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COORDINATION CHEMISTRY REVIEWS

3. Hafnium 1992

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CONTENTS

INTRODUCTION

This chapter surveys the literature published on the coordination chemistry of hafnium in 1992. It is comprehensive for the main journals, which were searched manually, and *via* Current Contents, the Cambridge Crystallographic Data Base and STN International searches. Those references from more obscure sources were reviewed using *Chemical Abstracts* (vol. 117, 118). Incorporated into this review, is a section which briefly covers catalytic uses of hafnium complexes.

3.1 HAFNIUM(IV)

3.1.1 Complexes with coordinating carbon ligands

The complex $(\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_{13}H_8)HfCl_2$ has been synthesised from the reaction of $HfCl_4$ and the dilithium salt of 2-cyclopentadienyl-2-fluorenylpropane (equ. (1)). When activated by methylalumoxane the complex is able to promote the polymerisation of propene to give highly syndiotactic polypropene. The stronger Hf-C bond results in slower monomer insertion and a lower propagation rate than that observed for the analogous zirconium complex [1].

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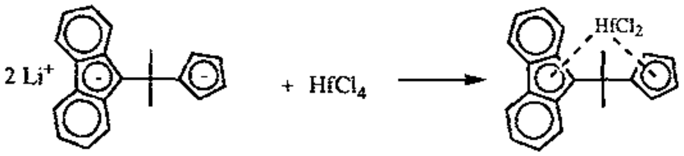
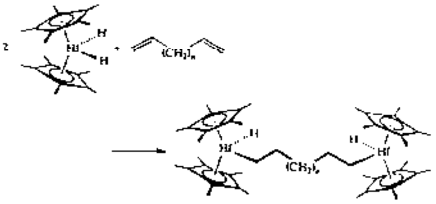


(1)

The reaction of $Cp^*{}_2HfH_2$ with a 2:1 molar ratio of the α,ω-dienes, 1,3-butadiene, 1,4-pentadiene, 1,5-hexadiene and 1,6-heptadiene, yields the novel dinuclear alkanediyl derivatives $[Cp^*{}_2(H)Hf(CH_2)_nHf(H)Cp^*{}_2]$ (n = 4 - 7) (equ. (2)). The 1:1 molar reactions of the same reagents give the mononuclear compounds $[Cp^*{}_2(H)Hf(\eta^3\text{-}CH_2CHCHCH_3)]$, $[Cp^*{}_2\overline{HfCH_2(CH_2)_2C}H(CH_3)]$, $[Cp^*{}_2\overline{HfCH_2(CH_2)_3C}H(CH_3)]$ and $[Cp^*{}_2(H)HfCH_2(CH_2)_4CH{=}CH_2]$ respectively (equ. (3)). The ratios of these products and their related dihafnocene complexes are temperature dependent in some cases. Allene reacts cleanly with $Cp^*{}_2HfH_2$ in equimolar amounts to give the allyl hydride derivative $[Cp^*{}_2(H)Hf(\eta^3\text{-}CH_2CHCH_2)]$ but in a 1:2 molar ratio to give a mixture of products containing $[Cp^*{}_2(H)Hf(CH_2)_3Hf(H)Cp^*{}_2]$. Surprisingly, the reaction of $Cp^*{}_2HfH_2$ with acetylene is not dependent on the reaction stoichiometry and yields $[Cp^*{}_2(H)HfCH{=}CH_2]$ even with an excess of the hafnocene dihydride [2].



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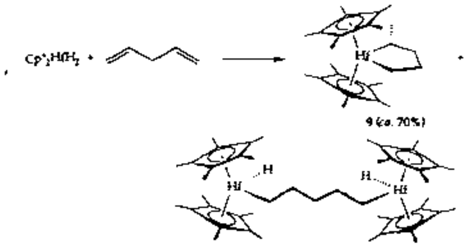


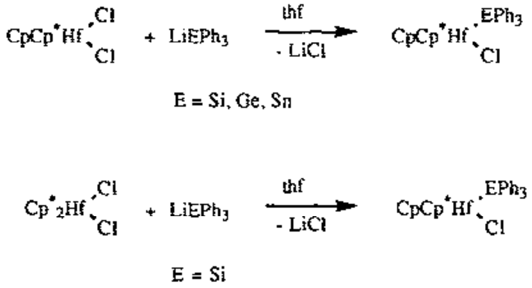
(3)

Reproduced with permission from ref. [2].

A systematic study of the third-order non-linear optical properties of some group 4 metallocene complexes Cp_2MX_2 has been undertaken (M = Ti, Zr, Hf; X = F, Cl, Br, CCC_6H_5). The third order non-linear optical susceptibilities, γ, were derived from the third harmonic generation efficiencies determined for given solutions using a Raman shifted Nd:YAG laser with a fundamental of 1.9μm. In the metallocene-halide complexes the lowest lying absorptions in the UV-VIS spectra arise from Cp-to-metal charge-transfers. The third order susceptibilities however are too low to be measured accurately ($\gamma \sim 5 \times 10^{-36}$ esu). In the acetylide complexes γ ranged from 30×10^{-36} to 5×10^{-36} esu. The decreasing trend in γ values (Ti>Zr>Hf) is rationalised by assuming that the Ti *d* orbitals are closer in energy to the alkynyl π orbitals which leads to more significant mixing between them to form an extended π system [3].

3.1.2 Complexes with silicon donor ligands

The σ-bond metathesis reactions of $CpCp'Hf(SiR_3)Cl$ ($Cp' = Cp$ or Cp^*, $R = Me$, $SiMe_3$) with hydrosilanes have been investigated e.g. the reaction of $CpCp^*Hf[Si(SiMe_3)_3]Cl$ with $RR'SiH_2$ gives the isolable metal silyl derivatives $CpCp^*Hf(SiHRR')Cl$ ($SiHRR' = SiH_2Ph$, $SiH_2(p\text{-tol})$, $SiH_2(p\text{-}MeOC_6H_4)$, $SiH_2(p\text{-}FC_6H_4)$, $SiH_2(2,4,6\text{-}Me_3C_6H_2)$, SiH_2CH_2Ph, SiH_2Cy, $SiHPh_2$, SiHMePh (mixture of diastereoisomers), $SiHPhSiH_2Ph$ (mixture of diastereoisomers). Primary and secondary silanes undergo such reactions when a less sterically hindered silyl ligand is introduced at hafnium but tertiary silanes e.g. Me_3SiH and Et_3SiH do not react. These hydrosilation reactions are accelerated by visible light *via* excitation of a low-intensity transition at 405 nm which appears to have considerable silyl-to-metal charge-transfer character. The crystallographically characterised compound, $CpCp^*Hf[Si(SiMe_3)_3]Cl$ was also found to react with bis(silyl) compounds to give 1,4-$CpCp^*(Cl)HfSiH_2C_6H_4SiH_2Hf(Cl)CpCp^*$ and 2,5-$CpCp^*(Cl)HfSiH_2(C_4H_2S)SiH_2Hf(Cl)CpCp^*$ and with alkoxyhydrosilanes ($HSi(OMe)_2R'$) to give $CpCp^*Hf(SiH_2Me)Cl$ and $CpCp^*(SiH_3)Cl$ [4].



$$CpCp^*HfCl_2 + LiEPh_3 \xrightarrow[-\,LiCl]{thf} CpCp^*Hf(EPh_3)Cl \qquad E = Si, Ge, Sn$$

$$Cp^*_2HfCl_2 + LiEPh_3 \xrightarrow[-\,LiCl]{thf} CpCp^*Hf(EPh_3)Cl \qquad E = Si$$

Scheme 1

The novel stable crystalline material $(thf)_3LiSiPh_3$, and its germyl and stannyl analogues have been employed as reagents in the preparation of triphenylsilyl, triphenylgermyl and triphenylstannyl derivatives of hafnium (Scheme 1). Trends in stability toward photochemical decomposition for these complexes were found to be Sn>Ge>Si. Reaction of $Cp^*_2Hf(SiPh_3)Cl$ with MeMgBr gives $Cp_2Hf(SiPh_3)Me$ which is thermally unstable, and with dihydrogen produces Cp^*_2HfHCl. The reaction of $CpCp^*Hf(EH_2Ph)Cl$ (E = Si, Ge) and 1 equivalent of $PhSiH_3$ under ambient room lighting gives the s-bond metathesis products $CpCp^*Hf(SiH_2Ph)Cl$ and $HEPh_3$. Similarly $CpCp^*Hf[Si(SiMe_3)_3]Cl$ reacts cleanly with $HSnPh_3$ to give $CpCp^*Hf(SnPh_3)Cl$. The reaction of $Cp^*_2Hf(SiPh_3)Cl$ with 1 equivalent of $PhSiH_3$ under ambient laboratory conditions gives quantitative amounts of Cp^*_2HfHCl and $HSiPh_3$, some unreacted $PhSiH_3$ and silane dehydrocoupling products after 2 days [5].

The electronic structure of complexes of the type $R''_nM{=}SiRR'$, (M = Zr, Hf) have been investigated using *ab initio* wave functions including the effects of electron correlation. Several conclusions have been made; firstly that the inclusion of electron correlation is necessary to describe the MSi π-bond, secondly the GVB overlap and MSi force constants increase on the electron withdrawing nature of the ligands (e.g. R = Cl) and thirdly that the MSi force constants vary, with Nb > Zr and Ta > Hf. Analysis of the molecular and electronic structural data using the MC/LMO/CI approach implies that stronger MSi double bonds occur when the MSi π-bond has more back-bonding character [6].

3.1.3 Complexes with nitrogen donor ligands

Eight coordinate complexes of ethylenedioxydiethylene dinitrilotetraacetate ($egta^{4-}$) [Zr(egta)] and [Hf(egta)] have been prepared in aqueous solution from the reaction of $M(OH)_4$ (M = Hf, Zr) and H_4egta (figure 1). The two compounds were isostructural in the solid state with distorted square antiprismatic coordination geometry. In [Hf(egta)] the $-N(CH_2CO_2)_2^-$ and $-NCH_2CH_2O-$ methylene groups give rise to signals in the ^1H NMR spectra that indicate some magnetic equivalence. This is in contrast to the zirconium analogue and it is thought to be a result of changes in the C-N-C angles with the two pairs of $N(CH_2CO_2)_2$ units or slight adjustments in the M-N bond lengths [7].

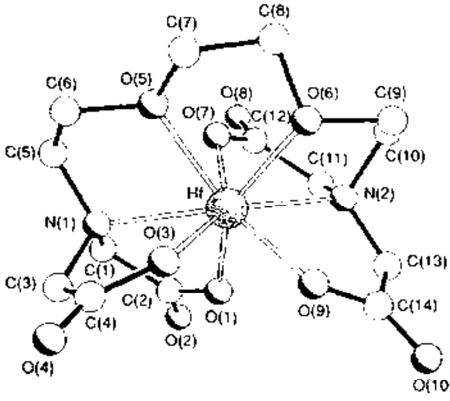


Figure 1. The X-ray structure of [Hf(egta)]. Reproduced with permission from ref. [7].

When the enediamide complex $Cp^*Hf[(\sigma^2,\pi\text{-}^iPr\text{-}DAB)]Cl$ ($Cp^* = \eta^5\text{-}C_5Me_5$, ^iPr-DAB = 1,4-diisopropyl-1,4-diaza-1,3-butadiene) is reacted with ^tBuCN in toluene at 120°C the hafnium complex $Cp^*Hf[^iPrNCH{=}CHNC(Me){=}CHC(^tBu){=}NH]Cl$ is produced. The structure of this compound has been determined by X-ray crystallography (figure 2) and shows that the Cp^*HfCl complex of this new dianionic tridentate ligand is formed by apparent insertion of the cyanide into an ^iPr b-C-H bond, accompanied by the loss of two H atoms. The compound $Cp^*Hf(s^2,\pi\text{-}^iPr\text{-}DAB)Cl$ was also found to react with a variety of ketones RR'C=O (R,R' = ^tBu, Me; R,R' = Ph, Ph) to form intensely yellow ene imine alkoxide complexes of general formula $Cp^*Hf(^iPrNCH{=}CHN{=}CMe_2)(OCHRR')Cl$ (Scheme 2) [8].

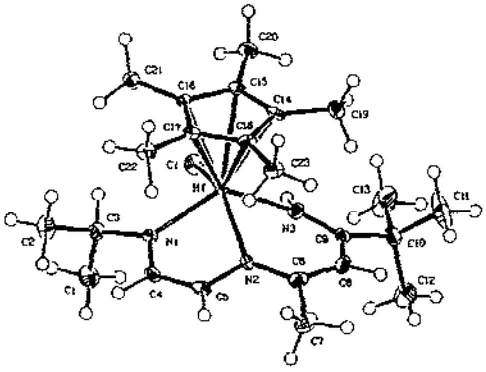
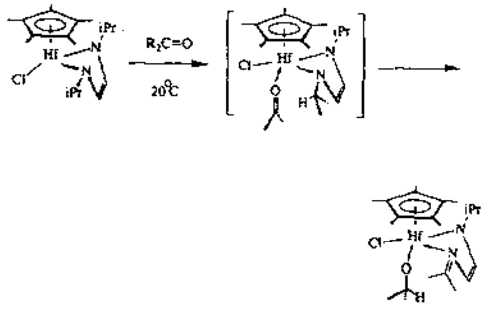


Figure 2. The X-ray structure of $Cp^*Hf[{}^iPrNCH{=}CHNC(Me){=}CHC({}^tBu){=}NH]Cl$. Reproduced with permission from ref. [8].



Reproduced with permission from ref. [8].

Scheme 2

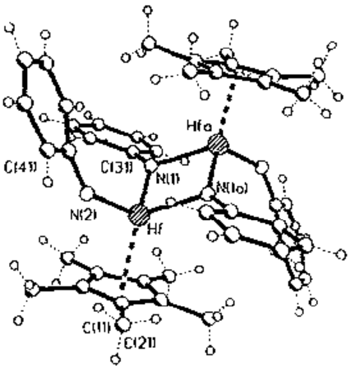
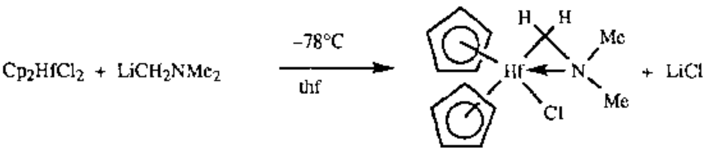


Figure 3. X-ray crystal structure of $[(\eta^5\text{-}C_5Me_5)Hf(NHPh)NPh]_2$. Reproduced with permission from ref. [9].

The chloride $HfCl_4$ reacts with $LiNH^tBu$ to give $[(^tBuNH)_2HfN^tBu]_2$ which oligomerises above 100°C with elimination of H_2N^tBu. The reaction of $(\eta^5\text{-}C_5Me_5)HfCl_3$ with LiNHR gives compounds of general formula $[(\eta^5\text{-}C_5Me_5)Hf(NHR)_3]$ ($R = {}^tBu$, 2,4,6-$Me_3C_6H_2$, 2,6-$^iPr_2C_6H_3$) and $[(\eta^5\text{-}C_5Me_5)Hf(NHPh)NPh]_2$. The latter has been structurally characterised as two crystallographically independent molecules (figure 3) [9].

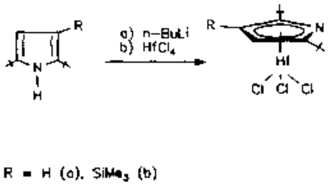
The complex $Hf(=NAr)Cl_2(thf)_2$ is prepared from the reaction of $HfCl_4(thf)_2$ with four equivalents of LiNHAr and two equivalents of Me_3SiCl in thf. This complex reacts with $K_2(C_8H_8)$ to provide $[(\eta^8\text{-}C_8H_8)Hf(=NAr)]_2$ in high yield. C.I. Mass spectrometric data and the solubility properties of the latter are consistent with its formulation as a dimer [10].

The synthesis of a (dimethylamino)alkylhafnium complex has been achieved by reacting Cp_2HfCl_2 with a suitable Group 1 amine (equ. (4)). The product is sensitive to hydrolysis but otherwise very unreactive. The complex is as shown in equ. (4), with an "inward pointing" nitrogen coordination as this binding mode has been established crystallographically for $Cp_2Zr(O_2CCF_3)CH(Ph)NMe_2$ [11].



(4)

A novel azacyclopentadienyl compound (2,5-$^tBu_2C_4HRNH$)$HfCl_3$ has been obtained, and ^{13}C NMR spectroscopic data imply that the ligand is π-coordinated to the metal centre (equ. (5)) [12].



(5)

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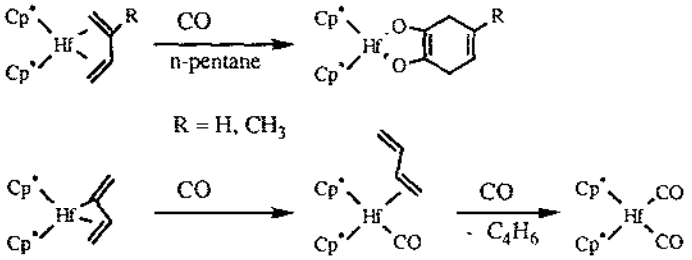
3.1.4 Complexes with phosphorus donor ligands

Tetrakis(tetrahydroborate)hafnium reacts with 4.5 equivalents of trimethylphosphine on prolonged treatment to give $Hf_3H_6(BH_4)_6(PMe_3)_4$. This complex engages in several dynamic exchange processes which could not be frozen out at −80°C. These are thought to include interconversions between didentate and tridentate $[BH_4]^-$ groups, and apparent rotation of a $H_3Hf(BH_3)_3$ unit about a hydride-bridged Hf···Hf vector. The dihafnium complex $(BH_4)H(Me_2PCH_2CH_2PMe_2)_2Hf(\mu\text{-}H)_3Hf(BH_4)_3$, prepared from $Hf_2H_3(BH_4)_5(PMe_3)_2$, retains the dinuclear Hf(μ-H)$_3$Hf unit and from comparison with the structurally characterised zirconium analogue, appears to have three of the BH_4^- ligands coordinated in a manner intermediate between η^2-BH_4^- and a η^3-BH_4^- bonding modes. Both $Me_2PCH_2CH_2PMe_2$ ligands are coordinated to one of the metal centres. The spectroscopic data confirm this formulation ($^{11}B\{^1H\}$ NMR C_7D_8 δ −11.4(s, 1B), δ −33.1(s, 1B); $^{31}P\{^1H\}$ NMR −80°C, δ 11.4(t), δ −6.5(t) J_{PP} = 21Hz) [13].

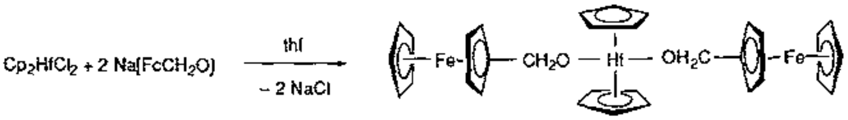
3.1.5 Complexes with oxygen donor ligands

The reactions of the *cis* and *trans* diene complexes of pentamethylcyclopentadienylhafnium with CO have been examined and the resulting endiolate and dicarbonyl products have been spectroscopically characterised (Scheme 3) [14].



Scheme 3

Hafnocene dichloride readily reacts with ferrocenylmethanoate to give the new spectroscopically characterised alkoxide complex (equ. (6)) [15].



(6)

The reaction of $Hf(BH_4)_4$ with ROH (R = Me, Et, ^{i}Pr, ^{t}Bu, Et_3C) in pentane occurs with the formation of the metal and boron alkoxides depending on the steric properties of R. Two new compounds were isolated namely $Hf(OCMe_3)_4.HB(OCMe)_2$ and $HB(OCEt_3)_2$ [16].

Compounds of general formula $MHfL.3H_2O$ (M = K, guandinium, H_5L = diethylenentriaminepentaacetic acid) were prepared and their structures determined from X-ray diffraction data. The potassium salts crystallise in a triclinic space group whereas the guandinium salts crystallise in a monoclinic space group [17].

Films of artificially controlled multi-layers of zirconium and hafnium phosphonates have been prepared on a silicon substrate by immersing a silicon wafer modified with $[OHSiMe_2$-$(CH_2)_3$-$PO_3H_2]$ as an anchoring agent into aqueous solutions of $ZrOCl_2$, $H_2O_3P(CH_2)_{10}PO_3H_2$(DBPA) (DBPA = 1,10-decanediylbis(phosphonic acid)), $HfOCl_2$, and DBPA [18].

3.1.6 Complexes with sulfur donor ligands

The complexes $(\eta\text{-RC}_5\text{H}_4)_2\text{Hf}(\text{S}_2\text{CN}(\text{CH}_2\text{Ph})_2)\text{Cl}$ (R = H, Me) were synthesised from the reaction of $(\eta\text{-RC}_5\text{H}_4)_2\text{HfCl}_2$ with the anhydrous sodium salts of dibenzyldithiocarbamate. These compounds were characterised by elemental analysis and IR and ^{1}H NMR spectroscopies [19].

Two new Ba/Hf/S phases of formula $\text{Ba}_5\text{Hf}_4\text{S}_{13}$ and $\text{Ba}_6\text{Hf}_5\text{S}_{16}$, the n = 4 and n = 5 members of the $\text{Ba}_{n+1}\text{Hf}_n\text{S}_{3n+1}$ Ruddlesden-Popper sulfides, have been prepared from BaS, Hf and elemental sulfur at 1050°C in BaCl_2 flux reactions [20].

3.2 HAFNIUM(II)

3.2.1 Complexes with nitrogen donor ligands

The electrochemical oxidation of the hafnium double-decker complexes Hf(OEP)_2 and Hf(TPP)_2 gives the mono and dications $[\text{Hf(OEP)}_2]\text{X}$, $[\text{Hf(OEP)}_2]\text{X}_2$, $[\text{Hf(TPP)}_2]\text{X}$ and $[\text{Hf(TPP)}_2]\text{X}_2$ ($\text{X} = \text{ClO}_4^-, \text{PF}_6^-$). These have near IR absorption bands that are ~2000 cm^{-1} higher in energy than those of the corresponding cerium complexes. Magnetic susceptibility measurements ($2\text{K} < T < 300\text{K}$) of the solids have been undertaken [21].

Solutions of $(\text{Me}_3\text{P})\text{Hf(CO)}_4$ readily undergo phosphine displacement in an excess of a macrocyclic triamines such as 1,4,7-triazacyclononane (tacn), to yield an air-sensitive but thermally stable, red to dark red microcrystalline material (equ. (7)). The IR spectrum of the tacn product has low frequency CO absorptions comparable to $[(\text{C}_5\text{Me}_5)\text{M(CO)}_4]^-$ species [22].

$$[(\text{Me}_3\text{P})\text{Hf(CO)}_4] + \text{tacn} \xrightarrow[\text{dme}]{-25^\circ\text{C}} [\text{tacnHf(CO)}_4] + \text{PMe}_3 \qquad (7)$$

3.2.2 Complexes with phosphorus donor ligands

The new triene compounds $[\text{Hf}(\eta\text{-C}_7\text{H}_8)\text{L}_2\text{Cl}_2]$ (L = PMe_3, PMe_2Ph) have been prepared. These similarly react with lithium indenide to give $[\text{Hf}(\eta\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)]$ which reacts with PMe_3 or $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ to form $[\text{Hf}(\eta\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)(\text{PMe}_3)]$ or $[\{\text{Hf}(\eta\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)\}_2(\mu\text{-Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)]$ respectively. The structure of the latter has been crystallographically determined (figure 4). Treatment of $[\text{Hf}(\eta\text{-C}_7\text{H}_8)(\text{PMe}_3)_2\text{Cl}_2]$ with NaCp gave red crystals of an isomeric mixture (equ. (8)) [23].

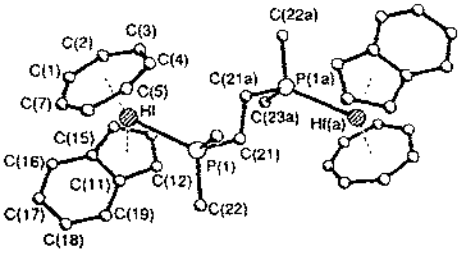
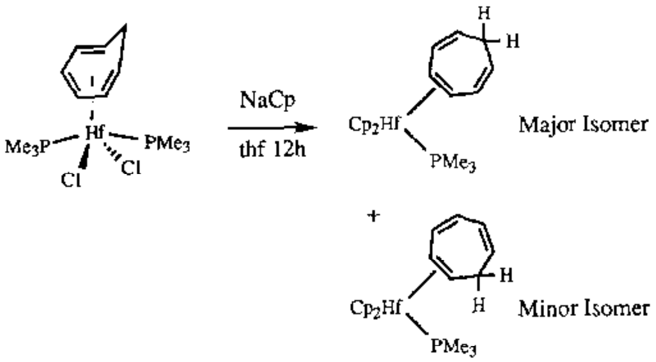


Figure 4. Molecular structure of $[\{\text{Hf}(\eta\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)\}_2(\mu\text{-Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)]$. Hydrogen atoms are omitted for clarity. Reproduced with permission from ref. [23]



(8)

The diene compounds [Hf(η^4-CH_2=CMeCMe=CH_2)(PMe_3)$_2$$Cl_2$] and [Hf($\eta^4$-$C_6H_8$)($PMe_3$)$_2$$Cl_2$] were prepared by reducing $HfCl_4$ using sodium amalgam in the presence of PMe_3 and the corresponding diene. Both compounds were characterised by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, but the structure of the former was obtained by low temperature (15K) neutron diffraction. The neutron diffraction data show that the carbon-carbon bond length sequence is inverted compared to the free diene and are consistent with a s^2, π-metallacyclopentene structure. Further evidence for this is provided by the fact that the diene methylene carbon atoms are closer to the hafnium than are the internal diene atoms. Treatment of this complex with lithium indenide gives [Hf(η^5-C_9H_7)$_2$(η^4-CH_2=CMeCMe=CH_2)], which appears from variable temperature ^{1}H NMR spectroscopic studies to undergo a diene flip fluxional process in solution [24].

3.3 HAFNIUM HETEROMETALLIC COMPLEXES

Bis(pentamethylcyclopentadienyl)calcium reacts with Cp$^*_2$$HfCl_2$ in toluene to yield a 1:1 adduct. Orange-yellow crystals of the resulting complex Cp$^*_2$HfCl(μ-Cl)CaCp$^*_2$ were grown in toluene. The structure shows that the two metallocene units are bent with a single bridging and terminal Cl on hafnium (figure 5). The bridging Cl atom is more closely associated with Hf than Ca (Hf-Cl = 2.463(3)Å, Ca-Cl = 2.864(3)Å). By using identical ligand sets on the *s* and *d* block metal atoms, the problem of ligand-exchange was eliminated. An alternative route to avoid ligand-exchange is to require that this reaction would result in unfavourable alkaline-earth to "soft" ligand interactions. Although other reagents were used, no reaction was observed between Cp$^*_2$Ca and Cp$^*_2$$HfH_2$ and only slight ^{1}H NMR spectroscopic shifts were observed for the reaction of Cp$^*_2$Ca and Cp$^*_2$HfHCl [25].

The reaction of Cp_2HfMe_2 with [Me_2AlCC(cyclo-C_6H_{11})]$_2$ in toluene at room temperature gave a mixture of Cp_2Hf[μ-η^1:η^2-MeCC(cyclo-C_6H_{11})][μ-CC(cyclo-C_6H_{11})]AlMe_2 and Me_3Al. The former was spectroscopically characterised and its structure was confirmed using single crystal X-ray diffraction methods (figure 6). The carbon atom C3 bridging the hafnium and aluminium metal centres is planar tetracoordinate. The four bond distances in the central plane to C3 are 1.280(9)Å C3-C1, 1.562(8)Å C3-C4, 2.091(6)Å C3-Al and 2.432(6)Å C3-Hf [26].

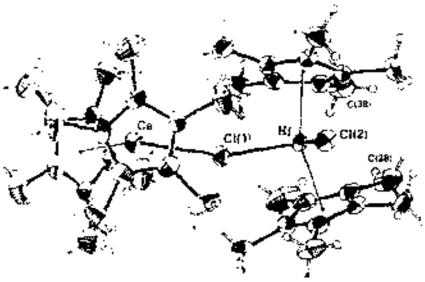


Figure 5. ORTEP view of $Cp^*_2HfCl(\mu\text{-}Cl)CaCp^*_2$, with the non-hydrogen atoms drawn at the 35% probability level. Reproduced with permission from ref. [25].

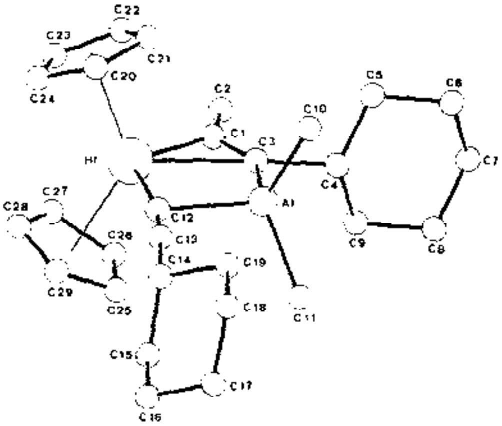
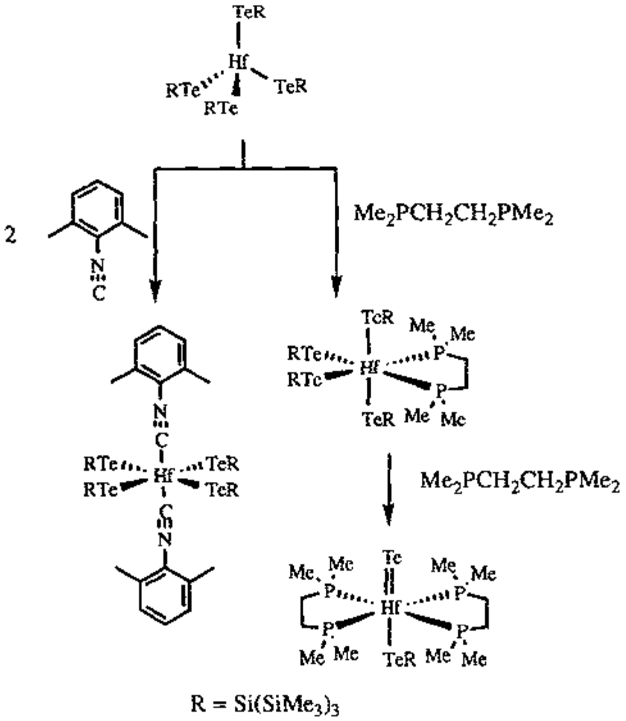


Figure 6. Molecular structure of $Cp_2Hf[\mu\text{-}\eta^1\text{:}\eta^2\text{-}MeCC(cyclo\text{-}C_6H_{11})][\mu\text{-}CC(cyclo\text{-}C_6H_{11})]AlMe_2$ showing the atom numbering scheme. Reproduced with permission from ref. [26].

The red homoleptic tellurolate $Hf[Te(Si(SiMe_3)_3)]_4$ has been prepared via tellurolysis of the metal tetraalkyl complex. This compound reacts cleanly with water and dry dioxygen to give the tellurol and ditelluride $Te_2[Si(SiMe_3)_3]_2$. The tellurolate compound has been characterised using ^1H, $^{13}C\{^1H\}$ and $^{125}Te\{^1H\}$ NMR spectroscopies and X-ray crystallography. The hafnium metal centre is surrounded by four tellurium atoms in a pseudo-tetrahedral array. The reactions of this species with a variety of Lewis bases have been studied and the products have been established spectroscopically in solution (Scheme 4) [27].



Scheme 4

3.4 HAFNIUM COMPLEXES AS CATALYSTS

The system Cp_2HfCl_2 / 2^nBuLi catalyses the condensation of $RSiH_3$ (R = Ph, ^nBu, ^nHex) to silicon oligomers. For reactions conducted at 50°C only one diastereomer of $H(^nBuSiH)_4H$ is observed [28].

The molecular weight and stereoregularity of the polymers produced on the homopolymerisation of 4-methyl-1-pentane is dependent on the nature and composition of the hafnium catalyst used. Similarly distinct behaviour was observed during the copolymerisation of 4-methyl-1-pentene with monoalkenes such as propene, 1-butene and 1-hexene [29].

The catalyst system *rac*-ethylene(bis-indenyl) hafnium dichloride-methyl aluminoxane and its zirconium analogue have been used for the homopolymerisation of ethene and the copolymerisation of ethene and 1-butene. In the case of Hf, the polymers obtained have average molecular weights ≤ 10 times higher than when Zr is used [30].

A chain transfer mechanism *via* β-CH_3 elimination has been proposed as the preferred mechanism for the polymerisation of propene by bis(pentamethylcyclopentadienyl)zirconium and hafnium dichloride/methylalumoxane catalysts at 50°C. The resulting atactic propene oligomers and low polymers have been shown by GC-MS and ^1H, ^{13}C NMR analysis to be mainly allyl and isobutyl terminated. The allyl/vinylidene ratio is 92/8 for Zr and 98/2 for Hf. In contrast the polymerisation of 1-butene occurs *via* exclusive β-H elimination and transfer to aluminium as with the non-substituted metallocenes Cp_2MCl_2 (M = Zr, Hf) [31].

An *ab initio* study of methane activation by Ti, Zr, Hf imido complexes $H_2M{=}NH$, has been completed and shows that the polarity of the metal-ligand bond in the products $H_2M(CH_3)(NH_2)$, formed initially is important in facilitating C-H scission [32].

In order to examine the relationship between agostic interactions at the metal-carbon bond in early transition metal organometallic complexes and their catalytic polymerisation of unsaturated hydrocarbons, a theoretical study using EH-MO calculations and relating $J_{(CH)}$ values obtained from a series of ethylene coordinated complexes has been undertaken. Experimental work on some new zirconocene and hafnocene systems includes a crystal structure of Cp_2Hf(*cis*-1,4-diphenyl-1,3-butadiene) [33].

The ethene polymerisation activity of $[(C_5H_4SiMe_3)_2MMe]^+$ catalysts (M = Ti, Zr, Hf) have been examined. The activity of the hafnium complex with $[CPh_3]^+[B(C_6F_5)_4]^-$ as co-catalyst was found to markedly increase with temperature and to give a corresponding decrease in the polymer molecular weight. This temperature dependence mirrored that of Cp_2MCl_2/MAO catalysts [34].

The effect of the presence of near-stoichiometric quantities of cyclic and acyclic alkenes on the $Cp_2MCl_2/^nBuLi$ (M = Ti, Zr, Hf) catalysed reactions of $PhMeSiH_2$ has been investigated. A surprising diversity of reactions including hydrosilylation of the alkene, isomerisation/hydrosilation of internal alkenes, dehydrocoupling of the silane with the alkene to form vinylsilanes was observed. Dehydrocoupling of cyclooctene and silane occurs to greatest extent with $Cp_2HfCl_2/^nBuLi$ systems [35].

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