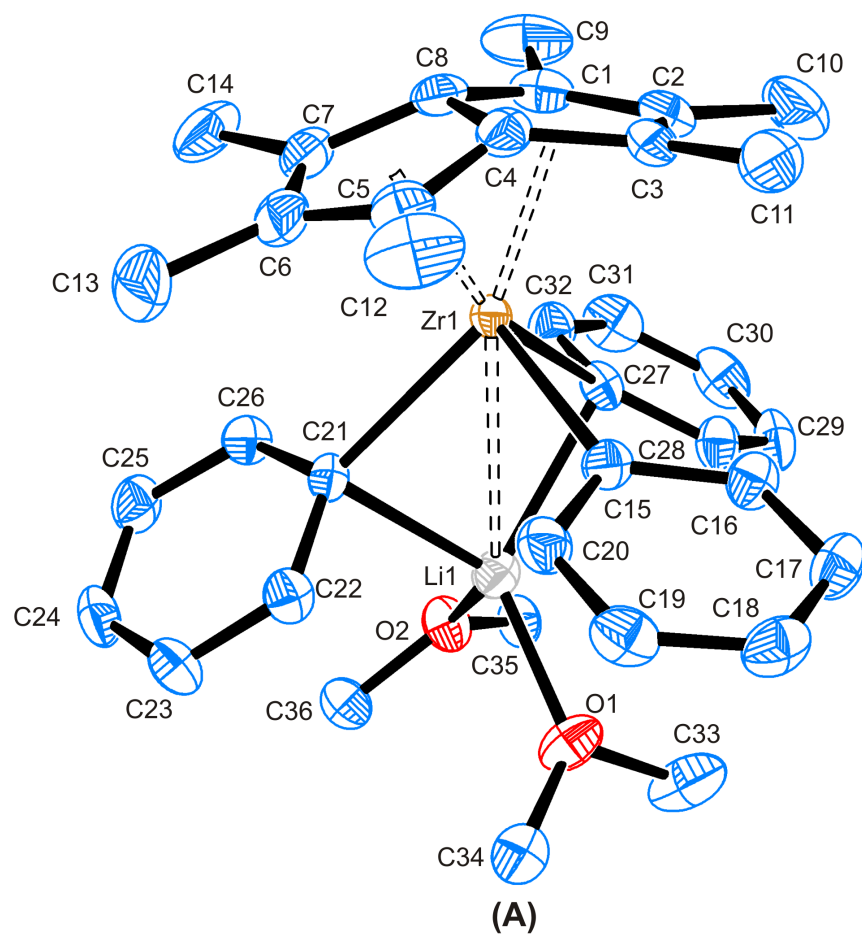


Figure 3.15: (A): The solid state molecular structure of an asymmetric unit of **3.8_{Zr}** (B): The polymeric structure of **3.8_{Zr}** viewed with respect to the (1 1 0) Miller Index. Thermal ellipsoids at 50 % probability and H-atoms omitted for clarity.

Table 3.13: Selected structural parameters for **3.8**. ESDs in parentheses

Bond lengths Å			
M-C(1)	2.472(2)	M-C(15)	2.336(2)
M-C(2)	2.684(2)	M-C(21)	2.404(2)
M-C(3)	2.609(2)	M-C(27)	2.403(2)
M-C(4)	2.315(2)	M-Li	3.172(3)
M-C(5)	2.609(2)	Li-C(21)	2.282(4)
M-C(6)	2.675(2)	Li-C(27)	2.290(4)
M-C(7)	2.454(2)		
M-C(8)	2.268(2)	M-Pn* _{cent.}	2.154(2)
Av. C _{ring} -Me	1.503	M-Pn* _{cent.}	2.148(2)
Bond angles °			
Fold Angle	27.9(2)		

Contained within the CSD there are 48 structures possessing a Zr-Ph bond, of which only one in combination with a coordinated lithium cation.⁷⁰ In this structure two Ph and two amidophenolate ligands coordinate to the Zr centre and two lithium cations are present - one covalently bonded to one of the Ph rings, the other is coordinated to both the Ph rings (figure 3.16).

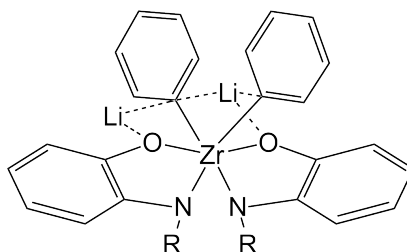


Figure 3.16: Schematic diagram of the only other example of a Ph bridging between a Zr centre and a lithium cation, substituents on phenolate rings and solvent coordinated to lithium cations removed for clarity.

The compound in figure 3.16 has two very different Zr-Ph bond lengths of 2.367 (4) Å and 2.450 (4) Å (the shorter being the one bound to the single lithium cation). Comparing this species to **3.8_{Zr}** (where the average Zr-Ph bond lengths is 2.404 Å) we see that **3.8_{Zr}**'s distances are equidistant between the two values seen in the compound

in figure 3.16. The C–Li distances in **3.8_{Zr}** (2.286 Å) are considerably shorter than those seen in the compound in figure 3.16 (2.397 Å). This is understandable due to there being two lithium cations in the above example being coordinated to two Ph rings, whereas in **3.8_{Zr}** there is only one lithium cation attached, thus allowing closer approach by electrostatic interactions.

The Zr–C(15) distance in **3.8_{Zr}** [2.336(2) Å] is only slightly longer than the distances found for ZrCp*₂Ph₂ (2.311 Å)^{71;72} and ZrCp₂Ph₂ (2.301 Å). Since all these examples are formally 16 e[−] complexes, the slight lengthening in **3.8_{Zr}** can presumably be attributed to increased steric crowding around the Zr centre.

Comparing the structural parameters of the Pn* ligand in **3.8_{Zr}** we see it is considerably flatter and has longer M–Pn*_{cent.} distances than most of the compounds seen so far in this chapter - indeed it is most comparable to the homoleptic sandwich **3.6_{Zr}**. Since **3.8_{Zr}** is formally a 16 e[−] complex this is presumably due of the increased steric demand due to the triple arylation leading to a longer M–Pn*_{cent.} distance.

3.6.4.2 NMR spectroscopy of **3.8**

The ¹H NMR spectrum of **3.8** consists of six resonances of 6:12:8:3:6:6 integral ratio (δ = 1.72, 1.93, 2.72, 7.10, 7.21 and 7.95 ppm for **3.8_{Zr}** and δ = 1.78, 2.05, 2.50, 7.05, 7.22 and 7.97 ppm for **3.8_{Hf}** respectively). These can be assigned to the WT- and NWT-Me, the 1,4-dioxane protons and the Ph protons respectively. Due to the integral ratios of **3.8_{Hf}** and the persistence of 1,4-dioxane within the product it is proposed **3.8_{Hf}** is isostructural with **3.8_{Zr}**. The presence of a single trio of resonances for the Ph ligands implies that in the solution phase all three are equivalent on the NMR timescale and the lithium is undergoing a fluxional process to bind to each Ph. The 1,4-dioxane is still present and prolonged subjection to a vacuum does not remove it. The ¹³C NMR spectrum shows the presence of ten resonances (five for Pn*, four for the Ph ring and a single resonance for the coordinated 1,4-dioxane) and the ⁷Li NMR shows a sharp singlet (δ = −1.12 or 1.06 ppm for **3.8_{Zr}** and **3.8_{Hf}** respectively).

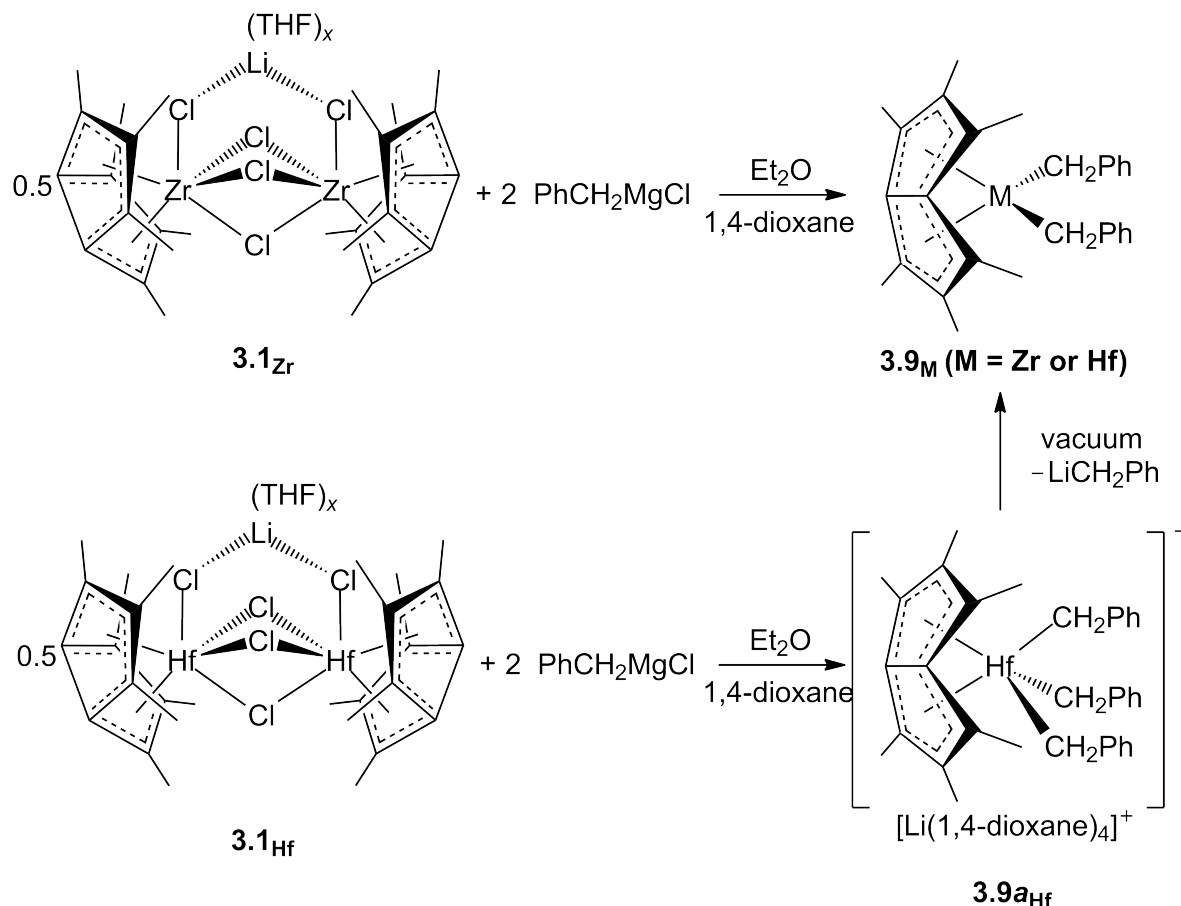
3.6.4.3 Other characterisation of **3.8**

Similarly to **3.7_{Zr}** the presence of σ -ligands in this complex prevented acquiring a signal corresponding to the mass ion in EI-MS. As a consequence the only signal seen is that of the Pn^* ring at 186 and its subsequent fragmentation pattern.

3.6.5 Synthesis of $\text{MPn}^*(\text{CH}_2\text{Ph})_2$ (**3.9**)

Of much interest in the chemistry of Zr and Hf are the benzyl derivatives (CH_2Ph), particularly due to their use as polymerisation and hydrogenation catalysts. In terms of the chemistry already seen in this chapter it would be of interest to see whether this species would exist as a monomer, or a dimer like **3.7** or a polymeric species like **3.8**.

Addition of just over four equivalents of PhCH_2MgCl in Et_2O to **3.1** in Et_2O results in the lightening of the colour of the yellow solution (scheme 3.13). Subsequently a small amount of 1,4-dioxane was syringed into the solution in order to precipitate out magnesium salts. At this point yellow crystals precipitated out from the Hf sample, which were suitable for single crystal X-ray analysis {identifying the compound as the intermediate: $[\text{HfPn}^*(\text{CH}_2\text{Ph})_3]^- [\text{Li}(1,4\text{-dioxane})]^+$, **3.9a_{Hf}**}. The bulk sample of **3.9_{Hf}** was subjected to a vacuum (removing the 1,4-dioxane and forcing the elimination of LiCH_2Ph , scheme 3.13) washed with hexane and isolated as a yellow amorphous powder, whereas **3.9_{Zr}** was crystallised from hexane.



Scheme 3.13: The syntheses of **3.9_M** (M = Zr or Hf).

3.6.6 Characterisation of **3.9**

3.6.6.1 Single crystal X-ray diffraction studies of **3.9_{Zr}**

In order to obtain single crystals suitable for X-ray diffraction of **3.9_{Zr}** a saturated hexane solution was slow cooled to $-38\text{ }^\circ\text{C}$ over three days. This resulted in the precipitation of a fine yellow powder. The supernatant was removed *via* filter cannula, concentrated and then again cooled to $-38\text{ }^\circ\text{C}$. This process was repeated once more to yield red crystals of **3.9_{Zr}** (in 53 % yield). **3.9_{Zr}** crystallises in the $P\ 2_1/n$ space group with a single molecule in the asymmetric unit of the unit cell. In contrast to **3.7_{Zr}** and **3.8_{Zr}**, **3.9_{Zr}** exists as a monomeric complex - a model of which is shown in figure 3.17. The metal centres adopt an approximately tetrahedral arrangement. It is assumed that **3.9_{Hf}** is isostructural with **3.9_{Zr}** however crystals of the Hf congener have not been isolated.

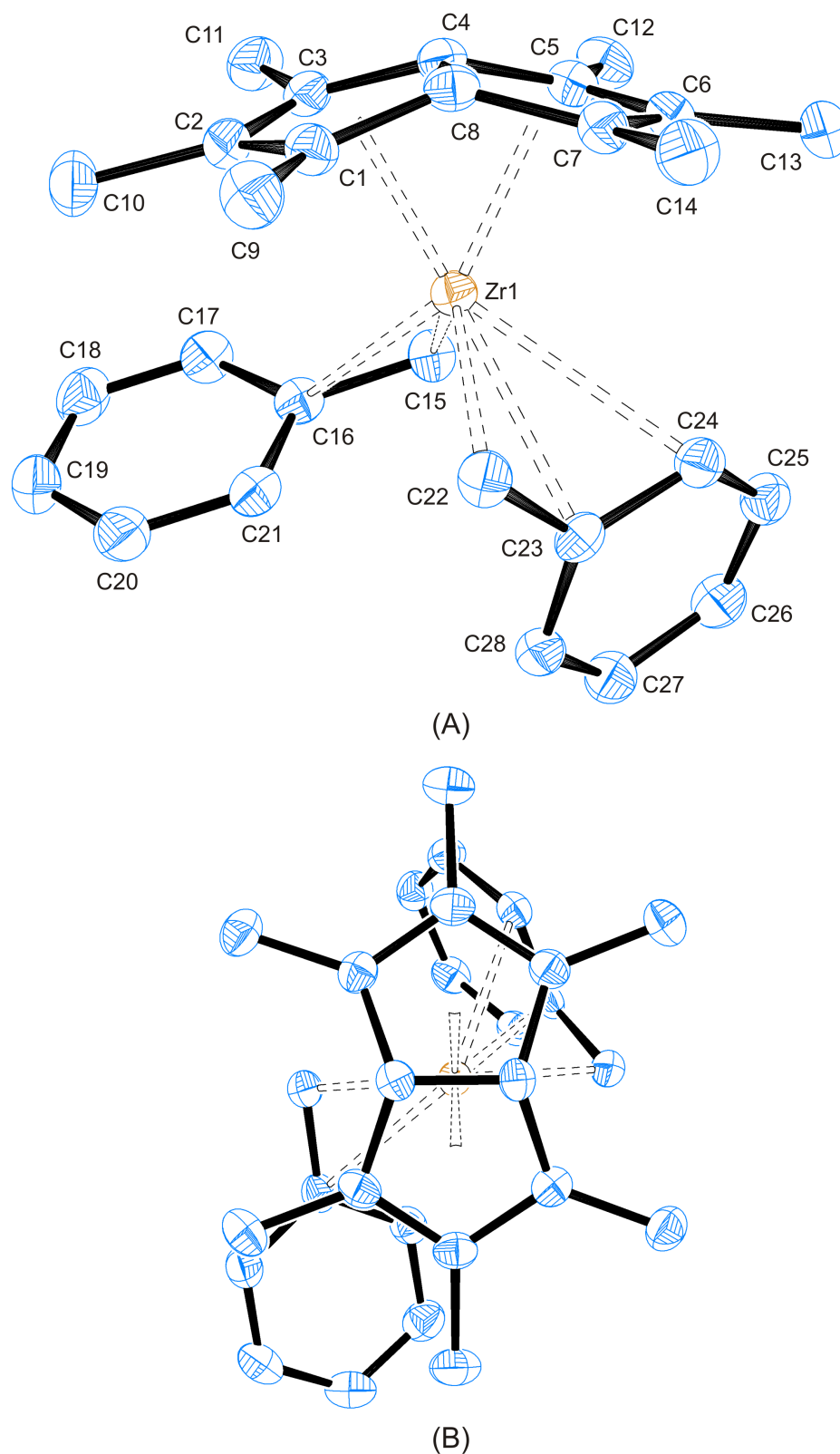


Figure 3.17: The solid state molecular structure of **3.9_{Zr}**, both (A) a side on view and (B) a top down view. Thermal ellipsoids at 50 % probability and H-atoms omitted for clarity.

The benzyl ligand has been found to bind to transition metal centre in large variety of modes, ranging from η^1 to η^7 . The manner in which it binds is a useful variable

for stabilising different electron deficient metal centres. However strict assignment of the hapticity was often a fairly subjective issue. Due to this, Parkin *et al.* have recently undertaken an in-depth investigation into the bonding in $\text{Zr}(\text{CH}_2\text{Ph})_4$ and other Zr-benzyl species found in the CSD.⁷³ In this work Parkin notes that there are two ways of distinguishing the bonding mode of the benzyl ligand: firstly by inspection of the deviation of the $\text{M}-\text{CH}_2-\text{Ph}$ bond angle from the idealised 109.5° (which can identify between η^1 and higher hapticities), and secondly by inspection of the difference between the $\text{M}-\text{CH}_2$ and $\text{M}-\text{C}_{\text{Ph}}$ distances (which can differentiate between the higher hapticities). To this end Parkin introduces the δ value (defined in figure 3.18). Using these two values Parkin was able to propose definitive assignment of binding modes of benzyl complexes (presented in table 3.14).

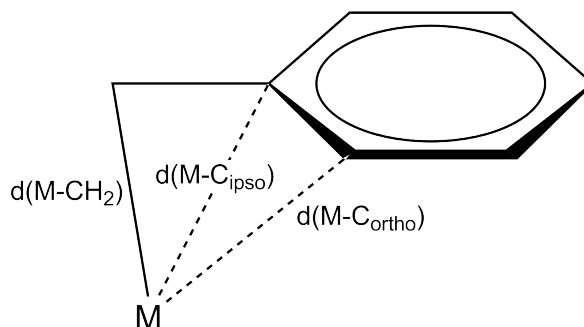


Figure 3.18: The definition of the δ value for the benzyl carbons: $\delta_{\text{ipso}} = d(\text{M}-\text{C}_{\text{ipso}}) - d(\text{M}-\text{CH}_2)$

Table 3.14: Criteria for assigning benzyl ligand coordination mode according to Parkin *et al.*⁷³

	$\text{M}-\text{CH}_2-\text{Ph}/^\circ$	$\delta_{\text{ipso}}/\text{\AA}$	$\delta_{\text{ortho}(\text{short})}/\text{\AA}$	$\delta_{\text{ortho}(\text{long})}/\text{\AA}$
η^1	> 97	> 0.5	> 0.5	> 0.5
η^2	≤ 97	≤ 0.5	> 0.5	> 0.5
η^3	≤ 97	≤ 0.5	≤ 0.5	> 0.5
η^4	$\ll 90$	< 0	≤ 0.5	≤ 0.5

Table 3.15: Selected structural parameters for **3.9_{Zr}**. ESDs are in parentheses.

Bond lengths Å			
Zr-C(1)	2.449(3)	Zr-C(15)	2.323(4)
Zr-C(2)	2.617(3)	Zr-C(16)	2.862(3)
Zr-C(3)	2.519(3)	Zr-C(21)	3.005(3)
Zr-C(4)	2.266(3)	Zr-C(22)	2.378(3)
Zr-C(5)	2.508(3)	Zr-C(23)	2.666(3)
Zr-C(6)	2.677(3)	Zr-C(24)	2.858(3)
Zr-C(7)	2.510(3)	Zr-C(25)	3.800(3)
Zr-C(8)	2.256(3)	Zr-Pn* _{cent.}	2.094(2)
Av. C _{ring} -Me	1.503	Zr-Pn* _{cent.}	2.122(2)
Bond angles °			
Fold Angle	28.8(3)	Zr(1)-C(15)-C(16)	95.47(18)
		Zr(1)-C(22)-C(23)	84.24(16)
δ values [C(15)-C(21)] Å			
Ipsos	0.539(4)	Para	2.713(4)
Ortho (short)	0.682(4)	Ortho (long)	1.693(4)
Meta (short)	2.631(4)	Meta (long)	1.857(4)
δ values [C(22)-C(28)] Å			
Ipsos	0.288(4)	Para	2.052(4)
Ortho (short)	0.480(4)	Ortho (long)	1.185(4)
Meta (short)	1.422(4)	Meta (long)	1.949(4)

Table 3.15 presents selected structural parameters for **3.9_{Zr}**, including the δ values for the benzyl ligands. Using Parkin’s parameters we are able to assign two different binding modes to each of the benzyl rings. Ligand C(22)-C(28) fits nicely into Parkin’s definitions, with the Zr(1)-C(22)-C(23) angle being less than 97 °, and the δ values for the *ipso* and nearer *ortho* carbons being less than 0.5 Å, and the value for the further *ortho* carbon being greater than 0.5 Å making it clearly an η^3 bonding situation. Indeed early DFT results on **3.9_{Zr}** clearly show a bonding interaction between the metal centre

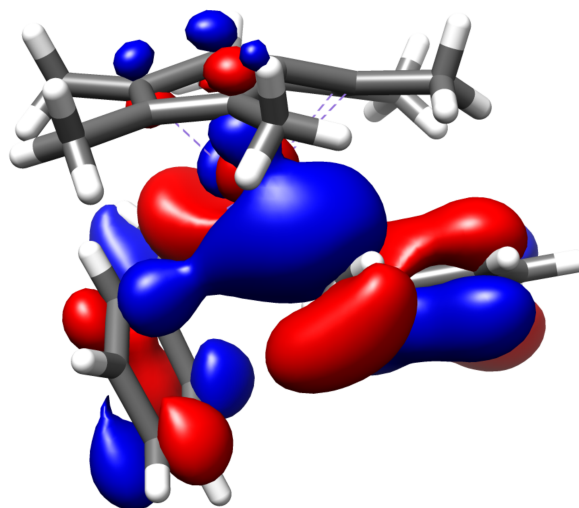


Figure 3.19: The HOMO-1 of **3.9Zr**. C atoms are rendered in grey, H atoms are rendered in white. Molecular orbital occupancy: Zr p_y 5.0 %; Zr d_{yz} 6.5 %; C(1) p_z 4.5 %; C(15) p_z 10.3 %; C(15) p_y 11.9 %; C(19) p_z 6.5 %; C(21) p_z 4.2 %; C(22) p_z 5.6 %; C(22) p_y 6.7 %. Isosurface limits: ± 0.025 .

and the nearer *ortho* carbon in the HOMO-1 (figure 3.19).

The bonding situation in the other benzyl ligand is less clear cut. The Zr-C(15)-C(16) angle is less than 97° , however all the δ values are greater than $0.5 \text{ \AA}$. It therefore appears that this ligand lies between Parkin's η^1 and η^2 definitions. Inspection of the molecular orbitals using DFT only finds one bonding interaction in the lowest energy of the valence orbitals (HOMO-9, figure 3.20); as such an η^2 bonding motif is tentatively assigned.

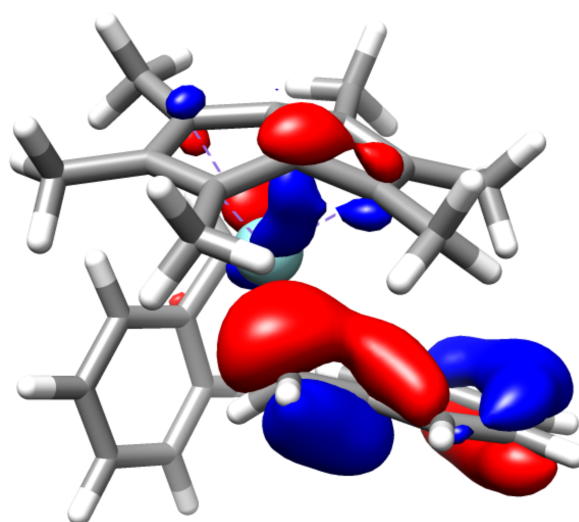


Figure 3.20: The HOMO-9 of **3.9Zr**. Zr atom is rendered in sky blue, C atoms are rendered in grey, H atoms are rendered in white. Molecular orbital occupancy: Zr d_{yz} 7.5 %; C(4) s 4.7 %; C(3) p_z 3.9 %; C(16) p_z 11.9 %; C(19) p_z 13.2 %; C(20) p_z 3.4 %. Isosurface limits: ± 0.040 .

The fold angle of $28.8(3)^\circ$, lies between the two other examples containing σ -bound ligands, **3.7_{Zr}** and **3.8_{Zr}** [average of 30.7° and $27.9(2)^\circ$ respectively]. This can be attributed partially to steric considerations, with the tri-substituted Ph (**3.8_{Zr}**) having a much greater steric bulk than a bis-substituted benzyl (**3.9_{Zr}**), which in turn has a greater steric bulk than $\text{ZrPn}^*(\mu\text{-CH}_2)(\mu\text{-Me}_2)$ (**3.7_{Zr}**). There is also a significant difference in the $\text{M-Pn}^*_{\text{cent.}}$ distances within **3.9_{Zr}**. This maybe due to the difference in binding modes of the two benzyl units. The η^3 bound benzyl must align the p -orbital of the near-side *ortho* carbon (C24) with the d -orbitals of the metal centre, this in turn increases the steric clash with the Pn^* WT- and NWT-Me on this side (C13/C14) thus pushing this side of the Pn^* out. The other benzyl does not have such orbital overlap and is therefore able to angle the aromatic ring away from the Pn^* ligand and therefore does not cause as much of a steric clash.

3.6.6.2 Single crystal X-ray diffraction studies of **3.9_{Hf}**

Interestingly during the synthesis of **3.9_{Hf}** an intermediate crystallised upon addition of 1,4-dioxane. Single crystal X-ray analysis identified this as $[\text{HfPn}^*\text{CH}_2\text{Ph}_3]^- [\text{Li}(1,4\text{-dioxane})_4]^+$ (**3.9_{aHf}**). **3.9_{Hf}** crystallised in the Cc space group with a single molecule in the asymmetric unit of the unit cell. This species involves an triply alkylated ‘ MPn^* ’ anionic metal fragment and a lithium counter-ion coordinated by four 1,4-dioxane molecules. Unlike **3.8_{Zr}** there appears to be no interaction between the anion and cation within the crystal structure and on application of vacuum the 1,4-dioxane was removed, subsequently precipitating LiCH_2Ph and forming **3.9_{Hf}** (demonstrated by ^1H NMR and ^7Li NMR). A model of the anion of **3.9_{aHf}** is shown in figure 3.21 and the pertinent structural parameters are summarised in table 3.16.

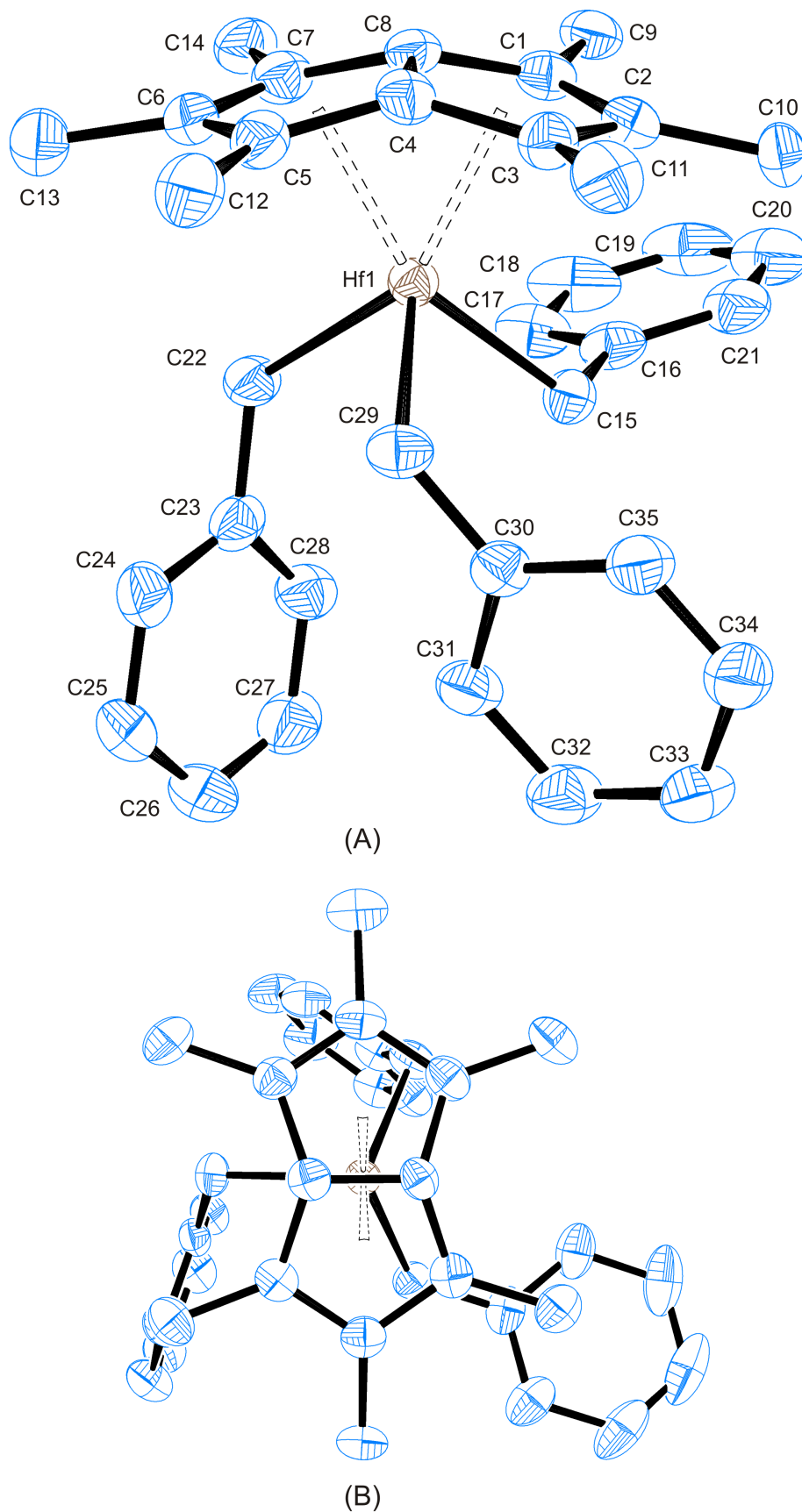


Figure 3.21: The single crystal X-ray structure of **3.9a_{Hf}**, both (A) side view and (B) top down view. Thermal ellipsoids at 50 % probability, H-atoms and counter-ion: [Li(1,4-dioxane)₄]⁺ omitted for clarity.

Table 3.16: Selected structural parameters for **3.9a_{Hf}**

Bond lengths Å			
Hf-C(1)	2.477(6)	Hf-C(15)	2.322(5)
Hf-C(2)	2.719(6)	Hf-C(16)	3.332(7)
Hf-C(3)	2.619(6)	Hf-C(22)	2.343(5)
Hf-C(4)	2.309(5)	Hf-C(23)	3.377(6)
Hf-C(5)	2.631(6)	Hf-C(29)	2.325(5)
Hf-C(6)	2.737(6)	Hf-C(30)	3.262(5)
Hf-C(7)	2.474(6)		
Hf-C(8)	2.267(6)	Hf-Pn* _{cent.}	2.164(3)
Av. C _{ring} -Me	1.504(8)	Hf-Pn* _{cent.}	2.173(3)
Bond angles °			
Fold Angle	24.7(6)	Hf(1)-C(15)-C(16)	121.4(4)
Hf(1)-C(22)-C(23)	122.6(4)	Hf(1)-C(29)-C(30)	117.1(4)
δ values [C(15)-C(21)] Å			
Ipsa	1.010(7)	Para	3.517(7)
Ortho (short)	1.567(7)	Ortho (long)	2.019(7)
Meta (short)	1.806(7)	Meta (long)	3.168(7)
δ values [C(22)-C(28)] Å			
Ipsa	1.034(7)	Para	3.560(7)
Ortho (short)	1.831(7)	Ortho (long)	1.840(7)
Meta (short)	3.054(7)	Meta (long)	3.047(7)
δ values [C(29)-C(35)] Å			
Ipsa	0.937(5)	Para	3.414(7)
Ortho (short)	1.696(7)	Ortho (long)	1.735(7)
Meta (short)	2.876(7)	Meta (long)	2.910(7)

The geometry about the Hf centre is approximately square-pyramidal with the two Pn*_{cent.}, C(22) and C(15) making up the square base. Of the three benzyl ligands two are aligned perpendicular to the Pn* ligand [C(22)-C(28) and C(29)-C(35)] and one

is lying parallel to it [C(15)-C(21)], which appears to be the result of crystal packing forces. It is clear by inspection of the bond angles at the CH₂ carbons (Hf-CH₂-Ph) that all three ligands are bound in an η^1 -fashion, something that is also confirmed by Parkin's δ parameters, all of which are over 0.5 Å (indeed all but one are over 1 Å). The Hf-C(15)/Hf-C(22)/Hf-C(29) bond lengths are all comparable to the Zr-C(15) lengths, however all the *ipso* carbons are further away. The Hf-CH₂ distances are approximately 0.05 Å longer than those seen for the related benzyl compounds HfCp₂(CH₂Ph)₂ [average = 2.293(7) Å]⁷⁴ and HfCp*(CH₂Ph)₃ [average = 2.26(3) Å],⁷⁵ presumably due to the anionic nature of this moiety.

Comparing the Pn* ligand of **3.9_{Hf}** to **3.9_{Zr}** we see a considerable increase in the M-Pn*_{cent.} distance in **3.9_{Hf}** (average distance 2.169 Å for **3.9_{Hf}** compared with 2.108 Å in **3.9_{Zr}**) and also a considerable flattening of the ligand [fold angle = 24.7(6)° for **3.9_{Hf}** compared with 28.8(3)° for **3.9_{Zr}**]. This difference is attributed both electronic factors; with **3.9_{Hf}** being anionic complex it would be expected that the ligands would be pushed further out, and also due to steric considerations, with **3.9_{Hf}** being triply alkylated whereas **3.9_{Zr}** is merely doubly alkylated.

3.6.6.3 NMR characterisation of **3.9**

Upon work-up and application of vacuum **3.9_{Hf}** loses 1,4-dioxane and subsequently precipitates LiCH₂Ph to form an analogous species with **3.9_{Zr}** (from careful inspection of the integrals in the ¹H NMR spectrum). Both congeners of **3.9** exhibit C_{2v} symmetry in solution, with six resonances in the ¹H NMR of 4:2:4:12:6:4 integral ratio, with the three lowest downfield lying in the aromatic region (δ = 6-7 ppm), and the three upfield lying in the aliphatic region (δ = 1-2 ppm). The ¹³C NMR possesses the 10 expected resonances, 5 for Pn* and 5 for the benzyl ligand. The VT-NMR spectra display little change in line shape - it is not wholly unexpected that it was not possible to freeze out the two different binding modes of the benzyl ligands, as facile exchange would be expected to take place. Latesky and co-workers noted that by inspection of the coupling constant of the α -CH₂ group and the chemical shift of the *ortho* protons one could probe the binding situation of the benzyl ligand, the corresponding data for compounds **3.9_M**

(M = Zr and Hf) are summarised in table 3.17.⁷⁶ In cases where there are significant π interaction between the benzyl ligand and the metal centre the chemical shift of the *ortho* protons migrates upfield and the $^1J_{(C-H)}$ increases. Both these effects are clearly seen in **3.9_{Zr}** where $\delta = 6.06$ ppm and $^1J_{(C-H)} = 135.0$ Hz and as such the proposed $\eta^3:\eta^1$ binding modes are reinforced. Use of Latesky's analysis for **3.9_{Hf}** implies the benzyl ligands to be bound with more η^1 character than **3.9_{Zr}**. However there is a slight increase in the $^1J_{C-H}$ coupling parameter and the *ortho* chemical shift is slightly upfield compared with species where the benzyl is bound in an explicitly η^1 fashion, therefore it is likely the binding mode lies somewhere in between the η^1 and η^2 modes.

Table 3.17: The 1H and ^{13}C NMR chemical shifts of the phenyl *ortho* nuclei and the $^1J_{C-H}$ of the CH_2 groups of **3.9_M** (M = Zr or Hf).

Species	δ (ppm) (1H)	δ (ppm) (^{13}C)	$^1J_{C-H}$ (Hz) (CH_2)
3.9_{Zr}	6.06	122.5	135.0
3.9_{Hf}	6.50	124.0	129.0

3.6.6.4 Other characterisation of **3.9**

Similarly to the other σ -bound ligand species synthesised in this chapter neither of the **3.9** species appear in EI-MS, with the only relevant signals seen being those belonging to Pn^* fragmentation.

3.7 Concluding remarks

A total of 20 novel group 4 species have been synthesised and characterised. Amongst them have been the important 'MPn*' synthons **3.1_{Zr}** and **3.1_{Hf}** which have subsequently been used to synthesise a number of mixed sandwich species (**3.2** - **3.4**), bis-allyl species (**3.5**) and three species involving a M-C σ -bond (**3.7** - **3.9**). Furthermore, the homoleptic sandwiches have been structurally characterised allowing a fascinating comparison with previous theoretical work and showing the effect of the increase crystallisability of the Pn^* ligand. The compounds synthesised in good yield will be tested for their ability to polymerise α -olefins in chapter four.

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4. POLYMERISATION STUDIES OF SYNTHESISED COMPLEXES

4.1 *Introduction*

4.1.1 *Polyolefins in industry and society*

Polyolefinic materials dominate the polymerisation industry with polypropylene (PP) and polyethylene (PE) forming the core.¹ PE has an extremely wide range of uses from artificial joints to adhesives, from petroleum additives to plastic bags. The reason for the pervasive nature of PE is its broad range of physical properties and its chemical stability. Indeed the latter has now become an issue with polyethylene forming a large proportion of waste going to landfill and not being readily biodegradable. Because of the broad range of usage, PE and PP have become the main tonnage of the polyolefin industry sector, with 72 million tonnes of PE and 48 million tonnes of PP produced globally (in 2010).

4.1.2 *The development of polyolefin catalysts*

Until the second half of the 20th-century, synthesis of polyolefins required extremely high temperatures and pressures but the 1950s saw the development of two, separate, catalytic systems. The first, discovered in 1951, was the Phillips catalyst (based on a chromium trioxide system); four years later, Ziegler and Natta separately developed a catalyst based on titanium halide/organoaluminium compounds, which worked under even milder conditions than the Phillips catalyst.²⁻⁵ Heterogenous titanium-based Ziegler-Natta catalysts have many advantages, polymerising propylene with a high degree of stereoselectivity and also able to co-polymerise ethylene with α -olefins. There are, however, drawbacks to heterogenous catalysis. Namely that polymerisation takes place at edges on TiCl_3 crystals and therefore many different types of active sites are present. This results in a broad molecular weight distribution.

Two years after the report of the synthesis of TiCp_2Br_2 and ZrCp_2Br_2 , group four metallocenes were investigated as potential polymerisation catalysts.⁶ The Natta and Breslow groups reported that titanocene dichloride (TiCp_2Cl_2) could be a catalyst for the polymerisation of ethylene using AlEt_3 or AlEt_3Cl as a co-catalyst, but they were slow and could not polymerise propylene.⁷⁻⁹ However, a fortuitous discovery was that a small amount of water added to the reaction mixture resulted in a tremendous increase in activity.¹⁰⁻¹² This led Sinn and co-workers to propose that replacing the aluminium-alkyl co-catalyst with the partially hydrolysed product methylaluminoxane (MAO) would improve activity.¹³ This breakthrough led to the burgeoning development of metallocene-based homogeneous catalysts through the 1980s and beyond.

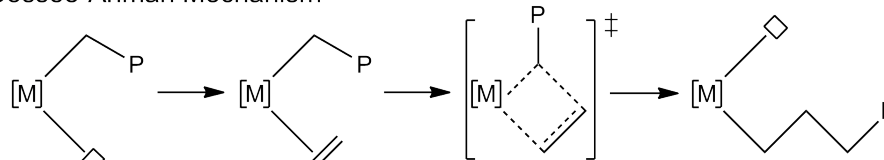
4.1.3 The mechanism of polymerisation catalysis

It was in 1964 that Cossee and Arlman proposed the first mechanism for olefin polymerisation by a titanium centre (figure 4.1).^{14;15} In their mechanism ethylene binds to a vacant co-ordination site on the metal centre. The metal binds to the π bonding-orbital and the π^* antibonding-orbital of the ethylene with the $d_{x^2-y^2}$ and the d_{yz} orbitals respectively [bonding first seen in Zeise's salt ($\text{C}_2\text{H}_4\text{PtCl}_3$)⁻].¹⁶ This is followed by migratory insertion of the olefin into the M-C alkyl bond to grow the polymer chain by two carbons and regenerate the vacant site.

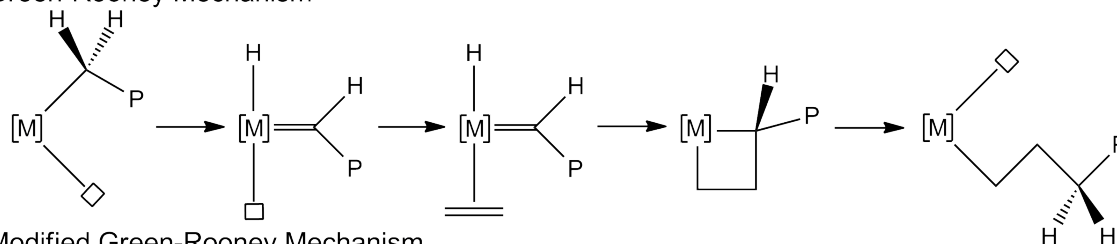
In 1978, a second mechanism was suggested by Green and Rooney proposing an alkylidene intermediate.^{17;18} In this mechanism the initial step is that of hydride migration from the alkyl chain to the metal centre to form the alkylidene species and a vacant site. The olefin binds on to this species and subsequently a metallo-cyclobutane complex is formed, which then reductively eliminates to grow the polymer chain by two and recreate the active centre. However, group four metallocenes, having no d electrons, are unable to undergo the oxidative addition required by the Green-Rooney mechanism.

Two intermediate mechanisms have also been proposed, both involving α -agostic interactions. The first, shown in figure 4.1, an adaptation of the Green-Rooney mechanism, posits the formation of an agostic interaction to stabilise the metal centre, which subsequently binds to an olefin, which then inserts into the M-C bond. The latter sug-

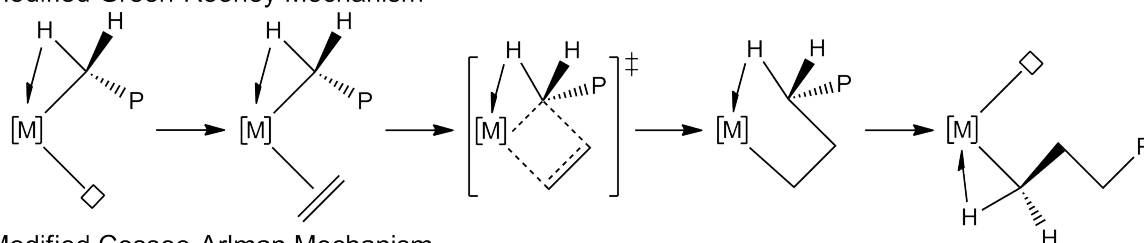
Cossee-Arman Mechanism



Green-Rooney Mechanism



Modified Green-Rooney Mechanism



Modified Cossee-Arman Mechanism

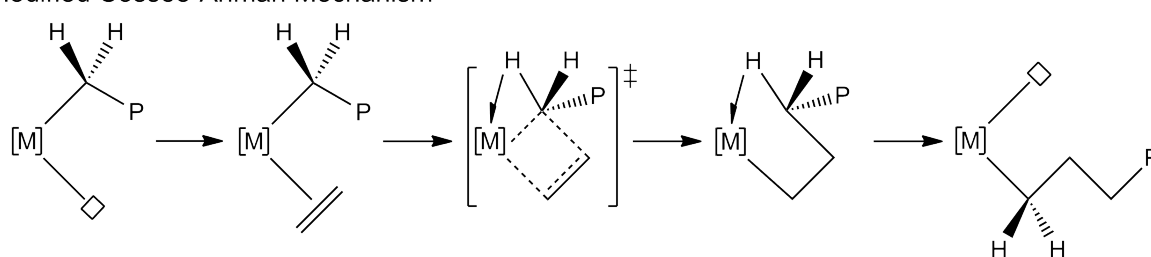
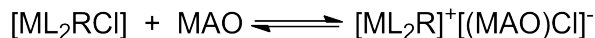


Figure 4.1: The four mechanisms for the polymerisation of ethylene.

gests olefin coordination happening first. The role of α -agostic interactions in Ziegler-Natta olefin polymerisation has been reviewed and have been shown to affect the rate and stereospecificity in catalytic systems where insertion of the olefin into the M-C bond is the rate limiting step.¹⁹

4.1.4 The role of MAO as the co-catalyst

All the mechanisms above have the pre-requisite of both a vacant binding site on the metal centre (for the olefin to bind to) and an alkyl chain (into which the olefin can insert). These two roles are both (usually) fulfilled by a co-catalyst (or activator). The most ubiquitous of these is MAO, the partial hydrolysis product of AlMe_3 . The exact constitution of MAO is unknown but it is believed to be of the general formula $[\text{Al}(\text{Me})\text{O}]_n$ and is thought to be made up of a mixture of linear and cyclic oligomers.²⁰ MAO is usually used with a dichloride system and fulfils a number of roles: firstly,



Scheme 4.1: The equilibrium in which MAO reacts with the pre-catalyst to form the active catalytic species. Addition of a large excess of MAO forces this equilibrium towards the right hand side.

it alkylates the metal centre, it then abstracts either the halide or the alkyl from the metal centre to activate the complex, and thirdly it acts as a scavenger of any impurities within the system.²¹ It is used in massive excess (*circa* 1000:1) to push any activation equilibria towards completion, making the catalyst as efficient as possible (scheme 4.1)

Use of such an excess of MAO has a number of drawbacks. Firstly, it is expensive. Secondly, MAO solutions usually contain a large amount of AlMe_3 , which has been shown to deactivate catalysts. Thirdly, the unclear chemical nature of MAO has hampered mechanistic investigations. Because of this a vast body of research has been undertaken in the search for different co-catalysts.²²

4.1.5 Measuring the performance of a catalyst

The ability of a complex to catalyse olefin polymerisation is called the activity of the complex. This parameter is a figure based on the mass of polymer produced, the amount of catalyst used, the time taken for the reaction, and the pressure of ethylene. It is commonly measured in the unit $\text{kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$. The activity of a complex is often classed by the Gibson scale (see table 4.1).²³

It should be noted that a catalyst cannot be judged on activity alone. Activity does not take into account temperature, concentration, stirring rate or the experimental set-up - all of which can have a profound effect on the yield of polymer. Furthermore,

Table 4.1: The categories of polymer ability by the Gibson scale.²³

Rating	Activity ($\text{kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$)
very low	< 1
low	1 - 10
moderate	10 - 100
high	100 - 1000
very high	> 1000

activity makes no judgement on the quality of the polymer produced in terms of molecular weight distribution - for this further analysis is required (high temperature GPC).

4.2 Initial polymerisation testing

4.2.1 Testing at 1 mg catalyst loading

Initially, all the compounds synthesised in this project, with the exception of the homoleptic sandwiches: MPn^*_2 ($\text{M} = \text{Zr}, \text{Hf}$) (due to lack of a pure sample), were tested for their ability to polymerise ethylene. Table 4.2 recalls the various chemical formulae for reference. All were subjected to an ethylene pressure of 2 bar, in 50 ml of hexane at 80 °C for one hour, with 1000 equivalents of MAO for 1 equivalent of complex ($[\text{MAO}]_0/[\text{M}]_0 = 1000$). The results are presented in table 4.3 and figure 4.2.

Table 4.2: Reference for chemical formulae of species (for $3.\text{X}_\text{M}$, $\text{M} = \text{Zr}$ or Hf)

Species	Formula
2.1	UPn^*_2
2.2	$[\text{UPn}^*(\mu\text{-Cl})_4]_2[\text{Li} \cdot \text{TMEDA}]$
2.3	$[\text{UPn}^*\text{Cp}^*(\mu\text{-Cl})_2][\text{Li} \cdot \text{TMEDA}]$
2.4	$[\text{UPn}^*\text{Cp}(\mu\text{-Cl})_2][\text{Li} \cdot \text{TMEDA}]$
2.5	UPn^*Cp_2
3.1_M	$[\text{MPn}^*(\mu\text{-Cl})_{3/2}]_2(\mu\text{-Cl})_2\text{Li} \cdot \text{THF}_x$
3.2_M	MPn^*CpCl
3.3_M	MPn^*Cp_2
3.4_M	$\text{MPn}^*\text{Cp}^*\text{Cl}$
3.5_M	$\text{MPn}^*(\text{C}_3\text{H}_5)_2$
3.7_{Zr}	$(\text{ZrPn}^*)_2(\mu\text{-Me})_2(\mu\text{-CH}_2)$
3.8_M	$\{\text{MPn}^*\text{Ph}(\mu\text{-Ph})_2[\text{Li} \cdot (\mu\text{-1,4-dioxane})]\}_n$
3.9_M	$\text{MPn}^*\text{CH}_2\text{Ph}$

Table 4.3: Polymerisation results of all compounds tested. Conditions employed: 80 °C, 1 hour, 2 bar ethylene, $[\text{MAO}]_0/[\text{M}]_0 = 1000$. * indicates stirring seized prematurely.

Species	Cat. used (μmol)	Yield (g)		Average Activity ($\text{kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$)
		run 1	run 2	
2.1	1.64	0.151	0.137	44.1
2.2	1.23	0.101	0.129	46.5
2.3	1.33	0.114	0.068	34.2
2.4	1.47	0.109	0.099	35.4
2.5	1.80	0.123	0.121	34.0
3.1_{Zr}	1.24	0.221	0.196	84.2
3.1_{Hf}	0.99	0.104	0.135	60.0
3.2_{Zr} *	2.66	1.061	1.120	944.9
3.2_{Hf} *	2.15	1.342	2.170	558.3
3.3_{Zr} *	2.46	1.507	2.148	803.1
3.3_{Hf}	2.02	1.630	1.809	426.6
3.4_{Zr}	2.24	0.617	0.787	156.5
3.4_{Hf}	1.87	0.358	0.226	78.3
3.5_{Zr}	2.79	0.289	0.334	55.8
3.5_{Hf}	2.23	0.240	0.249	54.8
3.7_{Zr}	1.68	1.116	0.900	300.5
3.8_{Zr}	1.66	0.218	0.274	74.1
3.8_{Hf}	1.45	0.129	0.128	44.5
3.9_{Zr}	2.18	0.367	0.416	89.7
3.9_{Hf}	1.82	0.188	0.206	57.0

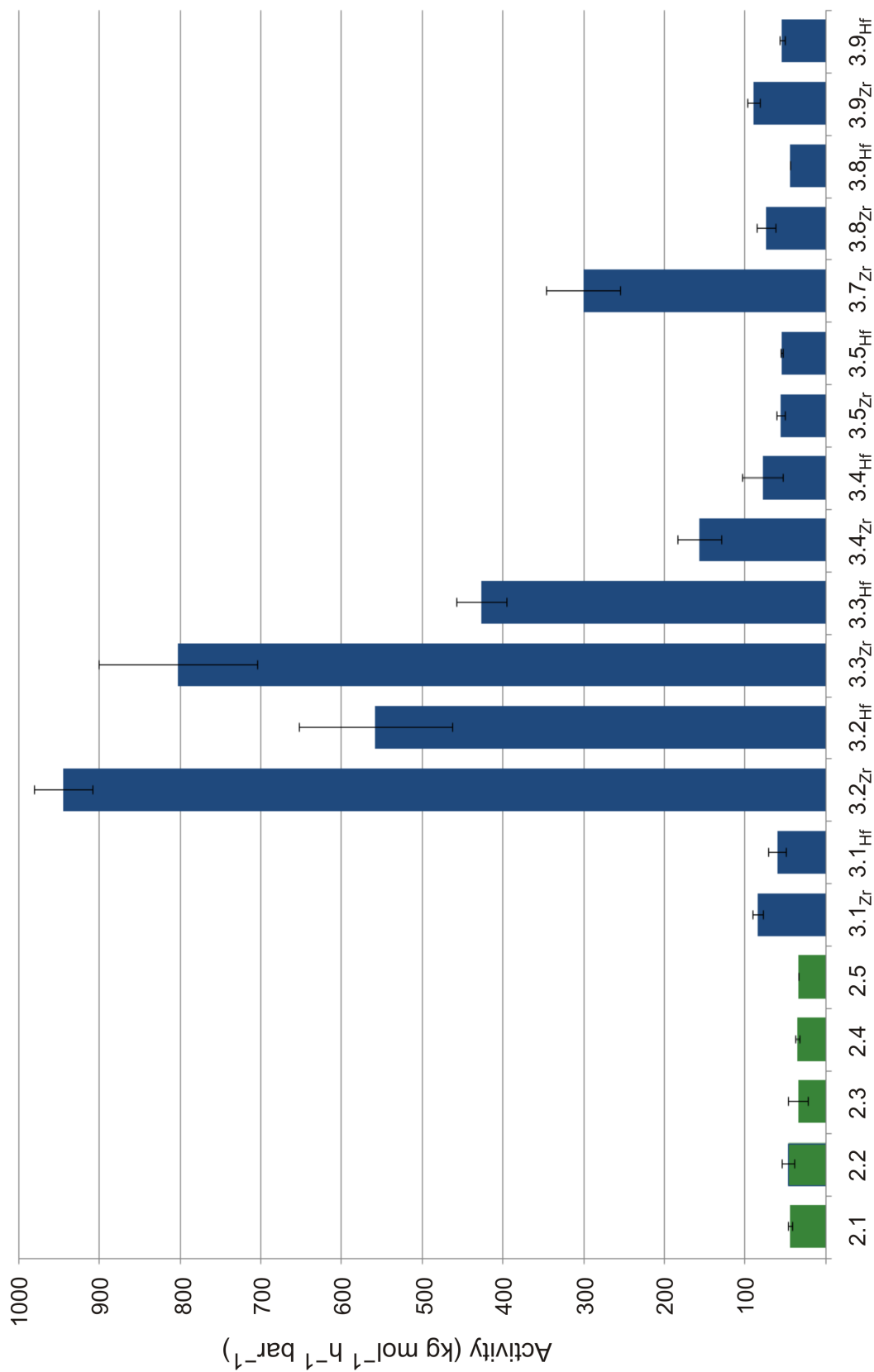


Figure 4.2: The activities of all compounds tested. Green bars are uranium compounds, blue bars are group four compounds. Conditions employed: 1 mg catalyst, 80 °C, $[MAO]_0/[M]_0 = 1000$. Samples of **3.2** and **3.3** seized prematurely (*vide infra*).

A number of trends are in the data presented above. Firstly, all the compounds have a moderate to high ability to catalyse the polymerisation of ethylene. Also, all the uranium-based catalysts (**2.1-2.5**) are worse than any of the group four catalysts. Indeed between the two most chemically comparable species: **2.5** and **3.3_M** the former has an activity of $34 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ whereas the two congeners of the latter species have activities of $803 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ and $426 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ (for Zr and Hf respectively).

Within the group four species there are again some trends. Firstly, the hafnium congener always produced lower amounts of ethylene and (despite the higher molecular weight) always had a lower activity. This is a well documented phenomenon within group four catalysts.²⁴⁻²⁶ Secondly, there is a clear group of catalysts which display considerably higher activity than any other, specifically those containing the MPn*Cp or MPn*Cp* motifs. These species all display high catalytic activity on the Gibson scale, with both congeners of **3.2** and **3.3_{Zr}** being so active that the stirring of the reaction vessel seized before an hour could be completed. The effect of permethylation of the Cp ring can be seen by comparing the activities of **3.2_M** and **3.4_M** ($944 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ and $157 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ for the Zr congener, 558 and $78 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ for the Hf congener). The proposed reason for this is the increased steric bulk around the metal centre of the catalyst results in hindered approach of the ethylene.²⁷

4.2.2 Testing at 0.1 mg catalyst loading

Because of the amount of polyethylene produced by **3.2** and **3.3** it was found that at 1 mg loading the reaction mixture could not be stirred effectively for an hour. Because of this, the measurement of activity of these two species cannot be considered reliable. It was therefore decided therefore to lower the catalytic loading to 0.1 mg. The MAO was kept at 1000 molar equivalents, and all other conditions were kept the same (*i.e.* 2 bar pressure of ethylene, 80 °C, 50 ml hexane as solvent). The results for these experiments are presented in table 4.4 and figure 4.3.

Table 4.4: Polymerisation results for **3.2** and **3.3** with 0.1 mg catalyst loading, $[\text{MAO}]_0/[\text{M}]_0 = 1000$, 80 °C, 2 bar ethylene, 1 hour reaction time.

Species	Cat. used (μmol)	Yield (g)		Average Activity ($\text{kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$)
		run 1	run 2	
3.2_{Zr}	0.27	2.366	2.076	4176
3.2_{Hf}	0.22	0.391	0.475	1009
3.3_{Zr}	0.25	2.020	2.111	4194
3.3_{Hf}	0.20	0.109	0.900	247

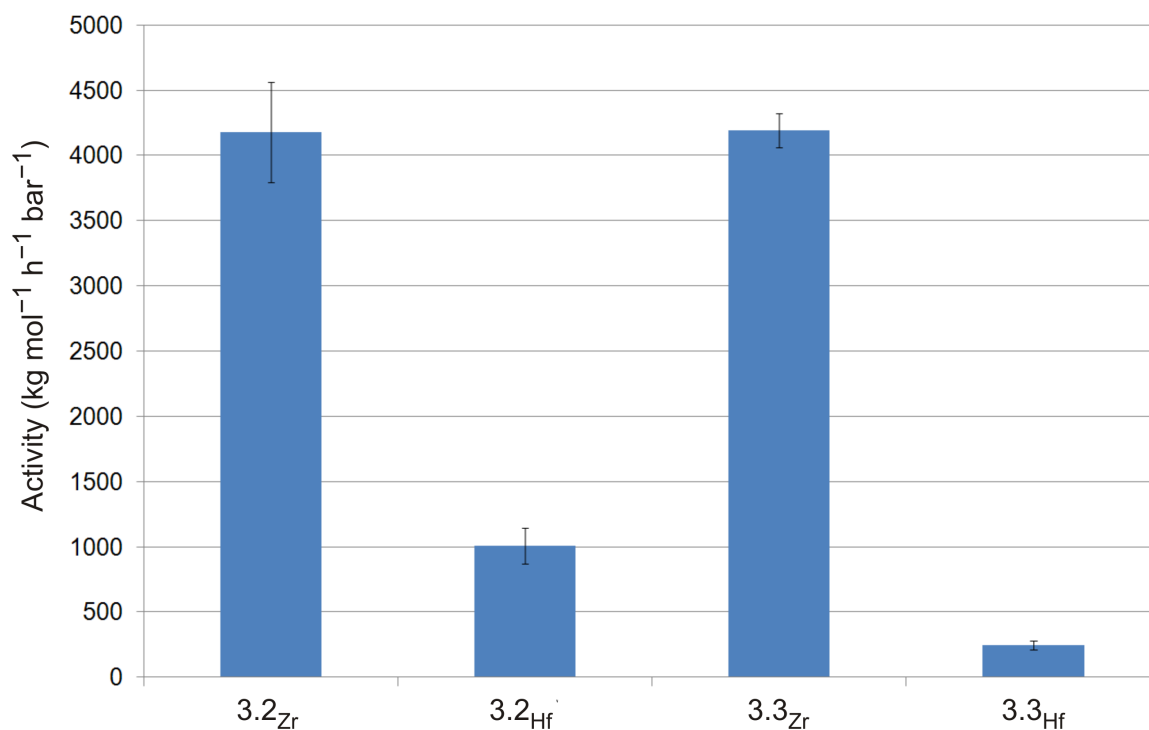


Figure 4.3: The activities of **3.2** and **3.3**. Conditions employed: 0.1 mg catalyst, $[\text{MAO}]_0/[\text{M}]_0 = 1000$, 80 °C, 2 bar ethylene, 1 hour reaction time.

Even with 0.1 mg loading of catalyst, the two zirconium congeners of **3.2** and **3.3** could not be stirred effectively for the entire hour with polyethylene aggregating on the magnetic follower. However, this issue was not as pronounced as with 1 mg loading, where stirring seized after just 13 minutes, and thus more accurate results were obtained.

From this round of testing it has been shown that **3.2_{Zr}**, **3.2_{Hf}** and **3.3_{Zr}** are all very highly active polymerisation catalysts (respective activities = 4176, 1009 and 4194 $\text{kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$) and **3.3_{Hf}** has high activity (247 $\text{kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$). The two zirconium congeners are approximately four times as effective as the highly active

hafnium species, and therefore small scale optimisation was carried out for these two species.

4.2.3 Altering the co-catalyst species and co-catalyst loading

The stirring problems encountered for **3.2_{Zr}** and **3.3_{Zr}** may arise from the co-catalyst that was being used (MAO). This may be addressed in several ways: firstly, by lowering the MAO to catalyst ratio, secondly, by using a different co-catalyst and thirdly, by supporting the co-catalyst on a solid (e.g. silica). Due to time constraints, this last option was not explored. Use of TIBA (tri-isobutylaluminium) instead of MAO (with $[\text{TIBA}]_0/[\text{M}]_0 = 1000$) was also investigated but yielded no polyethylene after one hour. Therefore, the polymerisation was repeated using $[\text{MAO}]_0/[\text{M}]_0 = 300$. The results are summarised in table 4.5 and figure 4.4.

Table 4.5: Polymerisation results for **3.2_{Zr}** and **3.3_{Zr}** with 0.1 mg catalyst loading, 80 °C, 2 bar ethylene, 1 hour reaction time, various MAO ratios.

Species	$[\text{MAO}]_0/[\text{M}]_0$	Yield (g)		Average activity ($\text{kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$)
		run 1	run 2	
3.2_{Zr}	1000	2.366	2.076	4176
3.2_{Zr}	300	1.143	1.548	2530
3.3_{Zr}	1000	2.020	2.111	4194
3.3_{Zr}	300	1.746	1.131	2921

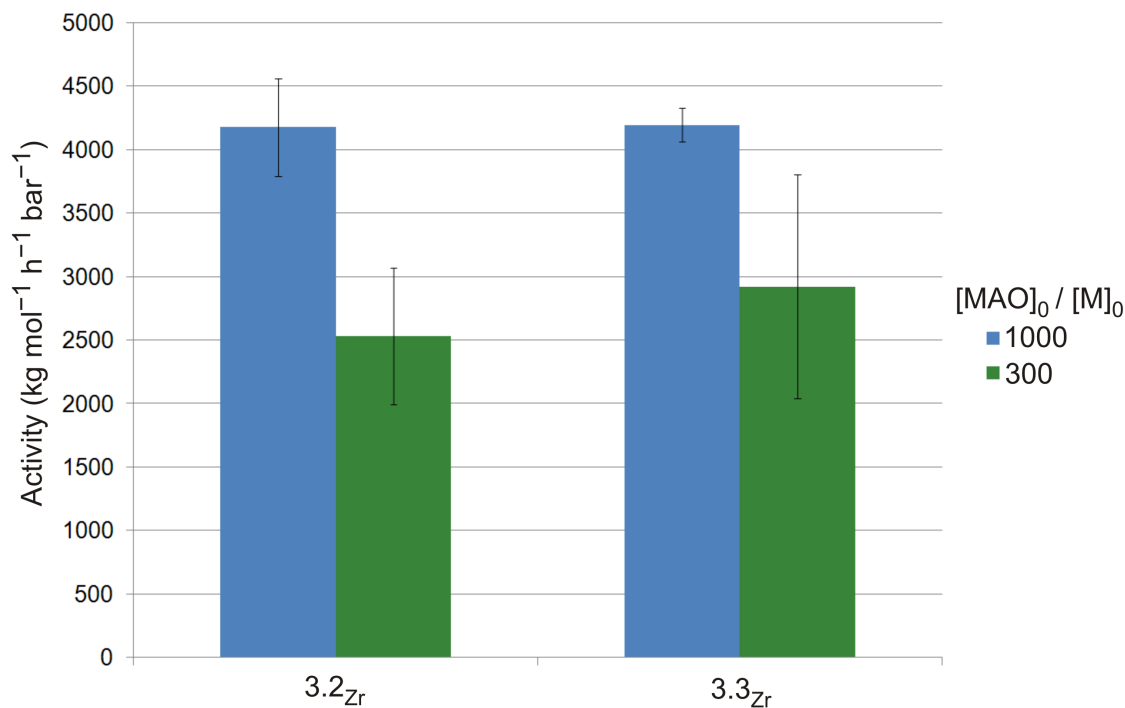


Figure 4.4: The activities of **3.2_{Zr}** and **3.3_{Zr}** with $[\text{MAO}]_0/[\text{M}]_0 = 1000$ or 300 . Other conditions employed: 0.1 mg catalyst, 80 °C, 1 hour reaction time, 2 bar ethylene.

As expected use of a lower MAO to catalyst ratio caused a drop in activity from 4176 to 2530 kg mol⁻¹ h⁻¹ bar⁻¹ for **3.2_{Zr}** and from 4194 to 2921 kg mol⁻¹ h⁻¹ bar⁻¹ for the hafnium congener. This has been attributed to both a lower amount of co-catalyst being available to scavenge impurities, and also less MAO resulting in the equilibrium in scheme 4.1 lying further to the left with more pre-catalyst and less active catalyst in the reaction mixture. Despite the lower ratio, polymer still aggregated around the magnetic follower and caused stirring to be problematic. Because of this, it was decided that use of 1000 equivalents of MAO would be employed for further tests.

4.2.4 Altering the time of polymerisation

The activity of metallocene based catalysts shows a peak in their activity/time profiles towards the beginning of the polymerisation process before settling to a constant activity.²⁷ The reason for this is that the catalyst is only truly homogeneous on the initial introduction of ethylene. As polymer is produced and precipitates rapidly the active complex gets embedded in a polymer matrix making it effectively a heterogeneous catalyst and leading to diffusion-controlled polymerisation. It was therefore decided to

investigate how the duration of polymerisation affected the activity of **3.2_{Zr}** and **3.3_{Zr}**.

The results of these experiments are summarised in table 4.6 and figure 4.5.

Table 4.6: Polymerisation results for **3.2_{Zr}** and **3.3_{Zr}** with 0.1 mg catalyst loading, $[\text{MAO}]_0/[\text{M}]_0 = 1000$, 80 °C, 2 bar ethylene over different time frames.

Species	Time (mins)	Yield (g)		Average activity (kg mol ⁻¹ h ⁻¹ bar ⁻¹)
		run 1	run 2	
3.2_{Zr}	15	0.622	0.555	4426
3.2_{Zr}	30	1.188	1.017	4146
3.2_{Zr}	60	2.076	2.366	4176
3.3_{Zr}	15	0.912	0.810	6993
3.3_{Zr}	30	1.462	1.469	5952
3.3_{Zr}	60	2.111	2.020	4101

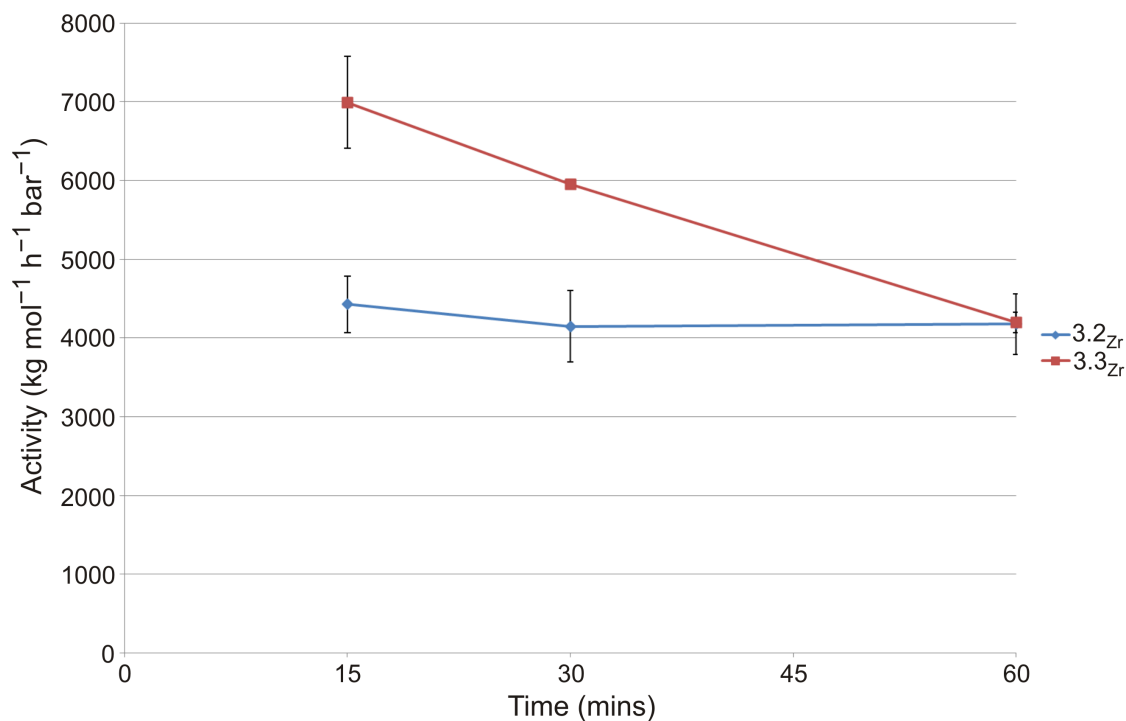


Figure 4.5: The activities of **3.2_{Zr}** and **3.3_{Zr}** over time. Other conditions employed: 0.1 mg catalyst, 80 °C, 2 bar ethylene, $[\text{MAO}]_0/[\text{M}]_0 = 1000$.

From figure 4.5 it is clear that by 15 minutes it appears that **3.2_{Zr}** is over its peak in activity and has approximately settled to the diffusion controlled limit. For **3.3_{Zr}** it takes an hour to reach the diffusion controlled limit. Both **3.2_{Zr}** and **3.3_{Zr}** have the same activity at the diffusion controlled limit since the rate limiting step does not

involve the electronic or steric effects of the catalyst but rather the transfer of the monomer unit through the polymer matrix. It was noted that effective stirring could not be reliably employed beyond 30 minutes and therefore for investigations into the effect of temperature on activity polymerisation experiments were limited to 30 minutes.

4.2.5 *Altering the temperature of polymerisation*

Altering the temperature of the polymerisation has two effects: it has a drastic influence on the molecular weight of the polymer and also affects the polymerisation ability of the catalyst. Due to the absence of high temperature GPC facilities, analysis of the polymer's molecular weight and molecular weight distribution was not possible, although it is expected that lower polymerisation temperatures would result in a high molecular weight polymer due to a lower rate of chain transfer.²⁶ An investigation into the relationship between catalytic activity and temperature was possible however.

The manner in which the activity is affected by temperature depends on a competition between the propagation and deactivation mechanisms at work. Optimum temperature is reached when the catalyst shows increased rates of propagation with relatively low rates of deactivation. Decreasing the temperature below the optimum results in a retardation of both propagation and deactivation and increasing the temperature above results in an increase in the deactivation resulting in lower activities in both cases. Polymerisation experiments were therefore undertaken between 40 °C and 100 °C at 20 °C increments. The results are presented in table 4.7 and figure 4.6.

Table 4.7: Polymerisation results for **3.2_{Zr}** and **3.3_{Zr}** with 0.1 mg catalyst loading, 30 min polymerisation time, 1000 equivalents of MAO over different temperatures.

Species	Temperature (°C)	Yield (g)		Activity (kg mol ⁻¹ h ⁻¹ bar ⁻¹)
		run 1	run 2	
3.2_{Zr}	40	0.873	0.605	2779
3.2_{Zr}	60	1.013	1.222	4202
3.2_{Zr}	80	1.188	1.017	4146
3.2_{Zr}	100	0.538	0.702	2332
3.3_{Zr}	40	0.916	1.071	4035
3.3_{Zr}	60	0.883	1.057	3939
3.3_{Zr}	80	1.462	1.469	5952
3.3_{Zr}	100	0.729	0.800	3105

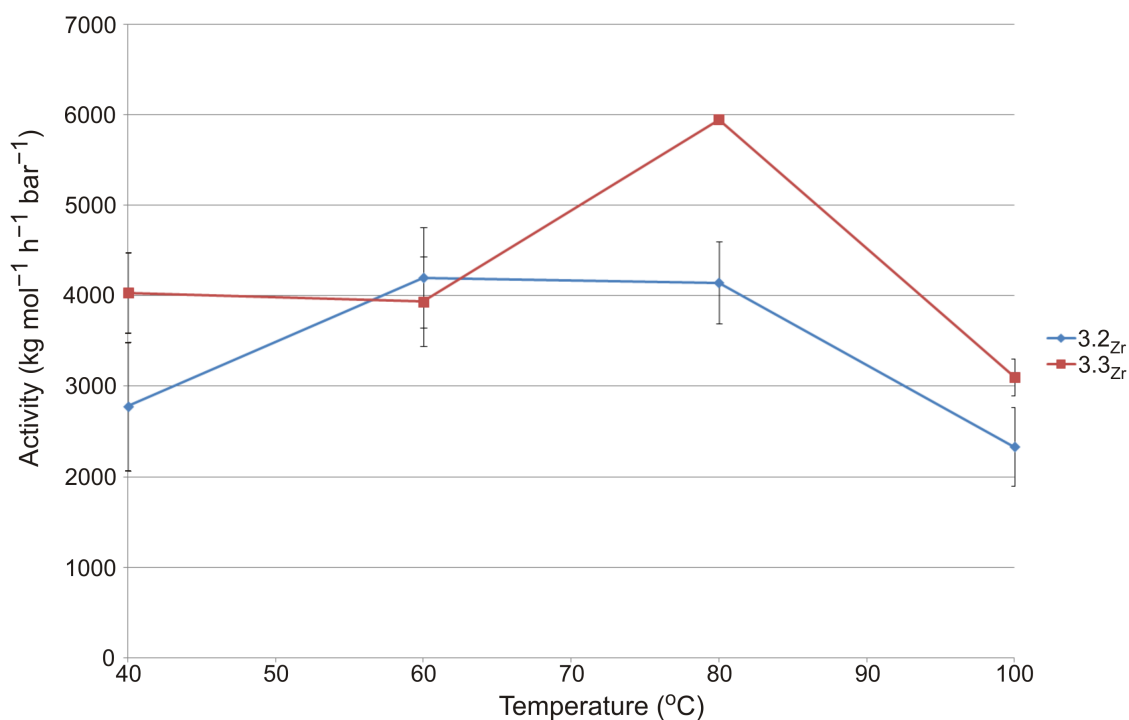


Figure 4.6: The activities of **3.2_{Zr}** and **3.3_{Zr}** at various temperatures. Other conditions employed: 0.1 mg catalyst, 30 minutes reaction time, 1000 equivalents MAO, 2 bar ethylene.

Even at only slightly elevated (40 °C) temperatures, both **3.2_{Zr}** and **3.3_{Zr}** still retain very high catalytic activity. **3.2_{Zr}** displays a significant drop in activity below 60 °C and **3.3_{Zr}** shows a considerable increase in activity at 80 °C. It is therefore proposed that the optimum temperature for **3.2_{Zr}** is approximately 70 °C whereas **3.3_{Zr}** has a

higher optimum temperature at 80 °C. Above these temperatures we see a sharp drop off in the activity of the complexes, as is expected as the rate of deactivation increases.

4.3 Concluding Remarks

The majority of the compounds synthesised in this project have been tested for their ability to polymerise ethylene in the solution phase, with most showing moderate or high activities according to the Gibson scale. However, ZrPn^{*}CpCl (**3.2_{Zr}**), HfPn^{*}CpCl (**3.2_{Hf}**) and ZrPn^{*}Cp₂ (**3.3_{Zr}**) all displayed *very* high catalytic activity with the zirconium species being approximately four times more active than the hafnium species (4176 kg mol⁻¹ h⁻¹ bar⁻¹ *vs.* 1009 kg mol⁻¹ h⁻¹ bar⁻¹). The zirconium species (**3.2_{Zr}** and **3.3_{Zr}**) were therefore used for an initial set of optimisation experiments where their activities at various times and temperatures were tested. These showed the expected drop off in activity over time for both species, however this was slower for **3.3_{Zr}** than **3.2_{Zr}**. The optimum temperatures (in terms of activity) were found to be approximately 70 °C and 80 °C respectively. The experiments were somewhat limited by practical considerations and further experiments in a purpose-built reactor should be undertaken. Nonetheless the initial analysis showed that **3.2_{Zr}** and **3.3_{Zr}** are excellent candidates for further study, both in terms of further optimisation for poly(ethylene) production and investigation into their use in propylene polymerisation.

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5. EXPERIMENTAL

5.1 *General Procedures and Physical Measurements*

5.1.1 *General Procedures*

All reactions were performed under an inert atmosphere of nitrogen or argon either using standard Schlenk techniques on a dual vacuum/inlet gas manifold or by employment of a Braun glove box. All glassware was heated in an oven at 180 °C for at least four hours prior to use.

Pentane, hexane, benzene, toluene and dichloromethane were dried and degassed using an MBraun SPS-800 solvent purification system and non-chlorinated solvents were stored in potassium mirrored ampoules. THF was distilled from a purple sodium/ benzophenone ketyl indicator and stored under nitrogen in oven-dried ampoules. Diethyl ether was distilled from a Na/K still which had been refluxing for at least five days and stored in potassium mirrored ampoules. All other solvents were dried over appropriate drying agents: 3 Å molecular sieves (TMEDA, 1,4-dioxane, pyridine), potassium (heptane) and stored over a potassium mirror where appropriate (1,4-dioxane and heptane).

Deuterated NMR solvents were purchased from Goss Scientific and were dried over the appropriate drying agent and freeze-thaw degassed three times: potassium (d^6 -benzene, d^8 -toluene), calcium hydride (d^8 -THF) and molecular sieves (d^1 -chloroform, d^2 -dichloromethane-, d^5 -pyridine).

Radioactive compounds were only handled in designated radiation supervised areas and a Mini Instruments Mini Monitor Series 900 Geiger-Muller counter was used to check for contamination. All contaminated glassware was cleaned with nitric acid and monitored until background levels were reached prior to the usual washing. Contaminated solid waste were disposed of in designated radioactive vessels. Radioactive organic waste was distilled then disposed of via the usual route and radioactive aqueous

waste was disposed of down a designated sink.

5.1.2 Crystal Structure Determination

Crystallographic data and parameters for the single crystal determinations of compounds presented in this thesis yet not included in the main text may be found in the electronic appendix. A typical crystal was mounted on a MiTeGen Micromounts using perfluoropolyether oil and cooled rapidly to 150 K in a stream of nitrogen gas using an Oxford Cryosystems Cryostream unit.¹ Data were collected with an Enraf-Nonius Kappa CCD diffractometer, using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Raw frame data were reduced using the DENZO-SMN package.² Intensity data were corrected using multi-scan method with SCALEPACK (within DENZO-SMN). The structures were solved using direct methods with SIR92³ and refined using full-matrix least squares refinement on all F² data using the CRYSTALS program suite.^{4,5} In general distances and angles were calculated using the full variance-covariance matrix. Dihedral angles were calculated using PLATON.⁶

5.1.3 Density Functional Theory Calculations

All DFT calculations were performed with the ORCA program package.⁷ The geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level of DFT.⁸⁻¹⁰ This hybrid functional often gives better results for transition metal compounds than pure gradient-corrected functionals, especially with regard to metal-ligand covalency.¹¹ For the geometry optimizations the all-electron Gaussian basis sets were those developed by the Ahlrichs group.¹²⁻¹⁴ Triple- ζ quality basis sets def2-TZVP with one set of polarization functions on the metals and on the atoms directly coordinated to the metal center were used. For the carbon and hydrogen atoms, slightly smaller polarized split-valence def2-SV(P) basis sets were used, that were of double- ζ quality in the valence region and contained a polarizing set of d-functions on the non-hydrogen atoms. Auxiliary basis sets were chosen to match the orbital basis.¹⁵⁻¹⁷ The RIJCOSX15 approximation was used to accelerate the calculations.¹⁸⁻²⁰ Orbitals were generated with the program Chimera.²¹

5.1.4 Electrochemistry

Electrochemical experiments were performed by Dr. Gregory Wildgoose of the University of East Anglia. Experiments were performed in dry THF containing 0.1 M [n Bu₄][NBF₄] as the supporting electrolyte using an Autolab PGStat 20 computer-controlled potentiostat (EcoChemie Utrecht, The Netherlands). Cyclic voltammetry experiments were performed using a three-electrode configuration with a Pt macrodisc electrode (99.99 %, Goodfellow, Huntingdon, U.K.) having an area of $(1.7 \pm 0.2) \times 10^{-3} \text{ cm}^2$ as the working electrode, a Pt gauze as the counter electrode, and a Ag wire as the pseudoreference electrode. The pseudoreference electrode was calibrated to the ferrocene/ferrocenium couple in THF, relative to which all of the standard potentials are reported.

5.1.5 Elemental Analysis

Elemental Analyses were carried out by Medac Ltd. for radioactive samples or by Dr. Stephen Boyer of London Metropolitan University for non-radioactive samples.

5.1.6 Infra-Red Spectroscopy

IR spectra were recorded on a Nicolet iS5 ThermoScientific spectrometer (range 4000-400 cm^{-1} , resolution 1 cm^{-1}) as KBr discs. Samples were prepared in the glovebox, mixed and ground with anhydrous KBr, then pressed into discs using an in-house, purpose built press and holder, the spectra were then recorded immediately.

5.1.7 Mass Spectrometry

Electron Impact (EI) and Field Ionisation (FI) mass spectra were recorded by Mr. Colin Sparrow of the Chemistry Research Laboratory, University of Oxford.

5.1.8 Solid State Magnetic Measurements

Solid-state magnetic susceptibility data were obtained using a Quantum Design MPMS-5 SQUID magnetometer. Accurately weighed samples (approx. 0.030 g) were placed into gelatine capsules and then loaded into nonmagnetic plastic straws before being

lowered into the cryostat. The field independence of the measurement was verified by measuring the susceptibility as a function of field between 5 and 5 T. Data were collected employing a field of 0.1 T and finally corrected for the inherent diamagnetism of the sample by use of Pascals constants and the thermally independent contribution to the paramagnetism.

5.1.9 Solution Phase NMR Spectroscopy

All air/moisture sensitive samples were prepared in a glovebox under a nitrogen atmosphere and sealed in 5 mm Youngs type concentric stopcocks. NMR spectra were obtained either on a Varian Mercury VX-Works 300 MHz spectrometer or a Varian Venus 300 MHz spectrometer. The Evans' measurements were carried out using a Varian Unity Plus 500 MHz spectrometer with the help of Dr. Nick Rees or on a Varian Venus 300 MHz spectrometer. ^1H and ^{13}C NMR spectra were referenced via the residual protio-solvent peak; ^7Li spectra were referenced externally to LiCl.

5.2 Starting Materials

5.2.1 Commercially Supplied Reagents

All reagents were used as received unless otherwise specified. Solvents were supplied by Rathburn, Fisher scientific or Sigma Aldrich. Deutero-solvents were supplied by Goss Scientific (with minimum 99.5at. % D). TMEDA, MeLi (1.6 M in Et_2O), MeLi · LiBr (1.5 M in Et_2O), K_{metal} , KBr (FT-IR grade, > 99 %), MeMgI (3.0 M in Et_2O), $\text{C}_3\text{H}_5\text{MgBr}$ (1.5 M in Et_2O), $\text{C}_6\text{H}_5\text{MgBr}$ (3.0 M in Et_2O), $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$ (1.5 M in Et_2O), ZrCl_4 , HfCl_4 , were all supplied from Sigma-Aldrich. Methylaluminoxane solution (10 wt. % in toluene) was dried *in vacuo* prior to use. Ethylene was supplied by BOC gases and passed through a high pressure drying column made of potassium wool. CO_2 was supplied Argo.

5.2.2 Literature Preparations

The following compounds were prepared according to published procedures: UCl_4 ,²² $\text{Li}_2\text{Pn}^*\cdot(\text{TMEDA})_x$,²³ NaCp ,²⁴ LiCp^* ,²⁵ $\text{HfCl}_4 \cdot 2 \text{THF}$,²⁶ $\text{ZrCl}_4 \cdot 2 \text{THF}$,²⁶ **3.1b_{Zr}**.²⁷

5.3 Experimental Details for Chapter Two

5.3.1 Synthesis of UPn^*_2 (**2.1**)

UCl_4 (0.673 g, 1.77 mmol) in THF (50 ml) was added to $Li_2Pn^*(TMEDA)_x$ (0.75 g, 3.54 mmol) in THF (50 ml) at room temperature and stirred for 2 h. The solution very quickly turned dark brown. The solvent was removed *in vacuo* and the solid dried by subjection to at least a 1×10^{-2} mbar vacuum overnight. The resulting black solid was dissolved in warm toluene (2×50 ml) and filtered through celite. The solution was reduced to minimum volume and cooled to -38 °C and left for 48 h which yielded black crystals which were washed with pentane (2×30 ml) to remove residual toluene and vacuum dried.

Yield = 0.422 g, (0.69 mmol, 39 %)

5.3.2 Synthesis of $[UPn^*(\mu-Cl_4)][Li(TMEDA)]_2$ (**2.2**)

A Schlenk was charged with UCl_4 (1 g, 2.64 mmol) and stirred up in benzene. To this an excess of TMEDA was added (2 ml, 1.55 g, 13.35 mmol) *via* syringe. The solution was stirred at room temperature for 1 h to allow formation of $UCl_4(TMEDA)_2$ *in situ* (demonstrated by the solution turning green). To this a slurry of $Li_2Pn^*(TMEDA)_x$ (0.573 g, 2.64 mmol) was added dropwise *via* cannula and then allowed to stir for 12 h. The green solution had turned to black upon return and was then filtered through celite and the solvent was removed *in vacuo*. The resultant dark solid was then redissolved in toluene and filtered *via* cannula and reduced to minimum volume the slow cooled to -38 °C over two days yielding dark murky green crystals.

Yield = 1.511 g (1.86 mmol, 70.5 %)

5.3.3 Synthesis of $[UPn^*(\eta^5-Cp^*)(\mu-Cl_2)][Li(TMEDA)]$ (**2.3**)

$LiCp^*$ (68 mg, 0.478 mmol) slurried in toluene (20 ml) at room temperature was added to $[UPn^*(\mu-Cl_4)][Li(TMEDA)]_2$ (350 mg, 0.432 mmol) dissolved in toluene (50 ml) and stirred for 12 h at 100 °C. The reaction mixture was then allowed to cool to room temperature before the solvent was removed *in vacuo* and the solid was washed with pentane at -78 °C, then dried by subjection to at least a 1×10^{-2} mbar vacuum

overnight. The dark solid was then taken up in hexane and filtered through celite before being reduced to minimum volume. The solution was cooled to $-38\text{ }^{\circ}\text{C}$ and yielded dark brown crystals which were unsuitable for single crystal X-ray diffraction. In order to achieve crystals of high enough quality the solid needed to be recrystallised from heptane and slow cooled to $-38\text{ }^{\circ}\text{C}$ over a period of four days.

Yield (before recrystallisation) = 156 mg (0.207 mmol, 48 %)

5.3.4 Synthesis of $[\text{UPn}^*(\eta^5\text{-Cp})(\mu\text{-Cl}_2)][\text{Li}(\text{TMEDA})]$ (**2.4**)

NaCp (36 mg, 0.409 mmol) dissolved in Et_2O (20 ml) at room temperature was added to $[\text{UPn}^*(\mu\text{-Cl}_4)][\text{Li}(\text{TMEDA})]_2$ (350 mg, 0.431 mmol) dissolved in Et_2O (50 ml) at room temperature and stirred for 2 h. The reaction mixture was then filtered through celite and the solvent was removed *in vacuo*. The resultant solid was washed with pentane at $-78\text{ }^{\circ}\text{C}$ and then dried by subjection to at least a 1×10^{-2} mbar vacuum overnight. Subsequent dissolution in toluene (3×50 ml), filtration *via* cannula, reduction to minimum volume *in vacuo* and subsequent slow cooling of the saturated solution to $-38\text{ }^{\circ}\text{C}$ led to the formation of black crystals. Due to the colour of the crystals it was not possible to find an appropriate single crystal for X-ray analysis.

Yield = 184 mg (0.270 mmol, 63 %)

5.3.5 Synthesis of $\text{UPn}^*(\eta^5\text{-Cp})_2$ (**2.5**)

NaCp (47.8 mg, 0.545 mmol) slurried in benzene (20 ml) was added to a solution of $[\text{UPn}^*(\mu\text{-Cl}_4)][\text{Li}(\text{TMEDA})]_2$ (200 mg, 0.247 mmol) in toluene (50 ml) at room temperature and then heated to $70\text{ }^{\circ}\text{C}$ whilst stirred for 12 h. The reaction mixture was then allowed to cool to room temperature and filtered through celite. The solvent was removed *in vacuo* and the subsequent solid was washed with pentane at $-78\text{ }^{\circ}\text{C}$ (3×30 ml) and then dried by subjection to at least a 1×10^{-2} mbar vacuum overnight. The solid was extracted with toluene (3×50 ml) yielding a black solution which was reduced to minimum volume before slow cooling to $-35\text{ }^{\circ}\text{C}$ over 3 days yielding **2.5** as an amorphous black powder.

Yield = 98 mg (0.177 mmol, 71.6 %)

5.4 Experimental Details for Chapter Three

5.4.1 Synthesis of $[\text{ZrPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{Et}_2\text{O})_x(\text{THF})_y$ (**3.1_{Zr}**)

$\text{ZrCl}_4 \cdot 2 \text{ THF}$ (7.12 g, 18.87 mmol) in benzene (50 ml) at room temperature was slurried onto $\text{Li}_2\text{Pn}^*(\text{TMEDA})_x$ ($x = 0.101$, 4.00 g, 18.87 mmol) in benzene (20 ml) and allowed to stir for 24 hours by which time the solution had turned dark brown and a large quantity of LiCl precipitate had formed. The precipitate was allowed to settle and the supernatant removed *via* cannula and the remainder extracted with benzene (3×50 ml). The volatiles were removed *in vacuo* leaving a brown solid. The residue was extracted with Et_2O to give an intensely brown solution that was reduced to minimum volume, which when cooled to -38°C yielded a golden-yellow solid. Removal of the mother liquor, followed by washing with -78°C pentane (2×20 ml) and subsequent drying *in vacuo* yielded a yellow solid. Analysis by ^1H NMR spectroscopy established/demonstrated it to be of the formula $[\text{ZrPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{Et}_2\text{O})_{0.245}(\text{THF})_{0.94}$. Yield = 3.897 g (4.723 mmol, 50.0 %) (taking into account the coordinated THF and Et_2O).

5.4.2 Synthesis of $[\text{HfPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{Et}_2\text{O})_x(\text{THF})_y$ (**3.1_{Hf}**)

Synthesis was carried out as above with the following alterations. The benzene solution was heated to 60°C during the reaction. The product was crystallised from THF in the first instance (though Et_2O may be used and the lower solubility of LiCl is advantageous) and yielded an orange-yellow solid. Amounts used: $\text{HfCl}_4 \cdot 2 \text{ THF}$ (3.00 g, 6.47 mmol), $\text{Li}_2\text{Pn}^*(\text{TMEDA})_x$ ($x = 0.080$, 1.35 g, 6.47 mmol).

Yield of $[\text{HfPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{THF})_{1.01}$: 76.2 % (2.43 g, 2.46 mmol).

5.4.3 Synthesis of $\{[\text{ZrPn}^*(\mu\text{-Cl})]_2(\mu^3\text{-Cl})(\mu\text{-Cl})_2\}_2\text{Mg}$ (**3.1_{aZr}**)

To an NMR tube charged with $[\text{ZrPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{Et}_2\text{O})_x(\text{THF})_y$ ($x = 0.245$, $y = 0.940$, approximately 10 mg) in d^8 -toluene an excess of Me_2Mg was added (approximately 5 mg), the tube was heated at 110°C overnight with a slight paling of the yellow solution. Slow evaporation of the solvent in a nitrogen atmosphere yielded small yellow crystals.

5.4.4 Improved synthesis of ZrPn^*CpCl (**3.2_{Zr}**)

A Schlenk was charged with $[\text{ZrPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{Et}_2\text{O})_x(\text{THF})_y$ ($x = 0.245$, $y = 0.940$, 200 mg, 0.242 mmol) and NaCp (45 mg, 0.509 mmol) and was cooled to -196°C before THF (50 ml) was added. The frozen mixture was allowed to warm to room temperature and stir for a further hour before volatiles were removed *in vacuo* and subjected to a dynamic vacuum ($< 1 \times 10^{-2}$ mbar) for four hours. The residue was extracted with toluene, reduced to minimum volume and slow cooled to -38°C precipitating yellow crystals.

Yield = 153 mg (0.405 mmol, 83.4 %).

5.4.5 Synthesis of HfPn^*CpCl (**3.2_{Hf}**)

Synthesis was carried out as above with the following alterations. Et_2O was used as the reaction solvent due to the lower solubility of the NaCl/LiCl by-product than in THF. The yellow reaction mixture was allowed to stir overnight and then crystallisation proceeded as above. Amounts used: $[\text{HfPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{Et}_2\text{O})_x(\text{THF})_y$ ($x = 0.677$, $y = 0.586$, 200 mg, 0.198 mmol), NaCp (35 mg, 0.397 mmol).

Yield of HfPn^*CpCl = 153.7 mg (0.330 mmol, 83.3 %)

5.4.6 Synthesis of $\text{ZrPn}^*(\eta^5\text{-Cp})(\eta^1\text{-Cp})$ (**3.3_{Zr}**)

Benzene (20 ml) was added to a mini Schlenk loaded with NaCp (44 mg, 0.502 mmol) and $[\text{ZrPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{Et}_2\text{O})_x(\text{THF})_y$ ($x = 0.315$, $y = 1.023$, 100 mg, 0.120 mmol) and was sonicated for a week resulting in formation of an orange solution with a pale precipitate. This was filtered *via* cannula and extracted with benzene (3×30 ml). Volatiles were removed *in vacuo* and subjected to a dynamic vacuum ($< 1 \times 10^{-2}$ mbar) for four hours. The residuum was extracted with hot hexane (60°C), reduced to minimum volume and slow cooled to -35°C , leading to crystallisation of $\text{ZrPn}^*(\eta^5\text{-Cp})(\eta^1\text{-Cp})$.

Yield = 83 mg (0.204 mmol, 85.2 %).

5.4.7 Synthesis of $\text{HfPn}^*(\eta^5\text{-Cp})(\eta^1\text{-Cp})$ (**3.3_{Hf}**)

Synthesis was carried out as above, however it was found that even with continued sonication it was not possible to form pure $\text{HfPn}^*(\eta^5\text{-Cp})(\eta^1\text{-Cp})$, instead it was formed in a 6:1 ratio with the mono-cyclopentadienyl derivative: $\text{HfPn}^*(\eta^5\text{-Cp})\text{Cl}$. Amounts used: $[\text{HfPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{Et}_2\text{O})_x(\text{THF})_y$ ($x = 0.677$, $y = 0.586$, 200 mg, 0.198 mmol), NaCp (87 mg, 0.990 mmol).

Yield of HfPn^*Cp_2 : 63 mg (0.127 mmol, 64.1 %).

5.4.8 Synthesis of $\text{ZrPn}^*\text{Cp}^*\text{Cl}$ (**3.4_{Zr}**)

$[\text{ZrPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{Et}_2\text{O})_x(\text{THF})_y$ ($x = 0.315$, $y = 1.023$, 200 mg, 0.239 mmol) was dissolved in toluene (30 ml) to which KCp^* (79 mg, 0.454 mmol) slurried up in toluene (30 ml) was added. The sample was allowed to stir overnight at 110 °C before being filtered *via* cannula and then reduced to dryness *in vacuo*. The resultant yellow solid was then washed with hexane (3×30 ml) before being subjected to a vacuum ($< 1 \times 10^{-2}$ mbar) for at least four hours. The solid was then taken up in toluene (3×30 ml) before being reduced to saturation. Single crystals were attained by cooling this solution to -35 °C.

Yield = 126 mg (0.282 mmol, 59.1 %).

5.4.9 Synthesis of $\text{HfPn}^*\text{Cp}^*\text{Cl}$ (**3.4_{Hf}**)

Synthesis was carried out as above. Amounts used: $[\text{HfPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li}(\text{Et}_2\text{O})_x(\text{THF})_y$ ($x = 0.677$, $y = 0.586$, 200 mg, 0.198 mmol), KCp^* (75 mg, 0.431 mmol).

Yield of $\text{HfPn}^*\text{Cp}^*\text{Cl}$ = 145 mg (0.270 mmol, 68.3 %).

5.4.10 Synthesis of $\text{ZrPn}^*(\eta^3\text{-C}_3\text{H}_5)_2$ (**3.5_{Zr}**)

$(\text{C}_3\text{H}_5)\text{MgCl}$ (2.0 M in THF, 0.502 ml, 1.004 mmol), was added to a solution of $[\text{ZrPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li}(\text{Et}_2\text{O})_x(\text{THF})_y$ ($x = 0.315$, $y = 1.023$, 200 mg, 0.239 mmol) in Et_2O (40 ml) whilst stirring at -78 °C. The yellow suspension on warming deepened in colour and at room temperature was a deep yellow solution with a white precipitate (presumably LiCl or MgCl_2). 1,4-dioxane (5 ml) was added to precipitate any remaining

magnesium salts, before all volatiles were removed *in vacuo* and subjected to a dynamic vacuum ($< 1 \times 10^{-2}$ mbar) for six hours. The residuum was extracted with hexane and filtered through celite before being reduced to minimum volume and slow cooled to -78 °C. A bright yellow crystalline solid was collected in 3 crops.

Yield = 102 mg (0.284 mmol, 59.0 %).

5.4.11 Synthesis of $\text{HfPn}^*(\eta^3\text{-C}_3\text{H}_5)_2$ (**3.5_{Hf}**)

A similar method as above was employed with the following alterations: $(\text{C}_3\text{H}_5)\text{MgCl}$ (1.0 M in Et_2O) was used and added to the reaction mixture at room temperature. The solution paled and an unidentified white precipitate (presumably LiCl) formed. The product was found to be yellow crystals. Amounts used: $[\text{HfPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{Et}_2\text{O})_x(\text{THF})_y$ (200mg, 0.198 mmol), $(\text{C}_3\text{H}_5)\text{MgCl}$ (1.0 M in Et_2O , 0.835 cm³, 0.834 mmol).

Yield: 128 mg in two crops (0.314 mmol, 72.2 %).

5.4.12 Synthesis of ZrPn^*_2 (**3.6_{Zr}**)

LiAlH_4 (94 mg, 2.472 mmol) was put into a slurry of Et_2O (50 ml) and cooled to -78 °C. To this $[\text{ZrPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li}(\text{Et}_2\text{O})_x(\text{THF})_y$ ($x = 0.140$, $y = 0.895$, 200 mg, 0.247 mmol) dissolved up in Et_2O (50 ml) at -78 °C was added. The solution was stirred at -78 °C for one hour before being allowed to warm to room temperature and stir for a further 16 hours. The solution remained grey with small metallic specks (presumably zirconium). The reaction mixture was filtered through celite to give an extremely pale yellow solution. The solvent was removed *in vacuo*, washed with -78 °C pentane and taken up in toluene (3×50 ml). The solution was filtered *via* cannula and reduced to minimum volume. Cooling this solution to -38 °C yielded **3.6_{Zr}** as an amorphous yellow powder in poor purity. In order to obtain crystals suitable for X-ray diffraction a d^8 -toluene NMR sample was allowed to slowly evaporate whilst under a N_2 atmosphere. Yield = 22 mg (0.0476 mmol, 9.6 %)

5.4.13 Synthesis of HfPn^*_2 (**3.6_{Hf}**)

$\text{HfCl}_4 \cdot 2 \text{ THF}$ (200 mg, 0.431 mmol) was stirred up in toluene (30 ml) to which a slurry of $\text{Li}_2\text{Pn}^*(\text{TMEDA})_x$ ($x = 0.083$, 361 mg, 1.724 mmol) in toluene (30 ml) was added at room temperature. The brown reaction mixture was heated at 110 °C for three days during which time it turned darker. The precipitate $[\text{LiCl}/\text{excess Li}_2\text{Pn}^*(\text{TMEDA})_x]$ was subsequently allowed to settle and the supernatant was removed *via* cannula. The remaining solid was washed with toluene and filtered through celite until no more colour was taken up (3×100 ml). The filtrate was combined with the previously removed solution and the solvent was removed *in vacuo* leaving a red solid. This solid was washed with pentane (3×30 ml), taken up in toluene (50 ml), filtered *via* cannula, and reduced to minimum volume. The saturated solution was cooled to -35 °C yielding **3.6_{Hf}** as an amorphous powder. In order to get crystals suitable for X-ray diffraction a d^6 -benzene NMR solution was allowed to slowly evaporate whilst under a N_2 atmosphere.

yield = 18 mg (0.0326 mmol, 7.6 %)

5.4.14 Synthesis of $[\text{ZrPn}^*(\mu\text{-Me})]_2(\mu\text{-CH}_2)$ (**3.7_{Zr}**)

MeMgI (3.0 M in Et_2O , 0.346 ml, 1.03 mmol) was added to a stirred solution of $[\text{ZrPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{Et}_2\text{O})_x(\text{THF})_y$ ($x = 0.140$ $y = 0.895$, 200 mg, 0.478 mmol) in Et_2O (30 ml) *via* syringe. The solution immediately turned a ruby red hue. After four hours stirring was ceased and 1,4-dioxane (5 ml) was added in order to precipitate magnesium salts. The subsequent opaque mixture was filtered through celite. Solvent was removed *in vacuo* and the solution was washed with pentane (2×50 ml) and subsequently dried by exposure to vacuum for two hours ($< 1 \times 10^{-2}$ mbar). The remaining solid was extracted with toluene (3×30 ml) and reduced to minimum volume before cooling to -38 °C. This yielded **3.7_{Zr}** as an orange-red amorphous powder. In order to obtain single crystals an NMR sample in d^8 -toluene was allowed to evaporate under a N_2 atmosphere.

Yield = 181.3 mg (0.304 mmol, 63.6 %)

5.4.15 Synthesis of $\text{ZrPn}^*\text{Ph}(\mu\text{-Ph})_2\text{Li} \cdot \text{dioxane}$ (**3.8_{Zr}**)

To a stirred suspension of $[\text{ZrPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{Et}_2\text{O})_x(\text{THF})_y$ ($x = 0.315$, $y = 1.023$, 130 mg, 0.155 mmol) in Et_2O (40 ml), PhMgCl (2.0 M in THF, 0.326 ml, 0.653 mmol) was added whilst stirring at -78°C , followed by warming to room temperature. The solution immediately turned deep yellow and upon warming a fine white precipitate formed. The suspension was allowed to stir for three hours at room temperature before 1,4-dioxane (5 ml) was added to precipitate any remaining magnesium salts. Volatiles were removed *in vacuo* and subjected to a dynamic vacuum ($< 1 \times 10^{-2}$ mbar) for 3 hours. The residue was extracted with pentane, filtered *via* cannula and cooled to -35°C to precipitate a red powder. Repeated recrystallisations from hexane allowed the isolation of red single crystals.

Yield = 97 mg (0.161 mmol, 52.0 %).

5.4.16 Synthesis of $\text{HfPn}^*\text{Ph}(\mu\text{-Ph})_2\text{Li} \cdot \text{dioxane}$ (**3.8_{Hf}**)

Synthesis was carried out as above. Amounts used: $[\text{HfPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li}(\text{Et}_2\text{O})_x(\text{THF})_y$ ($x = 0.677$, $y = 0.586$, 170 mg, 0.169 mmol), PhMgCl (3.0 M in Et_2O , 0.343 ml, 1.03 mmol).

Yield of $\text{HfPn}^*\text{Ph}(\mu\text{-Ph})_2\text{Li} \cdot \text{dioxane} = 81$ mg (0.117 mmol, 34.6 %).

5.4.17 Synthesis of $\text{ZrPn}^*(\text{CH}_2\text{C}_6\text{H}_5)_2$ (**3.9_{Zr}**)

$\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$ (1.0 M in Et_2O , 2.009 ml, 2.009 mmol) was added to a slurry of $[\text{ZrPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{Et}_2\text{O})_x(\text{THF})_y$ ($x = 0.315$, $y = 1.023$, 400 mg, 0.478 mmol) in Et_2O (60 ml) whilst stirring at -78°C . A white precipitate was formed which on warming to room temperature redissolved with the solution turning a deep orange colour. 1,4-dioxane (5 ml) was added to precipitate magnesium salts, then all volatiles were removed under reduced pressure and subjected to a dynamic vacuum ($< 1 \times 10^{-2}$ mbar) for 14 hours. The residue was extracted with hexane and filtered through celite before being reduced to minimum volume and cooled to -35°C . After 72 hours a fine white precipitate (presumably LiCl/Mg salts) had formed and the mother liquor was decanted and again cooled to -35°C . This procedure was repeated once more before

slow cooling to $-35\text{ }^{\circ}\text{C}$ producing a yellow crystalline solid after removal of supernatant and washing with $-78\text{ }^{\circ}\text{C}$ hexane. Yield = 233 mg (0.507 mmol, 53.0 %).

5.4.18 Synthesis of $[\text{HfPn}^*(\text{CH}_2\text{Ph})_3]^-[\text{Li}(1,4\text{-dioxane})_4]^+$ and $\text{HfPn}^*(\text{CH}_2\text{C}_6\text{H}_5)_2$
(**3.9a_{Hf}**) and (**3.9_{Hf}**)

Synthesis was carried out as above with the following alterations. Upon addition of 1,4-dioxane small yellow needles were formed, these were isolated and used for X-ray diffraction experiments (**3.9a_{Hf}**). Further work-up proceeded as above however the resultant yellow solid was not soluble in hexane and as such extracted with and crystallised from toluene. Amounts used: $\text{Pn}^*\text{Hf}(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li}(\text{Et}_2\text{O})_x(\text{THF})_y$ ($x = 0.677$, $y = 0.586$, 200 mg, 0.198 mmol), $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$ (1.0 M in Et_2O , 0.834 ml, 0.834 mmol). Yield of $\text{HfPn}^*(\text{CH}_2\text{C}_6\text{H}_5)_2 = 46\text{ mg}$ (0.0839 mmol, 42.3 %). Yield of $[\text{Pn}^*\text{Hf}(\text{CH}_2\text{Ph})_3]^-[\text{Li}(1,4\text{-dioxane})_4]^+ = 22\text{ mg}$ (0.220 mmol, 11.1 %).

5.5 Experimental Details for Chapter Four

5.5.1 Ethylene polymerisation conditions

5.5.1.1 Generic experimental technique

In a glovebox 10 mg of the given compound to be tested was dissolved up in 10 ml of toluene. A Rotaflo ampoule containing a stirrer bar was charged with 1000 molar equivalents of MAO and washed with 49 ml of hexane. To this 1 ml of the stock solution of compound was added (for 0.1 mg catalyst loading 0.1 ml of the stock solution was used, with 50 ml of hexane). The ampoule was quickly transferred onto a Schlenk line, degassed *in vacuo* for 5 minutes and then heated to $80\text{ }^{\circ}\text{C}$ with vigorous stirring. The ampoule was then pressurised with ethylene gas (2 bar) for one hour. Afterwards the polymerisation was quenched by removing the ethylene gas supply and exposing to ampoule to vacuum. The solution was then filtered in air and washed through with pentane ($3 \times 50\text{ ml}$). The specific amounts and conditions used are summarised in the tables below.

- Table 5.1 is split into three sections. The first two contain the masses of catalyst

and MAO used and the amount of polymer obtained for the broad spectrum testing at 1 mg catalyst loading, the first section being the uranium compounds, the second section being the group four compounds. The third section of the table comprises of the polymer testing at reduced catalytic and MAO loading.

- *Table 5.2* contains the masses and conditions of the reactions carried out over various time-scales.
- *Table 5.3* contains the masses and conditions of the reactions carried out at various temperatures.

Table 5.1: Amounts of catalyst and co-catalyst used in the initial testing. Other conditions 80 °C, 2 bar ethylene, 1 hour reaction time.

Species	Mass of catalyst (mg)	Amount of catalyst (mmol)	MAO equivalents	Mass of MAO (mg)	Yield (mg)		Activity	
					Run 1	Run 2	Run 1	Run 2
2.1	1	0.00164	1000	95	151	138	46.1	42.1
2.2	1	0.00123	1000	72	101	129	40.8	42.1
2.3	1	0.00133	1000	77	114	68	42.9	25.6
2.4	1	0.00147	1000	85	109	99	37.2	33.6
2.5	1	0.00180	1000	105	124	122	34.4	33.8
3.1_{Zr}	1	0.00124	1000	72	221	196	89.2	79.3
3.1_{Hf}	1	0.000994	1000	58	104	135	52.3	67.7
3.2_{Zr}	1	0.00266	1000	154	1061	1120	919.3	970.5
3.2_{Hf}	1	0.00215	1000	125	1342	2107	625.5	491.0
3.3_{Zr}	1	0.00246	1000	143	1507	2148	733.8	872.3
3.3_{Hf}	1	0.00202	1000	117	1630	1809	404.4	448.8
3.4_{Zr}	1	0.00224	1000	130	617	787	137.6	175.5
3.4_{Hf}	1	0.00187	1000	108	358	226	96.0	60.6
3.5_{Zr}	1	0.00279	1000	162	289	334	51.7	59.8
3.5_{Hf}	1	0.00223	1000	129	240	249	53.8	53.8
3.7_{Zr}	1	0.00168	1000	97	1116	900	332.7	268.3
3.8_{Zr}	1	0.00166	1000	96	218	274	65.6	82.5
3.8_{Hf}	1	0.00144	1000	84	129	128	44.7	44.3
3.9_{Zr}	1	0.00218	1000	128	367	416	84.1	95.3
3.9_{Hf}	1	0.00182	1000	106	188	206	51.5	56.5
3.2_{Zr}	0.1	0.000266	1000	15.4	2366	2076	4448.7	3903.4
3.2_{Zr}	0.1	0.000266	300	4.6	1548	1143	2910.6	2149.1
3.3_{Zr}	0.1	0.000246	1000	14.3	2111	2020	4286.6	4101.8
3.3_{Zr}	0.1	0.000246	300	4.3	1131	1746	2296.6	3545.4
3.2_{Hf}	0.1	0.000215	1000	12.5	391	475	911.2	1107.0
3.3_{Hf}	0.1	0.000215	1000	11.7	109	90	270.4	223.3

Table 5.2: Amounts of catalyst and co-catalyst used, and polymer obtained over different time scales. Other conditions: 1000 equivalents MAO, 80 °C, 2 bar ethylene.

Species	Mass of catalyst (mg)	Amount of catalyst (mmol)	Time (mins)	Mass of MAO (mg)	Yield (mg)		Activity	
					Run 1	Run 2	Run 1	Run 2
3.2_{Zr}	0.1	0.000266	15	14.3	622	555	4678.0	4174.2
3.2_{Zr}	0.1	0.000266	30	14.3	1188	1017	4467.5	3824.4
3.2_{Zr}	0.1	0.000266	60	14.3	2366	2076	4448.7	3903.4
3.3_{Zr}	0.1	0.000246	15	15.4	912	810	7407.6	6579.1
3.3_{Zr}	0.1	0.000246	30	15.4	1462	1469	5937.5	5965.9
3.3_{Zr}	0.1	0.000246	60	15.4	2111	2020	4286.6	4101.8

Table 5.3: Amounts of catalyst and co-catalyst used in the initial testing. Other conditions: 1000 equivalents MAO, 2 bar ethylene, 30 minutes reaction time.

Species	Mass of catalyst (mg)	Amount of catalyst (mmol)	Temperature (°C)	Mass of MAO (mg)	Yield (mg)		Activity	
					Run 1	Run 2	Run 1	Run 2
3.2_{Zr}	0.1	0.000266	40	14.3	873	605	3282.9	2275.1
3.2_{Zr}	0.1	0.000266	60	14.3	1013	1222	3809.4	4595.3
3.2_{Zr}	0.1	0.000266	80	14.3	1188	1017	4467.5	3824.4
3.3_{Zr}	0.1	0.000246	40	15.4	916	1071	3720.1	4349.5
3.3_{Zr}	0.1	0.000246	60	15.4	1057	883	4293.0	3586.0
3.3_{Zr}	0.1	0.000246	80	15.4	1462	1469	5937.5	5965.9

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6. CHARACTERISING DATA

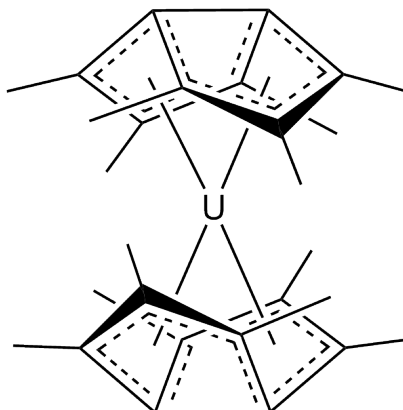
The data of the compounds synthesised are in the following order: firstly uranium compounds (2.1-2.5), then zirconium compounds (3.1_{Zr}-3.9_{Zr}), finally the hafnium compounds (3.1_{Hf}-3.9_{Hf}).

NMR Data, unless stated otherwise, were collected at room temperature.

Single crystal X-ray data may be found in the electronic appendix.

6.1 Characterising Data for Chapter 2

6.1.1 Characterising Data for UPn*₂ (**2.1**)



General Properties: Black Crystalline air-sensitive solid

Elemental Analysis found (calculated) for UC₂₈H₃₆ (MW = 610.33) (%):
C 54.46 (55.08) H 6.61 (5.94).

High Resolution MS (EI) found (calculated) for UPn*₂: 610.3321 (610.3325).

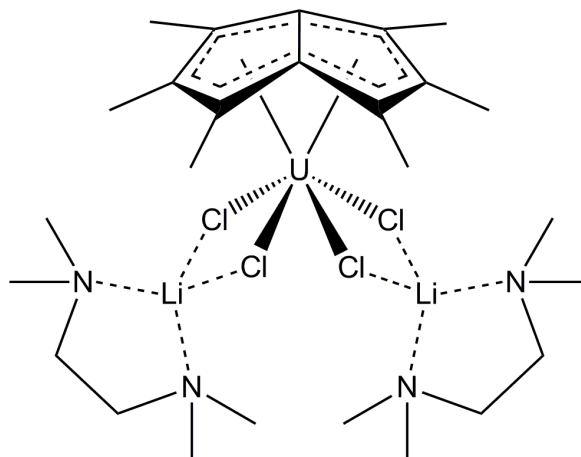
MS (EI): m/z = 610 ([UPn*₂]⁺, 100 %).

IR (KBr, cm⁻¹): 2931 (s), 2908 (s), 2855 (s), 1457 (m), 1437 (m), 1420 (m), 1379 (m),
1019 (m), 773 (m).

¹H NMR (C₆D₆) δ (ppm): 1.04 [(1, 3, 5, 7)-Me, 24H, s], -27.89 [(2, 6)-Me,
12H, s].

¹³C{¹H} NMR (C₆D₆) δ (ppm): 968.6 [(1, 3, 5, 7)-Me], 875 [(2, 6)-Me, unob-
served], 601.8 (quat.), 315.3 (quat.), 124.1 (quat.).

X-ray data: 2_1.cif

6.1.2 Characterising Data for $[UPn^*(\mu-Cl_4)][Li(TMEDA)]_2$ (**2.2**)

General Properties: Extremely dark green air sensitive crystalline solid

Elemental Analysis found (calculated) for $UC_{26}N_4Cl_4Li_2H_{50}$ (MW = 610.33)
 (%): C 37.45 (38.44) H 6.17 (6.20) N 6.87 (6.89).

High Resolution MS (EI) found (calculated) for $[UPn^*Cl_2]$: 494.1202 (429.1293).

MS (EI): $m/z = 494$ ($[Pn^*UCl_2]^+$, 80 %), 186 ($[Pn^*]^+$, 100 %) .

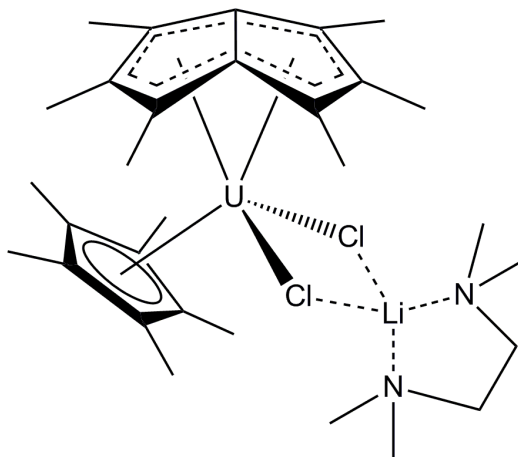
IR (KBr, cm^{-1}): 2958 (s), 2838 (br), 2795 (s), 1464 (s), 1291 (s), 1037 (s), 1019 (s), 7911 (s), 511 (s).

1H NMR (C_6D_6) δ (ppm): 10.73 [(**1**, **3**, **5**, **7**)- Me_4 , 12H, s], 8.18 [(**2**, **6**)- Me_2 , 6H, s], 4.20 (TMEDA- Me_8 , 24H, br, $\nu_{\frac{1}{2}} = 59.4$ Hz), 2.44 (TMEDA- $[CH_2]_4$, 8H, br, $\nu_{\frac{1}{2}} = 31.5$ Hz).

$^{13}C\{^1H\}$ NMR (C_6D_6) δ (ppm): 256.3 (quat.), 157.6 (quat.), 57.7 (TMEDA- CH_2), 47.7 (TMEDA- Me), 11.1 [(**2**, **6**)- Me , s], -78.3 [(**1**, **3**, **5**, **7**)- Me , s], -456.7 (quat.).

7Li NMR (194 MHz, C_6D_6) δ (ppm): -2.01 (s).

X-ray data: 2.2.cif

6.1.3 Characterising Data for $[\text{UPn}^*\text{Cp}^*(\mu\text{-Cl}_2)][\text{Li}(\text{TMEDA})]$ (**2.3**)

General Properties: Black air sensitive crystalline solid

High Resolution MS (EI) found (calculated) for $\text{UPn}^*\text{Cp}^*\text{Cl}$: 594.2778 (594.3108).

MS (EI): $m/z = 594$ ($[\text{UPn}^*\text{Cp}^*\text{Cl}]^+$, 10%), 494 ($[\text{UPn}^*\text{Cl}_2]^+$, 5 %), 458 ($[\text{UPn}^*\text{Cl}]^+$, 10 %), 186 ($[\text{Pn}^*]^+$, 100 %).

IR (KBr, cm^{-1}): 2962 (s), 2909 (s), 2854 (s), 1650 (m), 1461 (m), 1439 (m), 1370 (m), 1261 (m), 1096 (m), 1069 (m), 1018 (m), 803 (m).

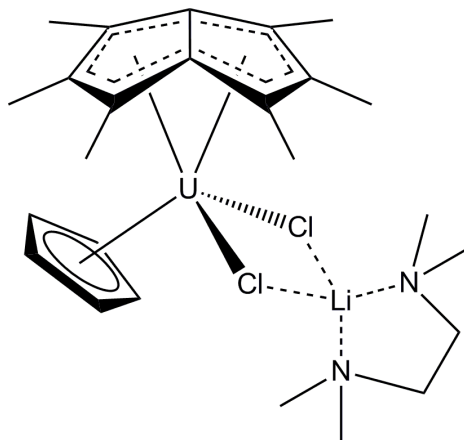
^1H NMR (C_7D_8) δ (ppm): 9.31 ($\text{Cp}^*\text{-Me}_5$, 15H, br, $\nu_{\frac{1}{2}} = 16.6$ Hz), -2.70 (TMEDA- Me_4 , 12H, br, $\nu_{\frac{1}{2}} = 27.1$ Hz), -3.914 (TMEDA- $[\text{CH}_2]_2$, 4H, br, $\nu_{\frac{1}{2}} = 28.2$ Hz), -14.04 [(**2,6**)- Me_2 , 6H, br, $\nu_{\frac{1}{2}} = 17.2$ Hz]. NWT-Me too broad for detection at room temperature.

^1H NMR (C_7D_8 , 193 K) δ (ppm): 72.66 (NWT- Me , 3H, br), 71.85 (NWT- Me , 3H, br), 14.16 ($\text{Cp}^*\text{-Me}_5$, 15H, s), -1.09 (NWT- Me , 3H, s), -3.32 (NWT- Me , 3H, s), -5.36 (TMEDA- Me_2 , 6H, s), -7.59 (TMEDA- Me_2 , 6H, s), -11.12 (TMEDA- $[\text{CH}_2]_2$, 4H, s), -30.58 [(**2, 6**)- Me_2 , 6H, d].

$^{13}\text{C}\{^1\text{H}\}$ NMR δ (ppm): Spectrum unattainable due to paramagnetism, poor solubility and fluxionality.

^7Li NMR (194 MHz, C_6D_6) δ (ppm): -43.50 (s).

X-ray data: 2.3.cif

6.1.4 Characterising Data for $[\text{UPn}^*\text{Cp}(\mu\text{-Cl}_2)][\text{Li}(\text{TMEDA})]$ (**2.4**)

General Properties: Black air sensitive crystalline solid

High Resolution MS (EI) found (calculated) for UPn^*CpCl : 524.3218 (524.1996).

MS (EI): m/z = 523 ($[\text{UPn}^*\text{CpCl}]^+ - \text{H}$, 10 %), 487 ($[\text{UPn}^*\text{Cp}]^+ - 2\text{H}$, 10 %), 338 ($[\text{UCpCl}]^+$, 10 %), 186 ($[\text{Pn}^*]^+$, 100 %)

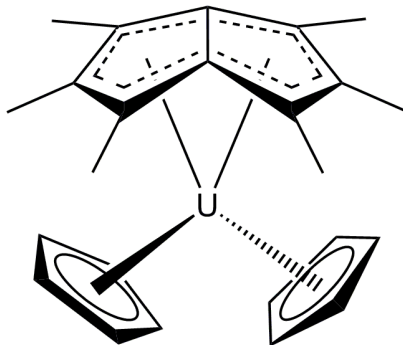
IR (KBr, cm^{-1}): 2961 (s), 2907 (s), 2868 (s), 2838 (s), 1465 (m), 1261 (s), 1097 (m), 1019 (m), 802 (m).

^1H NMR (C_7D_8) δ (ppm): 23.29 [(**1**, **3**, **5**, **7**)- Me_4 , 12H, br, $\nu_{\frac{1}{2}} = 104.7$ Hz], 3.69 (Cp , 5H, s), 1.10 (TMEDA- Me_4 , 12H, br, $\nu_{\frac{1}{2}} = 23.4$ Hz), -0.52 (TMEDA- $[\text{CH}_2]_2$, 4H, br, $\nu_{\frac{1}{2}} = 32.7$ Hz), -16.52 [(**2**, **6**)- Me_2 , 6H, s].

^1H NMR (C_7D_8 , 193 K) δ (ppm): 57.44 (NWT- Me_2 , 6H, br, $\nu_{\frac{1}{2}} = 181.5$ Hz), 8.08 (Cp , 5H, s, $\nu_{\frac{1}{2}} = 31.3$ Hz), 6.11 (NWT- Me_2 , 6H, br, $\nu_{\frac{1}{2}} = 180.9$ Hz), 0.35 (TMEDA- Me_2 , 6H, br, $\nu_{\frac{1}{2}} = 34.7$ Hz), -1.86 (TMEDA- Me_2 , 6H, br, $\nu_{\frac{1}{2}} = 399.4$ Hz), -2.90 (TMEDA- $[\text{CH}_2]_2$, 4H, br, $\nu_{\frac{1}{2}} = 191.1$ Hz), -34.12 [(**2**, **6**)- Me_2 , 6H, s, $\nu_{\frac{1}{2}} = 94.5$ Hz].

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ (ppm): 243.2, 84.6, 54.6, 44.3. Due to the paramagnetism resonances were unassignable.

^7Li NMR (194 MHz, C_6D_6) δ (ppm): -14.46 (s).

6.1.5 Characterising Data for UPn*Cp₂ (**2.5**)

General Properties: Black air sensitive crystalline solid

High Resolution MS (EI) found (calculated) for UPn*Cp₂: 554.3952 (554.2699).

MS (EI): m/z = 554 ([M]⁺, 30 %), 489 ([M]⁺–Cp, 100 %), 186 ([Pn*]⁺, 90 %).

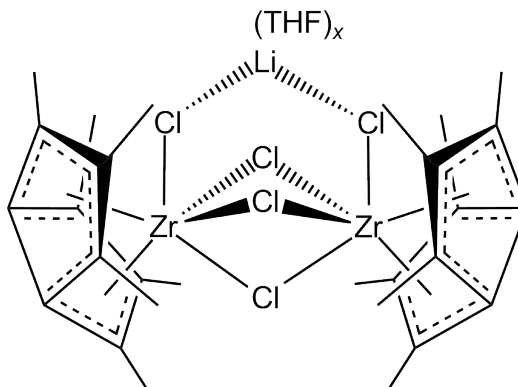
IR (KBr, cm^{–1}): 2958 (s), 2870 (m), 2794 (m), 1464 (s), 1291 (s), 1036 (s), 1019 (s), 791 (s), 511 (s).

¹H NMR (C₆D₆) δ (ppm): 42.05 [(**1**, **3**, **5**, **7**)–Me₄, 12H, s], –0.48 (Cp, 10H, s), –41.09 [(**2**, **6**)–Me₂, 6H, s].

¹³C{¹H} NMR (C₆D₆) δ (ppm): 545.4 [(**1**, **3**, **5**, **7**)–Me, s], 259.3 (Cp, s), 61.4 [(**2**, **6**), s], 45.6 [(**4**, **8**), s], –4.8 [(**1**, **3**, **5**, **7**), s], –95.1 [(**2**, **6**)–Me, s].

6.2 Characterising data for chapter 3

6.2.1 Characterising Data for $[\text{ZrPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{Et}_2\text{O})_x(\text{THF})_y$ (**3.1_{Zr}**)



General Properties: Golden-yellow air-sensitive crystalline solid.

Elemental Analysis found (calculated) for $[\text{ZrPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{THF})_y$ ($y = 1.72$) (MW = 863.26) (%): C 48.49 (48.53), H 5.83 (5.81).

High Resolution MS (EI) found (calculated) for ZrPn^*Cl_2 345.9834 (345.9833)

MS (EI): $m/z = 345$ ($[\text{ZrPn}^*\text{Cl}_2]^+$, 20 %); 310 ($[\text{ZrPn}^*\text{Cl}]^+$, 20 %).

IR (KBr, cm^{-1}): 2908 (m), 2726 (m), 1440 (m), 1379 (s), 1224 (s), 1099 (s), 1049 (m), 894 (m), 797 (m), 683 (m).

^1H NMR (C_6D_6) δ (ppm): 1.23 ($\beta\text{-CH}_2$, t), 1.86 [(**2**, **6**)- Me_4 , 12H, s], 2.12 [(**3**, **5**)- Me_4 , 12H, br s, $\nu_{\frac{1}{2}} = 3.6$ Hz], 2.18 [(**1**, **7**)- Me_4 , 12H, br s, $\nu_{\frac{1}{2}} = 3.8$ Hz], 3.52 ($\alpha\text{-CH}_2$, t).

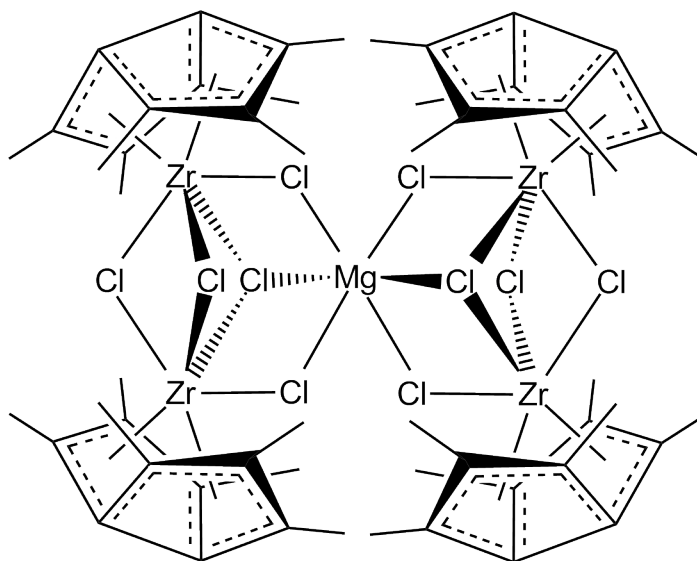
^1H NMR (C_7D_8 , 343 K) δ (ppm): 1.38 ($\beta\text{-CH}_2$, t), 1.87 [(**2**, **6**)- Me_4 , 12H, s], 2.11 [(**1**, **3**, **5**, **7**)- Me_8 , 24H, s], 3.55 ($\alpha\text{-CH}_2$, t).

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ (ppm): 10.7 [(**2**, **6**)- Me_4 , s], 13.0 [(**1**, **7**)- Me_4 , br, $\nu_{\frac{1}{2}} = 3.3$ Hz], 13.4 [(**3**, **5**)- Me_4 , br, $\nu_{\frac{1}{2}} = 3.3$ Hz], 25.2 ($\beta\text{-CH}_2$, t), 68.2 ($\alpha\text{-CH}_2$, t), 110.5 [(**3**, **5**), br, $\nu_{\frac{1}{2}} = 4.3$ Hz], 112.0 [(**1**, **7**), br, $\nu_{\frac{1}{2}} = 4.1$ Hz], 124.0 (**4**, s), 125.7 (**8**, s), 132.2 [(**2**, **6**), s].

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 343 K) δ (ppm): 10.7 [(**2**, **6**)- Me_4 , s], 13.4 [(**1**, **3**, **5**, **7**)- Me_8 , s], 25.4 ($\beta\text{-CH}_2$, s), 68.2 ($\alpha\text{-CH}_2$, s), 111.3 [(**1**, **3**, **5**, **7**), br, $\nu_{\frac{1}{2}} = 24.2$ Hz], 125.0 [(**4**, **8**), s], 132.6 [(**2**, **6**), s].

^7Li NMR (194 MHz, C_6D_6) δ (ppm): 1.17 (s).

X-ray data: 3.1Zr.cif

6.2.2 Characterising Data for $[\text{ZrPn}^*(\mu\text{-Cl})]_4[(\mu_3\text{-Cl})_2(\mu\text{-Cl})_2\text{Mg}]$ (**3.1azr**)

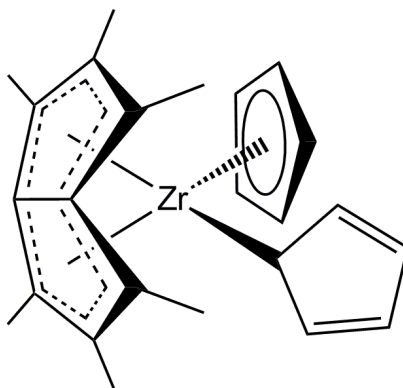
General Properties: Colourless air-sensitive crystalline solid.

MS (EI): $m/z = 346$ (ZrPn^*Cl_2 , 20 %); 310 (ZrPn^*Cl , 20 %); 173 ($\text{Pn}^*\text{-Me}$, 100 %).

^1H NMR (C_7D_8) δ (ppm): 1.86 [(**2, 6**)- Me_8 , 24H, s], 1.99 [NWT- Me_8 , 24H, s], 2.08 [NWT- Me_8 , 12H, s].

^1H NMR (C_7D_8 , 393 K) δ (ppm): 1.89 [(**2, 6**)- Me_8 , 24H, s], 2.02 [(**1, 3, 5, 7**)- Me_{16} , 48H, s].

X-ray data: 3.1aZr.cif

6.2.3 Characterising Data for $\text{ZrPn}^*(\eta^5\text{-Cp})(\eta^1\text{-Cp})$ (**3.3_{Zr}**)

General Properties: Yellow-orange crystalline solid, air-sensitive.

MS (EI): **3.3_{Zr}** gave no molecular ion signal in mass spectrum and all other signals could be attributed to co-crystallised **3.2_{Zr}**.

IR (KBr, cm⁻¹): 3110 (s), 3058 (s), 2949 (s), 2909 (s), 2864 (s), 1444 (m), 1382 (s), 1020 (m), 986 (s), 853 (s), 727 (s), 699 (s), 661 (s), 626(m).

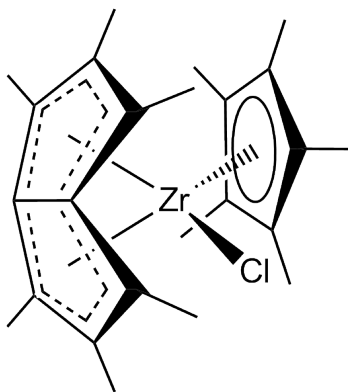
¹H NMR (C₇D₈) δ (ppm): 1.65 [(**2**, **6**)-Me₂, 6H, s], 1.82 [(**3**, **5**)-Me₂, 6H, br s, $\nu_{\frac{1}{2}} = 117.8$ Hz], 2.04 [(**1**, **7**)-Me₂, 6H, br s, $\nu_{\frac{1}{2}} = 120.1$ Hz], 4.90 ($\eta^5\text{-Cp}$, 5H, br s, $\nu_{\frac{1}{2}} = 44.6$ Hz), 5.89 ($\eta^1\text{-Cp}$, 5H, br s, $\nu_{\frac{1}{2}} = 50.5$ Hz).

¹H NMR (C₇D₈, 263 K) δ (ppm): 1.62 [(**2**, **6**)-Me₂, 6H, s], 1.75 [(**3**, **5**)-Me₂, 6H, br s, $\nu_{\frac{1}{2}} = 2.8$ Hz], 2.11 [(**1**, **7**)-Me₂, 6H, br s, $\nu_{\frac{1}{2}} = 3.2$ Hz], 4.92 ($\eta^5\text{-Cp}$, 5H, br s, $\nu_{\frac{1}{2}} = 2.4$ Hz), 5.98 ($\eta^1\text{-Cp}$, 5H, br s, $\nu_{\frac{1}{2}} = 3.2$ Hz).

¹H NMR (C₇D₈, 373 K) δ (ppm): 1.76 [(**2**, **6**)-Me₂, 6H, s], 2.01 [(**1**, **3**, **5**, **7**)-Me₄, 12H, br s, $\nu_{\frac{1}{2}} = 1.6$ Hz], 5.38 (Cp, 10H, br s, $\nu_{\frac{1}{2}} = 5.0$ Hz).

¹³C{¹H} NMR (C₇D₈), 263 K δ (ppm): 11.0 [(**2**, **6**)-Me₂], 12.3 [(**1**, **7**)-Me₂], 13.2 [(**3**, **5**)-Me₂], 104.3 [(**3**, **5**), br, $\nu_{\frac{1}{2}} = 3.6$ Hz], 108.6 [(**1**, **7**), br, $\nu_{\frac{1}{2}} = 3.1$ Hz], 111.6 ($\eta^5\text{-Cp}$, br, $\nu_{\frac{1}{2}} = 3.6$ Hz), 112.5 ($\eta^1\text{-Cp}$, br, $\nu_{\frac{1}{2}} = 20.6$ Hz), 117.2 (**4**, s), 123.4 (**8**, s), 124.7 [(**2**, **6**), s].

X-ray data: 3_3Zr.cif

6.2.4 Characterising Data for $\text{ZrPn}^*(\eta^5\text{-Cp}^*)\text{Cl}$ (**3.4_{Zr}**)

General Properties: Orange crystalline solid, air-sensitive.

High Resolution MS (EI) found (calculated) for $\text{ZrPn}^*\text{Cp}^*\text{Cl}$: 446.1305 (446.1318).

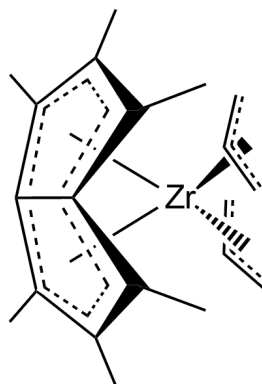
MS (EI): $m/z = 446$ ($[\text{M}]^+$, 20 %), 410 ($[\text{M-Cl}]^+$, 1 %), 311 ($[\text{M-Cp}^*]^+$, 30 %), 187 ($[\text{Pn}^*]$, 20 %).

IR (KBr, cm^{-1}): 2960 (s), 2905 (s), 2870 (m), 1437 (m), 1379 (s), 1261 (s), 1097 (s), 1024 (s), 801 (s).

^1H NMR (C_7D_8) δ (ppm): 1.67 [(**2**, **6**)- Me_2 , 6H, s], 1.77 [$\text{Cp}^*\text{-Me}_5$, 15H, s], 1.95 [(**3**, **5**)- Me_2 , 6H, s], 2.08 [(**1**, **7**)- Me_2 , 6H, s].

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8), δ (ppm): 10.2 [(**3**, **5**)- Me_2 , s], 11.1 [$\text{Cp}^*\text{-Me}_5$, s], 11.9 [(**1**, **7**)- Me_2 , s], 13.0 [(**2**, **6**)- Me_2 , s], 102.8 [(**3**, **5**) s], 112.9 [(**1**, **7**) s], 117.3 (Cp^* , s), 118.5 (**4**, s), 124.4 [(**2**, **6**), s], 125.6 (**8**, s).

X-ray data: 3_4Zr.cif

6.2.5 Characterising Data for $\text{ZrPn}^*[\eta^3-(\text{C}_3\text{H}_5)_2]$ (**3.5_{Zr}**)

General Properties: Bright Yellow air-sensitive crystalline solid.

Elemental Analysis found (calculated) for $\text{C}_{20}\text{H}_{28}\text{Zr}$ (MW = 359.66) (%):
C 66.75 (66.79), H 7.71 (7.85).

High Resolution MS (EI) found (calculated) for $\text{ZrPn}^*(\text{C}_3\text{H}_5)_2$: 358.1232 (358.1238).

MS (EI): m/z = 358 ($[\text{M}]^+$, 15 %); 317 ($[\text{M}-\text{C}_3\text{H}_5]^+$, 50 %); 276 ($[\text{M}-2\text{C}_3\text{H}_5]^+$, 100 %).

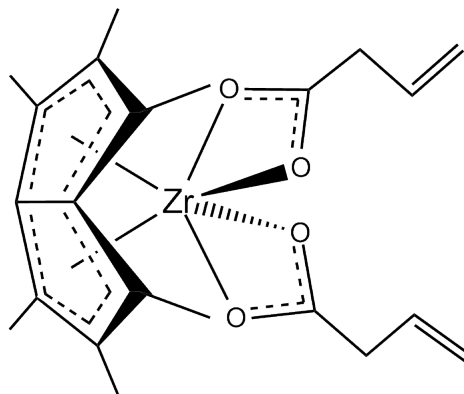
IR (KBr, cm^{-1}): 3065 (s), 2909 (m), 1506 (s), 1447 (m), 1243 (s), 1222 (s), 1026 (s), 1005 (s), 830 (s), 803 (s), 745 (s), 682 (s), 633 (s).

^1H NMR (C_7D_8 , 333 K) δ (ppm): 1.62 [(**2**, **6**)- Me_2 , 6H, s], 1.92 [(**1**, **3**, **5**, **7**)- Me_2 , 12H, br, $\nu_{\frac{1}{2}} = 24.7$ Hz], 2.22 [CH_2CHCH_2 , v. br, $\nu_{\frac{1}{2}} = 80.2$ Hz], 5.22 (CH_2CHCH_2 , quin, $^3J_{\text{H-H}} = 11.92$ Hz)

^1H NMR (C_7D_8 , 283 K) δ (ppm): 1.55 [(**2**, **6**)- Me_2 , 6H, s], 1.69 [(**1**, **5**)- Me_2 , 6H, s], 1.89 [(**17**, **20**)- CHH_{anti} , 2H, d, $^3J_{\text{H-H}} = 15.37$ Hz], 1.93 [(**15**, **18**)- CHH_{syn} , 2H, d, $^3J_{\text{H-H}} = 9.21$ Hz], 2.08 [(**3**, **7**)- Me_2 , 6H, s], 2.45 [(**17**, **20**)- CHH_{syn} , 2H, d, $^3J_{\text{H-H}} = 9.97$ Hz], 3.47 [(**15**, **18**)- CHH_{anti} , 2H, d, $^3J_{\text{H-H}} = 15.62$ Hz], 5.14 [(**16**, **19**)- CH_{meso} , 2H, m].

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 298 K) δ (ppm): 9.97 [(**2**, **6**)- Me_2 , s], 11.3 [(**1**, **5**)- Me_2 , s], 14.0 [(**3**, **7**)- Me_2 , s], 56.4 [(**15**, **18**)- CH_2CHCH_2 , s], 66.4 [(**17**, **20**)- CH_2CHCH_2 , s], 99.2 (**3**, **7**), 104.5 (**1**, **5**), 116.0 (**4**, **8**), 128.1 (**2**, **6**), 136.7 [(**16**, **19**)- CH_2CHCH_2 , s].

X-ray data: 3_5Zr.cif

6.2.6 Characterising Data for $\text{ZrPn}^*[\kappa^2\text{-(O}_2\text{CCH}_2\text{CHCH}_2)_2]$ (**3.5azr**)

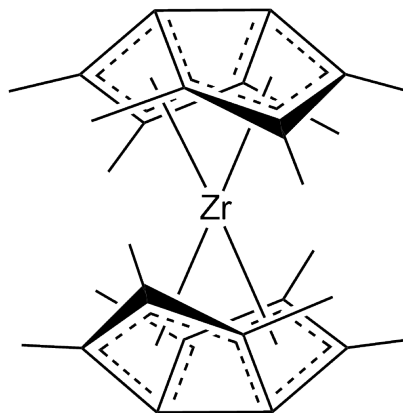
General Properties: Pale yellow air-sensitive solution.

High Resolution MS (EI) found (calculated) for $\text{ZrPn}^*(\text{O}_2\text{CCH}_2\text{CHCH}_2)_2$:
446.1035 (446.0925).

MS (EI): $m/z = 446$ ($[\text{M}]^+$, 10 %); 360 ($[\text{M}-\text{O}_2\text{C}_4\text{H}_5-\text{H}]^+$, 10 %); 186 ($[\text{Pn}^*]^+$, 10 %).

^1H NMR (C_6D_6) δ (ppm): 1.89 [(**2**, **6**)- Me_2 , 6H, s], 1.94 [(**1**, **3**, **5**, **7**)- Me_4 , 12H, s], 2.87 [(**16**, **20**)- CH_2 , 4H, d, $^3J_{\text{H-H}} = 6.7$ Hz, $^5J_{\text{H-H}} = 1.3$ Hz], 5.00 [(**18**, **22**)- $\text{RHC}=\text{CH}_{\text{cis}}\text{H}$, d, $^3J_{\text{H-H}} = 10.3$ Hz, $^1J_{\text{H-H}} = 1.7$ Hz], 4.88 [(**18**, **22**)- $\text{RHC}=\text{CH}_{\text{trans}}\text{H}$, d, $^3J_{\text{H-H}} = 15.6$ Hz, $^1J_{\text{H-H}} = 1.6$ Hz], 5.83 [(**17**, **21**) $\text{RHC}=\text{CH}_2$, 2H, m]

^{13}C { ^1H } NMR (C_6D_6) δ (ppm): 11.7 [(**1**, **3**, **5**, **7**)- Me_4], 12.3 [(**2**, **6**)- Me_2], 45.7 [(**16**, **20**)- $\text{O}_2\text{CCH}_2\text{CHCH}_2$], 107.7 (**1**, **3**, **5**, **7**), 117.5 [(**18**, **22**)- $\text{O}_2\text{CCH}_2\text{CHCH}_2$], 125.7 (**4**, **8**), 134.4 [(**17**, **21**)- $\text{O}_2\text{CCH}_2\text{CHCH}_2$], 136.0 (**2**, **6**), 179.8 [(**15**, **19**)- $\text{O}_2\text{CCH}_2\text{CHCH}_2$].

6.2.7 Characterising Data for ZrPn^*_2 (**3.6_{Zr}**)

General Properties: Orange air-sensitive crystalline solid.

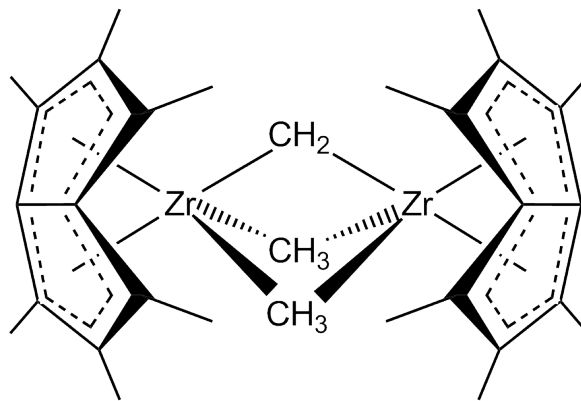
High Resolution MS (EI) found (calculated) for ZrPn^*_2 : 462.1864 (462.1864).

MS (EI): $m/z = 462$ ($[\text{M}]^+$, 20 %); 447 ($[\text{M}-\text{CH}_3]^+$, 10 %); 188 ($[\text{M}-\text{C}_{14}\text{H}_{16}-\text{Zr}]^+$, 100 %).

^1H NMR (C_6D_6) δ (ppm): 2.51 [(**1**, **3**, **5**, **7**)- Me_8 , 24H, s], 1.97 [(**2**, **6**)- Me_4 , 12H, s].

^{13}C NMR: Due to difficulties in purification it was not possible to record a ^{13}C spectrum.

X-ray data: 3.6Zr.cif

6.2.8 Characterising Data for $[\text{ZrPn}^*]_2[\mu\text{-Me}]_2[\mu\text{-CH}_2]$ (**3.7_{Zr}**)

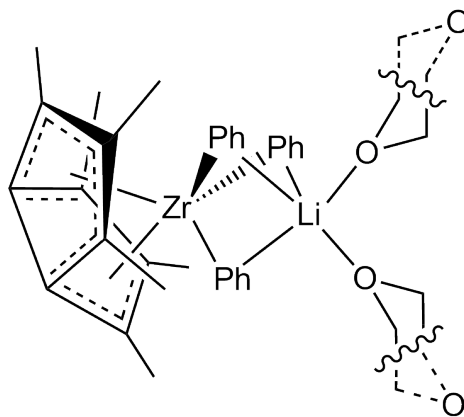
General Properties: Red air-sensitive crystalline solid.

IR (KBr, cm^{-1}): 2906 (s), 2856 (s), 2556 (m), 1385 (s), 1223 (s), 1194 (s), 1097 (m), 1023 (m), 802 (s), 728 (s), 684 (s), 573 (s).

^1H NMR (C_6D_6) δ (ppm): -0.36 [(**15**, **17**)-($\mu\text{-Me}$)₂, 6H, s], 1.92 [(**2**, **6**, **19**, **23**)- Me_4 , 12H, s], 1.96 [(**1**, **3**, **5**, **7**, **18**, **20**, **22**, **24**)- Me_8 , 24H, s], 2.72 [**16**-($\mu\text{-CH}_2$), 2H, s]

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ (ppm): 10.6 [(**2**, **6**)- Me_2 , s], 12.2 [(**1**, **3**, **5**, **7**)- Me_4 , s], 38.9 [$\mu\text{-Me}_2$, s], 104.5 [(**1**, **3**, **5**, **7**), s], 127.3 [(**4**, **8**), s], 127.9 [(**2**, **6**), s], 180.2 [($\mu\text{-CH}_2$), s]

X-ray data: 3_7Zr.cif

6.2.9 Characterising Data for $[\text{ZrPn}^*\text{Ph}(\mu\text{-Ph})_2\text{Li}(1,4\text{-dioxane})]_n$ (**3.8_{Zr}**)

General Properties: Yellow air-sensitive crystalline solid.

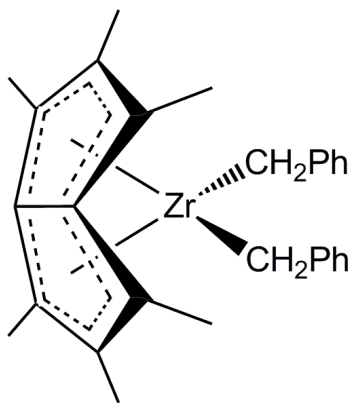
IR (KBr, cm^{-1}): 3038 (s), 2924 (m), 2925 (m), 2851 (m), 1460 (s), 1422 (m), 1382 (m), 1254 (s), 1124 (s), 1072 (s), 1046 (m), 864 (s), 704 (s).

^1H NMR (C_6D_6) δ (ppm): 1.72 [(**2**, **6**)-*Me*, 6H, s], 1.93 [(**1**, **3**, **5**, **7**)-*Me*, 12H, s], 2.72 (1,4-dioxane-*CH*₂, 8H, d), 7.09 (*p*-Ph, 3H, t, $^3J_{\text{H-H}} = 7.3$ Hz), 7.21 (*m*-Ph, 6H, t, $^3J_{\text{H-H}} = 7.6$ Hz), 7.96 (*o*-Ph, 6H, t, $^3J_{\text{H-H}} = 6.4$ Hz).

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ (ppm): 11.1 [(**2**, **6**)-*Me*₂, s], 12.9 [(**1**, **3**, **5**, **7**)-*Me*₄, s], 66.9 (1,4-dioxane), 106.3 (**1**, **3**, **5**, **7**), 126.7 (**4**, **8**), 126.81 (*p*-Ph), 127.1 (*m*-Ph), 131.7 (**2**, **6**), 139.5 (*o*-Ph), 179.0 (*i*-Ph).

^7Li NMR (194 MHz, C_6D_6) δ (ppm): -1.12 (s).

X-ray data: 3_8Zr.cif

6.2.10 Characterising Data for $\text{ZrPn}^*(\text{CH}_2\text{Ph})_2$ (**3.9_{Zr}**)

General Properties: Yellow air-sensitive crystalline solid.

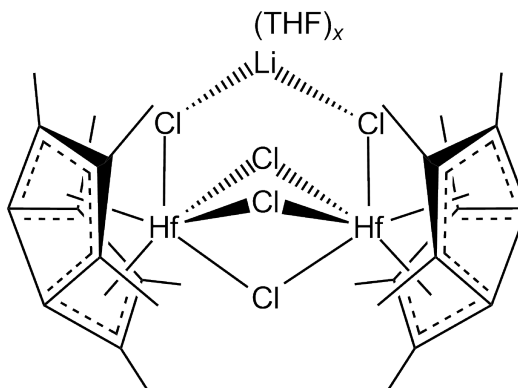
Elemental Analysis found (calculated) for $\text{C}_{28}\text{H}_{32}\text{Zr}$ (MW = 459.78) (%): C 72.94 (73.14), H 6.85 (7.02).

IR (KBr, cm^{-1}): 3045 (s), 2971 (m), 2939 (m), 2907 (s), 1589 (s), 1555 (s), 1476 (s), 1444 (m), 1381 (m). 1297 (m), 1217 (m), 1026 (m), 898 (s), 844 (s), 797 (s), 747 (s), 709 (m), 588 (m).

^1H NMR (C_6D_6) δ (ppm): 1.63 (ZrCH_2 , 4H, s), 1.69 [(**2**, **6**)- Me_2 , 6H, s], 1.81 [(**1**, **3**, **5**, **7**)- Me_4 , 12H, s], 6.06 (*o*-Ph, 4H, d, $^3\text{J}_{\text{H-H}} = 7.7$ Hz), 6.74 (*p*-Ph, 2H, t, $^3\text{J}_{\text{H-H}} = 7.3$ Hz) 6.96 (*m*-Ph, 4H, t, $^3\text{J}_{\text{H-H}} = 7.5$ Hz).

^{13}C NMR (C_6D_6) δ (ppm): 11.0 [(**2**, **6**)- Me_4 , q, $^1\text{J}_{\text{C-H}} = 126.4$ Hz], 12.2 [(**1**, **3**, **5**, **7**)- Me_4 , q, $^1\text{J}_{\text{C-H}} = 126.1$ Hz], 50.0 [ZrCH_2 , t, $^1\text{J}_{\text{C-H}} = 135.0$ Hz], 104.4 [(**1**, **3**, **5**, **7**), s], 121.8 (*p*-Ph, d, $^1\text{J}_{\text{C-H}} = 162.3$ Hz), 122.5 (*o*-Ph, d, $^1\text{J}_{\text{C-H}} = 152.9$ Hz), 123.9 [(**4**, **8**), s], 130.1 [(**2**, **6**, s], 131.6 (*m*-Ph, d, $^1\text{J}_{\text{C-H}} = 158.5$ Hz), 143.5 (*i*-Ph)

X-ray data: 3_9Zr.cif

6.2.11 Characterising Data for $[\text{HfPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{Et}_2\text{O})_x(\text{THF})_y$ (**3.1_{Hf}**)

General Properties: Golden-yellow air-sensitive crystalline solid.

Elemental Analysis found (calculated) for $[\text{HfPn}^*(\mu\text{-Cl})_{\frac{3}{2}}]_2(\mu\text{-Cl})_2\text{Li} \cdot (\text{THF})_y$ ($y = 1.01$, MW = 986.81) (%): 39.05 (38.96), 4.55 (4.50).

High Resolution MS (EI) found (calculated) for HfPn^*Cl_2 : 436.0246 (436.0251)

MS (EI): $m/z = 436$ ($[\text{HfPn}^*\text{Cl}_2]^+$, 100 %); 420 ($[\text{HfPn}^*\text{Cl}]^+$, 30 %).

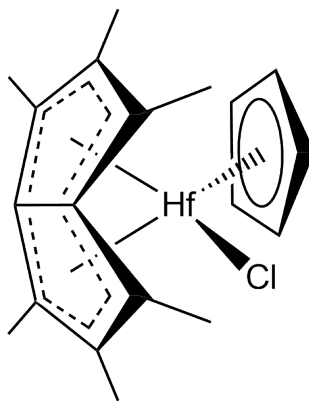
IR (KBr, cm^{-1}): 2969 (m), 1738 (s), 1447 (s), 1365 (s), 1273 (s), 1216 (s), 1093 (m), 1020 (m), 804 (s), 749 (s).

^1H NMR (C_6D_6) δ (ppm): 1.40 ($\beta\text{-CH}_2$, t), 1.90 [(**2**, **6**)- Me_4 , 12H, s], 2.26 [(**1**, **3**, **5**, **7**)- Me_8 , 24H, s], 3.59 ($\alpha\text{-CH}_2$, t).

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ (ppm): 10.5 [(**2**, **6**)- Me_4], 12.9 [(**1**, **3**, **5**, **7**)- Me_8], 25.4 ($\beta\text{-CH}_2$), 68.2 ($\alpha\text{-CH}_2$), 107.9 [(**1**, **3**, **5**, **7**), br], 120.8 (**4**, **8**), 130.5 (**2**, **6**).

^7Li NMR (194 MHz, C_6D_6) δ (ppm): 5.3 (s).

X-ray data: 3.1Hf.cif

6.2.12 Characterising Data for $\text{HfPn}^*(\eta^5\text{-Cp})\text{Cl}$ (**3.2_{Hf}**)

General Properties: Pale yellow crystalline solid, air-sensitive.

High Resolution MS (EI) found (calculated) for HfPn^*CpCl : 466.0956 (466.0954).

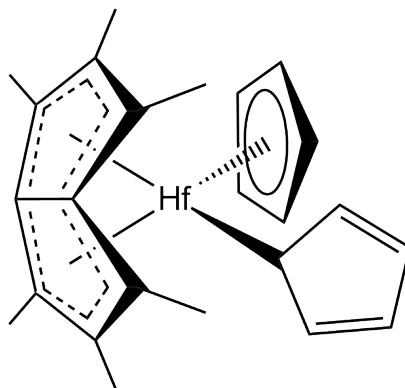
MS (EI): $m/z = 466$ ($[\text{M}]^+$, 10 %); 401 ($[\text{M-Cp}]^+$, 20 %), 187 ($[\text{Pn}^*]^+$, 100 %).

IR (KBr, cm^{-1}): 2951 (m), 2901 (s), 2878 (m), 1447 (m), 1382 (s), 1261 (s), 1097 (m), 1023 (s), 815 (s), 733 (m).

^1H NMR (C_7D_8) δ (ppm): 1.72 [(**2,6**)- Me_2 , 6H, s], 1.94 [(**3,5**)- Me_2 , 6H, s], 2.10 [(**1,7**)- Me_2 , 6H, s], 5.56 ($\eta^5\text{-Cp}$, 5H, s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8) δ (ppm): 11.2 [(**2, 6**)- Me_2 , s] 12.4 [(**3, 5**)- Me_2 , s], 13.0 [(**1, 7**)- Me_2 , s], 103.3 [(**1, 7**), s], 109.7 (Cp, s), 110.9 [(**3, 5**), s], 116.9 (**8**, s), 124.3 [(**2, 6**), s], 125.2 (**4**).

X-ray data: 3.2Hf.cif

6.2.13 Characterising Data for $\text{HfPn}^*(\eta^5\text{-Cp})(\eta^1\text{-Cp})$ (**3.3_{Hf}**)

General Properties: Yellow crystalline solid, air-sensitive.

MS (EI): **3.3_{Hf}** gave no molecular ion signal in mass spectrum and all other signals could be attributed to **3.2_{Hf}**.

IR (KBr, cm^{-1}): 3058 (s), 2910 (m), 1445 (m), 13382 (s) 1261 (s), 1028 (m), 982 (s), 811 (s), 735 (s), 667 (s).

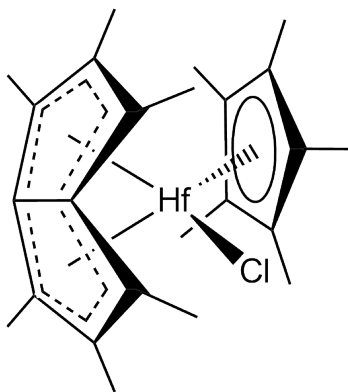
^1H NMR (C_7D_8 ; 253K) δ (ppm): 1.70 [(**2**, **6**)- Me_2 , 6H, s], 1.95 [(**3**, **5**)- Me_2 , 6H, s], 2.16 [(**1**, **7**)- Me_2 , 6H, s], 4.91 ($\eta^5\text{-Cp}$, 5H, s), 5.88 ($\eta^1\text{-Cp}$, 5H, s).

^1H NMR (C_7D_8 , 173 K) δ (ppm): 1.53 [(**2**, **6**)- Me_2 , 6H, s], 1.78 [(**3**, **5**)- Me_2 , 6H, s], 2.19 [(**1**, **7**)- Me_2 , 6H, s], 3.66 [$i\text{-}\eta^1\text{-Cp}$, 1H, br] 4.81 ($\eta^5\text{-Cp}$, 5H, s), 6.35 ($\alpha\text{-}\eta^1\text{-Cp}$, 2H, s), approx. 7 ($\beta\text{-}\eta^1\text{-Cp}$, 2H, s, obscured by solvent peak).

^1H NMR (C_7D_8 , 353 K) δ (ppm): 1.74 [(**2**, **6**)- Me_2 , 6H, s], 2.00 [(**1**, **3**, **5**, **7**)- Me_4 , 12H, s], 5.38 (Cp , 10H, br s, $\nu_{\frac{1}{2}} = 5.0$ Hz).

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 253 K) δ (ppm): 11.0 [(**2**, **6**)- Me_2], 12.5 [(**1**, **7**)- Me_2] 13.2 [(**3**, **5**)- Me_2], 102.6 [(**3**, **5**), br, $\nu_{\frac{1}{2}} = 3.6$ Hz], 107.2 [(**1**, **7**), br, $\nu_{\frac{1}{2}} = 3.1$ Hz], 109.7 ($\eta^5\text{-Cp}$, br, $\nu_{\frac{1}{2}} = 3.6$ Hz), 110.9 (**4**, s), 114.0 ($\eta^1\text{-Cp}$, br, $\nu_{\frac{1}{2}} = 20.6$ Hz), 120.4 (**8**, s), 123.4 [(**2**, **6**), s].

X-ray data: 3.3Hf.cif

6.2.14 Characterising Data for $\text{HfPn}^*(\eta^5\text{-Cp}^*)\text{Cl}$ (**3.4_{Hf}**)

General Properties: Orange crystalline solid, air-sensitive.

High Resolution MS (EI) found (calculated) for $\text{HfPn}^*\text{Cp}^*\text{Cl}$: 536.1740 (536.1736)

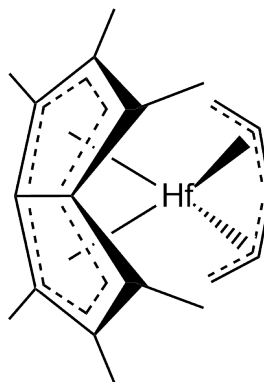
MS (EI): $m/z = 536$ ($[\text{M}]^+$, 5 %); 401 ($[\text{M}-\text{Cp}^*]^+$, 5 %), 187 ($[\text{Pn}^*]^+$, 100 %).

IR (KBr, cm^{-1}): 2958 (s), 2906 (s), 2961 (s), 1437 (m), 1379 (s), 1261 (s), 1228 (s), 1095 (m), 1021 (m), 807 (s), 594 (s).

^1H NMR (C_6D_6) δ (ppm): 1.66 [(**2**, **6**)- Me_2 , 6H, s], 1.80 ($\text{Cp}^*\text{-Me}_5$, 15H, s), 2.11 [(**3**, **5**)- Me_2 , 6H, s], 2.20 [(**1**, **7**)- Me_2 , 6H, s].

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8), δ (ppm): 10.2 [(**3**, **5**)- Me_2 , s], 11.2 [$\text{Cp}^*\text{-Me}_5$, s], 11.9 [(**1**, **7**)- Me_2 , s], 13.0 [(**2**, **6**)- Me_2 , s], 103.1 [(**3**, **5**) s], 111.8 [(**1**, **7**) s], 116.1 (Cp^* , s), 118.2 (**4**, s), 123.4 [(**2**, **6**), s], 128.7 (**8**, s).

X-ray data: 3_4Hf.cif

6.2.15 Characterising Data for $\text{HfPn}^*[\eta^3\text{-(C}_3\text{H}_5)_2]$ (**3.5_{Hf}**)

General Properties: Yellow air-sensitive crystalline solid.

High Resolution MS (EI) found (calculated) for $\text{HfPn}^*(\text{C}_3\text{H}_5)_2$: 448.1652 (448.1657).

MS (EI): $m/z = 448$ ($[\text{M}]^+$, 10 %); 407 ($[\text{M}-\text{C}_3\text{H}_5]^+$, 80 %); 363 ($[\text{M}-2\text{C}_3\text{H}_5]^+$, 40 %); 186 ($[\text{Pn}^*]^+$, 40 %); 173 ($[\text{Pn}^*-\text{Me}]^+$, 100 %).

IR (KBr, cm^{-1}): 3065 (s), 2962 (m), 2909 (m), 2859 (m), 1510 (s), 1448 (m), 1381 (s), 1261 (s), 1096 (m), 838 (m), 810 (s), 751 (s).

^1H NMR (C_7D_8 , 298 K) δ (ppm): 1.59 [(**2**, **6**)- Me_2 , 6H, s], 1.920 [(**1**, **3**, **5**, **7**)- Me_2 and CH_2CHCH_2 , v. br, $\nu_{\frac{1}{2}} = 91.14$ Hz], 5.164 [(**16**, **19**)- CH_2CHCH_2 , q, $^1\text{J}_{\text{H-H}} = 12.91$ Hz]

^1H NMR (C_7D_8 , 233 K) δ (ppm): 1.53 [(**2**, **6**)- Me_2 , 6H, s], 1.70 [(**1**, **5**)- Me_2 , 6H, s], 1.80 [(**17**, **20**)- CHH_{anti} , 2H, d, $^3\text{J}_{\text{H-H}} = 15.22$ Hz], 1.98 [(**15**, **18**)- CHH_{syn} , 2H, d, $^3\text{J}_{\text{H-H}} = 9.45$ Hz], 2.14 [(**3**, **7**)- Me_2 , 6H, s], 2.25 [(**17**, **20**)- CHH_{syn} , 2H, d, $^3\text{J}_{\text{H-H}} = 9.80$ Hz], 3.51 [(**15**, **18**)- CHH_{anti} , 2H, d, $^3\text{J}_{\text{H-H}} = 15.41$ Hz], 5.14 [(**16**, **19**)- CH_{meso} , 2H, m].

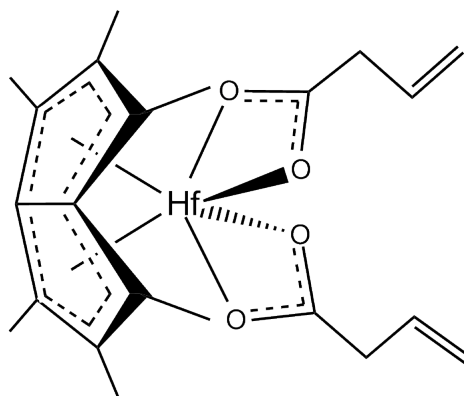
$^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 233 K) δ (ppm): 9.9 [(**2**, **6**)- Me_2 , s], 11.3 [(**1**, **5**)- Me_2 , s], 14.4 [(**3**, **7**)- Me_2 , s], 54.9 [(**15**, **18**)- CH_2CHCH_2 , s], 64.1 [(**17**, **20**)- CH_2CHCH_2 , s], 96.5 [(**3**, **7**), s], 103.2 [(**1**, **5**), s], 113.1 [(**4**, **8**), s], 127.5 [(**2**, **6**), s], 136.2 [(**16**, **19**)- CH_2CHCH_2 , s].

^1H NMR (C_7D_8 , 373 K) δ (ppm): 1.65 [(**2**, **6**)- Me_2 , 6H, s], 1.95 [(**1**, **3**, **5**, **7**)- Me_2 , 12H, s], 2.33 [(**15**, **17**, **18**, **20**)- CH_2 , 8H, d, $^3\text{J}_{\text{H-H}} = 12.25$ Hz], 5.21 [(**16**, **19**)- CH_{meso} , 2H, q, $^3\text{J}_{\text{H-H}} = 12.23$ Hz].

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 373 K) δ (ppm): 9.9 [(**2**, **6**)- Me_2 , s], 12.5 [(**1**, **3**, **5**, **7**)- Me_2 ,

s], 60.6 [(**15, 17, 18, 20**)-CH₂CHCH₂, s], 99.9 [(**1, 3, 5, 7**), s], 114.3 [(**4, 8**), s], 127.4 [(**2, 6**), s], 137.0 [(**16, 19**)-CH₂CHCH₂, s].

X-ray data: 3_5Hf.cif

6.2.16 Characterising Data for $\text{HfPn}^*[\kappa^2\text{-(O}_2\text{CCH}_2\text{CHCH}_2\text{)}]_2$ (**3.5a_{Hf}**)

General Properties: Very pale yellow air-sensitive solution.

High Resolution MS (EI) found (calculated) for $\text{HfPn}^*(\text{O}_2\text{CC}_3\text{H}_5)_2$: 536.1462 (536.1453).

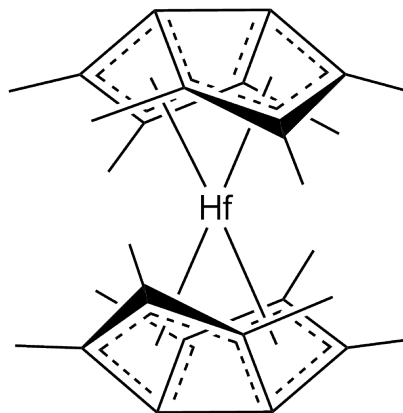
MS (EI): $m/z = 536$ ($[\text{M}]^+$, 30 %); 451 ($[\text{M}-\text{CO}_2\text{C}_3\text{H}_5]^+$, 10 %); 186 ($[\text{Pn}^*]^+$, 30 %); 173 ($[\text{Pn}^*-\text{Me}]^+$, 80 %).

^1H NMR (C_6D_6) δ (ppm): 1.89 [(**2**, **6**)- Me_2 , 6H, s], 1.99 [(**3**, **7**)- Me_2 , 6H, s], 2.29 [(**1**, **5**)- Me_2 , 6H, s], 2.76 [(**16**, **20**)- CH_2 , 4H, d, $^3J_{\text{H-H}} = 7.2$ Hz, $^5J_{\text{H-H}} = 1.8$ Hz], 4.83 [(**18**, **22**)- $\text{RHC}=\text{CH}_{\text{trans}}\text{H}$, d, $^3J_{\text{H-H}} = 16.9$ Hz, $^1J_{\text{H-H}} = 1.7$ Hz], 4.88 [(**18**, **22**)- $\text{RHC}=\text{CH}_{\text{cis}}\text{H}$, d, $^3J_{\text{H-H}} = 10.0$ Hz, $^1J_{\text{H-H}} = 1.3$ Hz], 5.82 [(**17**, **21**) $\text{RHC}=\text{CH}_2$, 2H, m]

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ (ppm): 10.1 [(**2**, **6**)- Me_2 , s], 10.8 [(**1**, **5**)- Me_2 , s], 10.9 [(**3**, **7**)- Me_2 , s], 41.7 [(**16**, **20**)- $\text{O}_2\text{CCH}_2\text{CHCH}_2$, s], 107.6 [(**1**, **5**), s], 108.0 [(**3**, **7**), s], 118.2 [(**18**, **22**)- $\text{O}_2\text{CCH}_2\text{CHCH}_2$, s], 124.7 (**4**, s), 126.7 (**8**, s), 130.2 [(**17**, **21**)- $\text{O}_2\text{CCH}_2\text{CHCH}_2$, s], 132.5 [(**2**, **6**), s], 191.3 [(**15**, **19**)- $\text{O}_2\text{CCH}_2\text{CHCH}_2$].

^1H NMR (C_7D_8 , 373 K) δ (ppm): 1.90 [(**2**, **6**)- Me_2 , 6H, s], 2.08 [(**1**, **3**, **5**, **7**)- Me_4 , 12H, s], 2.82 [(**16**, **20**)- CH_2 , 4H, d, $^3J_{\text{H-H}} = 6.79$ Hz], 4.93 [(**18**, **22**)- $\text{RHC}=\text{CH}_{\text{trans}}\text{H}$], 4.96 [(**18**, **22**)- $\text{RHC}=\text{CH}_{\text{cis}}\text{H}$], 5.80 [(**17**, **21**) $\text{RHC}=\text{CH}_2$, 2H, m]

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 373 K) δ (ppm): 10.0 [(**2**, **6**)- Me_2 , s], 10.6 [(**1**, **3**, **5**, **7**)- Me_4 , s], 41.8 [(**16**, **20**)- $\text{O}_2\text{CCH}_2\text{CHCH}_2$, s], 107.9 [(**1**, **3**, **5**, **7**), s], 117.9 [(**18**, **22**)- $\text{O}_2\text{CCH}_2\text{CHCH}_2$, s], 126.9 [(**4**, **8**), s], 130.5 [(**17**, **21**)- $\text{O}_2\text{CCH}_2\text{CHCH}_2$], 132.5 [(**2**, **6**), s], 191.1 [(**15**, **19**, s)- $\text{O}_2\text{CCH}_2\text{CHCH}_2$].

6.2.17 Characterising Data for HfPn^*_2 (**3.6_{Hf}**)

General Properties: Red air-sensitive crystalline solid.

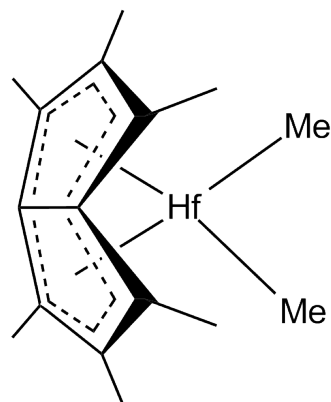
Elemental Analysis found (calculated) for $\text{C}_{28}\text{H}_{36}\text{Hf}$ (MW = 552.23) (%):
C 60.84 (60.8), H 6.57 (6.63).

High Resolution MS (EI) found (calculated) for HfPn^*_2 : 552.2288 (552.2287).

MS (EI): $m/z = 462$ ($[\text{M}]^+$, 10 %); 186 ($[\text{Pn}^*]^+$, 100 %).

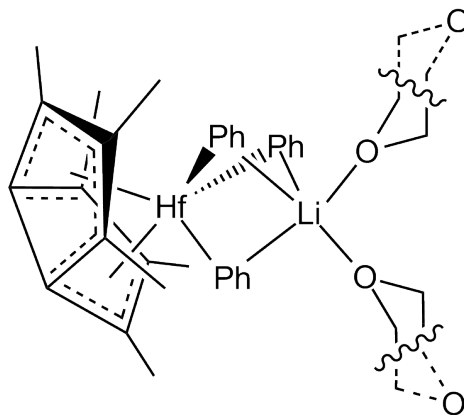
^1H NMR (C_7D_8) δ (ppm): 2.01 [(1, 3, 5, 7)- Me_8 , 24H, s], 1.45 [(2, 6)- Me_4 , 12H, s].

X-ray data: 3.6Hf.cif

6.2.18 Characterising Data for HfPn^*Me_2 

General Properties: Pale orange air and thermally-sensitive pyrophoric powder.

^1H NMR (C_6D_6) δ (ppm): -0.44 [$(\text{Hf}-\text{Me}_2)$, 6H, s], 1.96 [(2, 6)- Me_2 , 6H, s], 2.10 [(1, 3, 5, 7)- Me_4 , 12H, s].

6.2.19 Characterising Data for $[\text{HfPn}^*\text{Ph}(\mu\text{-Ph})_2\text{Li}(1,4\text{-dioxane})]_n$ (**3.8_{Hf}**)

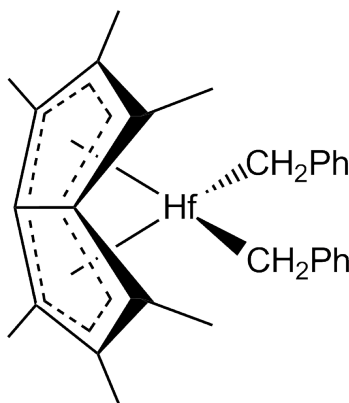
General Properties: Red air-sensitive amorphous powder.

IR (KBr, cm^{-1}): 3042 (s), 2964 (m), 2924 (m), 2857 (m), 1454 (m), 1412 (m), 1380 (m), 1260 (s), 1110 (s), 1078 (s), 1051 (m), 1021 (m), 872 (s), 709 (s).

^1H NMR (C_6D_6) δ (ppm): 1.78 [(**2**, **6**)-*Me*, 6H, s], 2.05 [(**1**, **3**, **5**, **7**)-*Me*₄, 12H, s], 2.50 (1,4-dioxane-*CH*₂, 8H, d), 7.06 (*p*-Ph, 3H, t $^3J_{\text{H-H}} = 7.4$ Hz), 7.22 (*m*-Ph, 6H, t, $^3J_{\text{H-H}} = 7.3$ Hz), 7.98 (*o*-Ph, 6H, t, $^3J_{\text{H-H}} = 6.9$ Hz).

^{13}C NMR (C_6D_6) δ (ppm): 11.0 [(**2**, **6**)-*Me*₂, s], 12.7 [(**1**, **3**, **5**, **7**)-*Me*₄, s], 66.3 (1,4-dioxane), 104.4 (**1**, **3**, **5**, **7**), 126.4 (**4**, **8**), 127.5 (*p*-Ph), 127.1 (*m*-Ph), 131.7 (**2**, **6**), 139.5 (*o*-Ph), 179.0 (*i*-Ph).

^7Li NMR (194 MHz, C_6D_6) δ (ppm): -1.06 (s).

6.2.20 Characterising Data for $\text{HfPn}^*(\text{CH}_2\text{Ph})_2$ (**3.9_{Hf}**)

General Properties: Orange air-sensitive crystalline solid.

Elemental Analysis found (calculated) for $\text{C}_{28}\text{H}_{32}\text{Hf}$ (MW = 548.19) (%):

IR (KBr, cm^{-1}): 3064 (m), 3007 (m), 2971 (s), 2857 (s), 1592 (s), 1481 (s), 1446 (m), 1256 (m), 1210 (s), 1123 (m), 1073 (m), 1027 (m), 984 (s), 874 (s), 803 (s), 749 (m), 698 (s), 616 (m).

^1H NMR (C_6D_6) δ (ppm): 1.28 (HfCH_2 , 4H, s), 1.69 [(**2**, **6**)- Me_2 , 6H, s], 1.99 [(**1**, **3**, **5**, **7**)- Me_4 , 12H, s], 6.50 (*o*-Ph, 4H, d $J_{\text{H-H}} = 7.3$ Hz), 6.82 (*p*-Ph, 2H, t, $J_{\text{H-H}} = 7.0$ Hz), 7.03 (*m*-Ph, 4H, t, $J_{\text{H-H}} = 7.6$ Hz).

^{13}C NMR (C_6D_6) δ (ppm): 10.7 [(**2**, **6**)- Me_4 , q, $^1J_{\text{C-H}} = 126.9$ Hz], 12.0 [(**1**, **3**, **5**, **7**)- Me_4 , q, $^1J_{\text{C-H}} = 126.9$ Hz], 55.0 [HfCH_2 , t, $^1J_{\text{C-H}} = 129.0$ Hz], 105.4 (**1**, **3**, **5**, **7**, s), 122.2 (*i*-Ph), 124.0 [(**4**, **8**), s], 129.4 [(**2**, **6**, s], 128.1 (*m*-Ph, d, $^1J_{\text{C-H}} = 70.7$ Hz), 131.1 (*p*-Ph, d of d, $^1J_{\text{C-H}} = 157.8$ Hz $^2J_{\text{C-H}} = 7.6$ Hz), 145.6 (*o*-Ph, only observed in decoupled spectrum).

X-ray data for **3.9a_{Hf}:** 3_9a.cif