

11. Zirconium and Hafnium 1994

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INTRODUCTION

This chapter reviews the coordination chemistry of zirconium and hafnium published during 1994. It was compiled by surveying work detailed in the major journals and less prominent sources were reviewed using the online searching facility of the University of Bath (BIDS).

The coordination chemistry of Zr and Hf involves many complexes with organic ligands. Cyclopentadienyl complexes are especially common. For the purpose of this review it was decided to include references to complexes having at least one donor atom other than carbon. These

references may also be cited in a complementary review of the organometallic chemistry of Zr and Hf for 1994 and therefore some overlap may occur.

The first section of the review is organised according to donor ligand going from left to right across the periodic table for compounds of Zr and Hf formally having an oxidation state of IV. This is followed by a section involving low oxidation state complexes. The latter half of the review is concerned with the solid state chemistry of Zr and Hf. It includes a subsection on layered phosphate and phosphonate complexes of Zr and Hf. The characteristic structural properties of these materials may find application in important areas such as ion exchange and catalysis. The final section deals with the reactions of Zr and Hf specifically related to catalytic processes. It is not intended as a comprehensive survey of the field but serves as a brief summary of the catalytic behaviour of Zr and Hf coordination complexes published during 1994.

11.1 ZIRCONIUM(IV) AND HAFNIUM(IV)

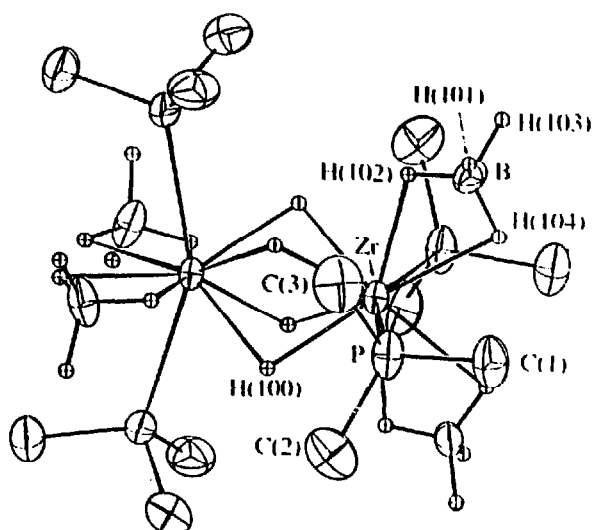
An extensive review has appeared on the chemistry of biscyclopentadienylzirconium(IV) and hafnium(IV) complexes with a variety of donor ligands including transition metal-centred anionic ligands [1].

11.1.1 Complexes with hydrogen donor ligands

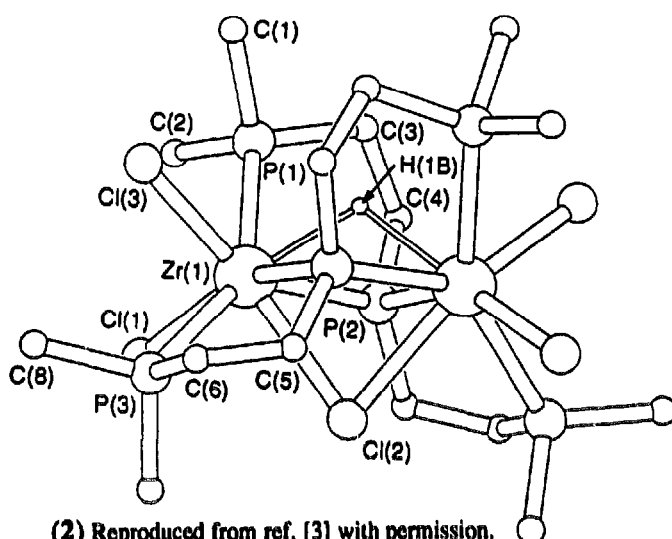
The dimeric compound $[\text{Zr}_2\text{H}_4(\text{BH}_4)_4(\text{PMe}_3)_4]$ (1) has been prepared by the reaction of $\text{Zr}(\text{BH}_4)_4$ with 16 equivalents of PMe_3 in pentane at 195 K. The crystal structure showed it to consist of two Zr atoms linked by four bridging hydride ligands. Each Zr is ligated by two PMe_3 ligands and two didentate BH_4^- groups. The Zr-Zr distance of 2.979(1) Å is significantly shorter than that seen in the related triple hydrogen-bridged dimer $[\text{Zr}_2\text{H}_3(\text{BH}_4)_5(\text{PMe}_3)_2]$ (Zr-Zr = 3.124(1) Å). This is consistent with a shortening of Zr-Zr contact distances on increasing the number of bridging hydrides between the metal centres [2].

Compounds of the form $[\text{ZrCl}_2\text{L}_2]$, $[\text{Zr}_2\text{Cl}_6\text{L}_2]$, $[\text{Zr}_2\text{Cl}_5\text{HL}_2]$ and $[\text{Zr}_2\text{Cl}_3\text{L}_2]$ ($\text{L} = \text{P}(\text{CH}_2\text{CH}_2\text{PMe}_2)_2$) have been prepared by the reaction of zirconium chloride and the deprotonated diphosphinophosphide, $\text{P}(\text{CH}_2\text{CH}_2\text{PMe}_2)_2\text{H}$. The complexes have been characterised by analytical and spectroscopic techniques. The crystal structure of $[\text{Zr}_2\text{Cl}_4(\mu\text{-Cl})(\mu\text{-H})(\text{P}(\text{CH}_2\text{CH}_2\text{PMe}_2)_2)_2]$ (2) has been determined. It is dinuclear and contains chloride, phosphide and hydride bridges. Complexes containing both hydride and dialkylphosphide groups are rare for early transition metals [3].

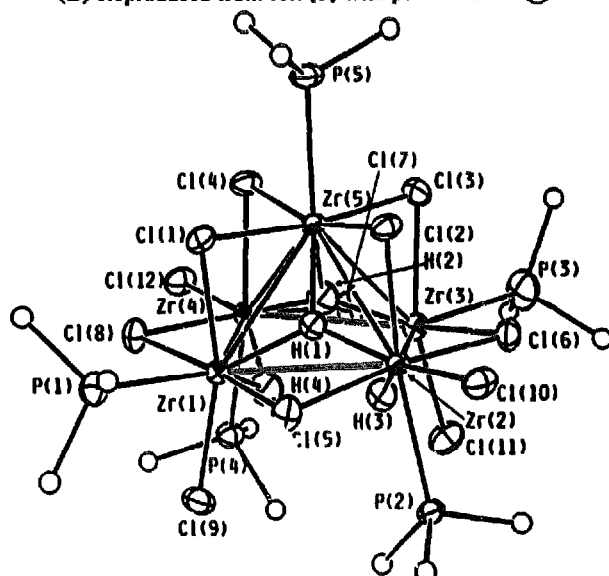
Compounds of composition $\text{H}_4\text{Zr}_5\text{Cl}_{12}(\text{PR}_3)_5$ have been prepared by the reaction of ZrCl_4 with Bu_3SnH (1:1.60) followed by 1 mole equivalent of PR_3 . Compounds with $\text{PR}_3 = \text{PMe}_3$ (3), PEt_3 (4) and PMe_2Ph (5) were characterised by X-ray crystallography and ^1H and ^{31}P (^1H) NMR spectroscopy. The compounds all have five Zr atoms arranged to form a distorted pyramid with a roughly rectangular base. Apart from the hydrogen atoms they all have core geometry $\text{Zr}_5\text{Cl}_{12}(\text{PR}_3)_5$ [4].



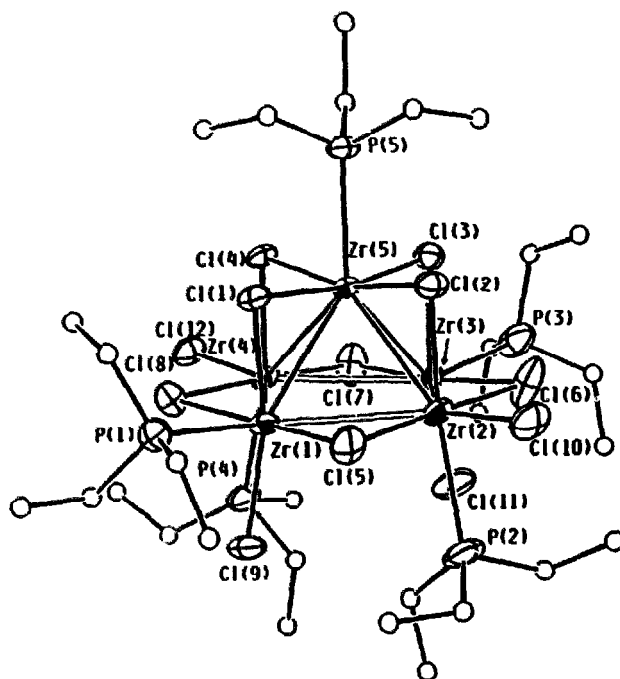
(1) Reproduced from ref. [2] with permission.



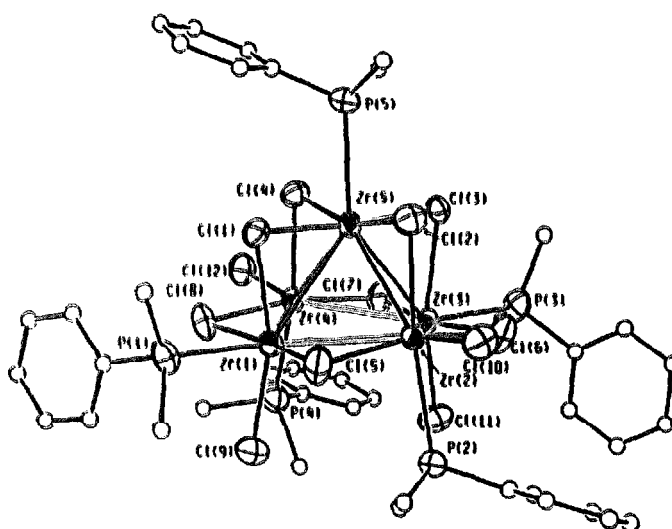
(2) Reproduced from ref. [3] with permission.



(3) Reproduced from ref. [4] with permission.



(4) Reproduced from ref. [4] with permission.



(5) Reproduced from ref. [4] with permission.

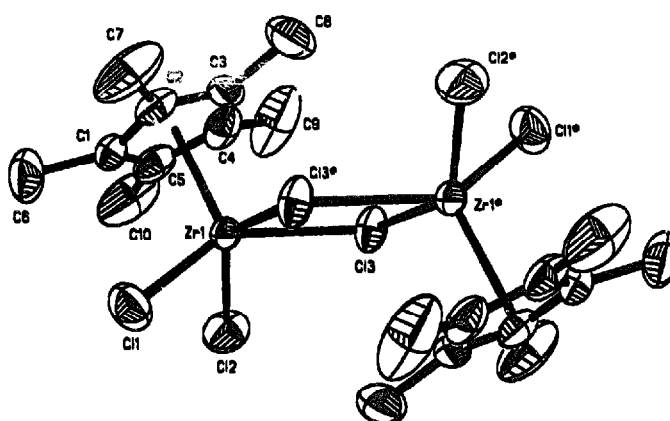
Silica-anchored hydride complexes, $[\text{Zr}]_5\text{-H}$, have been synthesised by the controlled hydrogenolysis of a tris(neopentyl)zirconium surface complex, prepared from tetrakis(neopentyl)zirconium and dehydroxylated SiO_2 . The hydride complexes have been characterised by infrared spectroscopy. Their chemical reactivity has been compared to related molecular analogues. The high reactivity and thermal stability of the complexes were considered to

be related to the presence around Zr of the 'solid' ligand. The influence of the ligand is discussed in terms of electronic and immobilising effects [5].

Silica-anchored alkyl zirconium complexes $[\text{Zr}]_5\text{-R}$ ($\text{R} = \text{cyclooctyl}$, Pr or Me) have also been prepared by the reaction of $[\text{Zr}]_5\text{-H}$ complexes with the relevant alkanes. Their stoichiometric reactivity towards molecules such as carbon monoxide and olefins was investigated in order to determine the potential of such systems to activate and functionalise alkanes catalytically [6].

11.1.2 Complexes with carbon donor ligands

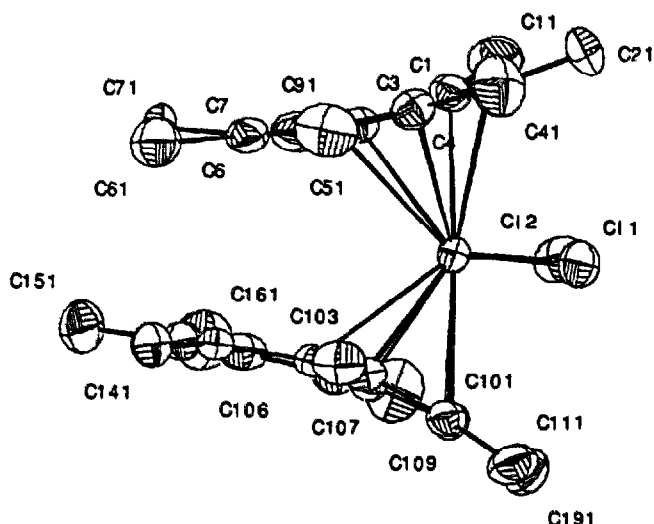
The compound Cp^*ZrCl_3 (**6**), prepared from the reaction of ZrCl_4 with Cp^*SiMe_3 , has been shown by crystallography to consist of dimeric units. The two Cp^*ZrCl_3 moieties are related by a centre of symmetry with two chlorine atoms bridging the two metals. The Zr–Zr intramolecular distance (4.119\AA) and Zr–Cl(bridging) distances are similar to those found in CpZrCl_3 which exists as a linear polymer [7].



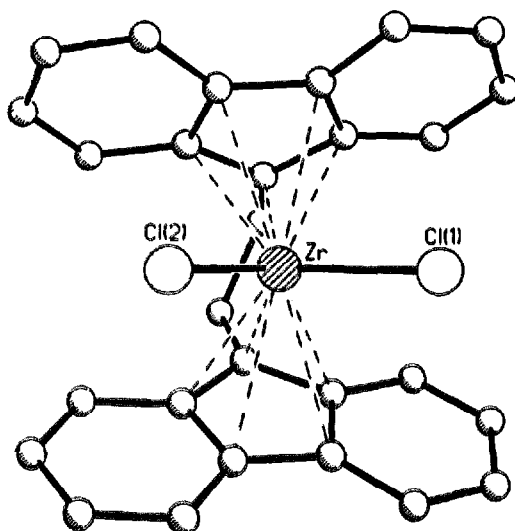
(6) Reproduced from ref. [7] with permission

The half-sandwich compounds $\text{M}(\eta^5\text{-C}_9\text{Me}_7)\text{Cl}_3$ ($\text{M} = \text{Zr}, \text{Hf}$) have been obtained by addition of 1-(trimethylsilyl)heptamethylindene ($\text{C}_9\text{Me}_7\text{SiMe}_3$) to a suspension of the anhydrous halides MCl_4 in thf . Replacement of a further Cl group yielding the metallocene derivatives $\text{M}(\eta^5\text{-C}_9\text{Me}_7)_2\text{Cl}_2$ was achieved by treatment of MCl_4 with 2 equivalents of lithium heptamethylindenide (LiC_9Me_7). An X-ray structure determination carried out on the Zr derivative, (**7**), showed the indenyl ligands to be symmetrically η^5 -bonded to the metal. The heptamethylindenyl rings assume a partially staggered arrangement with respect to each other and are oriented away from the chloride ligands resulting in a significant distortion from planarity of the rings by folding at the bridgehead carbon atoms as shown in figure (7) [8].

The first examples of *ansa*-bis(fluorenyl) complexes of group 4 metals have been prepared and their structures determined by X-ray diffraction (see figure (8)). The complexes, $(\text{C}_{13}\text{H}_8\text{-C}_2\text{H}_4\text{-C}_{13}\text{H}_8)\text{MCl}_2$ ($\text{M} = \text{Zr}, \text{Hf}$), were obtained from the reactions of MCl_4 with the dianion $[\text{C}_{13}\text{H}_8\text{-C}_2\text{H}_4\text{-C}_{13}\text{H}_8]^{2-}$, synthesised from 1,2-difluorenylethane and MeLi in a 1:2 stoichiometric ratio. The Zr derivative was found to show a high activity as a homogeneous polymerisation catalyst in combination with methylalumoxane (MAO) [9].



(7) Reproduced from ref. [8] with permission.

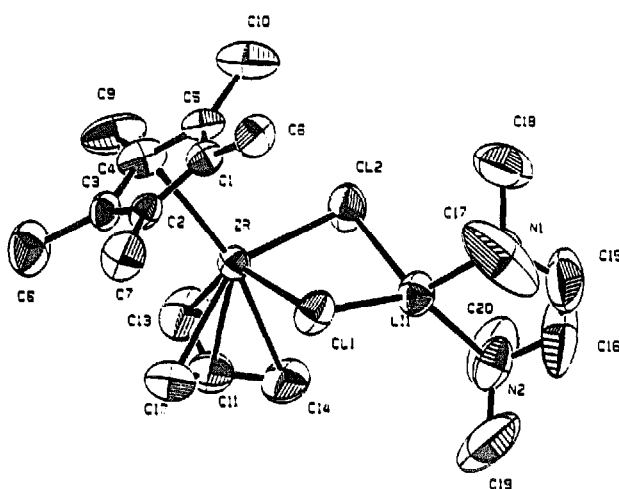


(8) Reproduced from ref. [9] with permission.

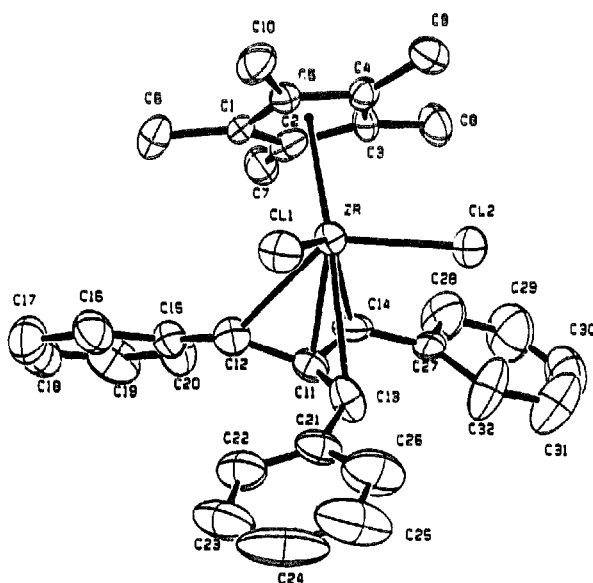
The recently reported complex $[(\text{Me}_2\text{C}(\eta^5\text{-C}_5\text{H}_4)(\eta^2\text{-C}_9\text{H}_6))\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$ **1** has been used to synthesise homo- and hetero-dimetallic complexes of Zr and Hf. The complexes isolated were $[(\eta^5\text{-C}_5\text{H}_5)\text{MCl}_2\{(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)\}\text{M}^*\text{Cl}_2(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Zr}$, $\text{M}^* = \text{Zr}$, Hf; $\text{M} = \text{Hf}$, $\text{M}^* = \text{Zr}$, Hf), $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)\}\text{ZrCl}_2(\eta^5\text{-C}_5\text{Me}_5)]$, $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)\}\text{Rh}(\text{CO})_2]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)\}\text{Mn}(\text{CO})_3]$. The preparations of the complexes are detailed and results of ^1H and ^{13}C NMR spectroscopy given. The results of the X-ray crystal structure of **1** are reported [10].

Two trimethylenemethane (TMM) complexes of zirconium have been synthesised and their structures determined by X-ray diffraction to study the effect of the TMM^{2-} ligand as a dianionic mimic for the $[\text{C}_5\text{R}_5]^-$ ligand in early transition metal chemistry [11]. The structure of the complex

$\text{Cp}^*(\text{TMM})\text{ZrCl}_2\text{Li}(\text{tmeda})$, (**9**), prepared from the reaction of equimolar quantities of Cp^*ZrCl_3 and $\text{TMM}(\text{Li.tmeda})_2$, has an overall geometry analogous to that of bent metallocenes. The TMM ligand is bound in a pyramidal $\eta^4\text{-syn}$ manner and the angles around the Zr atom are fairly normal for a bismetallocene type complex supporting the view that the TMM ligand acts as an isoelectronic but dianionic mimic of the Cp ligand. A further complex $\text{Cp}^*(\text{TBM})\text{ZrCl}_2\text{Li}(\text{tmeda})_2$, (**10**), was prepared by slow addition of $\text{Li}_2(\text{TBM})(\text{tmeda})_2$ (TBM = tribenzylidenemethane) to Cp^*ZrCl_3 . The X-ray structural study carried out on (**10**) showed that it is best described as a salt consisting of $[\text{Cp}^*(\text{TBM})\text{ZrCl}_2]^-$ anions with tetrahedral $[\text{Li}(\text{tmeda})_2]^+$ cations. It was assumed that coordination of the more bulky TBM ligand to Zr prevents a zwitterion arrangement as in (**9**) and the negative charge on the ion increases the distances between Zr and the carbon atoms of TBM relative to the Zr-TMM distances in (**9**) and results in significant distortion. High MW polyethene was obtained when (**10**) was treated with methylalumoxane (MAO) co-catalyst and ethene.



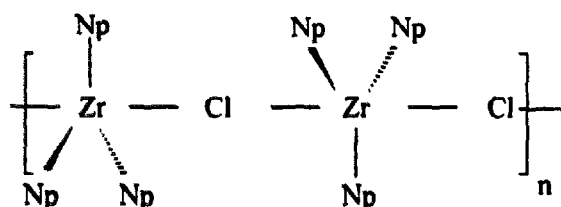
(**9**) Reproduced from ref. [11] with permission.



(**10**) Reproduced from ref. [11] with permission.

A detailed synthetic and structural report has been made on substituted acetophenone- $\text{Cr}(\text{CO})_3$ enolate complexes and their complexation by $[\text{Cp}_2\text{ZrCl}]^+$ cations with diastereoisomerism [12].

The first example of linear symmetric $-\text{X}-\text{M}-\text{X}-\text{M}-$ chains in which the metal has a d^0 configuration has been reported [13]. Three convenient syntheses are reported for chlorotrieneopentylzirconium, Np_3ZrCl (11) according to equations (i)–(iii) ($\text{Np} = \text{Me}_3\text{CCH}_2^-$). The X-ray crystal structure of (11) showed that the compound crystallises in polymeric chains with a linear symmetric repeating $-\text{Cl}-\text{ZrNp}_3-\text{Cl}-\text{ZrNp}_3-$ unit. The Zr atom adopts a trigonal bipyramidal geometry and the angles between the chlorine atoms and the neopentyl ligands are 90° indicating that the Zr-Cl bonds are perpendicular to the plane formed by the Zr and three α -carbon atoms.



(11)

The hydrozirconation adduct of C_{60} , $(\text{Cp}_2\text{ZrCl})_n\text{C}_{60}\text{H}_n$, ($n = 1-3$) formed according to equation (iv) has been allowed to react with *N*-bromosuccinimide (NBS) and *m*-chloroperbenzoic acid (*m*-CPBA). In each case a Diels-Alder addition was proved to have taken place with the formation of 1,2-dihydro[60]fullerenes. This was unlike the behaviour of $(\text{Cp}_2\text{ZrCl})_n\text{C}_{60}\text{H}_n$ with *N*-chlorosuccinimide which resulted in total decomposition to C_{60} [14].



Complexes containing carbon-donor ligands with boron are discussed together below. In order to understand the role of Lewis acidic co-catalysts such as MAO the organoborane $\text{B}(\text{C}_6\text{F}_5)_3$ has been used as an effective alternative cocatalyst capable of yielding isolable and characterisable catalysts with group 4 metallocenes. The compound $\text{B}(\text{C}_6\text{F}_5)_3$ is a relatively strong molecular Lewis acid and can form a variety of characterisable Lewis base adducts.

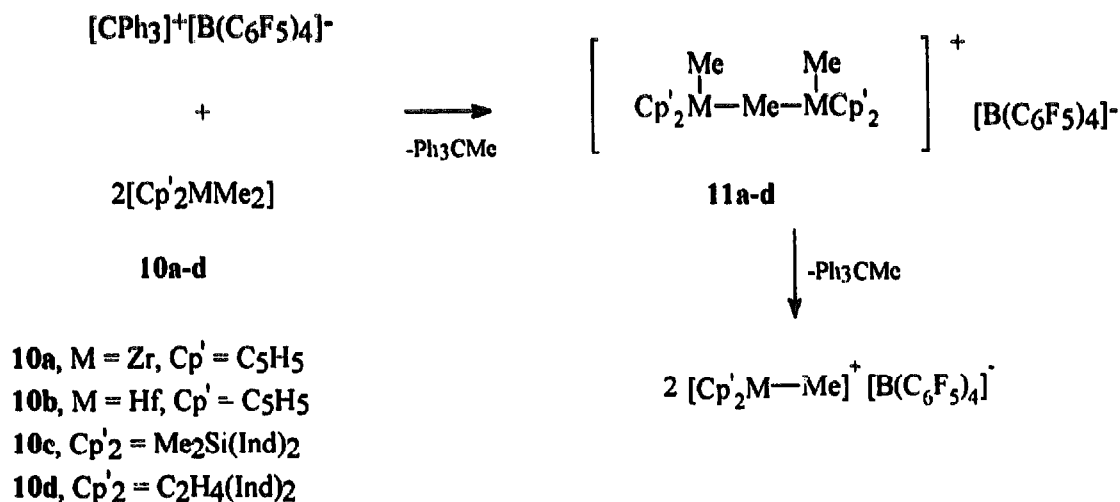
The reactions of a series of zirconocene dimethyl complexes, L_2ZrMe_2 ($\text{L} = \eta^5\text{-C}_5\text{H}_5$ 2, $\eta^5\text{-C}_5\text{H}_3\text{Me}_2$ 3, $\eta^5\text{-C}_5\text{Me}_5$ 4, $\eta^5\text{-C}_5\text{H}_3((\text{CH}_3)_3\text{Si})_2$ 5) with $\text{B}(\text{C}_6\text{F}_5)_3$ in hydrocarbon solvents were found to yield base-free cationic zirconium alkyl complexes $[\text{L}_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$. When $(^i\text{Bu}_2\text{C}_5\text{H}_3)_2\text{ZrMe}_2$ was used, the cationic metallacyclic product $\{(^i\text{Bu}_2\text{C}_5\text{H}_3)[^i\text{BuC}_5\text{H}_3\text{CMe}_2\text{CH}_2]\text{Zr}\}^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ 6 was obtained from a presumed

intramolecular C-H activation process. Complexes **4** and **6** were found to undergo rapid hydrogenolysis to yield the corresponding cationic hydrido complexes $[(\text{Me}_5\text{C}_5)_2\text{ZrH}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ **7**, $[(\text{Me}_5\text{C}_5)_2\text{ZrH}]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ **8** (stepwise) and $[(^i\text{Bu})_2\text{C}_5\text{H}_3)_2\text{ZrH}]^+[\text{MeP}(\text{C}_6\text{F}_5)_3]^-$ **9** respectively. Complexes **3-6** and **8**, have been characterised by X-ray diffraction. Complex **3** was found to undergo slow conversion to $\{[(\text{Me}_2\text{C}_5\text{H}_3)_2\text{ZrMe}]_2(\mu\text{-F})\}^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ in C_6D_6 in an inert atmosphere at 25°C . The X-ray structure of this complex was also determined. Complexes **2-5**, **7** and **8** were shown to be highly active homogeneous catalysts for the polymerisation of ethene with activities comparable with MAO-based zirconocene catalysts [15]. The same complexes were found to be active in the atactic polymerisation of propene.

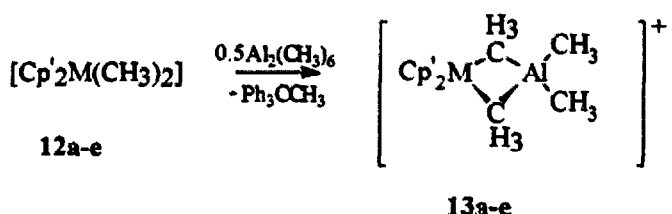
The reaction which is generally held to yield monomeric cationic 14-electron complexes used as polymerisation catalysts (see equation (v)) has been shown to be incomplete in describing the course of the reaction and can be shown to lead to dimeric complexes as the major products depending upon the reaction conditions [16].



The reaction of the methyl complexes $[\text{Cp}'_2\text{MMe}]^+$ **10a-d** with $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ at -60°C in CD_2Cl_2 led to the formation of dinuclear bridged complexes **11a-d** (scheme 1). In the presence of trimethylaluminium the cations $[\text{Cp}'_2\text{MMe}]^+$, **12a-e** formed preferentially the heterodinuclear complexes $[\text{Cp}'_2\text{M}(\mu\text{-Me})_2\text{AlMe}_2]^+$ (**13a-e**, scheme 2). The equilibria established between these dimeric homo- and heterodinuclear cationic complexes and their monomeric forms have been investigated in order to attempt to understand their catalytic activity.



Scheme 1



12a, M = Zr, Cp' = C₅H₅

12b, M = Hf, Cp' = C₅H₅

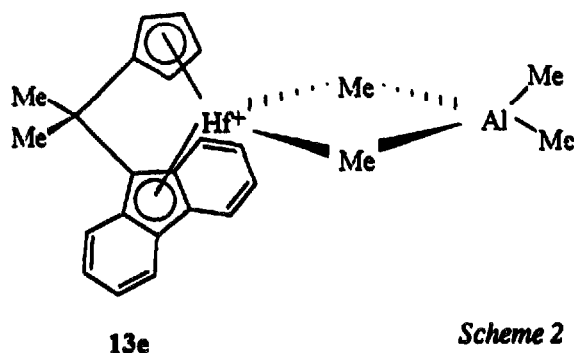
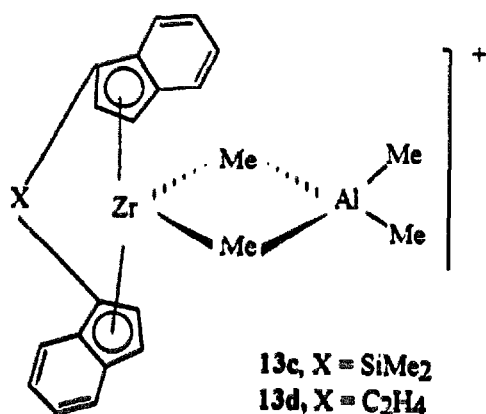
12c, M = Zr, Cp' = Me₂Si(Ind)₂

12d, M = Zr, Cp' = C₂H₄(Ind)₂

12e, M = Hf, Cp' = Me₂C(Cp)(Flu)

Ind = indenyl

Flu = fluorenyl

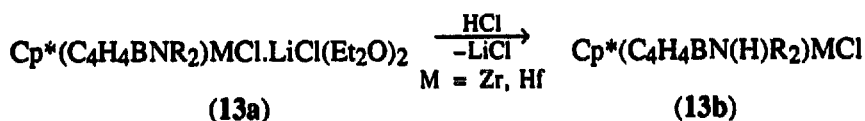
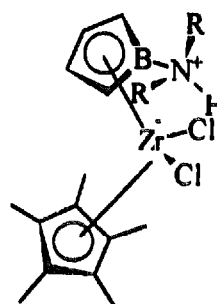
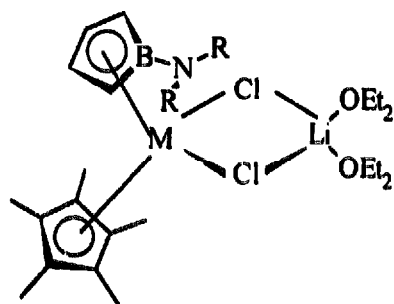
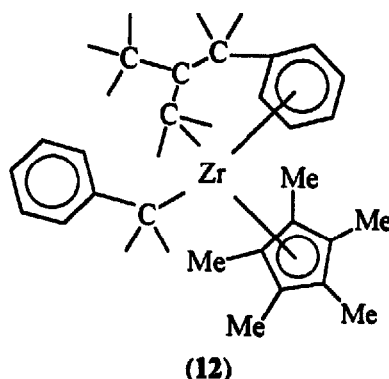


Scheme 2

Propene has been found to undergo insertion into the half-sandwich salt complex $[\text{Cp}^*\text{Zr}(\text{CH}_2\text{Ph})_2][\text{B}(\text{CH}_2\text{Ph})(\text{C}_6\text{F}_5)_3]$ to yield $[\text{Cp}^*\text{Zr}(\text{CH}_2\text{CHMeCH}_2\text{Ph})(\text{CH}_2\text{Ph})][\text{B}(\text{CH}_2\text{Ph})(\text{C}_6\text{F}_5)_3]$, (12). The crystal structure of (12) was shown to possess an unusual 'back-biting' η^6 -arene coordination to the metal, ascribed to the unexpected stability of the compound towards either further propene insertion or β -hydrogen elimination [17]. The structure, (figure (12)), consists of discrete cations and $[\text{B}(\text{CH}_2\text{Ph})(\text{C}_6\text{F}_5)_3]^-$ anions. The Zr atom, rather than being highly electron deficient as the formula of the complex would suggest, is saturated by intramolecular η^6 -coordination with the phenyl ring. There is therefore no significant cation-anion bonding interaction unlike in $[\text{CpZr}(\text{CH}_2\text{Ph})_2][\text{B}(\text{CH}_2\text{Ph})(\text{C}_6\text{F}_5)_3]$ in which coordination to Zr of the Ph rings of the anion was observed. The coordination around the Zr atom is pseudo-tetrahedral by the two C atoms and the centroids of the Cp* and Ph rings.

A group of aminoborollide derivatives of zirconium and hafnium having both Lewis acidic and basic sites in relatively close proximity has been prepared. The compounds $\text{Cp}^*[\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2]\text{MCl} \cdot \text{LiCl}$ (M = Zr, Hf) have been obtained by treatment of Cp^*MCl_3 with $\text{Li}_2[\text{C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2] \cdot \text{thf}$ in toluene. The X-ray crystal structure of the bis(diethyletherate) adduct of the zirconium complex, (13a), was determined and revealed that the borollide ligand is η^5 -bound to zirconium and the bulky $(\text{N}(\text{CHMe}_2)_2)$ group is rotated to the side of the metallocene wedge so that it points away from the Cp* ring and one of the coordinated ether

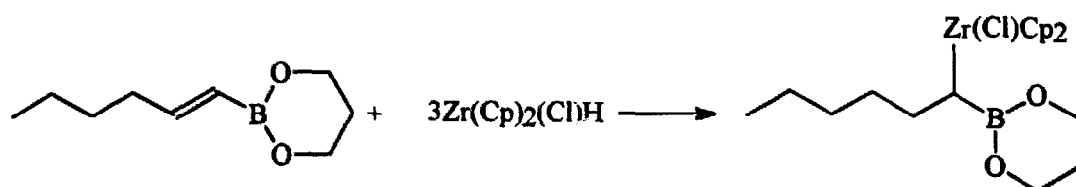
molecules. The two methine C atoms, the N, and the B of the borollide are co-planar which allows $p\pi$ - $p\pi$ interaction between the B and N atoms with the possibility of a resonance structure. Protonation of the borollide nitrogen of (13a) or the Hf analogue with 1 equiv. of HCl yielded the zwitterion dichlorides, $\text{Cp}^*(\text{C}_4\text{H}_4\text{BN}(\text{H})\text{R}_2)\text{MCl}_2$ (scheme 3). The X-ray structure of the hafnium derivative, (13b), was determined and showed the borollide ligand was also η^5 coordinated but in this case the N atom is pyramidal not planar as in (13a). There was some uncertainty in the location of the H atom, but protonation of the N atom as in (13b) eliminates any contribution from a resonance structure as in the case of (13a) [18].



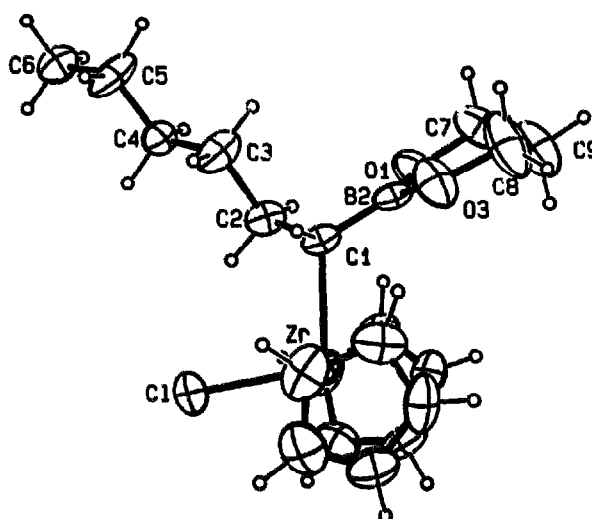
Scheme 3

Interest in the applications of 1,1-dimetallo compounds of zirconium, especially in olefin polymerisation reactions, has resulted in the isolation of the first Zr boronic ester 1,1-dimetallo compound, chlorobis(cyclopentadienyl)[1-(1,3,2-dioxaborinane-2-yl)hexyl]zirconium(IV) (14). The synthesis of the compound from alkenyl boronic ester, and 3 equivalents of $[\text{Zr}(\text{Cp})_2(\text{Cl})\text{H}]$ is outlined below in scheme 4. The structure of the compound (14) was found to consist of

approximately tetrahedral 4-coordinate zirconium ligated by two Cp rings, Cl and the aliphatic C(1). No inter- or intra-molecular interactions were detected between Zr and the B or O atoms [19]. The compound was found to be effective in catalysing the polymerisation of styrene without a co-catalyst. Further analytical information concerning these compounds has been reported [20].

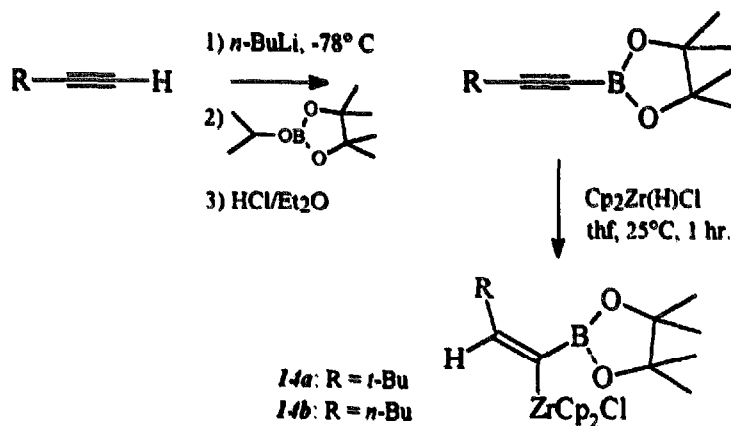


Scheme 4



(14) Reproduced from ref. [19] with permission

The same group has reported the first examples of stable 1,1-dimetalloalkenes of boron and zirconium also synthesised by hydrozirconation reactions using $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ as shown in scheme 5 [21]. The structure of the tert-butyl derivative **14a** was determined by X-ray crystallography. Two molecules, whose configurations are identical but differing in conformational details, were found per asymmetric unit. In both molecules the coordination spheres around the Zr atoms were almost regular tetrahedrons.

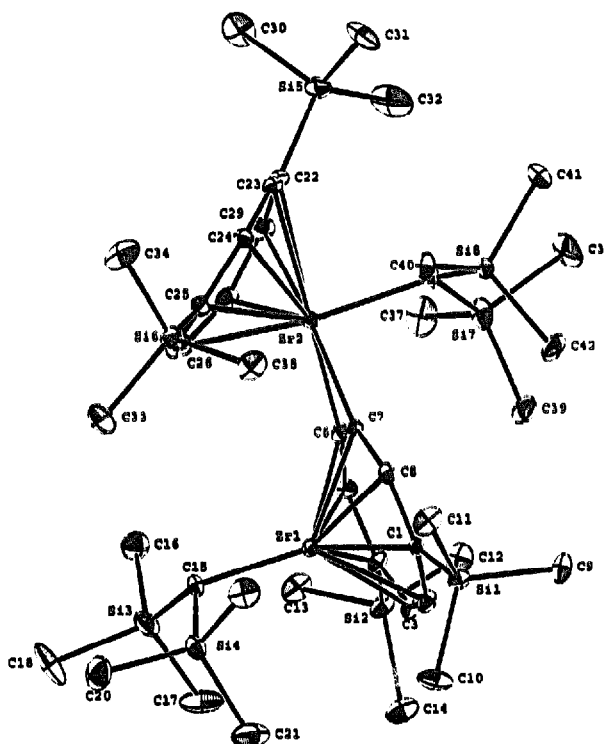


Scheme 5

11.1.3 Complexes with silicon containing ligands

The X-ray crystal structure of $[\text{C}_5\text{H}_2(\text{SiMe}_3)_3]_2\text{ZrCl}_2$ has been determined [22]. The complex was found to be monomeric in the solid state and crystallises with two independent molecules, the structures of which differ mainly in the relative staggered orientation of the $[\text{C}_5\text{H}_2(\text{SiMe}_3)_3]$ rings. The tris(trimethylsilyl)cyclopentadienyl rings were found to be staggered due to steric congestion resulting in a Cp(centroid)-Zr-Cp(centroid) angle of $135.4(2)^\circ$ and relatively short Zr-Cl bond lengths. The Cl atoms are symmetrically placed between the Cp rings in the plane containing the Cp ring centroid and the Zr atom. ESR spectroscopic evidence for a Zr(III) species was observed following reduction of $[\text{C}_5\text{H}_2(\text{SiMe}_3)_3]_2\text{ZrCl}_2$ with sodium amalgam.

The reaction between $[(\text{Zr}(\eta\text{-COT})\text{Cl}_2)_2]$ [COT = 1,4-bis(trimethylsilyl)cyclooctatetraene] and $[\text{LiCH}(\text{SiMe}_3)_2]$ in diethyl ether at -78°C yielded the dinuclear complex $[(\eta\text{-C}_8\text{H}_6(\text{SiMe}_3)_2)\text{Zr}\{\text{CH}(\text{SiMe}_3)_2\}(\mu\text{-}\eta^8\text{:}\eta^2\text{-C}_8\text{H}_4(\text{SiMe}_3)_2)\text{Zr}\{\text{CH}(\text{SiMe}_3)_2\}]$ (15). The X-ray crystal structure shows a bridging cyclooctatriene-ene ligand arising from double hydrogen abstraction from a COT ring. The diamagnetic nature of the complex suggests a zwitterionic structure involving cationic Zr(IV) and anionic Zr(II), or cationic Zr(IV) and also anionic Zr(IV) [23].

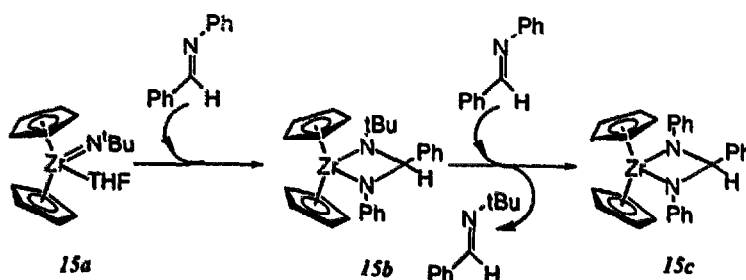


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11.1.4 Complexes with nitrogen donor ligands

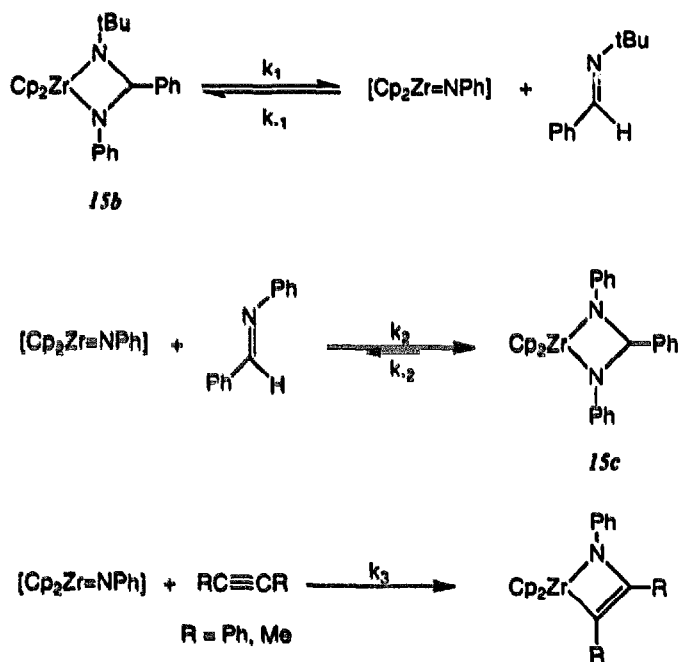
The compound $\text{Cp}_2\text{Zr}(=\text{N-}^t\text{Bu})(\text{thf})$ **15a** has been found to undergo a formal [2+2] cycloaddition reaction with benzaldehyde *N*-phenylamine to give the 2,4-diazametallacyclobutane **15b** (scheme 6). **15b** reacts with a second molecule of *N*-phenylamine to give the related

heterometallacycle **15c** with the release of benzaldehyde *N*-tert-butylamine. A preliminary study has been made of the reaction mechanism. The reaction proceeds, in analogy to olefin metathesis, by an initial dissociative process that generates a transient imido complex intermediate. The imido complex is trapped by alkynes, and even more efficiently by imines. Identical values for the saturation rate constant k_1 were obtained for the reactions of **15b** with imine and two alkynes, at high imine or alkyne concentrations, where diazametallacycle cleavage is rate determining. This evidence supported the mechanism proposed in scheme 7 [24].



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Scheme 6



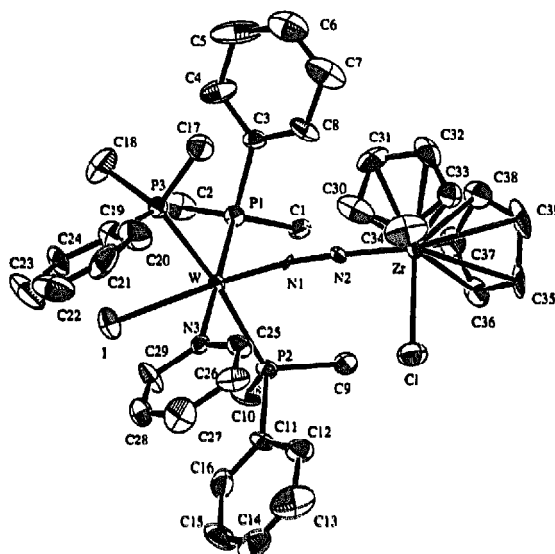
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Scheme 7

The formation of η^2 -imine-zirconocene complexes, $\text{Cp}_2\text{Zr}(\text{NR}^1\text{CR}^2\text{R}^3)$, by elimination of R^4H from $\text{Cp}_2\text{Zr}(\text{R}^4)(\text{NR}^1\text{CHR}^2\text{R}^3)$ has been investigated with regard to the variation in R^1 , R^2 , R^3 and R^4 . Special reference was made to the Hammett type structure/rate correlations (R^1 , R^2 , $\text{R}^4 = p\text{-XC}_6\text{H}_4$, $\text{X} = \text{Me}_2\text{N, MeO, H, Cl, CO}_2\text{Me}$; R^1 , $\rho = 3.2$; R^2 , $\rho = 0.5$; R^4 , $\rho = -1.6$). The data obtained suggested a cyclometallation involving deprotonation α to nitrogen by (R^4) . The relationship between the rate of reaction and the structure of the amine shows a marked dependency

on both electronic and steric effects. This is the first time that η^2 -imine complexes have been formed even from simple amines such as dibutylamine and trapped with an alkyne to form secondary allylic amines on workup. In the absence of a trap, η^2 -(PhN=CMe₂)ZrCp₂ rearranges by a rapidly reversible hydride shift to give an η^3 -azaallyl-zirconocene hydride [25].

The reactions of *cis*-[W(N₂)₂(PMe₂Ph)₄] with either [Cp₂TiCl₂] alone or a mixture of [Cp₂MCl₂] (M = Zr, Hf) and excess sodium iodide yielded heterodimetallic complexes with a bridging N₂ ligand, [WX(PMe₂Ph)₄(μ -N₂)MCp₂Cl] (M = Ti, X = Cl; M = Zr, Hf, X = I). The W-Zr complex was further converted to the dinitrogen complex [W(PMe₂Ph)₃(py)(μ -N₂)ZrCp₂Cl] (**16**), by treatment with excess pyridine. The structure of (**16**) has been determined and was found to contain a $\eta^1:\eta^1$ -dinitrogen bridge between the W and Zr atoms. The W atom has an octahedral configuration with three mutually meridional PMe₂Ph and one py ligand forming the basal plane. The remaining sites are occupied by mutually *trans* μ -N₂ and iodide ligands [26].

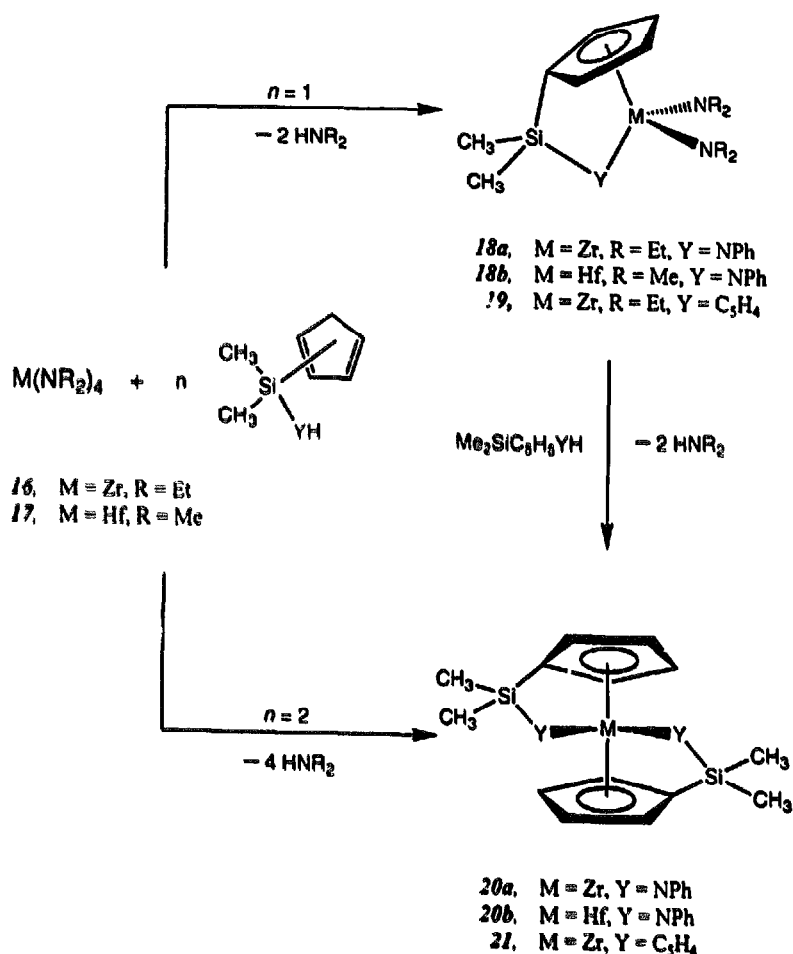


(**16**) Reproduced from ref. [26] with permission.

The homoleptic metal amides Ti(NEt₂)₄, Ti(NMe₂)₄ and Zr(NEt₂)₄ have been allowed to react with silyl-substituted cyclopentadienes Me₂Si(CpR)(NHR') (CpR = C₅H₅, R' = C(CH₃)₃; CpR = C₅H₅, R' = C₆H₅; CpR = C₅H₄CH₃, R' = C(CH₃)₃) and indine (CpR = C₉H₇, R' = C(CH₃)₃) to give nine new half sandwich complexes of type Me₂Si[CpR][NR']M(NR''₂)₂ (M = Ti, Zr; R'' = Me, Et). The new ligands were characterised by ¹H, ¹³C and ²⁹Si NMR and IR spectroscopies, and GC-MS with regard to sigmatropic rearrangements caused by hydrogen and silicon migration. The titanium and zirconium complexes were characterised by their ¹H, ¹³C and ²⁹Si NMR spectra, IR and mass spectroscopy [27].

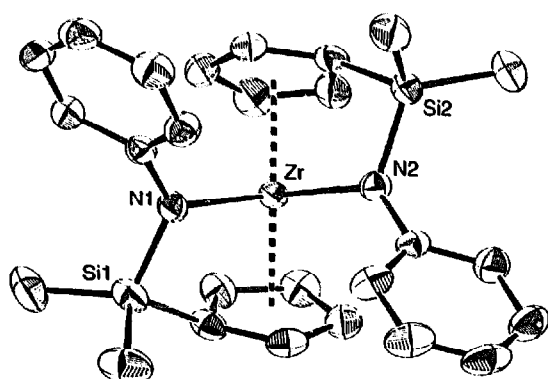
rac-Metallocene complexes **20a**, **20b** and **21** have been prepared by a new salt-free synthesis which avoids the formation of mixtures of *rac/meso* diastereomers (scheme 8) [28]. The method involved the treatment of homoleptic metal amides, [M(NR₂)₄] (**16**, **17**) with functionalised cyclopentadienes, Me₂SiC₅H₅YH (Y = NPh, C₅H₄). The reaction between 1 mol. of metal amide and 1 mol. of cyclopentadiene in toluene resulted in the formation of **18a**, **18b** and **19**. On further treatment with cyclopentadiene, **20a**, **20b** and **21** were obtained. Complexes **20a**,

20b and **21** can also be formed directly by the reaction of the metal amides with two moles of cyclopentadienes. The products were characterised by ^1H , ^{13}C and ^{29}Si NMR. The twofold bridging and steric bulk of the phenyl substituents did not cause substantial distortion of the framework. Metallocenes **20** therefore display the same characteristic features of common metallocenes such as $[(\text{C}_5\text{H}_5)_2\text{ZrCl}_2]$ and $[\text{Me}_2\text{Si}(\text{C}_6\text{H}_4)_2\text{ZrCl}_2]$. The structure of **20a**, figure (17), shows the distance of the Zr atoms from the Cp ring centroids, Z, (2.21 and 2.22 Å) are in the typical range for Z-Zr distances. The Z-Zr-Z angle agrees well with the usual values of 125.4–128.3°. The *ansa* analogue metallocene **21** has a dynamic structure in solution like Ti, Zr and Hf complexes of $[\text{M}(\text{C}_5\text{H}_5)_4]$. The ^1H and ^{13}C NMR spectra feign fourfold η^5 coordination. The X-ray crystal structure, figure (18), has been determined. It is $(\eta^5)_2:(\eta^1)_2$ coordinated as in $[\text{M}(\text{C}_5\text{H}_5)_4]$ (M = Ti, Hf). The presence of a bridging bis(cyclopentadienyl) ligand is new coordination behaviour for metallocene chemistry.



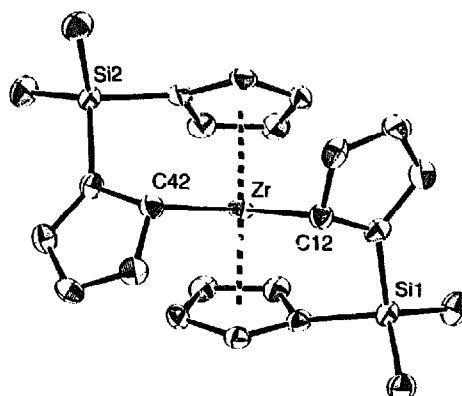
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Scheme 8



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(17)

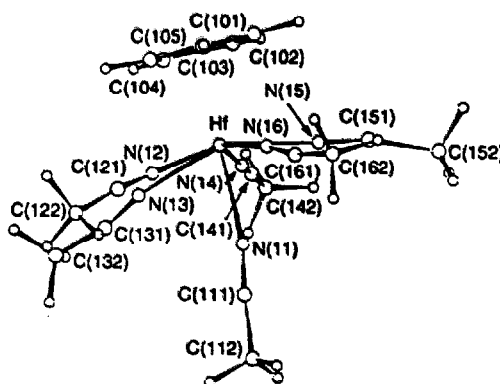


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(18)

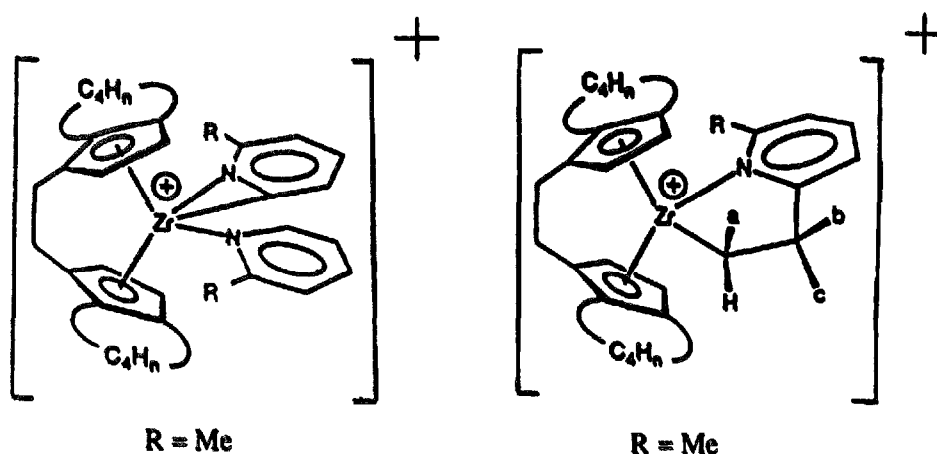
The first early-late heterodimetallic bridging imido complex $\text{Cp}_2\text{Zr}(\mu\text{-N-}^t\text{Bu})\text{IrCp}^*$ **22** has been synthesised in 65% yield by the sequential addition of $^t\text{BuLi}$ and $\text{Cp}^*\text{IrN-}^t\text{Bu}$ to Cp_2ZrCl_2 [29]. It was characterised by an X-ray diffraction study. The Ir-Zr bond distance was found to be 2.598(2) Å, and the Ir-N (1.887(13) Å) and Zr-N (2.084(13) Å) bond distances are comparable to those found in analogous homonuclear imido dimers. Cooperative reactivity studies, carried out on **22** showed it to undergo addition of both polar N-H, O-H, S-H and non-polar H-H, Si-H, C-H bonds across the Ir-Zr bond. Reaction of **22** with *p*-toluidine gave $\text{Cp}_2\text{Zr}(\text{NHAr})(\mu\text{-N-}^t\text{Bu})(\mu\text{-H})\text{IrCp}^*$ (**23**, 60% yield), with *p*-cresol gave $\text{Cp}_2\text{Zr}(\text{OAr})(\mu\text{-N-}^t\text{Bu})(\mu\text{-H})\text{IrCp}^*$ (**24a**, 56% yield) and *tert*-butyl alcohol gave $\text{Cp}_2\text{Zr}(\text{O-}^t\text{Bu})(\mu\text{-N-}^t\text{Bu})(\mu\text{-H})\text{IrCp}^*$ (**24b**, 74% yield). Complexes **23** and **24a** have been characterised by X-ray crystallography. Addition of diphenylphosphine and cyclohexylphosphine to **22** resulted in the unusual insertion of phosphide (PR_2) into the Ir-N rather than the Ir-Zr bond to give $\text{Cp}_2\text{Zr}(\mu\text{-N-}^t\text{Bu})\text{PEt}_2\text{Ir}(\text{H})\text{Cp}^*$ (**25a**, 63% yield) and $\text{Cp}_2\text{Zr}(\mu\text{-N-}^t\text{Bu})\text{PHCyIr}(\text{H})\text{Cp}^*$ (**25b**, 50% yield). An X-ray diffraction study of **25a** found an Ir-Zr bond distance of 2.642(1) Å, similar to that in **22**. With methyl triflate (MeOTf) the *tert*-butoxide complex **24b** gave $\text{CpZr}(\text{O-}^t\text{Bu})(\text{OTf})(\mu\text{-H})(\mu\text{-N-}^t\text{Bu})\text{IrCp}^*$ (**26**, 62% yield), as a result of the replacement of a single Zr-bonded Cp ligand with a triflate ligand. An X-ray diffraction study confirmed that the triflate ion was covalently bonded to zirconium.

The reaction of $[\text{M}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3(\text{MeCN})_2]$ ($\text{M} = \text{Zr, Hf}$) and SbCl_5 in CH_3CN solution is a convenient route to cationic monocyclopentadienyl metal(IV) species following halide extraction. The hexachloroantimonate(V) salts $[\text{M}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2(\text{MeCN})_3][\text{SbCl}_6]$, $[\text{M}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{MeCN})_4][\text{SbCl}_6]_2$ and $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_6][\text{SbCl}_6]_3$ were isolated and characterised. The structure of $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_6][\text{SbCl}_6]_3 \cdot 2\text{CH}_2\text{Cl}_2$ has been determined, and the cation is shown in figure (19). It is monoclinic and comprises two independent $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_6]^{3+}$ cations, six $[\text{SbCl}_6]^-$ anions and two lattice CH_2Cl_2 solvent molecules. It has seven-coordinate metal geometry, with an axial Cp ligand. Only a few cationic monocyclopentadienyl complexes have so far been structurally characterised [30].



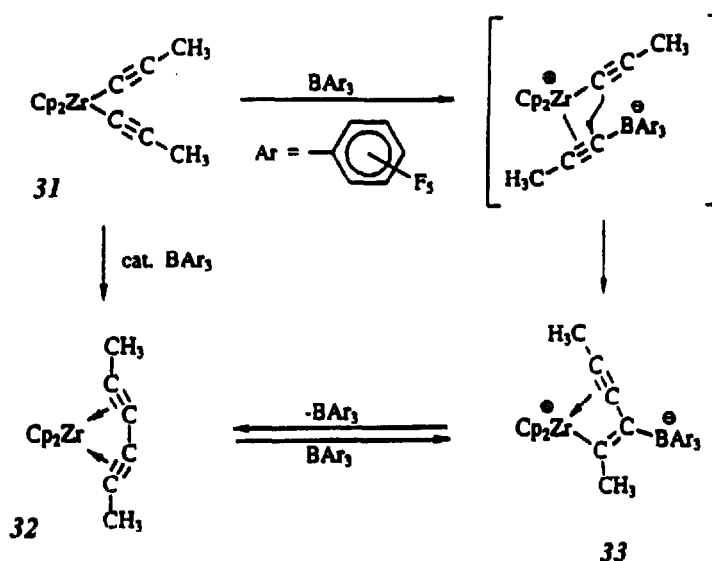
(19) Reproduced from ref. [30] with permission.

Chiral $\text{chCp}_2\text{Zr}(\eta^2\text{-pyrid-2-yl})^+$ (chCp_2 = chiral *ansa*biscyclopentadienyl) species derived from Brintzingers C_2 -symmetric *ansa*-zirconocene complexes $(\text{EBI})\text{ZrCl}_2$ (27, EBI = ethylenebisindenyl) and $(\text{EBTHI})\text{ZrCl}_2$ (28, EBTHI = ethylenebis(tetrahydroindenyl)) undergo highly regio- and stereospecific alkene insertion reactions [31]. For example, protonolysis of *rac*-(EBI) ZrMe_2 and *rac*-(EBTHI) ZrMe_2 with $[\text{HN}^n\text{Bu}_3][\text{BPh}_4]$ in the presence of 2-picoline gives the ion pairs *rac*-[(EBI) $\text{Zr}(\eta^2\text{-6-Me-pyrid-2-yl})(2\text{-picoline})][\text{BPh}_4]$ 29, $n = 4$, 91%) and *rac*-[(EBTHI) $\text{Zr}(\eta^2\text{-6-Me-pyrid-2-yl})(2\text{-picoline})][\text{BPh}_4]$ (29, $n = 8$, 91%). The complexes are obtained as mixtures of 'N-inside' and 'N-outside' isomers which differ in the orientation of the η^2 -pyridyl ligands, figure (20). At 23°C in CH_2Cl_2 , 29 ($n = 4, 8$) both insert propene and 1-hexene to give the azazirconacycles shown in figure (21). Compound 29 gives 30 ($30, a = b = \text{H}, c = \text{Me}, \text{Bu}$ respectively) with 83% de for both. Compound 29 ($n = 8$) reacts similarly, but with lower de. The β -substituent points towards the C_6 ring of the EBI/EBTHI ligand in the major diastereomer. Conversely, compounds 29 ($n = 4, 8$) undergo regio and stereospecific 2,1 styrene insertion to give *rac*-(EBI) $\text{Zr}(\eta^2\text{-CHPhCH}_2)(6\text{-Me-pyrid-2-yl})^+$ (30, $n = 4, a = \text{Ph}, b = c = \text{H}$) and *rac*-(EBTHI) $\text{Zr}(\eta^2\text{-CHPhCH}_2)(6\text{-Me-pyrid-2-yl})^+$ (30, $n = 8, a = \text{Ph}, b = c = \text{H}$) in which the α -Ph substituent points away from the EBI/EBTHI C_6 ring (de >98%). The stereoselectivity of these reactions is explained in terms of steric interactions between the EBI/EBTHI ligand, the η^2 -pyridyl group and the alkene substituent in the presumed intermediate alkene adducts.



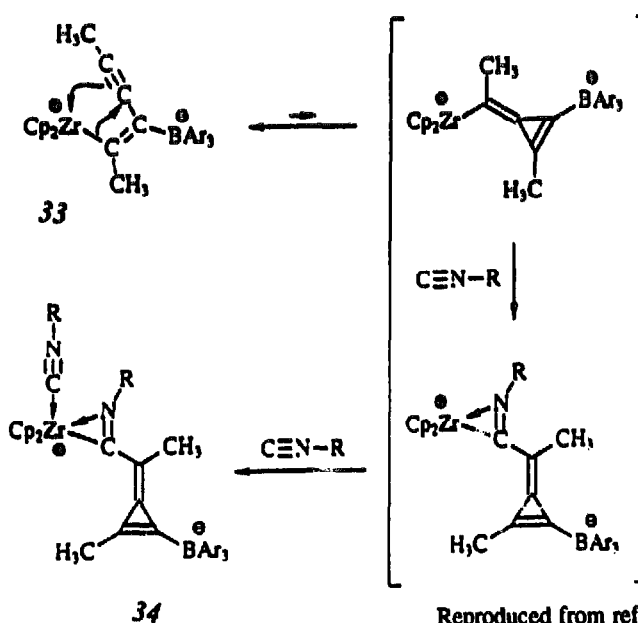
(20) Reproduced from ref. [31] with permission. (21)

Bis(propynyl)zirconocene (**31**), prepared by the reaction of $[\text{Cp}_2\text{ZrCl}_2]$ and 2 molar equivalents of propynyllithium, undergoes catalytic and stoichiometric coupling of the alkynyl ligands upon treatment with BAR_3 (tris(pentafluorophenyl)borane). BAR_3 (< 1 mol. %) catalyses the conversion of bis(propynyl)zirconocene to $(\eta^4\text{-2,4-hexadiyne})\text{zirconocene}$ (**32**) in toluene at room temperature [32]. A 1:1 molar ratio of **31** and BAR_3 under the same conditions results in the formation of $(\text{C}_5\text{H}_5)_2\text{Zr}(\mu\text{-2,4-hexadiyne})\text{BAR}_3$ betaine (**33**) in 83% yield. ^1H and ^{13}C NMR spectra are reported (scheme 9). Treatment of **33** with tert-butyl isonitrile did not give the expected CNR insertion into the reactive Zr-C σ -bond. Instead, **34** (figure (22)) was formed in good yield as a result of rearrangement of the framework and subsequent reaction with two isonitrile units (scheme 10).



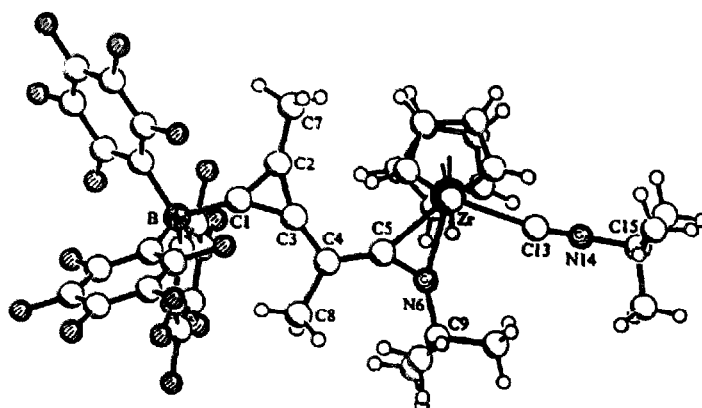
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Scheme 9



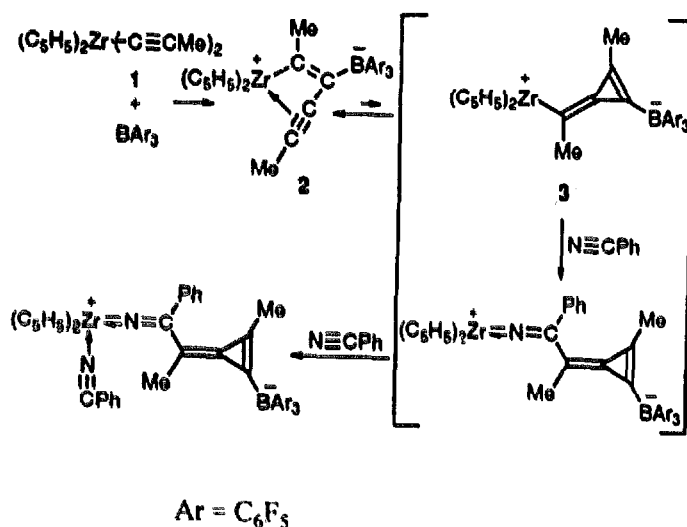
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Scheme 10



(22) Reproduced from ref. [32] with permission.

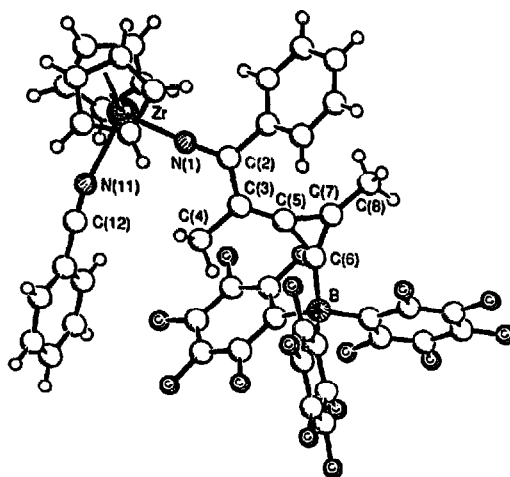
$(C_5H_5)_2Zr(\mu\text{-}2,4\text{-hexadiyne})BAr_3$ betaine reacts with benzonitrile to give a Zr/B bridging methylenecyclopropene derivative, figure (23), formed by intramolecular alkyne insertion into a Zr-C(sp²) σ -bond (scheme 11). The structure of (23) was determined by X-ray diffraction. It contains a substituted methylenecyclopropene framework bearing two methyl groups, a $B(C_6F_5)_3$ substituent and an *N*-metallated ketimino functionality. The complex is best described as an organometallic zirconium boron betaine [33].



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Scheme 11

The $(\mu\text{-formaldehyde})(Cp_2ZrCl)_2$ complex $[(Cp_2ZrCl)_2(\mu\text{-}\eta^1(O),\eta^2(C,O)\text{-CH}_2O)]$ reacts with alkyl isocyanides RNC (R = CH₂SiMe₃, CMe₃) with insertion into the Zr-C bond and opening of the metalla-oxirane unit by cleavage of the adjacent Zr-O bond to give the 'N-inside' (η^2 -iminoacyl) zirconocene complexes $[(Cp_2ZrCl)(CH_2OZrCp_2Cl)=NR]$. The compound $[(Cp_2ZrCl)(CH_2OZrCp_2Cl)=NCH_2SiMe_3]$ was characterised by X-ray diffraction [34].



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Multiple C-C coupling of isocyanides has been demonstrated by the ambient-pressure reactions of CNMe with $\text{Cp}_2\text{M}(\text{N}(\text{CMe}_3)\text{CC}(=\text{NCMe}_3)\text{CH}_2\text{SiMe}_2\text{CH}_2)$ and the high pressure reactions of CNCMe_3 with $\text{Cp}_2\text{M}(\text{CH}_2\text{SiMe}_2\text{CH}_2)$ which give the compounds $\text{Cp}_2\text{M}(\text{N}(\text{Me})\text{C}-\text{C}(=\text{NCMe}_3)\text{C}(=\text{NCMe}_3)\text{CH}_2\text{SiMe}_2\text{CH}_2)$ and $\text{Cp}_2\text{M}(\text{N}(\text{CMe}_3)\text{C}(=\text{C}=\text{NCMe}_3)\text{C}(=\text{NCMe}_3)-\text{CH}_2\text{SiMe}_2\text{CH}_2)$ ($\text{M} = \text{Zr}, \text{Hf}$) respectively [35].

The formation and structures of some cationic pyrazole and pyrazolyl zirconocene complexes have been reported [36]. On treatment of dimethylzirconocene with 1 molar equivalent of pyrazole, methane and (pyrazole-*N*)methylzirconocene **35** were formed. Treatment of **35** with tributylammonium tetraphenylborate gave cationic $(\eta^2\text{-pyrazolyl-}N,N')$ (tetrahydrofuran)-zirconocene **36**, isolated as the tetraphenylborate salt in >60% yield. The related $(\eta^2\text{-pyrazolyl-}N,N')$ ($\eta^1\text{-pyrazolyl-}N$)zirconocene tetraphenylborate salt was obtained by treating the methylzirconocene cation $[\text{Cp}_2\text{ZrCH}_3(\text{thf})]^+$ with pyrazole in CH_2Cl_2 . Cationic complex **36** reacts with acetylacetone by proton transfer to give (acetylacetonato)($\eta^1\text{-pyrazole-}N$)zirconocene tetraphenylborate (**37**). Complexes **36** and **37** were characterised by X-ray diffraction. Complex **36** was used as a Lewis-acid in the Mukaiyama aldol reaction between [(trimethylsilyl)oxy]cyclopentene and benzaldehyde.

A new class of organotitanium(IV) and organozirconium(IV) chelates with biologically active monofunctional didentate semicarbazones having the ON donor system has been prepared. Cp_2TiCl_2 and Cp_2ZrCl_2 were allowed to react in 1:1 and 1:2 stoichiometric proportions of the appropriate ligand, prepared by condensing heterocyclic ketones and semicarbazide hydrochlorides in the presence of NaOAc. Trigonal bipyramidal and octahedral structures were suggested for the 1:1 and 1:2 (M:L) complexes of Ti(IV) and Zr(IV), respectively, on the basis of spectral analysis [37].

The reaction of Cp_2ZrCl_2 with HL (HL = 2,3-dihydroxypyridine, 2-amino-3-hydroxypyridine) in water, followed by addition of $\text{K}^+[\text{ROCS}_2]^-$ produced the xanthate salts $[\text{Cp}_2\text{ZrL}]^+[\text{ROCS}_2]^-$ in 67–69% yields ($\text{R} = \text{Me}, \text{Et}, \text{Me}_2\text{CH}$). The salts were characterised by elemental analysis, conductance measurements, and IR and ^1H NMR spectroscopy [38].

Bis-[(*tert*-butylamidodimethylsilyl)cyclopentadienyl]zirconium, (${}^1\text{C}_4\text{H}_9\text{N-SiMe}_2\text{-C}_5\text{H}_4$) $_2\text{Zr}$, is formed as a spiranoide zirconacyclus by reaction of $\text{ZrCl}_4\cdot 2\text{thf}$ with (${}^1\text{C}_4\text{H}_9\text{N-SiMe}_2\text{-C}_5\text{H}_4$) Li_2 , irrespective of the molar ratio of the starting materials. The complex was investigated by means of ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectroscopy [39].

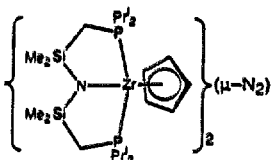
A series of silylamido complexes of zirconium, $\text{Cp}_2\text{Zr(X)(N}^t\text{BuSiMe}_2\text{H)}$ ($\text{X} = \text{H, I, Br, Cl, F}$) have been prepared. The complexes exhibit agostic $\beta\text{-Si-H}$ interactions with the metal centre, and have been characterised by spectroscopic and structural methods. Data obtained from NMR spectroscopy provided evidence for the interaction of the Si-H σ -bond with zirconium. The spectroscopic data also established a definite trend for the strength of the non-classical Zr-H-Si interaction in $\text{Cp}_2\text{Zr(X)(N}^t\text{BuSiMe}_2\text{H)}$: $\text{X} = \text{H} > \text{I} > \text{Br} > \text{Cl} > \text{F}$. This ordering directly reflects the relative electrophilicity of the zirconium centre. X-ray diffraction studies of the hydride and chloride complexes were also consistent with the coordination of the Si-H bond to the metal centre. Short Zr-Si distances and acute Zr-N-Si angles suggested severe bending of the silyl group towards zirconium, and the location of the amido group near the centre of the metallocene equatorial wedge is consistent with a Cp_2ML_3 coordination environment, not the Cp_2ML_2 geometry indicated by the formula $\text{Cp}_2\text{Zr(NR}_2\text{)(X)}$ [40].

N-N 1.301(3) Å

Zr-N_2 1.920(3) Å

Zr-N-N 170°

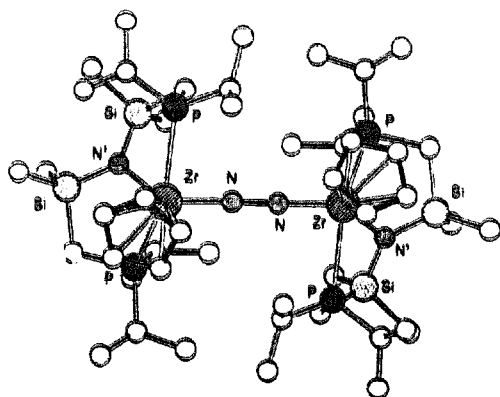
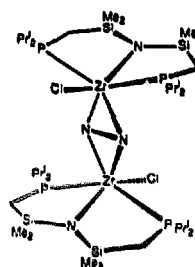
Zr-N^t 2.306(3) Å



N-N 1.548(7) Å

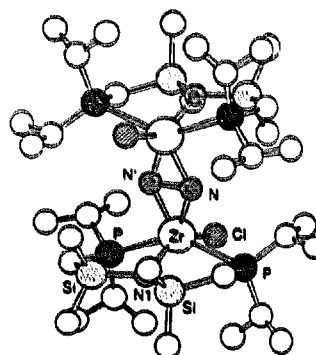
Zr-N 2.024(4) Å

Zr-N1 2.175(3) Å



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(24)



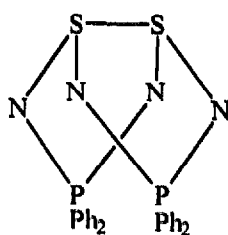
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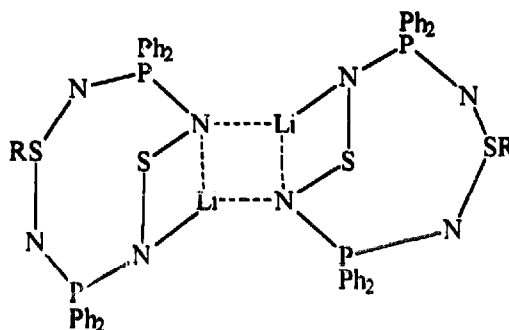
The vibrational properties of the bridging dinitrogen ligand in two different dinuclear zirconium complexes known to contain unusually long N-N bonds have been investigated by resonance Raman (RR) spectroscopy [41]. X-ray crystallography has shown that $\{[(\text{Pr}_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)$ (24), exhibits 'end-on' bridging dinitrogen, whilst $\{[(\text{Pr}_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{ZrCl}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$ (25), exhibits 'side-on' bridging dinitrogen. The RR spectrum of (24) showed a single intense peak at 1211 cm^{-1} , corresponding to the $\nu(\text{N-N})$ symmetric stretch. The peak shifted to 1172 cm^{-1} in the ${}^{15}\text{N}_2$ -enriched isotopomer. This value

corresponds to an N-N bond order between 1 and 2, consistent with the 1.301 Å N-N bond length in the crystal structure. Solid state and toluene solution spectra correlated well, indicating the structures are nearly identical. The solid state RR spectrum of **25** showed a peak at 731 cm^{-1} which was assigned to $\nu(\text{N-N})$. The low frequency of this stretch compared with that of $\nu(\text{N-N})$ in N_2H_4 implied that the N-N bond order is less than 1. Solution RR spectra in thf were more complicated, but the presence of isotope sensitive bands below 1111 cm^{-1} also supported an N-N bond order of less than 1. This is consistent with the 1.548 Å N-N bond length in the crystal structure.

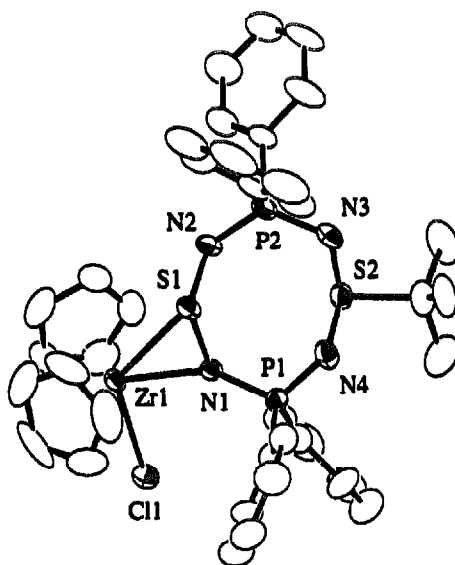
The synthesis and structure of the first zirconyl complex of the unsaturated $\text{P}_2\text{N}_4\text{S}_2$ ring (**26**) which exhibits a novel $\eta^2\text{-N,S}$ bonding mode has been reported. The reaction of the dilithocomplex (**27**) ($\text{R} = ^t\text{Bu}$) with 2 equivalents of Cp_2ZrCl_2 in thf at 0°C yielded $[\text{Cp}_2\text{ZrCl}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2^t\text{Bu})]$ (**28**) as highly air sensitive crystals. Complex (**28**) was characterised by ^1H , ^{13}C and ^{31}P NMR, and X-ray crystallography. The crystal structure showed that the $[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2^t\text{Bu}]$ ligand is coordinated to Zr *via* adjacent S and N atoms ($\eta^2\text{-N,S}$). This renders the Zr-S and Zr-N bonds highly susceptible to cleavage by electrophiles, and results in the production of $\text{P}_2\text{N}_4\text{S}_2$ rings with S-halogeno and N-H functionalities which are more difficult to make from the parent ring complex [42].



(26)



(27)



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Complexes of the type $\text{MCp}_2\text{Cl}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{R})$ have been prepared by the reaction of $[\text{Li}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{R})\text{thf}]_2$ ($\text{R} = \text{Me}, {}^t\text{Bu}, \text{Ph}, \text{CH}_2\text{PPH}_2$) with the metallocene dihalides MCp_2Cl_2 ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) in thf [43]. The X-ray crystal structure of $\text{ZrCp}_2\text{Cl}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2{}^t\text{Bu})$ has been determined. The $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2{}^t\text{Bu}^-$ ligand is attached to zirconium via adjacent sulphur and nitrogen atoms of an NSN unit on the opposite side of the ring from the ${}^t\text{Bu}$ group. The resulting three-membered metallacycle (zirconathiaaziridene) has the dimensions $d(\text{Zr-S}) = 2.634(2) \text{ \AA}$, $d(\text{Zr-N}) = 2.206(5) \text{ \AA}$, $d(\text{S-N}) = 1.697(6) \text{ \AA}$. Treatment of $\text{ZrCp}_2\text{Cl}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2{}^t\text{Bu})$ with electrophiles resulted in the regiospecific functionalisation of the $\text{P}_2\text{N}_4\text{S}_2$ ring. With methyl iodide or bromide it forms the unsymmetrical S,S' -diorgano derivative $\text{Ph}_4\text{P}_2\text{N}_4(\text{S}^t\text{Bu})(\text{SMe})$ and the S -bromo derivative $\text{Ph}_4\text{P}_2\text{N}_4(\text{S}^t\text{Bu})(\text{SBr})$, respectively. By contrast, the reaction of $\text{ZrCp}_2\text{Cl}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2{}^t\text{Bu})$ with 2 molar equivalents of HCl gas produces $[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2{}^t\text{BuH}_2]\text{Cl}$ in which the two nitrogen atoms, separated by the two-coordinate sulphur in the $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2{}^t\text{Bu}^-$ anion, have been protonated. $[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2{}^t\text{BuH}_2]\text{Cl}$ was characterised by ^{31}P and ${}^1\text{H}$ - ^{15}N HMQC NMR spectroscopy and by X-ray crystallography, which showed that it exists as a hydrogen bonded dimer in the solid state. An X-ray structural determination of $\text{Ph}_4\text{P}_2\text{N}_4(\text{SPh})(\text{SBr})$, prepared by the bromination of $[\text{Li}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Ph})\text{thf}]_2$ or $[\text{ZrCp}_2\text{Cl}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Ph})]$ revealed a relatively long S-Br distance of $2.573(5) \text{ \AA}$. Attempts to replace the Cl ligand in $\text{ZrCp}_2\text{Cl}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2{}^t\text{Bu})$ with strong nucleophiles such as $\text{Li}(\text{Et}_3\text{H})$ or LiMe were unsuccessful.

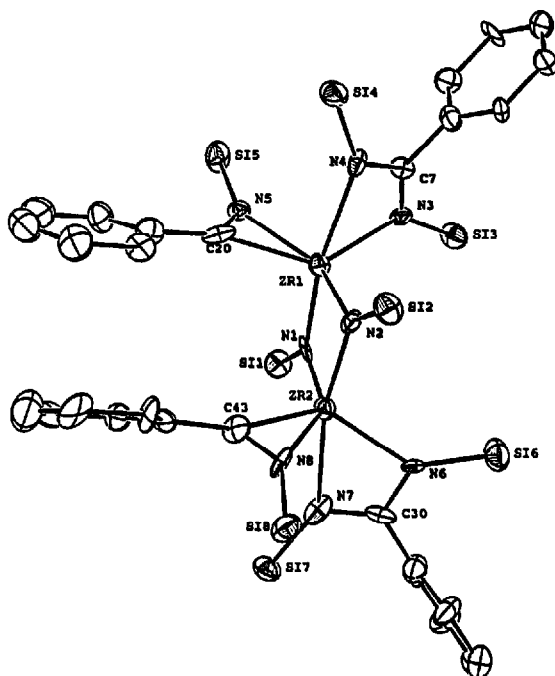
An *inter versus* intra isotope effect study has been carried out to determine whether methane binds to d^0 $({}^t\text{Bu}_3\text{SiNH})_2\text{Zr}=\text{NSi}^t\text{Bu}_3$ prior to C-H bond activation. Both mechanisms are plausible, but Occam's razor favours the smooth pathway for C-H versus C-D activation, given the lack of a significant isotope effect supporting methane binding [44].

The complex $[\text{Zr}(\text{dota})(\text{H}_2\text{O})]$ has been prepared by the reaction of $\text{Zr}(\text{OH})_4$, formed by the controlled hydrolysis of ZrOCl_2 , and excess H_4dota ($\text{H}_4\text{dota} = 1,4,7,10$ -tetraazocyclododecane- N,N',N'',N''' -tetraacetic acid). The solution structure of the complex has been determined by ${}^1\text{H}$ NMR at 293 K in D_2O . The results suggest that the structure is of lower symmetry than the mono-capped (H_2O) square antiprismatic structure shown by the solid state crystal structure of $\text{Na}[\text{Y}(\text{dota})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$. A minor isomer of the Zr complex was also observed [45].

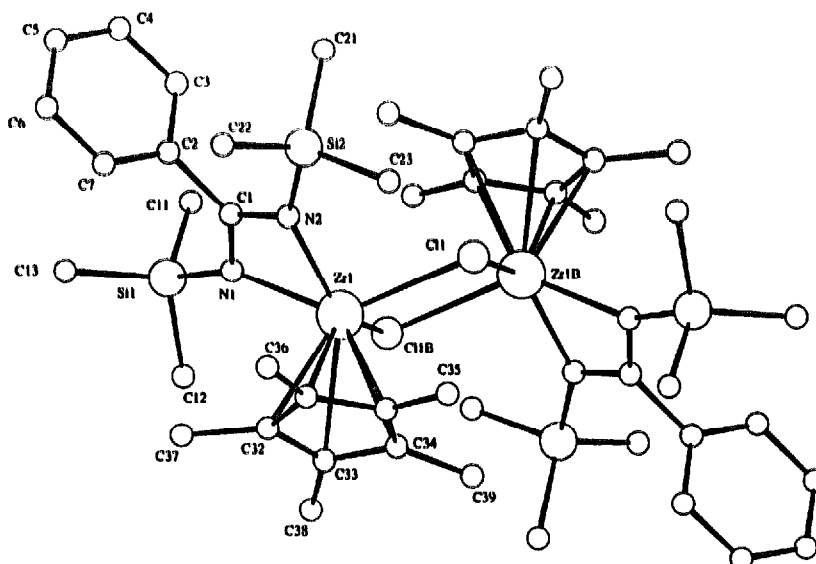
The complex $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{ZrCl}_2$ has been used to prepare a range of $\text{Zr}(\text{IV})$ derivatives based on N,N' -bis(trimethylsilyl)benzamidinate ligands by various routes. Reduction of the dichloride using Na/Hg gave a compound with empirical formula $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{Zr}\cdot 0.25(\text{hexane})$, which on analysis by X-ray means proved to be $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{Zr}(\eta^2\text{-PhCNSiMe}_3)(\mu\text{-NSiMe}_3)_2$ (29). In the molecule, each 6 coordinate Zr atom is bound to two bridging imido ligands, an η^2 -iminoacyl ligand and a didentate $[\text{PhC}(\text{NSiMe}_3)_2]$ ligand [46].

The compound $[\{\text{Zr}(\eta\text{-C}_5\text{Me}_5)(\eta\text{-CPh}(\text{N}(\text{SiMe}_3)_2)(\mu\text{-Cl})_2)[\text{B}(\text{C}_6\text{F}_5)_4]_2$ (30) was prepared by the reaction of $[\text{Zr}(\eta\text{-C}_5\text{Me}_5)(\eta\text{-CPh}(\text{N}(\text{SiMe}_3)_2)\text{Me}_2]$ and $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ in CH_2Cl_2 , with resultant abstraction of Cl from the solvent to give the unexpected chlorine bridged salt [47]. Treatment of $[\text{Zr}(\eta\text{-C}_5\text{H}_5)(\eta\text{-CPh}(\text{N}(\text{SiMe}_3)_2)\text{Me}_2]$ with $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ in CH_2Cl_2 resulted in the loss of C_6F_5^- from the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion in addition to chlorine abstraction from the solvent, forming $[\{\text{Zr}(\eta\text{-C}_5\text{H}_5)(\eta\text{-CPh}(\text{N}(\text{SiMe}_3)_2)(\mu\text{-Cl})_2)[\text{B}(\text{C}_6\text{F}_5)_3\text{Me}]_2$. The reaction

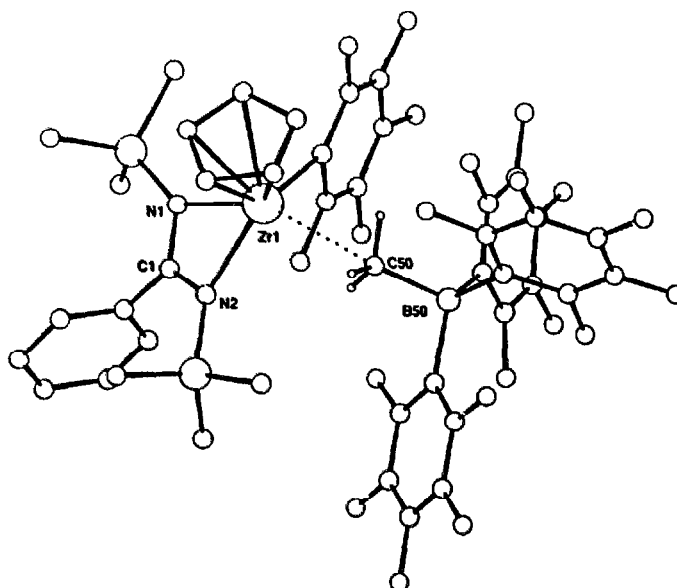
been transferred from B to Zr.



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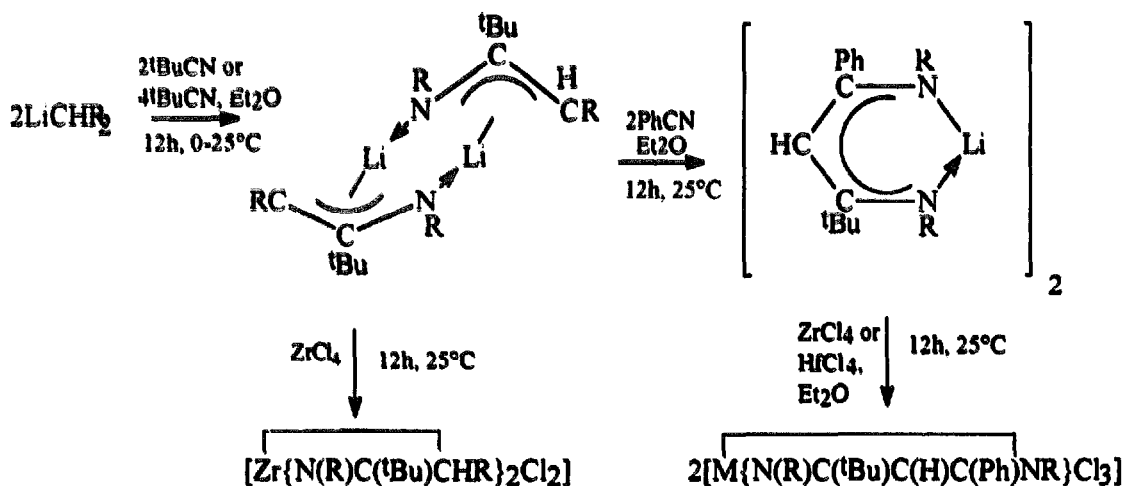


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(31) Reproduced from ref. [47] with permission.

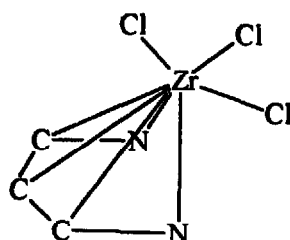
The η^3 -aza-allyl $[\text{Li}(\text{LL}')_2] \{[\text{N}(\text{R})\text{C}(\text{tBu})\text{CHR}]^- = [\text{LL}']^-\}$; $\text{R} = \text{SiMe}_3$, prepared by the reaction of LiCHR_2 with tBuCN , was allowed to react with ZrCl_4 to give the $\text{Zr}(\text{IV})$ η^3 -1-aza-allyl, $[\text{Zr}(\text{LL}')_2\text{Cl}_2]$ [48]. The β -diketiminates $[\text{M}\{\text{N}(\text{R})\text{C}(\text{tBu})\text{C}(\text{H})\text{C}(\text{Ph})\text{NR}\}\text{Cl}_3]$ ($\text{M} = \text{Zr}, \text{Hf}$) were obtained from $[\text{Li}(\text{LL}')_2]$ with 2PhCN via MCl_4 (scheme 12). The X-ray structure of the Zr analogue was determined. The Zr atom was found to be five coordinate in a distorted trigonal bipyramidal environment as shown in (32).



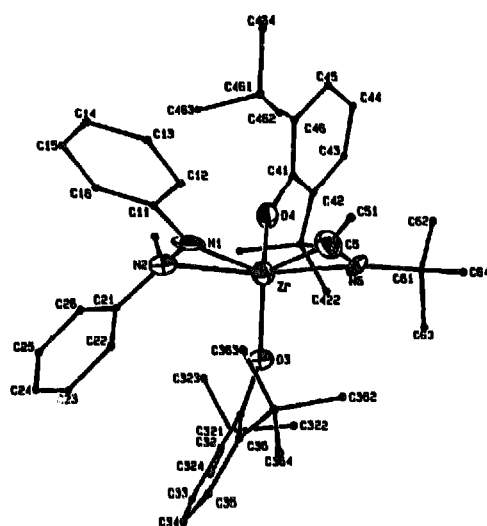
Scheme 12

The synthesis and reactivity of zirconium hydrazido complexes containing aryloxy ligands have been investigated. $[(\text{ArO})_2\text{Zr}(\text{Me})(\eta^2\text{-NPhNPh})]$ ($\text{ArO} = 2,6\text{-di-}t\text{butylphenoxide}$) was prepared by treating $[(\text{ArO})_2\text{Zr}(\text{Me})_2]$ with 1 equivalent of 1,2-diphenylhydrazine in hydrocarbon solvents at ambient temperature; 1 equivalent of methane is eliminated. Reaction of

$[(\text{ArO})_2\text{Zr}(\text{Me})(\eta^2\text{-NPhNHPPh})]$ with 1 equivalent of ${}^t\text{BuNC}$ led to a mixed hydrazido, iminoacyl complex $[(\text{ArO})_2\text{Zr}(\eta^2\text{-NPhNHPPh})(\eta^2\text{-}{}^t\text{BuCNCH}_3)]$ (33). The crystal structure of this complex shows both hydrazido and iminoacyl groups to be η^2 -bound to the metal with a PhN-NHPPh distance of $1.47(2)$ Å [49].



(32)



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Homoleptic 1,2:5,6-di-*O*-isopropylidene- α -D-glucofuranose (HL) complexes of aluminium and group 4 metals (Ti, Zr or Hf) have been synthesised by ligand displacement from AlEt_3 and $[\text{M}(\text{PhCH}_2)_4]$ ($\text{M} = \text{Ti, Zr or Hf}$) with HL. The products were characterised by ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectroscopies which showed the sugar ligands to be equivalent and free to rotate about the M-O bond, even at 193 K. Pyridine adducts of all the complexes were obtained. The X-ray crystal structure of the zirconium adduct $[\text{ZrL}_4(\text{py})_2]$ was determined. It is monomeric, and coordination around the Zr atom is pseudo octahedral, involving four carbohydrate and two pyridine ligands in a *cis* configuration [50].

Complexes of the general formula $\text{ZrCl}_4\cdot\text{DAD}$ have been obtained by the reaction of 1,4-diazabutadienes ($\text{DAD} = \text{RN}=\text{CPh-CPh}=\text{NR}$; $\text{R} = \text{C}_6\text{H}_5, \text{CH}_3\text{C}_6\text{H}_4, \text{CH}_3\text{OC}_6\text{H}_4$) with $\text{ZrCl}_4\cdot 2\text{thf}$ as shown in equation (vi). When the products were allowed to react with lithium diazadienides, Li_2DAD , deep coloured complexes of formula $\text{Zr}(\text{DAD})_3$ were formed as in equation (vii). The complexes were characterised by elemental analysis and IR, ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectroscopy [51].



The first substituted bis(porphyrin) complexes $\text{Zr}(\text{porph})(\text{porph-X})$ ($\text{X} = \text{NO}_2, \text{NH}_2$, where X replaces one of the β -pyrrole hydrogens) have been prepared. Electronic spectroscopy and cyclic voltammetry provided evidence that introduction of an electron withdrawing or donating group alters the electronic structure of the molecule. The electronic spectra of the π radical cations and dications confirmed that the interporphyrin π - π interactions are affected by β -substitution. ^1H NMR spectroscopic studies of $\text{Zr}(\text{porph})(\text{porph-X})$ show that the two porphyrin macrocycles do not rotate with respect to one another even at 150°C [52].

The dialkyl chlorides $(\text{Me}_3\text{SiCH}_2)_2\text{MCl}_2(\text{EtO})_2$ ($\text{M} = \text{Zr}, \text{Hf}$) synthesised from stoichiometric amounts of alkyl lithium and MCl_4 , have been used to prepare $(\text{P})\text{M}(\text{CH}_2\text{SiMe}_3)_2$ derivatives ($\text{PH}_2 = \text{tetra-}p\text{-tolylporphyrin}$ or OEPH_2) in good yields by reaction with the dilithium porphyrate. NMR spectroscopic studies carried out on the complex show that the Zr atom is displaced out of the porphyrin plane and that the ligands are *cis* to each other. Protonolysis of the OEP derivatives with one equivalent of $[\text{HNMe}_2\text{PH}][\text{BPh}_4]$ generated the cationic species of $[(\text{OEP})\text{M}(\text{CH}_2\text{SiMe}_3)][\text{BPh}_4]$ [53].

11.1.5 Complexes with phosphorus donor ligands

The dimer $[\text{Zr}_2\text{Cl}_8(\text{PMe}_3)_4]$ (34) has been obtained by the reaction of ZrCl_4 with 2 equivalents of PMe_3 in benzene. The Zr atoms are bridged by Cl atoms forming bipolyhedra arising from Cl-Cl edge sharing between $\text{ZrCl}_5(\text{PMe}_3)_2$ face capped octahedra. In the same study of edge sharing bioctahedral type complexes, the complex *trans*- $[\text{ZrI}_4(\text{PMe}_2\text{Ph})_2]$ (35) was obtained by allowing ZrI_4 to react with two equivalents of PMe_2Ph in benzene. This complex is mononuclear with octahedral geometry. The I-Zr-I and I-Zr-P angles are near to the octahedral value of 90° , and the PMe_2Ph ligands are *trans* to each other [54]. A related Zr(III) complex, $\text{Zr}_2\text{Cl}_6(\text{PMe}_3)_4$, has also been prepared (Section 11.2).

The reaction of $\text{Cp}^0_2\text{ZrCl}_2$ ($\text{Cp}^0 = \eta^5\text{-C}_5\text{Me}_4\text{Et}$) with one or two equivalents of $\text{LiPH}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)$ in thf yielded $\text{Cp}^0_2\text{Zr}\{\text{P}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{P}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\}$ as dark green crystals. X-ray crystallography showed the *trans*-(2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$) $\text{P}=\text{P}$ (2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$) ligand to be coordinated 'side-on'. This ligand is unstable when not coordinated to a metal centre. $\text{Cp}^0_2\text{Zr}\{\text{P}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{P}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\}$ has two identical Zr-P bond lengths of 2.650(3) Å, and a P-P bond length of 2.188(3) Å. The P-P bond length corresponds more closely to observed values for P-P single bonds, rather than for P-P double bonds [55]. The same group has reported the reaction of Cp_2ZrCl_2 with solvent free $\text{LiPH}(2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2)$. The terminal zirconocene phosphido complexes $\text{Cp}_2\text{Zr}(\text{Cl})\{\text{PH}(2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2)\}$, were formed by a 1:1 reaction, and $\text{Cp}_2\text{Zr}[\text{PH}(2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2)]_2$ by a 1:2 reaction. $\text{Cp}_2\text{Zr}[\text{PH}(2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2)]_2$ is more readily obtained by the reaction of Cp_2ZrCl_2 with $\text{H}_2\text{P}(2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2)$ in the presence of

The compounds $\text{Cp}_2\text{M}(\text{PR})_3$ ($\text{M} = \text{Zr}$, $\text{R} = \text{Ph}$ **38**, Cy **39**; $\text{M} = \text{Hf}$, $\text{R} = \text{Cy}$ **40**) and $\text{Cp}^*_2\text{Zr}(\text{PCy})_3$ **41** have been prepared by the known reactions of the metallocene dihalide with

primary phosphide salts [57]. Complexes **38**, **39** and **41** were also prepared by activation of the P-H bonds of a primary phosphine by zirconocene. Stabilised metallocene(II), $\text{Cp}_2\text{Zr}(\text{SMe}_2)_2$, and metallocene(II) generated *in situ* by the reduction of Cp_2ZrCl_2 or Cp^*ZrCl_2 , were both used. The compounds were characterised by ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{31}P and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Identification of the intermediates of these reactions was attempted. The reaction of Cp_2ZrCl_2 with LiPPh in the presence of NEt_4Br gave $[\text{Cp}_2\text{ZrBr}(\text{PPh})_2][\text{NEt}_4]$ **42**. These results suggested a mechanism of formation of the $\text{M}(\text{PR})_3$ derivatives involving phosphinidene $\text{M} = \text{Pr}$ and $\text{M}((\text{PR})_2)$ intermediates. Complexes **38–42** have been characterised by X-ray crystallography.

The synthesis, structure and bonding in zirconocene primary phosphido (PHR^-), phosphinidene (PR^{2-}) and phosphide (P^{3-}) derivatives have been investigated [58]. $\text{Cp}_2\text{Zr}(\text{PH}(\text{C}_6\text{H}_2\text{-2,4,6-}^t\text{Bu}_3))\text{Cl}$ **43** and $\text{Cp}_2\text{Zr}(\text{PH}(\text{C}_6\text{H}_2\text{-2,4,6-Me}_3))\text{Cl}$ **44** were prepared from LiPHR and Cp_2ZrCl_2 (1:1). In reactions of $\text{PH}_2(\text{C}_6\text{H}_2\text{-2,4,6-Me}_3)$ or PH_2SiMe_3 with Cp_2ZrHCl , the respective bridging phosphinidine derivatives $(\text{Cp}_2\text{ZrCl})_2(\mu_2\text{-PC}_6\text{H}_2\text{-2,4,6-Me}_3)$ and $\text{Cp}_2\text{Zr}(\mu_2\text{-PSiPh}_3)(\mu_2\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)\text{ZrCpCl}$ **45**, having planar phosphorus atoms, were obtained. Reaction of $\text{PH}(\text{C}_6\text{H}_2\text{-2,4,6-}^t\text{Bu}_3)$ with excess Cp_2ZrHCl resulted in the formation of planar, trinuclear $(\text{Cp}_2\text{Zr})_2(\mu_2\text{-Cl})(\mu_3\text{-P})(\text{ZrCp}_2\text{Cl})$ **46**, which could also be prepared by the addition of $\text{PH}(\text{C}_6\text{H}_2\text{-2,4,6-}^t\text{Bu}_3)$ to a mixture of Cp_2ZrCl_2 and Mg. It is a mixed valent compound, having an EPR spectrum typical of $\text{Zr}(\text{III})\text{-P}$ species. Diamagnetic $(\text{CpZr}(\mu_2\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4))_3(\mu_3\text{-P})$ was obtained under similar conditions, but with prolonged exposure to Mg. This complex was shown to be pyramidal at the phosphorus, in contrast to **46**. The terminal phosphinidene complexes $\text{Cp}_2\text{Zr}(\text{P}(\text{C}_6\text{H}_2\text{-2,4,6-}^t\text{Bu}_3))(\text{PMe}_3)$ and $\text{Cp}_2\text{Zr}(\text{P}(\text{C}_6\text{H}_2\text{Me}_3))(\text{PMe}_3)$ were formed by the reaction of **43** or **44** with KH and PMe_3 . The X-ray crystal structures of **43**, **45** and **46** were determined. Some of the mechanistic aspects of the chemistry are considered.

α -Phosphino enolates have been prepared by deprotonation of acyldiphenylphosphines using $^n\text{BuLi}$ and allowed to react with Cp_2ZrCl_2 , giving $[\text{Cp}_2\text{Zr}(\text{Cl})\text{O}(\text{CH}_2)\text{CPh}_2]$ and $[\text{Cp}_2\text{Zr}(\text{Cl})\text{O}(\text{CHMe})\text{CPh}_2]$. The latter complex was isolated as pure *E*- and *Z*-isomers. The reaction of $[\text{Cp}_2\text{Zr}(\text{Cl})\text{O}(\text{CH}_2)\text{CPh}_2]$ with $[\text{Cr}(\text{CO})_5\text{thf}]$ gave the dimetallic α -phosphino enolato complex $[\text{Cp}_2\text{Zr}(\text{Cl})\text{OC}(\text{CH}_2)\text{P}(\text{PH})_2\text{Cr}(\text{CO})_5]$ in which the nucleophile ' CH_2 ' unit is maintained free for further reactivity. Complexes $[\text{Cp}_2\text{Zr}(\text{Cl})\text{O}(\text{CHMe})\text{CPh}_2]$ and $[\text{Cp}_2\text{Zr}(\text{Cl})\text{OC}(\text{CH}_2)\text{P}(\text{PH})_2\text{Cr}(\text{CO})_5]$ were characterised by X-ray crystallography [59].

Hydride abstraction carried out on a mixture of $\text{Cp}_2\text{Zr}(\text{PMe}_3)$ complexes resulted in the formation of a zirconium complex of tropyne. Reaction of the $\text{Cp}_2\text{Zr}(\text{PMe}_3)$ complexes with 2-butyne followed by hydride abstraction gave the first example of a transition-metal metallacycle with the π framework of an azulene [60].

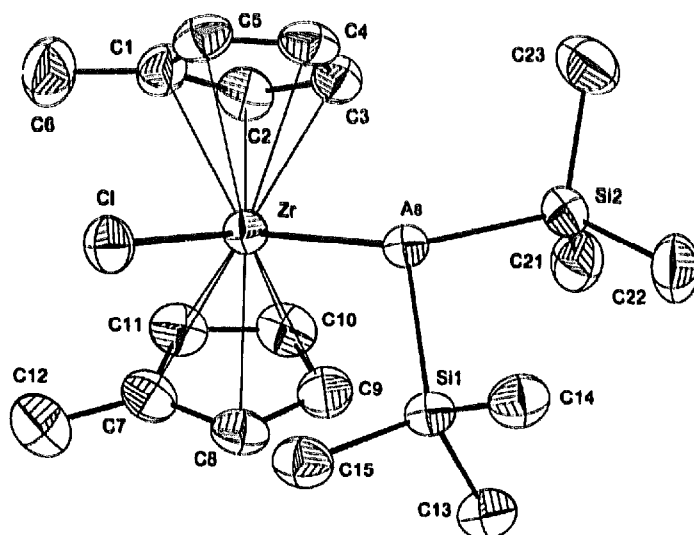
The $(\eta^2\text{-phosphatabenzyne})\text{dicyclopentadienylzirconium- trimethylphosphine adduct}$ $\text{Zr}(\text{Cp})_2(\text{PMe}_3)\text{C}_5\text{HPMe}_2$ was obtained as a stable complex by the thermal loss of RH from a $\text{Cp}_2\text{Zr}(\text{R})\text{-2-substituted phosphine}$ ($\text{R} = \text{Me}$ or Ph) in the presence of PMe_3 . Insertion of alkynes and ketones was found to take place selectively into the $\text{Zr-C}_2(\text{ring})$ bond of $\text{Zr}(\text{Cp})_2(\text{PMe}_3)\text{C}_5\text{HPMe}_2$ [61].

The reactions of ZrCl_4 with lithium phosphinomethanimides have been investigated [62]. With $\{(\text{tmeda})\text{Li}[\text{C}(\text{PMe}_2)(\text{SiMe}_3)]\}_2$ **47** a mixture of compounds $\text{Cl}_{4-n}\text{Zr}[\text{CH}(\text{PMe}_2)(\text{SiMe}_3)]_n$

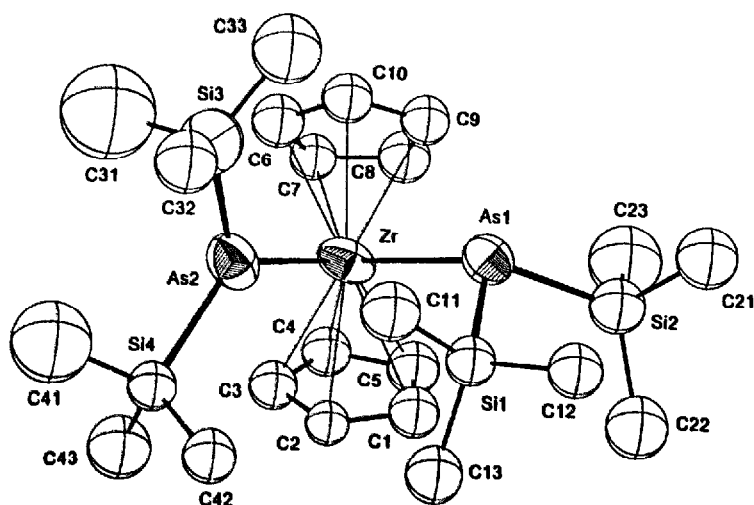
($n = 1-4$) **48a-d** was obtained and characterised by NMR spectroscopy. With (tmeda){Li[CH(PMe₂)(SiMe₃)₂]}₂ **49**, only the disubstituted product, Cl₂Zr[C(PMe₂)(SiMe₃)₂]₂ **50** was obtained in good yield. In toluene solution, insertion of CO into the Zr-C bond of **50** occurs, and after a subsequent 1,2-silyl shift, forms a phosphino enolato complex which dimerises to {Cl₂Zr[C(PMe₂)(SiMe₃)₂][OC(SiMe₃)=C(SiMe₃)PMe₂]}₂, **51**. Compound **50** also undergoes insertion of CO in thf solution. Spectroscopic evidence suggested the formation of the phosphorus ylide (Me₃Si)(Me₃SiO)C=C(PMe₂)(PMe₂=C(SiMe₃)₂), (L), **52** and LZrCl₂. With the lithium diphosphinomethanides (D)Li[C(PR₂)₂(SiMe₃)] (D = nothing, R = Me, **49a**; D = tmeda, R = Ph, **49b**; D = tmeda, R = Me, **49c**) the hexacoordinate complex Cl₂Zr[C(PMe₂)₂(SiMe₃)]₂ **53** and ionic species [(tmeda)₂Li]{Cl₃Zr[C(PR₂)₂(SiMe₃)]₂} **54**, (R = Ph) and **55**, (R = Me) with heptacoordinate Zr were obtained. Complexes **50**, **51**, **54** and **55** have been characterised by X-ray crystallography [62].

11.1.6 Compounds with arsenic donor ligands

The zirconocene arsenido complexes [Cp'₂Zr{As(SiMe₃)₂}(Cl)] (Cp' = C₅H₄Me) (**37**) and [Cp₂Zr{As(SiMe₃)₂}]₂ (**38**) have been obtained by the reaction of [Cp'₂ZrCl₂] or [Cp₂ZrCl₂] with Li(thf)₂As(SiMe₃)₂. The complexes were both characterised by IR, NMR and mass spectroscopy. The structures have been determined by X-ray crystallography. The values of the bond lengths in [Cp₂Zr{As(SiMe₃)₂}]₂ suggest the presence of one single and one double Zr-As bond at the central Zr atom which is in a distorted tetrahedral environment. In the monoarsenidocomplex the As(SiMe₃)₂ group was thought to be singly bonded to the Zr atom [63].



(**37**) Reproduced from ref. [63] with permission.



(38) Reproduced from ref. [63] with permission.

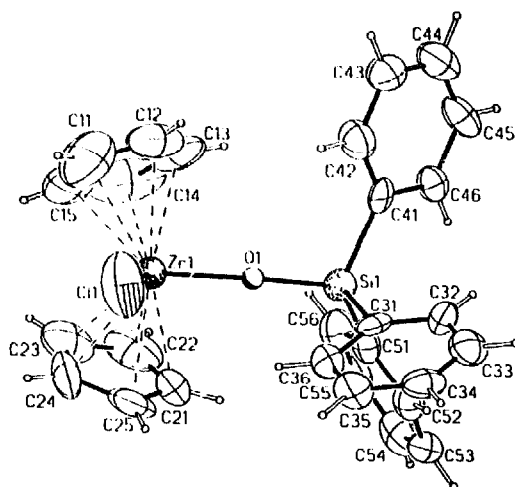
11.1.7 Complexes with oxygen donor ligands

The reactivity of Zr and Hf σ -bonds towards silanols has stimulated investigation into zirconium silanol complexes. There is evidence to suggest that silanols on Si surfaces promote catalytic activity and it is assumed that incorporation of Zr would have a cooperative effect in activating the substrate by forming a metal-siloxy complex. Compounds resulting from the interaction of silanols with metal containing moieties are of interest as models for metal to surface interaction in heterogeneous silicon-oxide based catalysts. This work has resulted in the isolation of two new Zr silanol complexes outlined below.

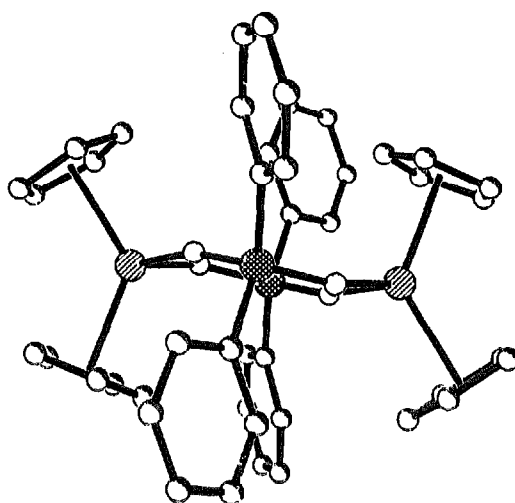
The compound $\text{Cp}_2\text{ZrCl}(\text{OSiPh}_3)$ (39) has been prepared from the reaction of Cp_2ZrCl_2 with triphenylsilanol (Ph_3SiOH) in diethyl ether in the presence of piperidine (pip) according to equation (viii). The structure of (39), as determined by X-ray crystallography, was found to consist of 3 symmetry-independent monomeric molecules differing only slightly in geometry. An average Zr-O bond distance of $1.964(6)\text{\AA}$ and Si-O bond distance of $1.621(6)\text{\AA}$, with a $\angle\text{Zr-O-Si}$ of $173.7(4)^\circ$ were found [65].



The reaction of Cp_2MMe_2 ($\text{M} = \text{Zr}, \text{Hf}$) with $\text{Ph}_2\text{Si}(\text{OH})_2$ yields the eight membered ring $[\text{Cp}_2\text{M}(\mu\text{-OSiPh}_2\text{O})]_2$. A single crystal X-ray determination of the structure of the Zr analogue (40) showed the 8-membered ring to be non-planar, the Cp_2Zr units being bent by 20° out of the Si_2O_4 plane to give a "chaise-longue" conformation. The Zr-O distances of $1.974(2)\text{\AA}$ and $1.983(2)\text{\AA}$ were found to be significantly longer than those reported in other Zr-O-Si compounds. EHMO calculations carried out on the structure found evidence to support the known reactivity of silanols towards complexes containing Zr-C or Hf-C σ -bonds [66].



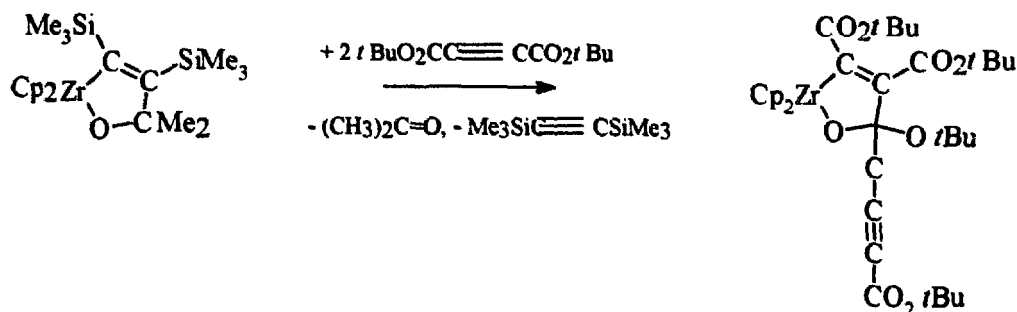
(39) Reproduced from ref. [65] with permission.



(40) Reproduced from ref. [66] with permission.

The dihydrofuran **56** (scheme 13), upon exposure to di-*tert*-butyl acetylenedicarboxylate in *n*-hexane, undergoes cleavage of bis(trimethyl)silylacetylene and acetone and the resultant "Cp₂Zr" moiety reacts with two equivalents of acetylenedicarboxylate according to reaction scheme 13. The product was not the expected substituted metallocyclopentadiene. Instead, insertion of an ester carbonyl group from the second molecule of alkyne produced the zirconadihydrofuran **57** [67]. The X-ray crystal structure of the thf adduct of this molecule was determined and showed the central structural element to consist of a near planar zirconadihydrofuran ring with two Cp ligands and a coordinated thf molecule. When **56** was treated with bis(trimethylsilyl) acetylenedicarboxylate only one alkyne molecule per zirconocene unit underwent reaction to yield the dimeric zirconadihydrofuran complex **58** as shown in reaction scheme 14. In the reaction the trimethylsilyl group undergoes an unusual 1,3-migration to a carbon atom. The X-ray crystal structure of **58** was

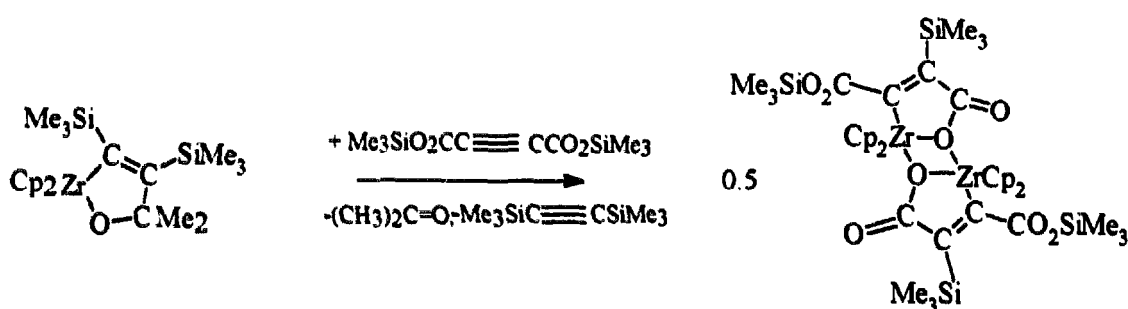
also determined and was shown to consist of a centro-symmetric four membered Zr-O-Zr-O planar ring. Possible mechanisms are cited for the intramolecular migration of the trimethylsilyl group.



56

57

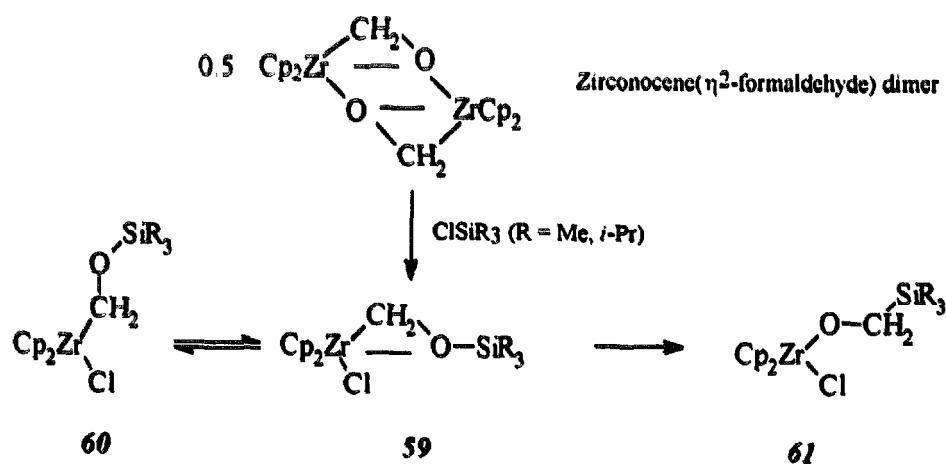
Scheme 13



56

58

Scheme 14



60

59

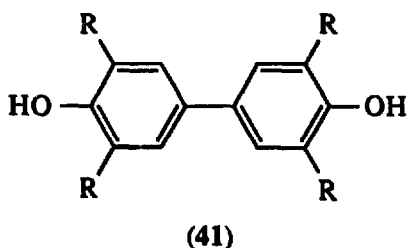
61

Scheme 15

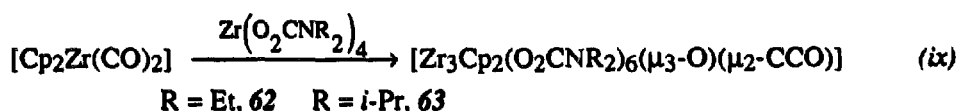
The zirconocene (η^2 -formaldehyde) dimer, $(\text{Cp}_2\text{ZrOCH}_2)_2$, was found to react with the trialkylchlorosilanes, R_3SiCl ($\text{R} = \text{Et, Me, } i\text{-Pr}$) to yield the (η^2 -(trialkylsiloxy)methyl)zirconocene complexes, $\text{Cp}_2\text{ZrClCH}_2\text{OSiR}_3$, 59. The complexes were found to have the metalloxirane

structural type with internal O-coordination. Thermolysis of **59** ($R = \text{Me}$ and $i\text{Pr}$) at 110° led to equilibration with the isomers **60** and **61** as shown in reaction scheme 15. Complexes **60** are the acyclic $\text{Cp}_2\text{ZrClCH}_2\text{OSiR}_3$ isomers of **59** whereas the complexes **61**, $\text{Cp}_2\text{ZrClOCH}_2\text{SiR}_3$, are formed from dyotropic rearrangement. The kinetics of the thermally induced rearrangement are reported [68].

Reaction between Cp_2ZrCl_2 and the 4,4'-biphenolate ligand, $(\text{Me}_4\text{BIPOH}_2)$, (**41**) in toluene resulted in the bismetallocene chloride complex $\text{Cp}_2\text{Zr}(\text{Me}_4\text{BIPO})\text{Cl}$ [69].



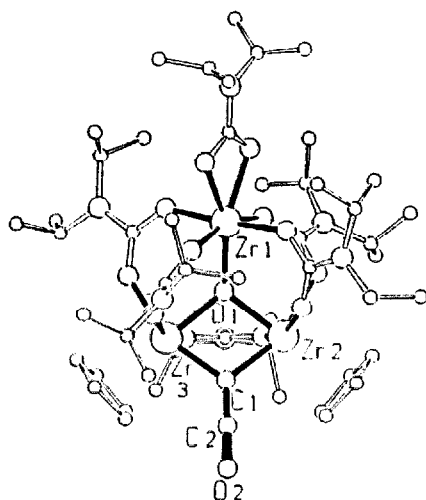
Formation of C-C bonds from feedstock CO is a fundamental reaction in organometallic chemistry with only one previous report to date of CO reduction to the ketylidene (CCO) ligand. However the reaction of the Zr(II) complex, $[\text{Cp}_2\text{Zr}(\text{CO})_2]$, with $[\text{Zr}(\text{O}_2\text{CNR}_2)_4]$ ($R = \text{Et}$, $i\text{Pr}$) in toluene has been reported to yield colourless crystals of the diamagnetic μ -ketylidene complexes, $[\text{Zr}_3\text{Cp}_2(\text{O}_2\text{CNR}_2)_6(\mu_3\text{-O})(\mu_2\text{-CCO})]$, according to equation (ix). Investigation of the IR spectra of



62 and **63**, shown in equation (ix), revealed that an absorption at 2013 cm^{-1} shifts to 1951 cm^{-1} in the ^{13}C -labelled compound (prepared using $[\text{Cp}_2\text{Zr}(^{13}\text{CO})_2]$) indicating that the C atoms of the μ -ketylidene ligand originate from the carbonyl group of the Zr(II) complex. The formation of the μ -ketylidene ligand by internal reduction of the carbonyl groups results from oxidation of Zr(II) within the carbonyl complex. This discovery rendered complexes of the type **62** and **63** as possible models for CO reductive cleavage on metal surfaces and supports suggestions that ketylidene might act as a surface bonded species. The X-ray crystal structure of **63** has been determined and was found to consist of a $\mu_3\text{-O}$ bridged triangle of zirconium atoms as shown in figure (42). Two of the metal atoms (Zr2 and Zr3) are coordinated to bridging carbamates and to the cyclopentadiene ring and $\mu\text{-CCO}$ ligands. The third zirconium atom (Zr1) has bridging and terminal carbamate ligands. The μ -ketylidene ligand is substantially linear [$\text{C-C-O} = 179.1^\circ$]. In an analogous reaction to that of the $\alpha\text{-C}$ atom in organic ketenes the Zr(IV) ketylidene complex **63** reacts with substrates containing the $>\text{C=O}$ group to give the μ -oxo complex $[\text{Zr}_3\text{Cp}_2(\text{O}_2\text{CNi-Pr}_2)_6(\mu_3\text{-O})(\mu_2\text{-O})]$. The structure is similar to that of **63** except that the $\mu_2\text{-CCO}$ group in **63** is replaced by the $\mu_2\text{-oxo}$ ligand [70].

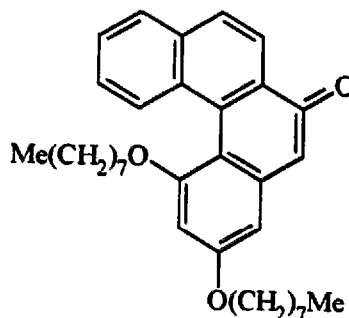
The adduct formed between CpZrCl_3 and a biaryl lactone, (**43**), has been studied in toluene solution by Zr K- α X-ray absorption spectroscopy. Results showed the adduct,

$[\text{CpZrCl}_2(\text{lactone})(\mu\text{-Cl})]_2$, to be dimeric in toluene with each Zr atom pseudo octahedrally coordinated to the metal at a distance of 2.14 Å [71].



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(42)



(43)

Complexation of Zr(IV) by acetic acid has been studied by NMR, IR and Raman spectroscopy in zirconium oxide chloride aqueous solutions. The position of the $\nu(\text{C-C})$ stretching band of the acetic acid group suggested that only one type of acetate complex was formed. Complexation is thought to occur through simple oxo bridges from acetic acid to the zirconium atom with the formation of 1:1 complexes, as supported by evidence from Raman and ^{13}C NMR spectroscopies [72].

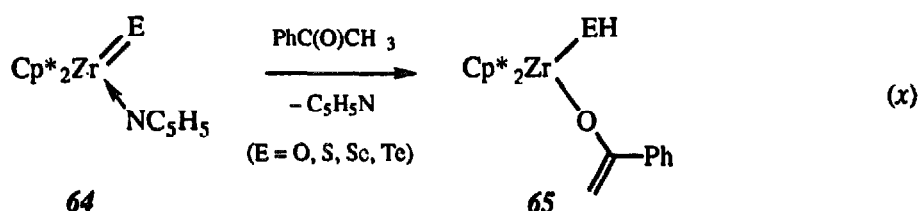
The synthesis of binary fluorosulfates, $\text{Zr}(\text{SO}_3\text{F})_4$ and $\text{Hf}(\text{SO}_3\text{F})_4$, has been achieved by oxidation of the metal powders with bis(fluorosulfonyl)peroxide, $\text{S}_2\text{O}_6\text{F}_2$, in fluorosulfuric acid. Solvolysis of ZrCl_4 with excess HSO_3F at 25°C was not successful in producing completely substituted products. The vibrational spectra of the products were recorded but the fluorosulfates were not sufficiently soluble in HSO_3F to allow conductivity or NMR spectroscopic studies to be carried out [73].

11.1.8 Complexes with sulfur, selenium and tellurium donor ligands

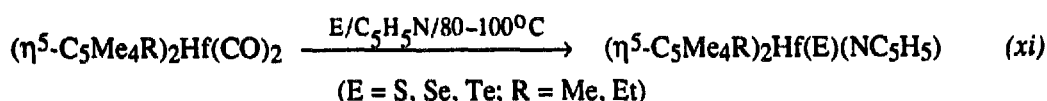
Attempts to produce a Zr analogue of the well known molybdenum $\text{Mo}=\text{S}$ chromophore has stimulated interest in zirconium sulfur chemistry. Acidification of $\text{Zr}(\text{BH}_4)_4$ by $^t\text{BuSH}$ resulted in the formation of the polynuclear clusters $\text{Zr}_3\text{S}_3(^t\text{BuS})_2(\text{BH}_4)_4(\text{thf})_2$ and $\text{Zr}_6\text{S}_6(^t\text{BuS})_4(\text{BH}_4)_8(\text{thf})_2$. When $\text{Zr}(\text{CH}_2\text{Ph})_4$ was used as the source of the metal, the cluster $\text{Zr}_3(\text{S})(^t\text{BuS})_{10}$, was obtained in a similar reaction. In each complex the sulfido group is derived from the Zr-coordinated $^t\text{BuS}^-$ ligands as a result of C-S bond activation followed by heterolytic bond cleavage. When the reaction between $\text{Zr}(\text{CH}_2\text{Ph})_4$ and PhSiH was carried out in the presence

of $\text{H}_2\text{CPhMgCl}$ a cluster with the formula $(\text{Mg}(\text{thf})_6)[\text{Zr}_2(\text{SPh})_{7.2}(\text{CH}_2\text{Ph})_{1.8}]_2 \cdot 3\text{thf}$, in which the S^{2-} ligands have been lost, was obtained. The difference in behaviour was attributed to the stronger C-S bond in the Zr coordinated PhS^- ligands. In $(\text{Mg}(\text{thf})_6)[\text{Zr}_2(\text{SPh})_{7.2}(\text{CH}_2\text{Ph})_{1.8}]_2 \cdot 3\text{thf}$ the C-S bond does not undergo a cleavage reaction to generate S^{2-} ligands [74].

The first complete set of terminal chalcogenido complexes of zirconium, $(\eta^5\text{-C}_5\text{Me}_4\text{R})_2\text{Zr}(\text{E})(\text{NC}_5\text{H}_5)$, ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$; $\text{R} = \text{Me}, \text{Et}$) has been successfully prepared by the reactions of $(\eta^5\text{-C}_5\text{Me}_4\text{R})_2\text{Zr}(\text{CO})_2$ with either N_2O or the elemental chalcogen in the presence of pyridine. The Te complex reacts instantly with N_2O to give the oxo-derivative. The hydrido-chalcogenido derivatives $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{EH})(\eta^1\text{-OC(Ph)=CH}_2)$, have been obtained by reactions of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{E})(\text{NC}_5\text{H}_5)$ with PhC(O)CH_3 (equation (x)), thus demonstrating the basicity of the chalcogenido ligand in these complexes. The X-ray crystal structures of the complexes $(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{Zr}(\text{E})(\text{NC}_5\text{H}_5)$ ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$), **64**, and hydrido-chalcogenido complexes, **65**, ($\text{E} = \text{O}, \text{S}, \text{Se}$) have been determined. The aim was to compare the Zr-E single and



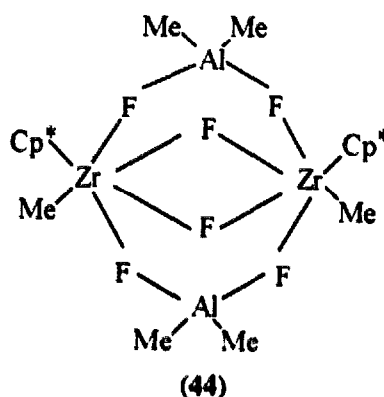
Zr=E double bond lengths with respect to the differences in the single and double bond covalent radii in the chalcogens. This led to the conclusion that the double bond covalent radius in the $(\eta^5\text{-C}_5\text{R}_5)_2\text{Zr}$ system is about 0.07 Å shorter than the single bond covalent radius. Values of Zr-E and Zr=E could be predicted fairly well for the heavier chalcogens (S, Se, Te) on the basis of the sum of covalent radii. However, for oxygen both the Zr-O and Zr=O bond lengths are anomalously short which is consistent with a coulombic stabilisation from an ionic contribution of the form $\text{Zr}^{\delta+}\text{-O}^{\delta-}$ which is more significant for the smaller more electronegative elements than heavier ones [75]. The same authors have also reported the syntheses and structures of the first complete series of terminal chalcogenido complexes of hafnium, $(\eta^5\text{-C}_5\text{Me}_4\text{R})_2\text{Hf}(\text{E})(\text{NC}_5\text{H}_5)$, ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$; $\text{R} = \text{Me}, \text{Et}$). For $\text{E} = \text{S}, \text{Se}$ or Te , the method used to prepare the Zr chalcogenido complexes was adapted (equation (xi)) and led to the hafnium derivatives $(\eta^5\text{-C}_5\text{Me}_4\text{R})_2\text{Hf}(\text{E})(\text{NC}_5\text{H}_5)$ in ca. 70 to 95% yield. The hafnium oxo complex was obtained by reaction of the tellurido derivative $(\eta^5\text{-C}_5\text{Me}_4\text{R})_2\text{Hf}(\text{Te})(\text{NC}_5\text{H}_5)$ with N_2O at room temperature in an analogous reaction to that of the Zr complex. The structures of the series of complexes $(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{Hf}(\text{E})(\text{NC}_5\text{H}_5)$ ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$) have been determined by X-ray diffraction. The values for Hf=E bond lengths were found to be very similar to those of the analogous Zr complexes as would be expected on the basis of lanthanide contraction [76].



The reactions of Cp_2HfCl_2 with 2-thiophenecarboxylic acid (2-TCH), 2-thiopheneacetic acid (2-TAH), 3-thiophenecarboxylic acid (3-TCH), 3-thiopheneacetic acid (3-TAH) and 4-(2-thienyl)butyric acid (2-TBH) in various stoichiometric ratios have been investigated. Magnetic susceptibility measurements carried out on the complexes $\text{Cp}_2\text{Hf}(\text{L})\text{Cl}$ and $\text{CpHf}(\text{L})_2\text{Cl}$ (L = didentate thiophene carboxylate ion) formed showed them to be diamagnetic [77].

11.1.9 Zirconium halide clusters and halo-salts

The compound $[\text{Cp}^*\text{ZrF}_3]$ when used with methylalumoxane (MAO), has been shown to have catalytic activity in the polymerisation of ethene. In order to explain the catalytic activity, selective exchange reactions of the fluorine groups in $[\text{Cp}^*_2\text{ZrF}_3]$ by alkyl groups have been studied [78]. Reaction of $[\text{Cp}^*\text{ZrF}_3]$ with AlMe_3 in a 1:1 molar ratio resulted in methyl group transfer from the Al to the Zr with the formation of a Zr-Al-C cluster, $[(\text{Cp}^*\text{ZrMeF}_3)_2(\text{AlMe}_2\text{F})_2]$, (44).

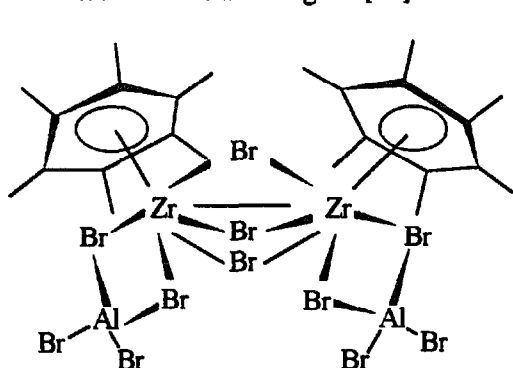


The structure can be seen to be a Zr-Al-F cluster having both Zr-F-Zr and Zr-F-Al bridges. The Zr atom is in a distorted octahedral and the Al in a distorted tetrahedral environment. ^{19}F NMR spectra showed only the *cis* form to be obtained. Reaction of either $[\text{Cp}^*\text{ZrF}_3]$ or $[(\text{Cp}^*\text{ZrMeF}_3)_2(\text{AlMe}_2\text{F})_2]$ with excess AlMe_3 led to immediate elimination of methane and the formation of a Zr-Al-C cluster, $[(\text{Cp}^*\text{Zr})_3\text{Al}_6\text{Me}_8(\text{CH})_5(\text{CH}_2)_2]$, among other intractable products. In $[(\text{Cp}^*\text{Zr})_3\text{Al}_6\text{Me}_8(\text{CH})_5(\text{CH}_2)_2]$ total replacement of the F atoms has occurred giving a $\text{Zr}_3\text{Al}_6\text{C}_7$ cluster which is remarkable for some very short metal-metal contacts (mean Zr-Al = 2.978(2) Å).

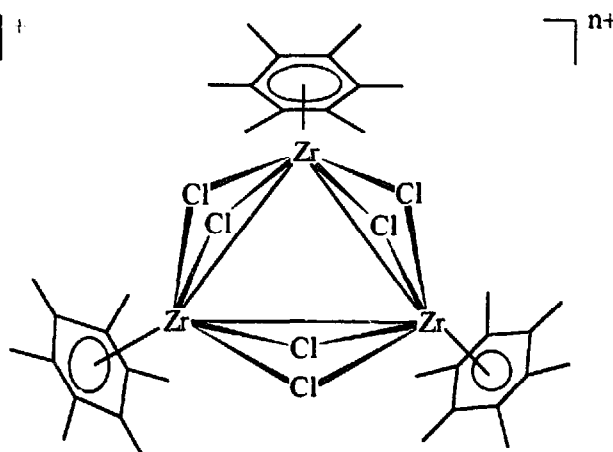
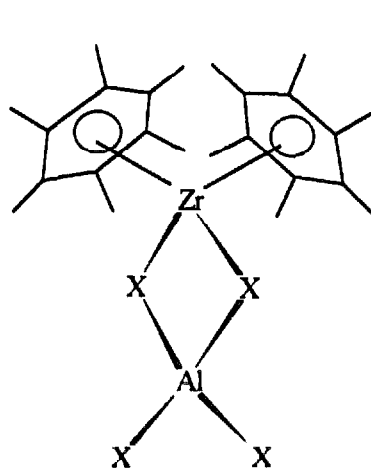
A method has been reported which leads to inner halide exchange in M_6X_{12} clusters. Using a Lewis base chloroaluminate $\text{ImCl}/\text{AlCl}_3$ melt with $\text{Zr}_6\text{Br}_{14}\text{Fe}$ at 160°C for 2–3 hours the compound $(\text{Im})_4[(\text{Zr}_6\text{Fe})\text{Cl}_{18}]$ was isolated (ImH = imidazole). The X-ray structure of the product showed that both inner and outer bromide atoms had been replaced by chlorides. In extending the method to other Zr cluster compounds $(\text{Im})_5[(\text{Zr}_6\text{Mn})\text{Cl}_{18}] \cdot 1.5\text{CH}_3\text{CN}$ has been obtained from $\text{Li}_2\text{Zr}_6\text{Cl}_{15}\text{Mn}$ and was structurally characterised [79].

Synthetic methods and main structural types of arene complexes of Zr and Hf in oxidation states from IV to 0 have been reviewed and compared with those of Ti. Cationic Zr complexes of the type (45a), (45b) and (45c) and neutral complexes of the type (46a) and (46b) were considered.

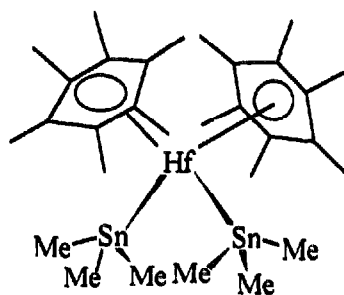
The general conclusion made was that the stability of the arene complexes increases with increasing substitution of the arene ligand [80].



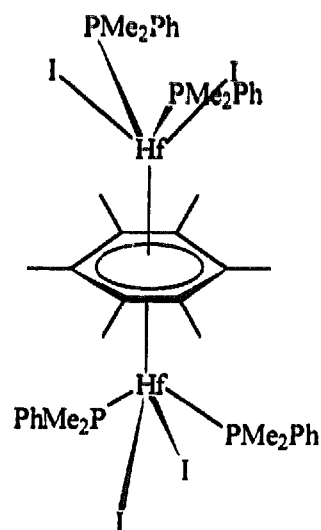
(45a)

(45b) $n = 1, 2, 3$ 

(45c)



(46a)

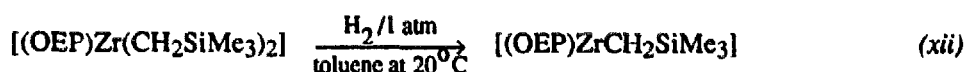


(46b)

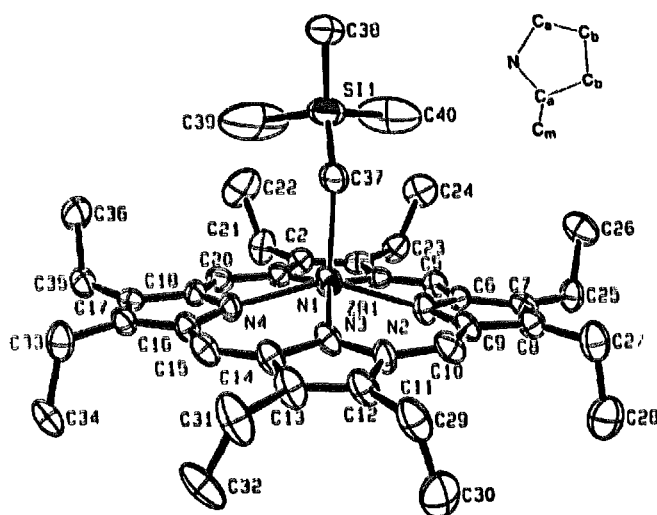
Zirconium and hafnium hexachloro salts, $[\text{TeCl}_3]_2[\text{MCl}_6]$ have been formed from the reactions between TeCl_4 and MCl_4 ($\text{M} = \text{Zr}, \text{Hf}$) [81]. The complexes were found to be isostructural and orthorhombic with M-Cl distances in the range 2.41–2.49 Å.

11.2 LOW OXIDATION STATE COMPLEXES OF ZIRCONIUM AND HAFNIUM

The alkyl Zr(III) complex, $[(\text{OEP})\text{ZrCH}_2\text{SiMe}_3]$, (**47**), has been obtained in an unprecedented hydrogen reduction reaction of the Zr(IV) compound $[(\text{OEP})\text{Zr}(\text{CH}_2\text{SiMe}_3)_2]$ in toluene according to equation (xii). The X-ray crystal structure of (**47**) showed the Zr atom to be 5-coordinate with the alkyl group in the axial position. The Zr atom is displaced by 0.63 Å out of the

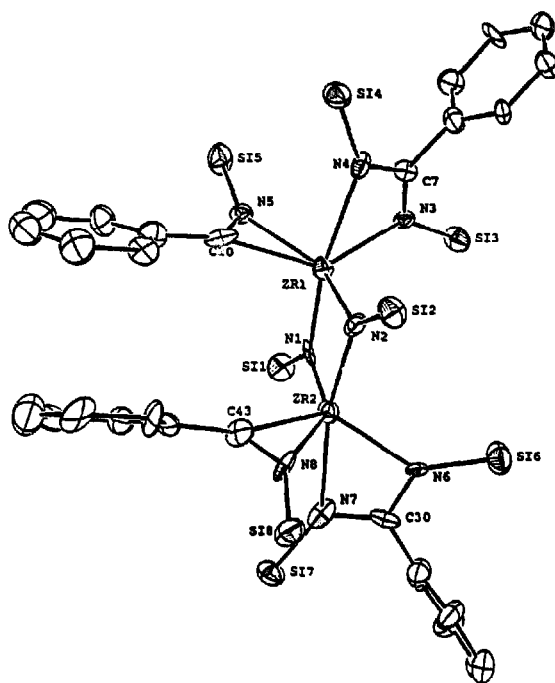


mean plane of the N atoms of the porphyrin ring. The distance is rather short compared with the analogous length in the dialkyl precursor $[(\text{OEP})\text{Zr}(\text{CH}_2\text{SiMe}_3)_2]$ (cf. 0.93 Å). The difference is ascribed to a relief of steric strain brought about by loss of the *cis*-ligand [82].



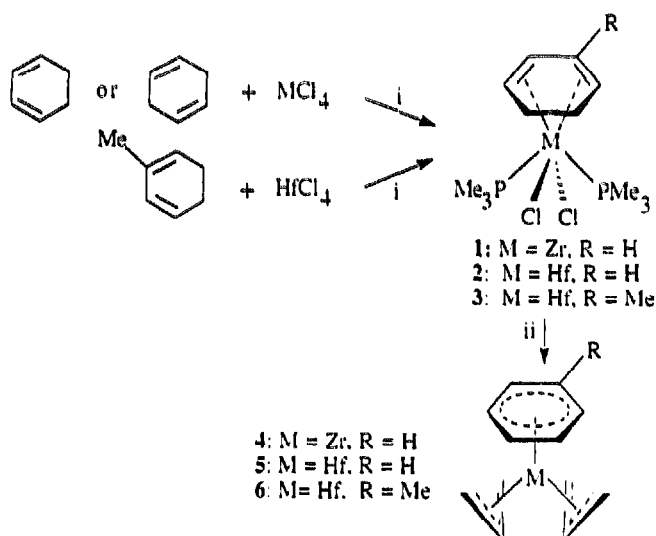
(**47**) Reproduced from ref. [82] with permission

A range of Zr(IV) derivatives with *N,N'*-bis(trimethylsilyl)benzamidinate ligands has been prepared with $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{ZrCl}_2$ as the starting material. Reduction of the dichloride in the presence of excess diphenylacetylene gave $[\text{PhCN}(\text{SiMe}_3)_2]\text{Zr}(\eta^2\text{-C}_6\text{Ph}_4)$. Orange crystals of the μ -imido- η^2 -iminoacyl species, $\{[\text{PhCN}(\text{SiMe}_3)_2]\text{Zr}(\eta^2\text{-PhCNSiMe}_3)(\mu\text{-NSiMe}_3)\}_2$ (**48**), were obtained in the absence of acetylene [83]. In the complex each Zr atom is six coordinate being bound to two bridging imido ligands, an η^2 -iminoacyl and a didentate $[\text{PhC}(\text{NSiMe}_3)_2]$ ligand. In the solid state the Zr_2N_2 four membered ring is almost planar.



(48) Reproduced from ref. [83] with permission

The compound $[\text{Hf}(\eta^4\text{-1-methylcyclohexa-1,5-diene})(\text{PMe}_3)_2\text{Cl}_2]$ has been prepared by reduction of HfCl_4 in the presence of trimethylphosphine and 2-methylcyclohexa-1,4-diene. The divalent zirconium compound $[\text{Zr}(\eta^6\text{-C}_6\text{H}_6)(\eta\text{-C}_3\text{H}_5)_2]$ was prepared by the reaction of $[\text{Zr}(\eta^4\text{-cyclohexa-1,3-diene})(\text{PMe}_3)_2\text{Cl}_2]$ with allylmagnesium bromide at 0°C . The divalent hafnium compounds $[\text{Hf}(\eta^6\text{-C}_6\text{H}_5\text{R})(\eta\text{-C}_3\text{H}_5)_2]$ ($\text{R} = \text{H}, \text{Me}$) were prepared in a similar manner (scheme 16). Analytical and spectroscopic data are reported [84].


 Reproduced from ref. [84]
 with permission.
 Scheme 16

The dinuclear Zr(III) compound $\text{Zr}_2\text{Cl}_6(\text{PMe}_3)_4$ has been recrystallised from benzene, and an X-ray structure examination showed evidence for a single Zr-Zr bond [85]. The compound

$\text{Zr}_2\text{Cl}_4(\eta^6\text{-C}_6\text{H}_5\text{PMe}_2)_2(\text{PMe}_2\text{Ph})_2$ has been prepared by the reaction of ZrCl_4 with PMe_2Ph in the presence of Na/Hg amalgam in toluene. The compound consists of two identical units $(\text{PMe}_2\text{Ph})\text{Cl}_2\text{Zr}(\eta^6\text{-C}_6\text{H}_5\text{PMe}_2)$ connected by the coordination of the P atom of each $(\eta^6\text{-C}_6\text{H}_5\text{PMe}_2)$ moiety to the Zr atom of the other. The structure is similar to those reported in 1991 of $\text{Hf}_2\text{Br}_4(\eta^6\text{-C}_6\text{H}_5\text{PMe}_2)_2(\text{PMe}_2\text{Ph})_2$ and $\text{Zr}_2\text{I}_4(\eta^6\text{-C}_6\text{H}_5\text{PMe}_2)_2(\text{PMe}_2\text{Ph})_2$ [86].

A cyclic voltammetric study of the Hf and Zr phthalocyanines, $(\text{OH})_2\text{MPc}(\text{Cl})$ ($[(\text{Cl})\text{Pc}]^{2-}$ = chlorinated phthalocyanine dianion, $\text{M} = \text{Zr, Hf}$) has been carried out and showed that one oxidation couple and two reduction couples exist in the presence of a variety of solvent electrolyte systems. All the redox processes were found to be centred on the Pc ring rather than the metal [87].

11.3 SOLID STATE COMPLEXES OF ZIRCONIUM AND HAFNIUM

11.3.1 Compounds with layer structures containing phosphate and phosphonate ligands

Considerable interest has been shown in the preparation and characterisation of layered zirconium phosphates and phosphonates. Compounds of this type often have ion exchange properties which enable them to imitate the reactions of zeolites and other microporous solids. They also have expandable pore size, in one direction, owing to the weak interactions between layers. These properties make them of interest for a number of applications, including as catalysts, catalyst supports and separation materials. The use of layered metal phosphonate compounds to prepare organic and inorganic materials with predetermined solid state structures has been reviewed [88]. The emphasis is on tetravalent metal ions, especially Zr(IV). The synthesis and optical properties of three forms of compounds, microcrystalline solids, multilayer thin films and porous solids, are described.

The crystal structure of the totally sodium ion exchanged phase of α -zirconium phosphate, $\text{Zr}_2(\text{NaPO}_4)_4 \cdot 6\text{H}_2\text{O}$, has been determined from X-ray powder diffraction data. The crystals are triclinic, space group P1. The layer structure was found to be similar to that of the parent α -zirconium phosphate, $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, in terms of metal coordination and the bridging nature of the phosphate group. The parent compound has monoclinic symmetry. The lower triclinic symmetry of the sodium compound occurs as a result of rearrangement of the layers. There are four independent Na^+ ions in the molecule, although the empirical formula is $\text{Zr}(\text{NaPO}_4)_2 \cdot 3\text{H}_2\text{O}$. The Na^+ are surrounded by the O atoms of both the water molecules and the phosphate groups [89].

The compound $\text{Zr}(\text{PO}_4)\text{F}(\text{OSMe}_2)$ has been prepared by adding a solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in aqueous HF to a solution of H_3PO_4 in dmsO and heating at 120°C for several days. The crystal structure was solved *ab initio* using X-ray powder diffraction data, and refined by the Rietveld method. $\text{Zr}(\text{PO}_4)\text{F}(\text{OSMe}_2)$ crystallises in the tetragonal space group P4/n . It has a layered structure, with the metal atoms and phosphate groups being almost planar. The O atoms of the phosphate group are involved in metal coordination. The axial sites of the metal octahedra are occupied by the charge neutralising fluoride ion and the O atom of the dmsO molecule [90].

The compounds $(M^I)(Zr)_2(PO_4)_3$ and $(M^I)(Hf)_2(PO_4)_3$ ($M = Ag, Cu$) have been synthesised in solid state reactions at temperatures between 900–1000°C ($M = Ag$) and 1000–1200°C ($M = Cu$) for 3–4 days. The compounds have Nasicon-like structures. Cell parameters, vibrational spectra and ionic conductivities are given. These materials are of interest as ionic conductors, ceramics with low thermal expansion, and luminescent materials [91].

Structural models have been proposed for the Cu complexes of two intercalated compounds of α -Zr(HPO₄)₂·H₂O with 1,10-phenanthroline and 2,2'-bipyridyl. The models were calculated by consideration of unit-cell geometry changes undergone by α -Zr(HPO₄)₂·H₂O upon insertion of first the organic molecules and then Cu using the comparison method [92].

The first incorporation of a crown ether, N-(2-ethylphosphonic)aza-18-crown-6, into γ -zirconium phosphate has been reported. ³¹P NMR spectroscopic data and powder XRD pattern are given [93].

The oxidative polymerisation of aniline has been accomplished using both the copper zirconium phosphate $CuZr(PO_4)_2$, and the mixed zirconium phosphonate $Zr[O_3P(CH_2)_3COOH]_{0.75}(O_3POH)_{1.25}$ as catalysts. With $CuZr(PO_4)_2$, the non-conducting emeraldine base form of polyaniline (PANI) formed on the surfaces of the phosphate microcrystals. When exposed to HCl, the solid $CuZr(PO_4)_2$ ·PANI turned from violet to green, indicating the formation of a protonated conducting polymer. With $Zr[O_3P(CH_2)_3COOH]_{0.75}(O_3POH)_{1.25}$ a violet product was also obtained, with the interlayer spacing of the solid increasing significantly, indicating polymerisation within the interlamellar region. The solid product did not react with HCl. IR spectra indicated a slightly different form of PANI included in $Zr[O_3P(CH_2)_3COOH]_{0.75}(O_3POH)_{1.25}$ than on the surface of $CuZr(PO_4)_2$ [94].

Several zirconium phosphates, $Zr(O_3PR)_2$ ($R = (CH_2)_3COOH, CH_2C_6H_5, (CH_2)_2Cl, CH=CH_2, (CH_2)_2CH=CH_2$) with reactive functional groups have been synthesised and structurally characterised. Small molecules and ions from solution could not be incorporated into the structure despite relatively weak interlayer interactions. Some mixed phosphonates of composition $Zr(O_3PCH_2C_6H_5)_x(O_3PCH_3)_{2-x}$ and $Zr(O_3P(CH_2)_3COOH)_x(O_3POH)_{2-x}$, where x varies from 1 to 2, were also prepared. These compounds were found to crystallise with inefficient interlayer ordering, resulting in porous structures [95]. The X-ray powder structure analysis of $[Zr_2(PO_4)\{O_3PCH_2N(CH_2CO_2H)_2\}\{O_3PCH_2N(CH_2CO_2H)(CH_2CO_2)\}(H_2O)_2]$, a new mixed phosphate/phosphonate layered zirconium compound, has been reported [96]. The light atoms were located and refined using synchrotron powder diffraction data collected with a Ge(111) monochromator and Ge(220) analysing crystal. The phosphate group is situated nearly in a plane, and bridges four Zr atoms which are arranged slightly above and below the plane. The octahedral coordination of each Zr is completed by an oxygen atom from each of 2 phosphate groups, the three oxygen atoms of a phosphonate group, and the oxygen atom of a water molecule. $[Zr_2(PO_4)\{O_3PCH_2N(CH_2CO_2H)_2\}\{O_3PCH_2N(CH_2CO_2H)(CH_2CO_2)\}(H_2O)_2]$ has an unusual Zr:P ratio of 2:3. However, it shows some similarities to well-known α - and γ -zirconium phosphates. The bridging by the phosphate resembles γ -ZrP, while the bonding of the phosphonate group to the metal atoms is similar to α -ZrP. The structure contains an additional H₂PO₄ group

which links to only two metal atoms. The compound $[\text{Zr}_2(\text{PO}_4)\{\text{O}_3\text{PCH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2\}\{\text{O}_3\text{PCH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2)\}(\text{H}_2\text{O})_2]$ is believed to be the only Zr-phosphate layer compound so far identified to contain a metal-coordinating water molecule.

Pillared compounds of γ -Zr(IV) phosphates, $\text{Zr}^{(\text{IV})}\text{PO}_4(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$, have been obtained by a topotactic reaction between the γ -zirconium phosphate and diphosphonic acids with a long rigid diphosphonate e.g. 4,4'-biphenyldiphosphonic acid. The aim was to identify stable phases with a concentration of pillars sufficiently low for creation of interlayer microporosity. Samples, prepared under different conditions, were characterised by chemical analysis and X-ray powder diffraction. Thermal stability was determined by thermogravimetry, evolved gas analysis (EGA) and X-ray diffraction with a high temperature camera [97].

The structure of the zirconium phenylphosphonate $\text{Zr}(\text{O}_3\text{PC}_6\text{H}_5)_2$ has been solved using a combination of modelling techniques and Patterson methods. Powder diffraction data were collected using synchrotron radiation ($\lambda = 1.3087 \text{ \AA}$). In the c axis projection the structure was found to closely resemble α -zirconium phosphate. The phenyl groups are inclined by about 30° to the c axis and tilted from the ab plane. The C-centre related phenyl groups form rows along the a axis in such a way that the adjacent rings are not in the same plane [98].

The intercalation of α,ω -alkyldiamines $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ ($n = 2$ –10) in layered zirconium (carboxyethyl)phosphonate, and the subsequent interlayer amidation have been investigated [99]. The intercalation and interlayer amidation properties of the α,ω -alkyldiamines were found to depend significantly on the number and parity of carbon atoms in the chain. Each alkyldiamine was found to form one or two intercalated phases in which the diamine molecules are arranged as a monolayer with their two ammonium termini bridging to the carboxyl groups of any two adjacent phosphonate layers. The axes of the molecules in the monolayers are tilted relative to the inorganic layer by 19° or 59° to form two groups of intercalates. For diamines $n \leq 7$, even numbers of carbon atoms produce high chain tilt forms, and odd numbers low chain tilt forms, although both forms coexist for $n = 4, 6$ and 7 . For diamines of chain length >7 , only the high chain tilt form was observed. At 120°C all the diammonium exchanged solids were condensed into their amide-functionalised forms, accompanied by partial desorption of the amine guests. Amidated phases were grouped into high or low chain tilt forms depending on the carbon chain length. Changes were observed in the interlayer distances.

A series of zirconium polyimine phosphonates has been synthesised from mono- and diphosphonic acids of polyamines in HCl with zirconyl chloride. The interlayer spacings for some representative complexes are reported. For the monophosphonates the interlayer spacing was found to depend on the degree of protonation and the drying conditions used. The compounds showed excellent complexing behaviour for anionic species or cation/anion pairs [100].

Studies have been carried out on the role of a zirconium octadecylphosphonate Langmuir Blodgett (LB) film on the organisation of self-assembled organophosphonate monolayer and multilayer films [101]. IR and XPS spectroscopy showed that the template layer was well-ordered and close-packed, with a Zr:P ratio of 1:1. Polarised ATR-FTIR measurements revealed that the alkyl chains were tilted by 31° from the surface normal. Octadecylphosphonic acid was self-

assembled at the zirconated LB template to produce a zirconium octadecylphosphonate bilayer. Spectroscopic measurements showed that the self-assembled layer was close-packed with a Zr:P ratio of 1:2. The alkyl chains were in an all-*trans* configuration. Every template Zr^{4+} site bound one octadecylphosphonic acid molecule from solution. The tilt angle of alkyl chains was 22° . Multilayer films of 1,10-decanediylldiphosphonic acid (DDPA) were also assembled at the zirconated LB template. ATR-FTIR spectroscopy showed that in the first few layers the diphosphonic acid molecules bridged the Zr template sites, but that a constant rate of deposition was achieved after three or four layers. The rigid α,ω -diphosphonic acid quaterthiophenediphosphonic acid (QDP) was also self-assembled at the zirconated LB template. UV-VIS analysis indicated that the same amount of material was deposited after each deposition cycle. X-ray diffraction was used to demonstrate the layered nature of the film.

Grazing angle X-ray diffraction and ellipsometry have been used to characterise the film thickness, thickness uniformity, density, and index of refraction of multilayer hafnium-1,10-decanediylbis(phosphonate) (Hf-DBP) films grown on silicon wafers. The results indicated that Hf-DBP multilayers vary considerably in individual layer thicknesses from sample to sample, and are generally not as similar to the assumed structure of the bulk compound with respect to the density and mode of metal-phosphonate binding as was previously suggested by the analogous Zr-DBP films [102].

The synthesis and polar film formation of two nonlinear chromophores has been reported [103]. The two phosphonate-terminated polar azo dyes, one that is substantially rigid and the other with a large molecular hyperpolarizability, were designed and incorporated into some zirconium-based surface multilayers. Second harmonic generation (SHG) was observed from the multilayers as a function of incident and polarisation angles and compared with that from the previously reported aminophenylazophenylphosphonic acid chromophore. The new dyes are analogous to moieties commonly used in electric field-poled polymers, and comparisons were also made between the polymers and the multilayers.

11.3.2 Zirconium complexes formed with phosphoric acid and phosphate extractants

Using IR spectroscopic methods the following associations were found in extracts of zirconium by tributylphosphate (TBP): $[(\text{TBP})_2\text{H}]^+[\text{Zr}(\text{NO}_3)_5]^-$, $[\text{TBP}.\text{H}_3\text{O}(\text{H}_2\text{O})_n]^+[\text{Zr}(\text{NO}_3)_5]^-$ ($n = 1, 2$) and $\text{Zr}(\text{NO}_3)_4(\text{TBP})_2$. The concentration of $\text{Zr}(\text{NO}_3)_4(\text{TBP})_2$ was less than those of $[(\text{TBP})_2\text{H}]^+[\text{Zr}(\text{NO}_3)_5]^-$ and $[\text{TBP}.\text{H}_3\text{O}(\text{H}_2\text{O})_n]^+[\text{Zr}(\text{NO}_3)_5]^-$. The shift of the equilibrium:



towards $[\text{TBP}.\text{H}_3\text{O}(\text{H}_2\text{O})_n]^+[\text{Zr}(\text{NO}_3)_5]^-$ is caused by an increase of the nitric acid concentration, and a decrease in the zirconium concentration [104].

The mechanism of zirconium extraction by di-2-ethylhexylphosphoric acid (HA) and solid extractant TVEKS-di-2-ethylhexylphosphoric acid (TVEKS-HA) has been studied using ^{31}P NMR spectroscopy [105]. With 0.3 or 1.875M solutions of HA in CCl_4 , Zr^{4+} in 2.2–8.1 M

aqueous nitric acid was extracted into the organic phase as $\text{Zr}(\text{NO}_3)(\text{HA})_2$ and $\text{ZrA}(\text{NO}_3)_3(\text{HA})_2$. These two complexes were also identified during the extraction of Zr^{4+} by TVEKS-HA. The differences in the mechanism of zirconium extraction by HA and TVEKS-HA are discussed.

11.3.3 Other solid state complexes

The intercalated organometallic sandwich compounds $\text{Co}(\eta\text{-C}_5\text{H}_5)_2$, $\text{Cr}(\eta\text{-C}_5\text{H}_5)_2$, $\text{Co}(\eta\text{-C}_5\text{H}_4\text{CH}_3)_2$, $\text{Mo}(\eta\text{-C}_6\text{H}_6)_2$, $\text{W}(\eta\text{-C}_7\text{H}_7)(\eta\text{-C}_5\text{H}_4\text{CH}_3)$ and $\text{Ti}(\eta\text{-C}_8\text{H}_8)(\eta\text{-C}_5\text{H}_5)$ in ZrS_2 have been investigated by X-ray spectroscopy, neutron diffraction and ^2H NMR spectroscopy. The aim was to determine the orientation of guest molecules within metal chalcogenide layer hosts. The results suggest that the molecules all adopt a preferred orientation in which their metal-ring centroid axes lie parallel to the host layer planes [106].

Crystals of the new borate $\text{K}_2\text{Zr}(\text{BO}_3)_2$ have been grown, and X-ray analysis has shown that it crystallises in the trigonal structure of the mineral buetschliite. The K and Zr atoms are distributed between the planar sheets of BO_3 groups. The K atom occupies a distorted hexagonal base-trigonal base O environment, and the Zr atom has a distorted octahedral coordination. The birefringence of the material was found to be 0.026 [107].

$\text{KZr}_2(\text{O}^i\text{Bu})_9$ has been prepared by the reaction of KO^iBu with $\text{Zr}(\text{O}^i\text{Bu})_4$ in a 1:2 molar ratio. The compound decomposed on sublimation yielding $[\text{KZr}(\text{O}^i\text{Bu})_5]_n$ which can also be prepared using equimolar KO^iBu and $\text{Zr}(\text{O}^i\text{Bu})_4$. $[\text{KZr}(\text{O}^i\text{Bu})_5]_n$ was studied by single crystal X-ray diffraction. It is a dimer, $\text{K}_2\text{Zr}_2(\text{O}^i\text{Bu})_{10}$, composed of two five-coordinate Zr-centres, each having trigonal bipyramidal geometry. The axes of the trigonal bipyramids are orthogonal and the $\text{Zr}(\text{O}^i\text{Bu})_5^-$ units encapsulate both K atoms. Due to fluxionality, the species appears as a singlet in ^1H NMR in d_8 -toluene, even at 75°C . Interconversions between, and possible dissociative mechanisms of, $\text{KZr}_2(\text{O}^i\text{Bu})_9$ and $[\text{KZr}(\text{O}^i\text{Bu})_5]_2$ were tested experimentally [108].

The synthesis, characterisation, thermal decomposition and full hydrolysis of $\text{Cu}_2\text{Zr}_2(\text{O}^i\text{Pr})_{10}$, $\text{Cu}_4\text{Zr}_4\text{O}(\text{O}^i\text{Pr})_{18}$ and $\text{Cu}_{14}\text{Zr}_4\text{O}_3(\text{O}^i\text{Pr})_{18}$ have been reported. $\text{Cu}_2\text{Zr}_2(\text{O}^i\text{Pr})_{10}$ is hydrolysed to $\text{Cu}_4\text{Zr}_4\text{O}(\text{O}^i\text{Pr})_{18}$. $\text{Cu}_{14}\text{Zr}_4\text{O}_3(\text{O}^i\text{Pr})_{18}$ is formed by oxidation of $\text{Cu}_2\text{Zr}_2(\text{O}^i\text{Pr})_{10}$ and $\text{Cu}_4\text{Zr}_4\text{O}(\text{O}^i\text{Pr})_{18}$ with dioxygen. The molecular structure of $\text{Cu}_4\text{Zr}_4\text{O}(\text{O}^i\text{Pr})_{18}$ consists of two $[\text{Cu}_2(\mu_2\text{-OR})_2\text{Zr}_2(\mu_2\text{-OR})_3(\text{OR})_4]^+$ fragments bound together by a pseudo-tetrahedron $\mu_4\text{-O}^{2-}$ bridging the copper centres. The X-ray structure of $\text{Cu}_{14}\text{Zr}_4\text{O}_3(\text{O}^i\text{Pr})_{18}$ consists of a planar $\text{Cu}_4\text{O}(\text{O}^i\text{Pr})_2^{4+}$ fragment capped by two $\text{Zr}_2\text{O}(\text{O}^i\text{Pr})_8^{2-}$ face-sharing bioctahedral units. The central oxo of the copper fragment is rigorously square planar. Magnetic and spectroscopic studies are reported [109].

The structure of $\text{Zr}(\text{OH})_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ has been determined *ab initio* by conventional powder diffraction. The structure was found to consist of zig-zag chains in the [001] direction formed by edge-sharing 8-fold coordinated zirconium polyhedra in the shape of a bicapped trigonal prism. The sulfate tetrahedra bridge within chains and a network of H-bonding stabilises interchain interactions to form corrugated sheets parallel to the [100] plane. Free water molecules lie between the sheets which play a major part in the H-bonding network [110].

The compound $\text{Cs}_4\text{Zr}_3\text{Te}_{16}$ has been synthesised at 900°C by the reaction of Zr with a $\text{Cs}_2\text{Te}_3/\text{Te}$ melt as a reactive flux. Single crystal X-ray data show that the structure of $\text{Cs}_4\text{Zr}_3\text{Te}_{16}$ comprises infinite one-dimensional chains of Zr-centred polyhedra that extend along the [100] plane and are separated from each other by Cs^+ cations. Each Zr atom is eight coordinate. There are four unambiguous Te-Te single bonds in the range $2.754(1)$ – $2.768(1)$ Å, and further interactions in the range $2.930(1)$ – $2.966(1)$ Å. The wide range of Te-Te interactions means that no simple order can be ascribed to the bonding in the chain. The compound shows weak semiconducting behaviour along the Zr/Te chains [111].

The only reduced binary hafnium telluride, Hf_3Te_2 has been prepared by the reaction of stoichiometric amounts of the elements in sealed Nb capsules [112]. The Nb capsules were sealed in evacuated and flame baked silica tubes, the temperature of which was increased uniformly to 1000°C over five days. After heating for at least ten days at 1000°C , Hf_3Te_2 was formed in quantitative yield. Single crystal X-ray crystallography studies have shown that Hf_3Te_2 is formally an insertion phase related to that of the bulk body-centred cubic metal. After every three layers of hafnium, two layers of tellurium are inserted. This produces a layered structure in which slabs are made up from three square nets of hafnium and sandwiched between two layers of tellurium. The Hf-Te₃-Hf sandwiches are stacked, with only weak interlayer interactions, to form the 3D structure. Within the net, the more oxidised metal centres are those bound to four tellurium atoms at the exterior of the layer. Each of these four metal atoms forms four bonds to hafnium atoms in the central net ($3.1229(4)$ Å) and one longer bond through the slab ($3.4454(12)$ Å) to a symmetry-equivalent atom. Each tellurium atom is five-coordinate with respect to hafnium atoms in the same slab.

The Pd(II) ternary fluorides PdMF_6 ($M = \text{Zr}, \text{Hf}$) have been synthesised and exhibit an ordered LiSbF_6 type structure. A structural phase transition was detected. A cubic high temperature form was characterised for PdZrF_6 and PdHfF_6 . All three phases show antiferromagnetic behaviour [113].

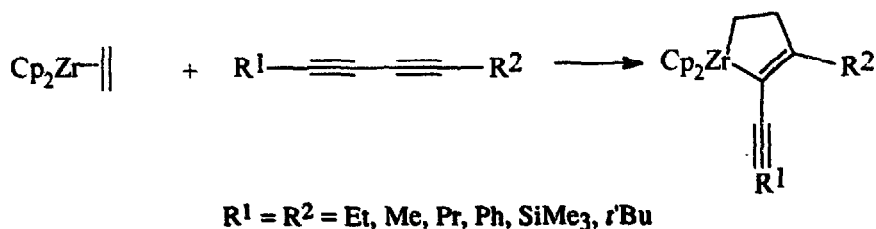
11.4 ZIRCONIUM AND HAFNIUM COMPLEXES AS CATALYSTS

Two reviews on recent developments in the uses of zirconium complexes in catalysis have been published in the past year [114, 115].

Both monocyclopentadienyl and dicyclopentadienyl Zr complexes have been used increasingly in many types of catalytic reactions. The catalytic activity of a range of metallocene-type mononuclear complexes of Zr containing mixed cyclopentadienyl or *ansa*-cyclopentadienyl ligands (Cp_2MX_2) ($X = \text{Cl}, \text{Me}, \text{CH}_2\text{SiMe}_3, \text{CH}_2\text{PPh}_2, \text{CH}_2\text{Ph}, \text{Ph}, p\text{-MeC}_6\text{H}_4, \text{PPh}_2$) in the hydrogenation of different types of olefins has been studied [116].

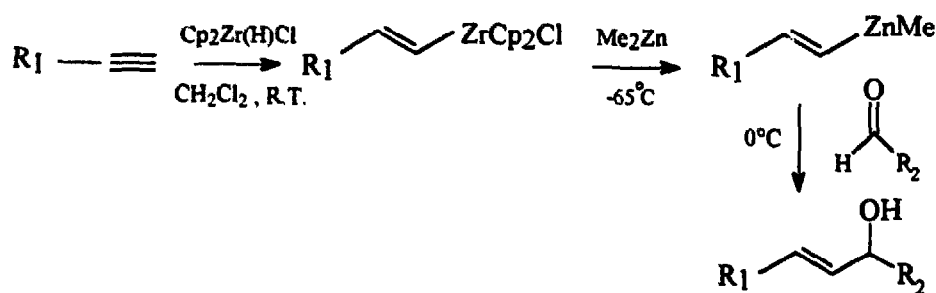
The complex Cp_2ZrCl_2 has been used to catalyse C-C bond formation reactions of diynes with EtMgBr in the first example of the formation of a C-C triple bond with EtMgBr . Certain diynes were found to react stoichiometrically with ethene zirconocene to give zirconacyclopentenes

with alkynyl substituents in the α -position with high regioselectivities as shown in scheme 17 [117].



Scheme 17

In the course of investigations on transmetalation reactions the additions of alkenyl zirconocene complexes to zinc species have been investigated. It was reported that the method significantly accelerates the addition of organozirconocenes to aldehydes, thus offering a new pathway to stereo-controlled C-C bond formation (scheme 18) [118].



Scheme 18

Zirconium alkyne complexes and zirconacyclopentenes have been used to catalyse regioselective C-C bond formation in vinyl ether derivatives [119]. The Zr complexes, prepared *in situ*, were allowed to react with acrolein diethyl acetal to afford vinyl ether derivatives in which C-C bond formation took place exclusively at the β -position of the α,β -unsaturated acetal. This was also found to be the case in the Zr catalysed reactions of α,β -unsaturated acetals with EtMgBr . The reaction of zirconocene-1-trimethylsilyl-1-octyne-trimethylphosphine, $(\text{Me}_3\text{P})\text{Cp}_2\text{Zr}-\text{C}_6\text{H}_{13}\text{C}:\text{CSiMe}_3$, with $(\text{EtO})_2\text{CHCH}:\text{CH}_2$ affords 75% *syn*- $\text{Me}_3\text{SiCH}:\text{C}(\text{C}_6\text{H}_{13})\text{CH}_2\text{CH}:\text{CHOEt}$.

Methylalumoxane (MAO) activated *rac*[1,2-bis(η^5 -(9-fluorenyl))-1-phenylethane]zirconium dichloride has been used for propene polymerisation using a constant monomer pressure at temperatures of 30, 50 and 70°C. Isotactic polypropene having irregularities dependent upon the polymerisation temperature was obtained [120].

Various copolymerisation reactions catalysed by Zr complexes on a MAO activator have been effected. For example copolymers of propene and the polar monomer 6-*t*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol were obtained using *rac*-[1,1'-(dimethylsilylene)bis(η^5 -4,5,6,7-tetrahydro-1-indenyl)] zirconium dichloride as a catalyst on a MAO activator [121].

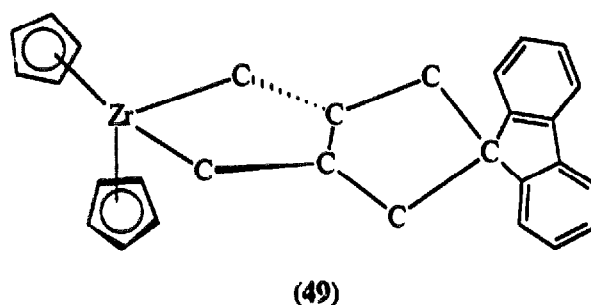
A series of seven new silyl-bridged zirconocenes has been synthesised and their performance as co-catalysts with MAO in the polymerisations of propene and ethene tested. The presence of aromatic substituents in appropriate positions in the zirconocene ligand frame was

Replacement of Ti compounds by analogous Zr ones was found to lead to lower yields in the preparation of syndiotactic polystyrene [126]. Carbon-carbon bond formation from multiple bonds using Zr and other transition metals has become recognised as a powerful synthetic method, particularly for the preparation of enynes, dienes and diynes. The reactions are known to proceed *via* fairly stable intermediate metallacycles from which highly regio- and stereocontrolled products can be obtained by treatment of the metallocycles with protons, halogens, isonitriles, CO and O₂. In a new synthesis of *N*-heterocycles, perhydroindole derivatives have been prepared from enynes by using Zr promoted reductive cyclisation [127]. The same group has reported the catalytic cyclisation of the diene **66** by Cp₂ZrCl₂ in the presence of BuMgBr to **67** and **68** according to scheme 19 [128]. The stereochemistry of the zirconacycle product formed under kinetic conditions was found to be different from that formed under stoichiometric conditions.

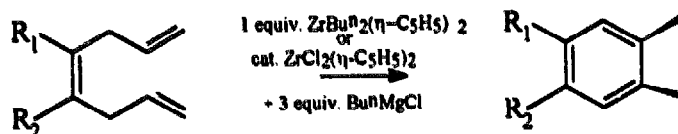


A further report on the catalytic cyclisation of dienes by Cp_2ZrCl_2 has been made. In the presence of excess butylmagnesium chloride this complex was found to be an effective catalyst precursor for the stereoselective cyclisation of non-conjugated dienes containing terminal alkoxide substituents. The products obtained are carbocyclic rings containing adjacent vinyl and methyl substituents with *trans* stereochemistry [129].

In an attempt to investigate the mechanisms involved in the zirconocene-catalysed cyclisation of non-conjugated dienes with organomagnesium reagents a variety of methods including kinetics, stoichiometric model reactions and stereochemical studies have been employed [130]. The key step in the catalytic reaction is thought to involve the transmetallation of a zirconacyclopentane derivative. Thus the zirconacyclopentane derived from 9,9'-diallylfluorene, (49) was prepared and structurally characterised. The kinetics of the catalytic cyclomagnesiation of 9,9'-diallylfluorene have been examined and the stereochemistry of the products was found to depend upon a variety of factors including the substrate, the magnesium reagent and its concentration and the temperature.

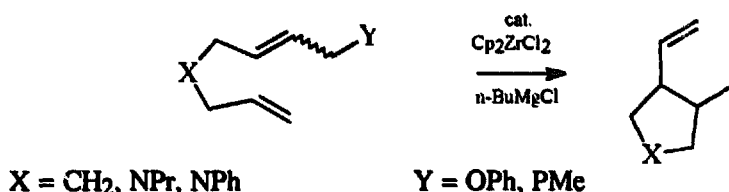


Zirconium-promoted reductive cyclisation has been used to synthesise the alkaloid (–)-dendrobine from (+)-calvone [131]. A highly stereoselective cyclisation of 1,4,7-trienes has been achieved using stoichiometric or catalytic amounts of zirconocene compounds. In the stoichiometric reactions ZrBu_2Cp_2 was used whereas in the catalytic reactions ZrCl_2Cp_2 was used to yield only *cis*-stereoisomers with over 98% stereoselectivity of cyclised products according to the general equation given in scheme 20 [132].



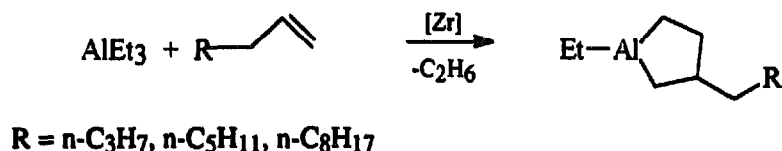
Scheme 20

The compound ZrCp_2Cl_2 has been used catalytically to effect the intramolecular cyclisation reactions of $\text{YCH}_2\text{CH}=\text{CHCH}_2\text{XCH}_2\text{CH}=\text{CH}_2$ ($\text{X} = \text{CH}_2$, NPr , NPh ; $\text{Y} = \text{PhO}$, MeO) to 2-methyl-1-vinylcyclopentane, 4-methyl-1-propyl-3-vinylpyrrolidine and 4-methyl-1-phenyl-3-vinylpyrrolidine respectively according to scheme 21 [133].



Scheme 21

A novel approach to the synthesis of aluminacyclopentanes and aluminacyclopentenenes based on the cycloalumination of olefins and disubstituted acetylenes assisted by Zr catalysts has been reported [134]. The catalytic reaction is claimed to be a major achievement in organoaluminium chemistry as it permits synthesis of 5 membered organoaluminium heterocycles with high regio- and stereoselectivity. Reactions to produce the cyclopentanes involved the treatment of the α -olefin (1-hexene, 1-octene, 1-undecene) and AlCl₃ with Cp₂ZrCl₂ (2 mol%) under an inert gas at room temperature. After 6–8 hours elimination of an equimolar amount of ethane occurred in a reaction which demonstrates a high selectivity for the formation of only 3-substituted aluminacyclopentanes as shown in scheme 22.



Scheme 22

The complex [Zr(tmtaa)(OTf)₂], bistriflatedibenzotetramethyltetraazaannulene zirconium(IV), prepared from the reaction of [Zr(tmtaa)Cl₂] with AgOSO₂CF₃ in CH₂Cl₂, has been found to be effective in promoting aldol condensation reactions and allylations in reasonable yields [135].

A report has been made on the use of Zr (IV) ethoxide and other alkoxides as catalysts in the conversion of a range of carboxylic esters and acids to the corresponding alcohol by polymethylhydrosiloxane [136].

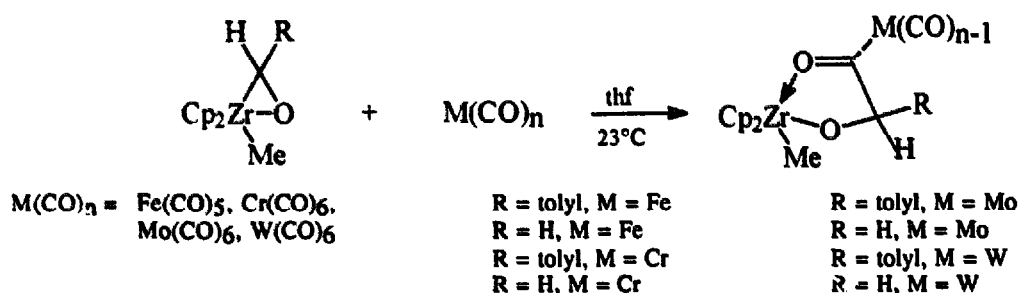
The chlorides ZrCl₄ and HfCl₄ have been used successfully to facilitate the regioselective rearrangement of adducts between ketones and the anion derived from [(methoxymethyl)sulfonyl]benzene [137].

The unstable zirconium borohydride, Zr(BH₄)₄, stabilised on poly(4-vinylpyridine) as a supported polymer, has been used in the reduction of carbonyl compounds such as heptanal, benzaldehyde and acetophenone to alcohols, in good yields [138]. The supported polymer was prepared by the exchange reaction between the poly(4-vinylpyridine) supported zirconium chloride complex and lithium borohydride in dimethoxyether.

Zirconocene derived catalysts have been used with tris(pentafluorophenyl)borane, (C₆F₅)₃B, in the dehydrocoupling of phenylsilane. Multinuclear NMR spectroscopic studies on the

catalytic species suggested that they are zirconocene(IV) hydride bridged dimers, with a "cation-like" silylium ligand on each zirconium; $[\text{Cp}_2\text{Zr}(\text{SiHPh})(\mu\text{-H})_2][\text{Bu}_2(\text{C}_6\text{F}_5)_2\text{B}]_2$ [139].

In an attempt to understand the mechanism for homogeneously catalysed carbon monoxide hydrogenation to polyols the reactions of anionic zirconocene η^2 -aldehyde complexes with metal carbonyls have been studied. During the course of the investigations nine new dimetallic complexes were obtained. Reaction of the anionic formaldehyde or *p*-tolualdehyde complexes with 1 equivalent of simple mononuclear metal carbonyls was found to proceed rapidly and quantitatively at RT in thf to give the heterodimetallic complexes containing a newly formed carbon-carbon bond, according to reaction scheme 23 [140].



Scheme 23

An *in-situ* IR spectroscopic study has been carried out on the interaction between group 6 metal carbonyls ($\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$) with dehydroxylated active ZrO_2 . Two kinds of adsorption sites on the ZrO_2 support were identified as having different Lewis acid acceptor character. The formation of surface adducts was found to labilise CO ligands and reversible decarbonylation of the adsorbed metal carbonyls was observed on pumping at RT. Hexacarbonyl adducts were regenerated on admitting CO into the cells. The stability of the adducts towards decarbonylation was in the order $\text{W}(\text{CO})_6 > \text{Cr}(\text{CO})_6 > \text{Mo}(\text{CO})_6$ [141].

Methane conversion to higher hydrocarbons ($\text{C}_2\text{-C}_5$) at temperatures of 100–400°C has been studied using a ruthenium catalyst loaded on $\text{Zr}_3(\text{PO}_4)_4$ [142]. An increase in reaction temperature favoured the formation of hydrocarbons with higher values of *n*.

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