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3. Hafnium 1991

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CONTENTS

INTRODUCTION

This chapter surveys the coordination chemistry of hafnium reported during 1991. The last review of hafnium which appeared in *Coordination Chemistry Reviews* covered the published work of 1983 with that of zirconium [1]. This review is not a comprehensive survey of hafnium, but the literature was surveyed using *Current Contents*, the Cambridge Crystallographic Data Base and STN International searches. A table from the relevant papers contained in the journals has been included as a quick reference point for interested readers. The less readily available journals were independently covered from *Chemical Abstracts* (Volumes 114, 115 and 116). Organometallic complexes are covered in this review.

The catalytic ability of hafnium complexes and the highly resistive superconductors of hafnium alloys have been mentioned, but are not extensively covered here as they are not strictly relevant to this coordination chemistry review.

3.1 HAFNIUM(IV)

3.1.1 Complexes with hydride ligands.

Several novel tetrahydrido dimeric hafnium species have been prepared and are useful starting materials for the synthesis of cationic hydride complexes. The bridged hydride dimers

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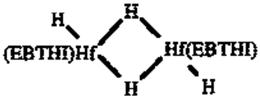
$[(\mathrm{EBTHI})\mathrm{MH}(\mu\text{-H})]_2$ (EBTHI= ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-inenyl); M= Zr or, for (1), M = Hf) are examples and were synthesised from (EBTHI)$\mathrm{MCl_2}$ (M= Zr or Hf) by the addition of two equivalents of Na[$\mathrm{Et_3BH}$] in C_6H_6. The dimethylhafnium complex (EBTHI)$\mathrm{HfMe_2}$ is formed when (1) is treated with MeLi in C_6H_6. Complex (1) can be protonated with weak acids to give the corresponding monomeric cationic hydride species. These metal hydride cations are of interest as possible intermediates in the polymerisation and hydration of alkenes [2].

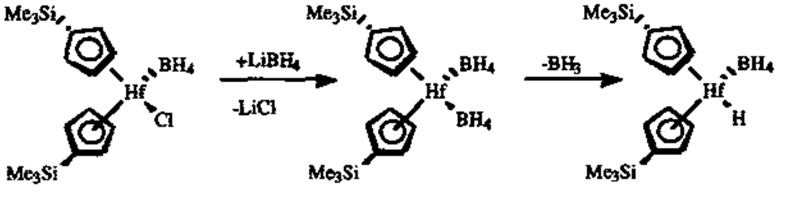


(1)

A new route for the synthesis of hafnocene and zirconocene silyl hydride complexes has been developed. The compound $\mathrm{Cp_2Hf(H)(SiPh_3)(PMe_3)}$ was synthesised and a mechanism for the formation of this complex was presented. The reaction chemistry of these complexes has also been examined [3].

3.1.2 Complexes with borohydride ligands

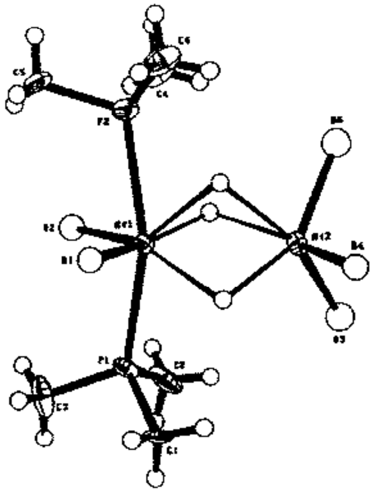
Some new $\mathrm{Me_3SiCp}$ complexes of hafnium have been prepared using a strategy analogous to that known for the reaction of $\mathrm{Cp_2HfCl_2}$ with nucleophiles, in which the $\mathrm{Cl^-}$ ligands are replaced by other anionic ligands. On treatment of $\mathrm{(Me_3SiCp)_2HfCl_2}$ with $\mathrm{LiBH_4}$, the compounds $\mathrm{(Me_3SiCp)_2Hf(Cl)BH_4}$, (2) and $\mathrm{(Me_3SiCp)_2Hf(H)(BH_4)}$, (3) were isolated. Although the expected bis(borohydride) complex $\mathrm{(Me_3SiCp)_2Hf(BH_4)_2}$, (4) was not obtained, the ^{11}B NMR spectrum of the reaction mixture showed it to be an intermediate species, which with loss of $\mathrm{BH_3}$ formed (3) (scheme 1). In a similar method the alkoxide and alkyl derivatives of $\mathrm{(Me_3SiCp)_2HfCl_2}$ were prepared [4].



(2) (4) (3)

Scheme 1

New polyhydride boride complexes of Zr and Hf have been prepared by the addition of trialkyl phosphines to $\mathrm{Zr(BH_4)_4}$ or $\mathrm{Hf(BH_4)_4}$. Two different classes of compounds were formed, namely, dinuclear products with bridging hydrides, and mononuclear products with terminal hydrides. The NMR spectra of these compounds were seen to be dynamic and temperature dependent. The variable-temperature NMR spectra of $Zr_2H_3(BH_4)_3(PMe_3)_2$ and $Hf_2H_3(BH_4)_5(PMe_3)_2$ (5) showed no direct evidence of dynamic behaviour. However the asymmetric structures of these complexes are only consistent with these spectra if there is a specific exchange process between the η^2-BH_4^- and η^3-BH_4^- groups on the hafnium or zirconium metal centres since they are chemically equivalent in the NMR spectra [5].



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(5)

Other metal borides have been prepared and have been found to have uses in ceramic, electronic, and optical industries [6].

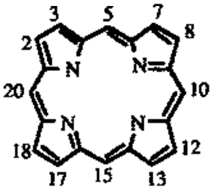
3.1.3 Complexes with nitrogen donor ligands

The new nitrate complexes $Cp_2HfBr(NO_3)$, $CpHfBr(OH)NO_3.H_2O$ and $CpHf(NO_3)_2(OH)$.THF were obtained from the reaction of $(Cp_2HfBr)_2O$ and Cp_4Hf with nitric acid. Depending on the type of complex, it was found that the bonding of the nitrate group with the metal can be realised in different ways [7].

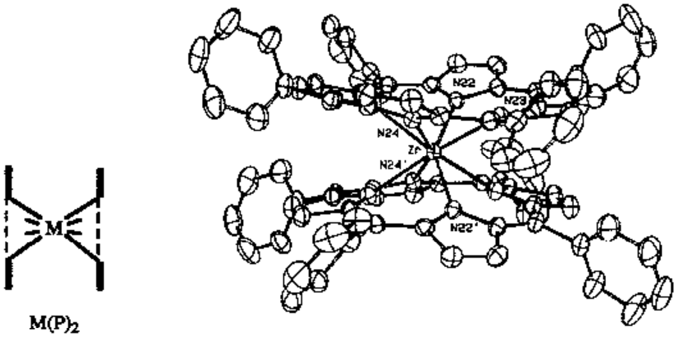
Zirconium and hafnium bis(porphyrinate) double decker complexes $M(P)_2$ (M= Zr, Hf; P = OEP, TPP) (see Table 1) have been synthesised from the reaction given in equ. (i). These structures can best be described as containing a sandwich-like metal centre with Zr or Hf bridging two porphryins (6). These complexes have been structurally characterised and show some potential as models for the special pair of bactereio-chlorophyll molecules effecting the transformation of light [8].

$$MCp_2Cl_2 + 2Li_2(P) \xrightarrow{\text{TCB, 200°C}} M(P)_2 + 2LiCl + 2LiCp \qquad \text{(i)}$$

Table 1. *Specification of Porphyrins*



Nr.	P	R in positions 2-20
1	OEP	C_2H_5 in 2, 3, 7, 8, 12, 13,17, 18
2	TPP	C_6H_5 in 5, 10, 15, 20



(a). schematic representation of $M(P)_2$

(b). crystal structure of $Zr(TPP)_2$ *Reproduced from ref. 8 with permission.*

(6)

3.1.4 Complexes with nitrogen and phosphorus donor ligands

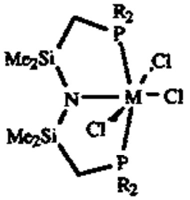
The fine tuning of Group 4 transition metal centres has been achieved by reaction with the tridentate ligand L^- where $HL = HN(SiMe_2CH_2PR_2)_2$. Under specific conditions the monomeric complex (7) could be isolated (scheme 2) and was found to be amenable to further elaboration either by $LiBH_4$, Grignard or other organometallic reagents.

A series of binuclear hafnium hydrideborohydrides were prepared starting from the tris(tetrahydroborate)complex $Hf(BH_4)_3(N(SiMe_2CH_2PMe_2)_2)$ (8) (scheme 3). Butadiene complexes of zirconium and hafnium have also been generated *via* two reductive procedures (scheme 4) [9].

$$MCl_4 + LiN(SiMe_2CH_2PR_2)_2 \xrightarrow[\text{(- LiCl)}]{\text{toluene 1-5 days}} MCl_3[N(SiMe_2CH_2PR_2)_2]$$

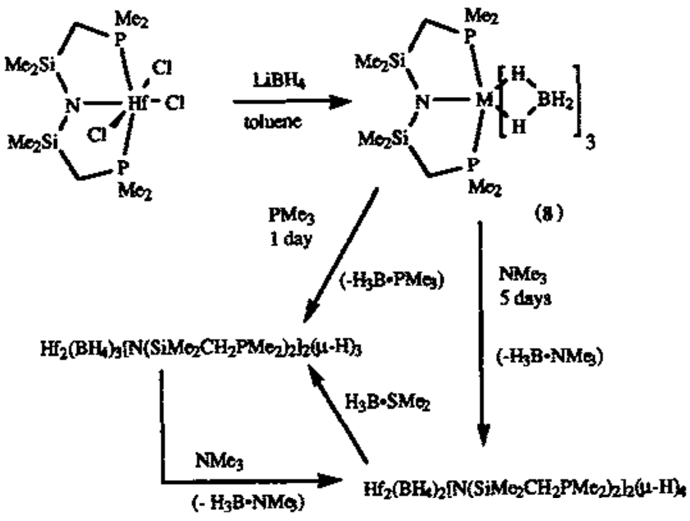
M = Zr, Hf

R = Me, Pr^i, Bu^t

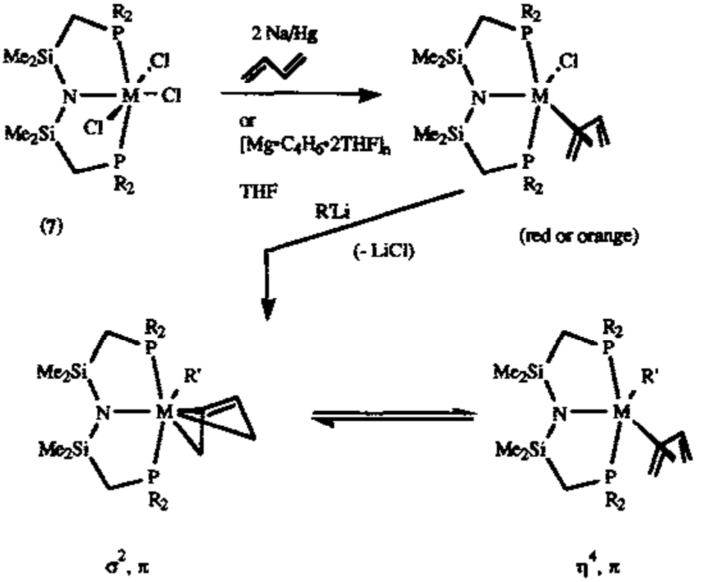


(7)

Scheme 2



Scheme 3

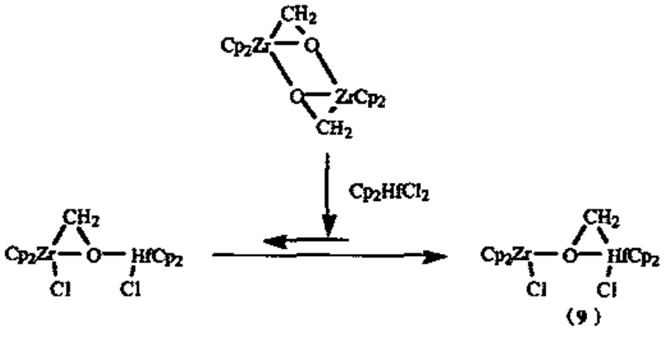


Scheme 4

3.1.5 Complexes with oxygen and sulfur donor ligands

3-Indole carboxylic acid derivatives of bis(cyclopentadienyl)hafnium(IV) dichloride have been synthesised and characterised. Complexes of the type $Cp_2Hf(L)Cl$ and $CpHf(L)_2Cl$, (where L is the didentate 3-indole carboxylate ion) were obtained. The 3-indole acetic acid and the 3-indolebutyric acid derivatives can be used as anticancer and antitumor agents, and their biological activity is enhanced upon binding to metal centres [10].

An alternative means of synthesising $\mu(\eta^1\text{-O}:\eta^2\text{-C,O-formaldehyde})$metallocene complexes has been found. It makes use of the specific reactivity of the (η^2-formaldehyde)zirconium dimer. This route has allowed the synthesis of the previously unattainable $[(Cp_2ZrCl)(Cp_2HfCl)(\mu\text{-}CH_2O)]$. This product could be one of two isomers, shown in scheme 5. No X-ray diffraction results are available but from thermochemical considerations it is suggested that methyl migration from zirconium to hafnium occurs to give (9), the more favoured Hf-C product [11].



Scheme 5

Didentate sulfur bridged compounds such as $(\eta^5\text{-}C_5H_5R)_2MS_2C_6H_6S_2M(\eta^5\text{-}C_5H_4R)_2$ (R= $SiMe_3$; M= Ti, Zr, Hf), were synthesised by the reaction of tetrasodium 1,2,4,5-tetramercaptobenzene with the 1,1'-bis(trimethylsilyl)metallocene dichlorides $M(\eta^5\text{-}C_3H_4R)_2Cl_2$ [12].

3.1.6 Organometallic complexes

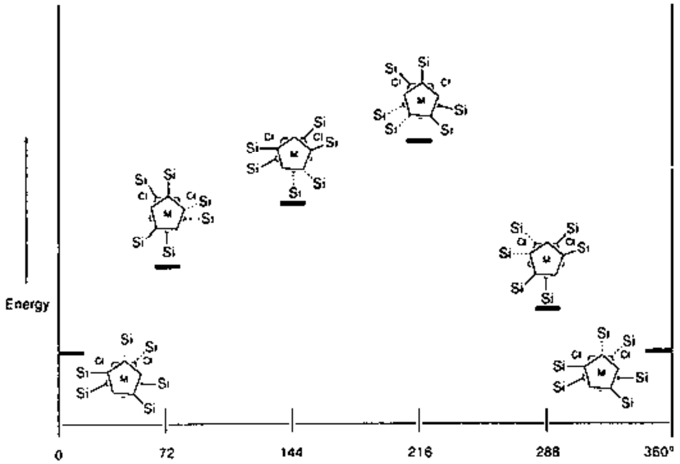
Investigations into the dynamics of hafnium compounds containing allyl and butadiene ligands were carried out. The compounds CpHf(1,2,3-Me_3allyl)(1,2-Me_2butadiene) and CpHf(1,1,2-Me_3allyl)(2,3-Me_2butadiene) were synthesised and studied. It was found that CpHf(1,2,3-Me_3 allyl)(1,2-Me_2butadiene) remains static on the NMR spectroscopic time scale in toluene-d^8 up to 84°C, whereupon it undergoes rapid decomposition. The static behaviour of CpHf(1,2,3-Me_3 allyl)(1,2-Me_2butadiene) contrasts with that of CpHf(1,1,2-Me_3allyl)(2,3-Me_2butadiene) which was found to display three separate dynamic processes and two different isomeric forms in toluene-d_8 solution. It was found that the methylation had a profound effect on the structural and dynamic properties of these CpHf(allyl)(butadiene) complexes. The allyl and butadieneyl groups have their orientation (supine or prone) determined predominantly by the non-bonded repulsions involving the methyl groups on these ligands [13].

The compounds $(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}CH_2CMeCMe_2)HfBr_2$ were prepared by a Grignard reaction of RMgX with $(\eta^5\text{-}C_5Me_5)HfCl_3$. These compounds were examined by single crystal X-ray crystallography and were found to have a bent metallocene-type geometry, with steric congestion in $(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}CH_2CMeCMe_2)HfBr_2$ causing the greatest distortion yet observed for an η^3-allyl ligand towards the η^1-binding mode of a early transition metal complex [14].

The reactions of a number of silylated cyclopentadienes with zirconium and hafnium have been investigated. Monocyclopentadienyl zirconium and hafnium trichlorides were synthesised. The reaction of tris(trimethylsilyl)cyclopentadiene with $ZrCl_4$ or $HfCl_4$, followed by the regiospecific silyl cleavage reaction of tris(trimethylsilyl)cyclopentadiene yields (1,3-bis(trimethylsilyl)-cyclopentadienyl)MCl_3 (M= Zr or Hf) exclusively. This seems to be due to the extremely large profile of the metal centres, which does not allow for the approach of a second bulky tris(trimethylsilyl)cyclopentadiene. In contrast, the related reactions of bis(trimethylsilyl)cyclopentadiene with $ZrCl_4$ or $HfCl_4$ affords the metallocene dichlorides. Verification of the 1,3-regiochemistry of (1,3-bis(trimethylsilyl)cyclopentadienyl)MCl_3 (M= Zr or Hf) was obtained by reaction with 1,3-bis(trimethylsilyl)cyclopentadiene. This yielded the previously structurally characterised 1,1',3,3'-tetrakis(trimethylsilyl)metallocene dichloride. These monocyclopentadienyl zirconium and hafnium trichlorides should prove important in relation to the preparation of highly soluble organometallic Lewis acids [15].

1,1',2,2',4,4'-Hexakis(trimethylsilyl)metallocene dichloride complexes of hafnium have been synthesised. These compounds were seen to show hindered rotation of the cyclopentadienyl ligands. This rotational process was compared to that of the 1,1',3,3'-tetrakis(trimethylsilyl)metallocene dichlorides of hafnium (and zirconium). In the case of the tetrakis-compounds, the long metal-cyclopentadienyl distances allow a facile "gear mesh" rotational

mechanism. In the case of the 1,1',2,2',4,4'-hexakis(trimethylsilyl)metallocene dichlorides however, this rotation involves the eclipsing of two trimethylsilyl groups, and the "gear mesh" mechanism was less favourable as indicated in (10). Hence a high barrier to rotation was observed [16].

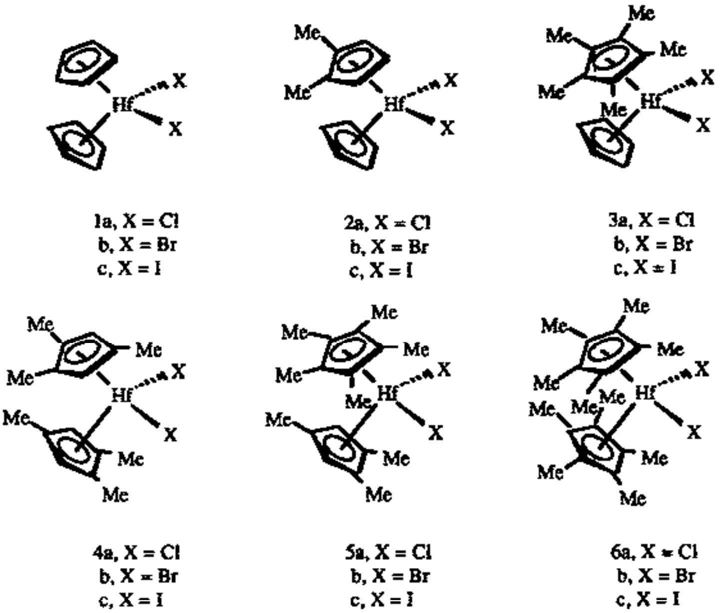


(10)

Qualitative energy diagram for cyclopentadienyl rotation in 1,1',2,2',4,4'-hexakis(trimethylsilyl)metallocene dichloride. *Reproduced from ref. 16 with permission.*

The dilithium salt of the 1,4-dicyclopentadienyl-1,1,4,4-tetramethyl-1,4-disilabutylene dianion, $[C_5H_4Si(CH_3)_2CH_2]^{2-}$ was synthesised and its reactions with the metal chlorides MCl_4 (M= Ti, Zr, Hf) were studied. For M = Hf, this reaction yielded hafnocene derivative with an intranuclear 1,1,4,4-tetramethyl-1,4-disilabutylene bridge. The identity of the new compound has been documented by analytical as well as by spectroscopic (IR, MS, ^1H and ^{13}C NMR) data [17].

A series of hafnocene dihalide derivatives was prepared (1-6, (a), (b), (c), (**11**)), with varying degrees of methyl substitution through the use of cyclopentadienide, 1,2,3-trimethylcyclopentadienide, 1,2,3,4,5-pentamethylcyclopentadienide, and a combination thereof as ligands. The decrease in $Hf(4f_{7/2})$ binding energy per methyl group was examined by XPS. The correlation of binding energies and the degree of methyl substitution for a series of hafnocene dichlorides was found to be linear. A series of hafnocene dibromides was examined by X-ray crystallography and it was shown that no structural distortion was seen as a result of addition of the methyl groups. These are shown in structures (**12**) and (**13**). It was thus concluded that the linearly additive electron donating ability of the methyl substituents was the reason for the decrease in binding energy of the $Hf(4f_{7/2})$ electrons [18].



1a, X = Cl
b, X = Br
c, X = I

2a, X = Cl
b, X = Br
c, X = I

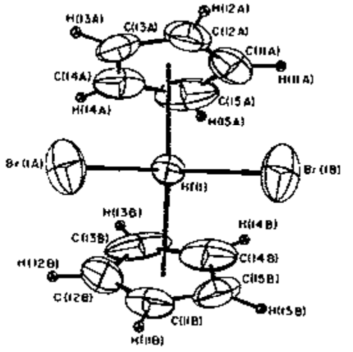
3a, X = Cl
b, X = Br
c, X = I

4a, X = Cl
b, X = Br
c, X = I

5a, X = Cl
b, X = Br
c, X = I

6a, X = Cl
b, X = Br
c, X = I

(11)



(12)
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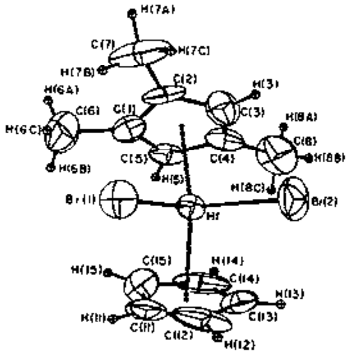

(13)
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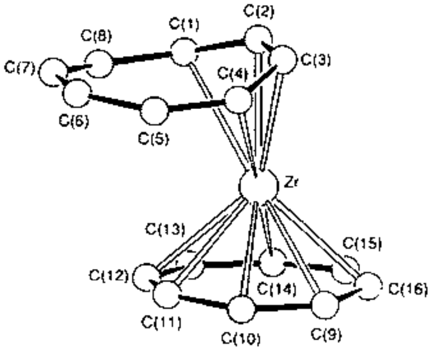
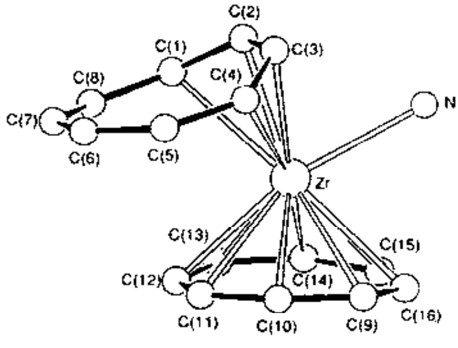
Studies of $Hf(C_8H_8)_2$ and its zirconium analogue have been reported. The structure of bis(cyclooctatetraenyl)zirconium, $Zr(C_8H_8)_2$ has been investigated. In solution, the NMR spectroscopic data suggested a symmetric sandwich structure, as all the hydrogen and carbon atoms were seen to be equivalent and no line broadening due to the decoalescence of a fluxional process was noted. However the CPMAS ^{13}C NMR spectrum contained two resonances and the X-ray crystallographic results unambiguously revealed a structure with one η^8- and one η^4-C_8H_8 ring (**14**). Similar conclusions were also been drawn for $Hf(C_8H_8)_2$, the hafnium analogue [19].



(14) A SCHAKAL drawing of complex $Zr(C_8H_8)_2$. *Reproduced with permission from ref. 20.*

The complexes $Zr(C_8H_8)_2$, $Hf(C_8H_8)_2$ and the complexes $M\{\eta^8\text{-}C_8H_6(SiMe_3)_2\}\{\eta^4\text{-}C_8H_6(SiMe_3)_2\}$ (M= Hf or Zr) were synthesised and the η^8 and η^4 binding modes were verified for the four compounds using the same methods as before. The crystal structure of $Hf\{\eta^8\text{-}C_8H_6(SiMe_3)_2\}\{\eta^4\text{-}C_8H_6(SiMe_3)_2\}$ has been determined. These complexes have now been shown to act as Lewis acids in the presence of thf, NH_3, and Bu^{t}NC and the adducts $Hf(\eta^8\text{-}C_8H_8,\eta^4\text{-}C_8H_8)(CNBu^t)$ and $Zr(\eta^8\text{-}C_8H_8,\eta^4\text{-}C_8H_8)L$ (L = NH_3, CNBu^t, thf), (complex (**15**) for L = NH_3), have been isolated and characterised. The X-ray crystallographic structures of $Zr(\eta^8\text{-}C_8H_8,\eta^4\text{-}C_8H_8)L$ (L = NH_3, CNBu^t) have been studied; data showed that one ring had no C(5)-C(8) to metal bonding and that the M-C(1) and M-C(4) bonds were longer than the M-C(2) and M-C(3) bonds which may suggest an alternative η^2 bonding mode through the C(2) and C(3) atoms, (**16**) [20].

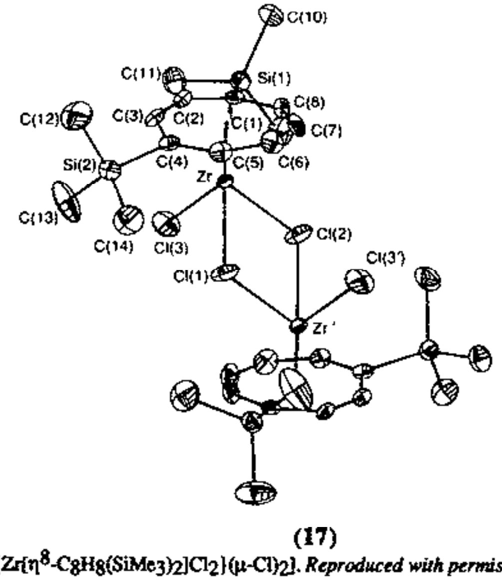


(15) A SCHAKAL drawing of complex $Zr(\eta^8\text{-}C_8H_8,\eta^4\text{-}C_8H_8)(NH_3)$.
Reproduced with permission from ref. 20.

(16)

3.1.7 Complexes with bridging halide ligands

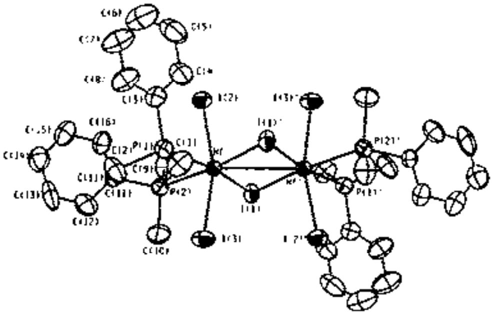
A new high yield synthesis of the half-sandwich monocyclooctatetraene 14-valence electron derivative [Hf(η^8-C_8H_8)Cl_2] and the solvated form [Hf(η^8-C_8H_8)Cl_2thf] has been developed based on a ligand redistribution reaction between [Hf(η^8-C_8H_8,η^4-C_8H_8)] and [$HfCl_4(thf)_2$]. Parallel chemistry occurs for zirconium. This new synthesis is reliable yet inexpensive and means that these complexes can now be used more readily in the study of organic transformations induced by zirconium and hafnium. These have advantages over the cyclopentadienyl analogues M(η^5-C_5H_5)$_2X_2$ in that they are unsaturated, both electronically and co-ordinatively. This new reaction proved valuable in the synthesis of substituted cyclooctatetraenes such as [{Zr[η^8-$C_8H_8(SiMe_3)_2$]Cl_2}(μ-Cl)$_2$] (**17**) [21].



(17)

[{Zr[η^8-$C_8H_8(SiMe_3)_2$]Cl_2}(μ-Cl)$_2$]. *Reproduced with permission from ref. 21.*

The reduction of HfI_4 or ZrI_4 with one equivalent of Na/Hg amalgam, followed by two equivalents of phosphine, produced, in moderate yields, the edge-sharing bioctahedral complexes $Hf_2I_6(PMe_2Ph)_4$ (**18**), or $Zr_2I_6(PMe_3)_4$ (**19**) and $Zr_2I_6(PMe_2Ph)_4$. It was thought that these iodine bridged complexes would not contain a metal-metal bond. However, from molecular orbital calculations on the model complex $Zr_2I_6(PH_3)_4$, it was found that the HOMO is in fact metal-metal bonding in character and is mainly composed of metal d_{z^2} and $d_{x^2-y^2}$ σ-type orbitals. Thus it was seen that even though the M-M distance was long ~ 3.4Å for all three complexes, in fact bonding character should be present [22].



(18)
$Hf_2I_6(PMe_2Ph)_4$
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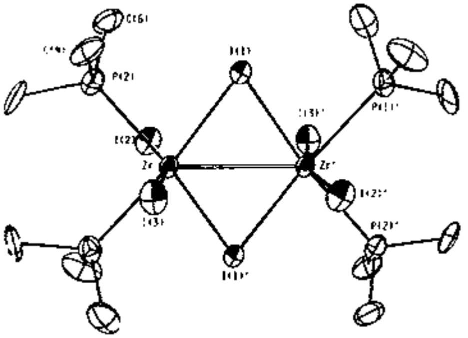

(19)
$Zr_2I_6(PMe_3)_4$
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3.1.8 Complexes used as organic catalysts

Many compounds of hafnium including $(C_5H_5)_2Hf(CH_3)_2$ [23] have been used as catalysts for polymerisation. Other compounds have also been used for polymerisation [24-28] and some are used as hydration catalysts for unsaturated polymers [29].

Syntheses of Fischer-type vanadium complexes have been achieved *via* the formation of metallocyclic (hafnoxycarbene)vanadium complexes from $CpV(CO)_4$ and the removal of hafnium. The complex (*s-trans*-butadiene)zirconoxycarbene adds to a carbonyl ligand of $CpV(CO)_4$ to give the [(π-allyl)Zirconoxycarbene]vanadium complex $Cp_2\overline{ZrOC[=VCp(CO)_3]C}_4H_6$. The complex $(butadiene)HfCp_2$ reacts similarly to give a mixture of the [(π-allyl)hafnoxycarbene]- and seven-membered metallocyclic [(σ-allyl)hafnoxycarbene]-vanadium species. These complexes can subsequently add a ketone to yield nine membered metalloxycarbene vanadium complexes, such as $Cp_2\overline{ZrOC[=VCp(CO)_3]CH_2CH{=}CHCH_2C(CH_3)_2O}$, exhibiting analogous chiral *trans*-cycloalkene dioxametallo-*trans*-cyclonene frameworks. The hafnium metal centre could be removed from the relevant complexes by treatment with tetrabutylammonium fluoride trihydrate in thf solution. The remaining Vanadium acylmetallate complexes were then *O*-alkylated to yield ordinary Fischer-type (carbene)vanadium complexes that could not be synthesised by conventional synthetic methods [30].

Investigations on the copolymerisation of a linear α-alkene, (1-hexene), with a branched alkene, (4-methyl-1-pentene), in the presence of hafnium or titanium supported on $MgCl_2$ were carried out. It was found that the hafnium catalysts gave higher regiospecifity and higher molecular weights, but had a lower activity than the titanium catalysts. The higher degree of polymerisation obtained when hafnium was present can be explained by the higher stability of the Hf-C σ-bond to transfer reactions without influencing the copolymer sequence distribution. It seems that a similar fraction of hafnium atoms actually take part in the polymerisation process and it is this that leads to the difference in activity. The steric effect is not fully understood [31].

The oligomerisation of ethane with other α-alkenes to form linear alkenes has been achieved in the presence of a catalyst system containing bis(cyclopentadienyl)-group 4 transition metal compounds with a substituent capable of reacting with a cation, and a non-coordinating compound containing a bulky anion with at least one boron atom and a cation [32].

Other research into hafnium metallocenes working as catalysts for specific polymerisation has been carried out using the catalyst bis(dimethylsilylene)bis(1,2,3,3*a*,7*a*-η-1*H*-indene-1-ylidene)$HfCl_2$. The products formed on polymerisation have been examined and a hypothesis for the reaction mechanism involved was given [33]. The same complex has been reported to act as a catalyst for the block polymerisation of ethylene with propylene [34].

The complexes $(BuO)_4Hf$ and hafnium 1,1'-bis(2-naptholate)bibutanolate were used in combination with dialkylmonochloroaluminium for the homogeneous polymerisation of ethene in order to understand the features of these systems in the basic polymerisation steps. These systems were then compared with the similar titanium based systems. The results, as in the heterogeneous case [31], led to the conclusion that hafnium based systems when activated with aluminium alkyls provide higher molecular weight polymers than analogous titanium systems, but have lower activity [35] than the titanium analogue.

Silane or germane bridged metallocene catalysts including those of hafnium have also been used as soluble catalyst systems for the polymerisation of alkenes [36].

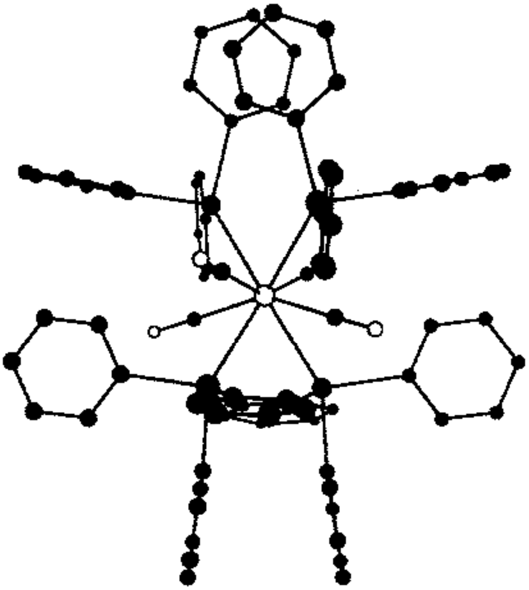
High resistant and/or superconducting mixed metal compounds of hafnium have been synthesised and examined *e.g.* HfO_2-modified alumina fibres [37] and aluminium-lithium-hafnium alloy powders [38]. These, however, are not reviewed in detail here.

3.2 HAFNIUM(II)

3.2.1 Complexes with carbonyl ligands

Carbonyl compounds of hafnium (and zirconium) containing only the triphenylstannyl ligand as a stabilising group have been prepared. These new complexes which formally contain divalent hafnium (or zirconium), are dianions of composition $[(Ph_3Sn)_4M(CO)_4]^{2-}$ (M= Hf or Zr). These are in fact the first examples of eight-coordinate metal carbonyls containing only monodentate ligands. The basic synthetic procedure is given in equation (ii). The exact role of the phosphine is not fully understood, but without it the carbonylation step fails. A view of the hafnium complex $[(Ph_3Sn)_4Hf(CO)_4]^{2-}$ (**20**) emphasises the relatively high symmetry of these dodecahedral species [39].

$$HfCl_4 \cdot 2thf + 2NaC_{10}H_8 \xrightarrow[CO]{4PMe_3,\ 4Ph_3SnNa} Na_2[(Ph_3Sn)_4Hf(CO)_4] + 2C_{10}H_8 \qquad \text{(ii)}$$

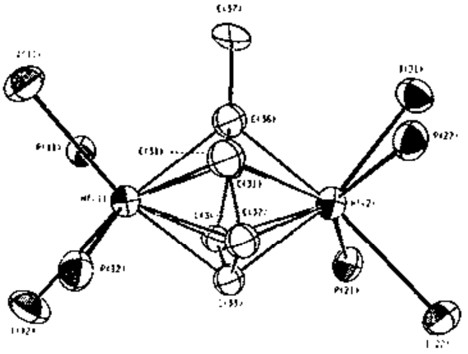


(20)

3.2.2 *Complexes with unsaturated ligands*

Hafnium(II) complexes are often stabilised by coordinated arene ligands, for example, $Hf_2I_2(PMe_2Ph)_4(\mu\text{-}\eta^{12}\text{-arene})$ where the arene is benzene or toluene; the structure of $Hf_2I_2(PMe_2Ph)_4(\mu\text{-}\eta^{12}\text{-}C_6H_5Me)$ (21) has been determined. These compounds were synthesised by an initial reduction of HfI_4 in the appropriate arene and then addition of two equivalents of dimethylphenylphosphine. These complexes are unique in two ways; firstly they are molecular compounds of hafnium which do not contain an $\eta^5\text{-}C_5H_5$ group, and secondly they contain a six-membered ring simultaneously and equivalently bonded to two metal atoms lying above and below the ring opposite to each other [40].

Complexes related to the ones described above have been reported and they include the dihafnium species $Hf_2Br_4(\eta^6\text{-}C_5H_5PMe_2)(PMe_2Ph)_2$ (22). Pyramidal HfX_2P_2 units are bound to a phenyl substituent of a phosphine ligand through all six carbon atoms . These compounds were formed by a similar MX_4 reduction procedure to that described above but here the metal-metal distance is quite long and indicates the possibility of forming mononuclear complexes of this nature [41].



(21)

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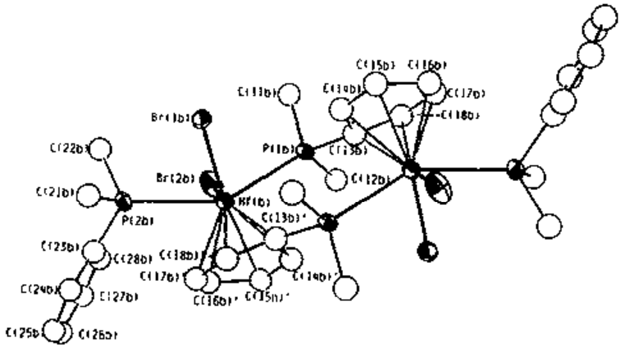

(22)

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Table of Reference Data

*	NMR	IR	XRD+	MS‡	UV/Vis	Raman	M.O.†	E.C.§
[2]	√							
[3]	√	√	√					
[4]	√			√				
[5]	√	√	√					
[7]	√					√		
[8]			√		√			√
[9]	√							
[10]	√	√						
[12]	√	√	√					
[13]	√		√					
[14]	√		√					
[15]	√							
[16]	√							
[17]	√	√		√				
[18]	√		√	√				
[19]	√		√					
[20]	√		√					
[21]	√		√					
[31]	√							
[39]	√	√	√					
[40]	√		√				√	
[41]			√				√	

* Number refers to reference paper ; + X-ray structure determination ; ‡ Molecular orbital theory calculation; § Electrochemical characterisation.