

## 4. Zirconium 1991

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## CONTENTS

INTRODUCTION .....	189
4.1 ZIRCONIUM(IV) .....	190
4.1.1 Complexes with ligands containing boron .....	190
4.1.2 Complexes with carbon-based ligands .....	192
4.1.3 Complexes with ligands containing silicon .....	199
4.1.4 Complexes with ligands containing tin .....	199
4.1.5 Complexes with nitrogen donor ligands .....	200
4.1.6 Complexes with nitrogen and phosphorus donor ligands .....	205
4.1.7 Complexes with phosphorus donor ligands .....	205
4.1.8 Complexes with oxygen donor ligands .....	207
4.1.9 Complexes with sulfur donor ligands .....	214
4.1.10 Complexes with halide ligands .....	216
4.1.11 Cationic complexes .....	217
4.2 ZIRCONIUM(III) .....	220
4.2.1 Complexes with phosphorus donor ligands .....	220
4.2.2 Complexes with chloride ligands .....	221
4.3 ZIRCONIUM(II) .....	221
4.3.1 Complexes with phosphorus donor ligands .....	221
4.3.2 Complexes with chloride ligands .....	222
4.4 Zirconium complexes as catalysts .....	223
REFERENCES .....	227

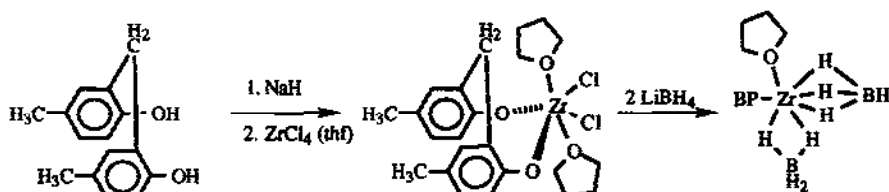
## INTRODUCTION

This review covers the literature published in 1991 on zirconium coordination complexes. It is comprehensive for the main journals but those references from more obscure sources were reviewed using *Chemical Abstracts* (vol. 114, 115, 116). There is, necessarily, some overlap with the chemistry of hafnium and this article should be read in conjunction with the accompanying chapter which surveys the coordination chemistry of hafnium for the same period. A survey of the catalytic behaviour of these complexes has been incorporated into this review, but layered intercalation materials containing zirconium, e.g. the structurally characterised chain complex  $K_4Zr_3Te_{17}$ , have not been included. Some organometallic chemistry has been included in this survey.

#### 4.1 ZIRCONIUM(IV)

##### 4.1.1 Complexes with ligands containing boron

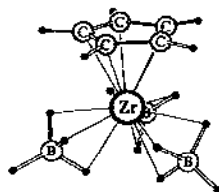
Tetrahydroborate derivatives of zirconium(IV) and titanium(IV) bonded to the bisphenoxo dianion (BP) (scheme 1) have been synthesised. Results of  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectroscopy showed



Scheme 1

the complex to undergo rapid dynamic behaviour even at 193K. The solid state IR spectrum indicated the presence of one didentate and one tridentate  $\text{BH}_4^-$  group. This was confirmed from a single crystal X-ray structure; the Zr-H distances that range between 2.00 and 2.16Å. The dioxametallacycle is puckered with a boat conformation [1].

The complex  $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{BH}_4)_3$  (1) was successfully synthesised from  $(\text{C}_5\text{H}_5)_2\text{ZrBr}_2$  and  $\text{LiBH}_4$ . Electron diffraction studies on similar organometallic derivatives of tetrahydroborates  $\text{L}_x\text{M}(\text{BH}_4)_y$  have indicated that the vibrational spectra of di- and tridentate groups differ in their B-H stretching mode and in their M-B distances. The gas-phase molecular structure of this novel complex was determined by electron diffraction at a nozzle temperature of 115°C. The IR spectral data and EHMO calculations indicate the presence of triple hydrogen bridges but the diffraction data are inconclusive [2].

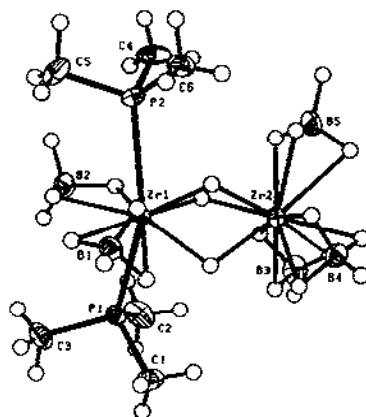


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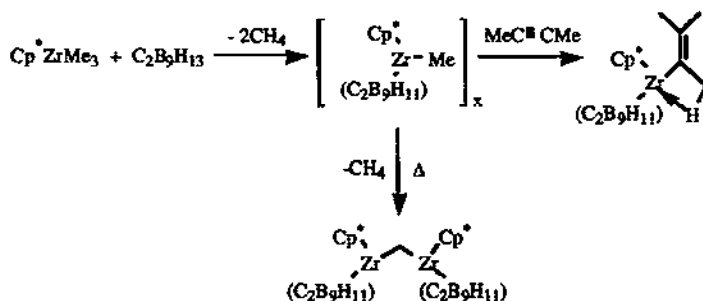
Treatment of  $\text{Zr}(\text{BH}_4)_4$  with  $\text{PMe}_3$  yields amber crystals of the new polyhydride  $\text{Zr}_2\text{H}_3(\text{BH}_4)_5(\text{PMe}_3)_2$  (2), which has been extensively studied in the solid state by X-ray diffraction and in solution by  $^1\text{H}$ ,  $^{11}\text{B}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. In contrast, treatment of the tetrahydroborate complex with a didentate phosphine, 1,2-bis(dimethylphosphino)ethane, dmpe, gives the mononuclear hydride,  $\text{ZrH}(\text{BH}_4)_3(\text{dmpe})$  or  $\text{ZrH}_2(\text{BH}_4)_2(\text{dmpe})$  depending on

stoichiometry. The IR and NMR spectroscopic data on these complexes are consistent with the monohydride having a pseudo-octahedral geometry in which three mutually *fac*-BH<sub>4</sub><sup>-</sup> groups are exchanging and the dihydride having a trigonal dodecahedral ligand arrangement with C<sub>2</sub> symmetry. Above 25°C the dihydride was fluxional, but the exchange barrier of 15.6 kcal mol<sup>-1</sup> was unusually high for a complex with such a high coordination number [3].



(2)

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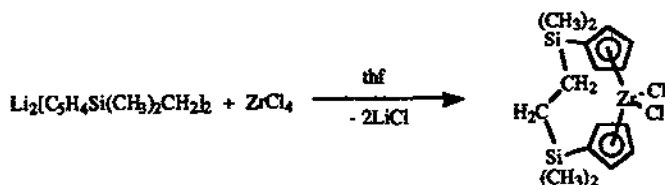
Scheme 2

The reaction of equimolar amounts of C<sub>2</sub>B<sub>9</sub>H<sub>13</sub> and Cp\*Zr(Me)<sub>3</sub> results in Zr-C bond cleavage and reformation to give {(Cp\*)(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)Zr(Me)}<sub>x</sub> as shown in scheme 2. Although the exact nature of this complex is unconfirmed due to its insolubility in hydrocarbon solvents, subsequent reaction with 2-butyne yields the monomeric alkenyl complex (Cp\*)(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)Zr(C(Me)=CMe<sub>2</sub>). A single crystal X-ray structure of this complex shows it to have a bent metallocene type geometry (centroid-Zr-centroid angle = 141.3°) similar to that observed for [(C<sub>5</sub>R<sub>5</sub>)<sub>2</sub>Zr(R)]<sup>n+</sup> complexes. The alkenyl group lies in the plane between the two η<sup>5</sup> ligands and is distorted by an agostic interaction involving one of the β-CH<sub>3</sub> hydrogens. This complex has olefin and acetylene insertion reactivity and will polymerise ethyne and propylene. Thermolysis



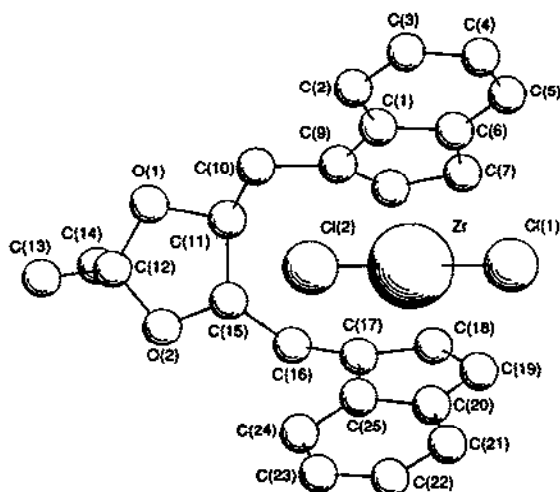
Reaction of two equivalents of 1,2,4-tris(trimethylsilyl)cyclopentadienyllithium with  $\text{ZrCl}_4$  in refluxing toluene yields 1,1',2,2',4,4'-hexakis(trimethylsilyl) zirconocene dichloride, 53% after chromatography. The temperature dependence of the  $^1\text{H}$  NMR spectra of this complex were explained in terms of full rotation of the substituted cyclopentadienyl ligands with a barrier to rotation of  $11.0 \pm 0.02 \text{ kcal mol}^{-1}$ . This contrasts with the analogous silylated ferrocenes and cobaltocenes where the steric interactions of the ligands are much greater [8].

A bridged zirconocene species has been synthesised from the reaction of the dilithium salt of 1,4-dicyclopentadienyl-1,1,4,4-tetramethyl-1,4-disilabutylene dianion  $[\text{C}_5\text{H}_4\text{Si}(\text{CH}_3)_2\text{CH}_2]_2^{2-}$  and  $\text{ZrCl}_4$  (scheme 3). The product (yield ~ 30%) is monomeric but other presently spectroscopically uncharacterised polymeric species are also formed [9].



Scheme 3

The lithium salts of the dianions of general type  $[(\text{C}_5\text{H}_4)\text{CHR}(\text{Cp}') ]_2^{2-}$  ( $\text{R} = \text{Me}$  or  $^t\text{Bu}$ ;  $\text{Cp}' = \text{C}_5\text{H}_4$ ,  $\text{C}_9\text{H}_6$ , or  $\text{C}_{13}\text{H}_8$ ) react with  $\text{ZrCl}_4$  in thf to give the complexes  $(\text{C}_5\text{H}_4)\text{CHR}(\text{Cp}')\text{MCl}_2$  which were characterised by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy [10].



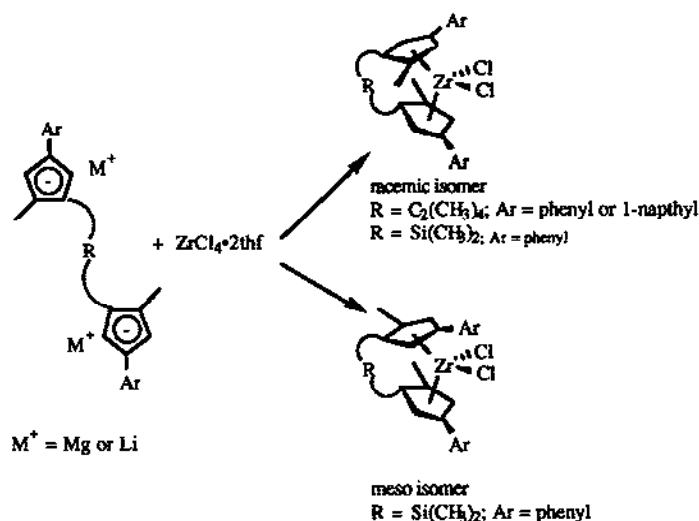
(4)

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The chiral indene derivative (4*S*,5*S*)-*trans*-4,5-bis(1*H*-inden-3-ylmethyl)-2,2-dimethyl-1,3-dioxolane ( $\text{H}_2\text{L}$ ) has been prepared after purification from optically pure 2,2-dimethyl-4,5-

bis(toluene-*p*-sulfonyloxymethyl)-1,3-dioxolane in diethyl ether and a suspension of indenyl magnesium bromide in toluene. The sodium salt of this compound reacts with  $\text{ZrCl}_4$  to yield  $\text{ZrLCl}_2$ . The molecular structure of this chiral zirconium derivative (4) shows the dihedral angle between the indene rings to be  $37^\circ$  as a result of the bridging unit twisting one of the indene rings to one side. Hydrogenation of this complex with  $\text{PtO}_2$  as catalyst gives the bis(4,5,6,7-tetrahydroinden-1-ylmethyl) derivative  $\text{ZrL}'_2\text{Cl}_2$ , which along with the non-hydrogenated starting material, is an active catalyst for the polymerisation of ethene and propene in the presence of methylaluminoxane [11].

Titanocene and zirconocene complexes with a phenyl or 1-naphthyl substituent in one of the  $\beta$ -positions of each cyclopentadienyl ligand and with an interannular tetramethylethano- or dimethylsilano-bridge have been prepared (scheme 4). Confirmation of the nature of the racemic isomers was obtained using  $^1\text{H}$  NMR spectroscopy and X-ray crystallography. In contrast to other ansa-metalloenes bearing bulkier tertiary alkyl  $\beta$ -substituents, the interannular bridges were found to lie close to the rear extension of the  $\text{ZrCl}_2$  bisector axes, and possess a much more accessible coordination site. In accord with this, very high activities as  $\alpha$ -alkene polymerisation catalysts were observed for these aryl-substituted complexes [12].

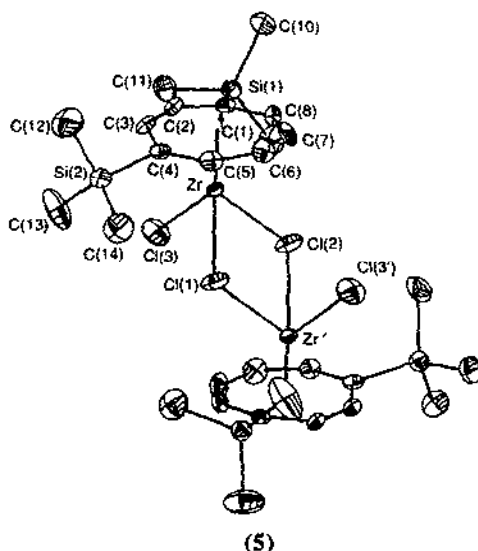


Scheme 4

The complex  $\text{Zr}\{\eta^8\text{-C}_8\text{H}_6(\text{SiMe}_3)_2\}\{\eta^4\text{-C}_8\text{H}_6(\text{SiMe}_3)_2\}$  was prepared from reducing  $\text{C}_8\text{H}_8(\text{SiMe}_3)_2\text{-1,4}$  with two equivalents of  $\text{BuLi}$  and then reacting with  $[\text{ZrCl}_4(\text{thf})_2]$ . The unsubstituted derivative was prepared from a similar reaction but solvated thf had to be removed by heating the complex in the solid state. The absence of solvation in the former is thought to be due to steric crowding provided by the two substituted cyclooctatetraene ligands rather than any decreased acidity of the metal. Both compounds appear fluxional in solution; even at 203K, only a single  $\text{C}_8\text{H}_8$  environment was observed in the  $^1\text{H}$  NMR spectrum of  $\text{Zr}(\eta^8\text{-C}_8\text{H}_8)(\eta^4\text{-C}_8\text{H}_8)$ . The zirconium metal centres act as Lewis acids and readily form adducts with thf,  $\text{NH}_3$  and  $\text{Bu}^t\text{NC}$ ; (see also the discussion of related hafnium complexes in Chapter 3 of this series of articles). The single crystal

X-ray structures of the latter two adducts were obtained and confirm the  $\eta^8$  and  $\eta^4$  coordination mode of the cyclooctatetraene ligands although the distribution of the C-C bond lengths is not consistent with those found in  $\text{Fe}(\eta^4\text{-C}_8\text{H}_8)(\text{CO})_3$  or  $\text{Ru}(\eta^4\text{-C}_8\text{H}_8)(\text{CO})_3$ . The zirconium-to-ring-carbon bond lengths in these structures increase on coordination of  $\text{NH}_3$  or  $\text{Bu}^t\text{CN}$  indicating a weakening of the metal-to- $\text{C}_8\text{H}_8$  interaction [13].

An alternative to the study of  $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2\text{X}_2$  complexes is that of the half-sandwich monocyclooctatetraene zirconium derivatives  $\text{Zr}(\eta^8\text{-C}_8\text{H}_8)\text{Cl}_2$ . Both the solvated and non solvated forms are now readily synthesised from the reaction of  $\text{Zr}(\eta^8\text{-C}_8\text{H}_8)(\eta^4\text{-C}_8\text{H}_8)$  with  $\text{ZrCl}_4(\text{thf})_2$ . The bistrimethylsilylated derivative gave the structurally characterised complex  $\{\text{Zr}(\eta^8\text{-C}_8\text{H}_6(\text{SiMe}_3)_2\text{Cl})\}(\mu\text{-Cl})_2$  which possesses a plane of symmetry that bisects the two bridging chlorine atoms as shown in structure (5) [14].

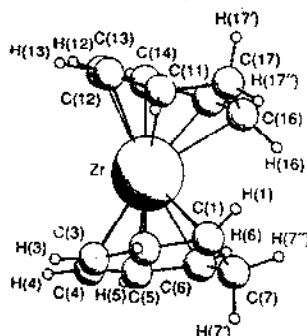


(5)  
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The structure of  $\text{Zr}(\text{C}_8\text{H}_8)_2$  has been investigated using variable temperature solution and solid state NMR spectroscopy and X-ray crystallography. The X-ray crystal structure unequivocally shows that one  $\text{C}_8\text{H}_8$  ring is  $\eta^8$ - and the other  $\eta^4$ -coordinated to the zirconium atom. The  $^{13}\text{C}$  and  $^1\text{H}$  NMR solution spectra show all the protons and carbon atoms to be equivalent. The barrier to the proposed fluxionality of the rings is estimated to be  $< 7.5 \text{ kcal mol}^{-1}$  in solution and  $> 13.5 \text{ kcal mol}^{-1}$  in the solid state. A second fluxional process involves 1,2-shifts of the  $\eta^4\text{-C}_8\text{H}_8$  ring [15].

Reduction of  $\text{ZrCl}_4$  with sodium amalgam in the presence of cycloheptatriene gives the complex  $\text{Zr}(\eta^6\text{-C}_7\text{H}_8)_2$  (6) in ca. 40% yield. The molecular structure of this complex was confirmed crystallographically and shows the cycloheptatrienyl ligands to have a non-parallel arrangement with a dihedral angle of  $25.6^\circ$ . On reaction with carbon monoxide,  $\text{Sn}_2\text{Me}_6$  or  $N,N,N',N'$ -tetramethylethylenediamine, the compound  $\text{Zr}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)$  was produced. The electronic structure of this complex has been investigated by PES and extended Hückel molecular

orbital calculations. The complex  $\text{Zr}(\eta^6\text{-C}_7\text{H}_8)_2$  reacts with  $\text{PMe}_3$  or the didentate phosphine 1,2-bis(dimethylphosphino)ethane (dmpe) to give  $\text{Zr}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)(\text{PMe}_3)$  and  $\{\text{Zr}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)\}_2(\text{dmpe})$ , respectively. These compounds have been extensively studied using  $^{31}\text{P}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopies. Reaction of  $\text{Zr}(\eta^6\text{-C}_7\text{H}_8)_2$  with the Lewis acid  $(\text{AlEt}_2\text{Cl})_2$  in thf for 1 week gave a compound proposed to be the zirconium dimer  $(\text{Zr}(\eta^7\text{-C}_7\text{H}_7)(\text{thf})(\mu\text{-Cl}))_2$  which acts as a good source of the  $\{\text{Zr}(\eta^7\text{-C}_7\text{H}_7)\}$ -fragment in subsequent reactions [16].



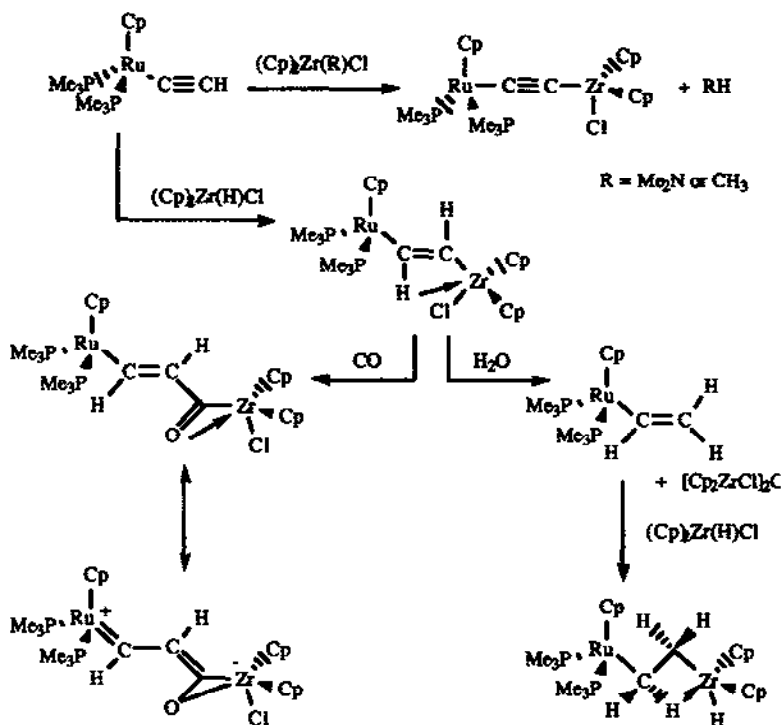
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(6)

A series of dimetallic ruthenium/zirconium complexes of general formula  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}_n\text{CH}_n\text{ZrClCp}_2$  ( $n = 0, 1, 2$ ) have been prepared from  $\text{Cp}(\text{PMe}_3)_2\text{RuC}\equiv\text{CH}$  (see scheme 5). Two of the products are  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CHZrClCp}_2$  and  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}_2\text{CH}_2\text{ZrClCp}$  and each exhibits a three-centre two-electron agostic interaction between the zirconium and a CH that is  $\beta$  to zirconium atom. These complexes are important as they represent a rare example of a  $\text{C}_2$ -unit bridging an electron rich metal atom and an electron deficient metal centre. The spectroscopic and structural data on an  $\eta^2$ -acyl complex obtained on carbonylation of  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CHZrClCp}_2$  indicate a substantial contribution from a Zwitterionic resonance form in which a formal positive charge exists on the Ru and a negative charge on the zirconium portion [17].

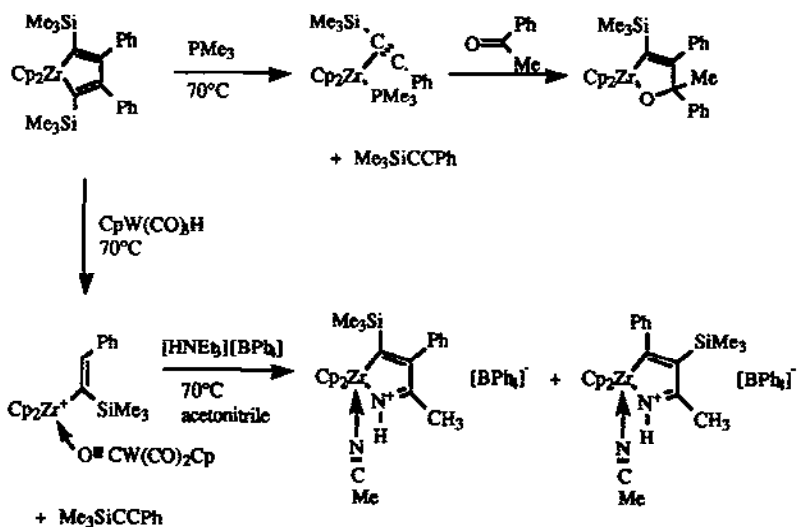
The five membered metallacycle  $\text{Cp}_2\text{Zr}(\text{CSiMe}_3\text{CPhCSiMe}_3\text{CPh})$  appears from its addition reactions with a ketone or a nitrile, or on protonation to be a suitable starting material for the *in situ* generation of the reactive complex  $\text{Cp}_2\text{Zr}(\eta^2\text{-C}(\text{SiMe}_3)\text{C}(\text{Ph}))$ . This was evident from the spectroscopic characterisation of the products and the systematic loss of free  $\text{Me}_3\text{SiCCPh}$  in each case. Reactions are summarised in scheme 6 [18].

When a slurry of  $[\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8][\text{CpZrCl}_2]_2$  in thf is treated with an excess of  $(\eta^3\text{-C}_3\text{H}_5)\text{MgCl}$  at room temperature, the dinuclear fulvalene zirconium allyl derivative *anti*- $[\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8][\text{CpZr}(\eta^1\text{-CH}_2\text{CHCH}_2)(\eta^3\text{-CH}_2\text{CHCH}_2)]_2$  is formed. The solid state structure of this complex shows the fulvalene to be planar and each zirconium atom to be coordinated to one  $\eta^5$ -Cp ring, two allyl groups and the fulvalene, in pseudo-tetrahedral geometry. In solution a fluxional process occurs and is thought to involve an  $\eta^1$ - $\eta^3$ -allyl rearrangement. Attempts to prepare the complex  $[\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8][\text{CpZrR}_2]_2$  (where R = tolyl) failed, spectroscopic data indicating the presence of  $\eta^1\text{-}\eta^5\text{-C}_5\text{H}_4$  rings [19].



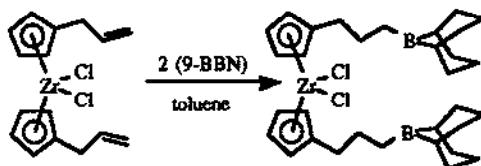


Scheme 5



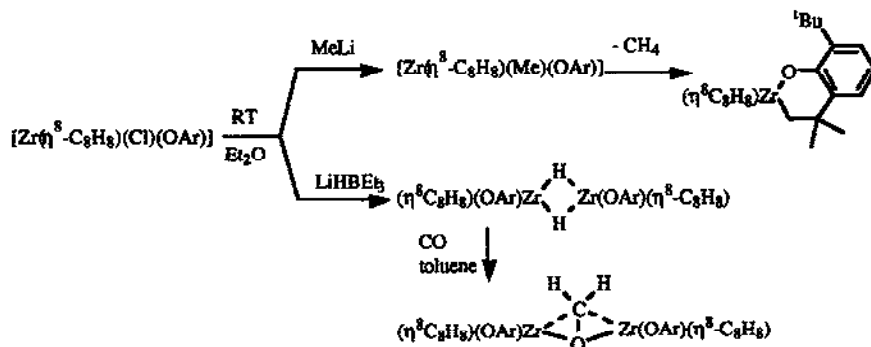
Scheme 6

The addition of 9-borabicyclo[3.3.1]nonane (9-BBN) to  $(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2)_2\text{ZrCl}_2$  yields  $(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_3(9\text{-BBN}))_2\text{ZrCl}_2$  (scheme 7). One of the Cp-bonded allyl ligands of this allyl cyclopentadienylzirconium dichloride couples with butadiene. Similar zirconium systems  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}=\text{C}(\text{CH}_3)\text{R})_2\text{ZrCl}_2$  ( $\text{R} = \text{CH}_3, \text{Ph}$ ) also undergo addition reactions with 9-BBN to give  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}(9\text{-BBN})\text{CH}(\text{CH}_3)\text{R})_2\text{ZrCl}_2$  ( $\text{R} = \text{CH}_3$  *rac/meso*  $\sim 1:1$ ) ( $\text{R} = \text{Ph}$ , *threo/erythro*  $\sim 1:1$ ). The mixtures of diastereoisomers were separated by fractional crystallisation [20].



Scheme 7

The yield of the complexes  $\text{Cp}^*(\text{R})\text{ZrX}_2$  ( $\text{Cp}^* = (\text{CH}_3)_5\text{C}_5$ ,  $\text{R} = \text{C}_3\text{H}_5$ ,  $\text{X} = \text{Cl}$ ;  $\text{R} = 1,1,2$ -trimethylallyl,  $\text{X} = \text{Br}$ ;  $\text{R} = 1,2,3$ -trimethylallyl,  $\text{X} = \text{Br}$ ) is dependent on the number of Me substituents at the terminal positions on the allyl ligand. These compounds were synthesised from the reaction of allyl Grignards or allyl lithium reagents with  $\text{Cp}^*\text{ZrCl}_3$  and their reactivity towards  $[\text{MCp}(\text{CO})_2]^-$  ( $\text{M} = \text{Fe}, \text{Ru}$ ) and  $\text{LiCH}_2\text{PPh}_2$  were investigated. The X-ray crystal structures of  $\text{Cp}^*(\eta^3\text{-C}_3\text{H}_5)\text{ZrCl}_2$  and  $\text{Cp}^*(\text{R}')(\eta^2\text{-CH}_2\text{PPh}_2)\text{Zr}$  ( $\text{R}' = 1,2$ -dimethylbutadiene) are reported and the dynamic behaviour of the latter was examined by variable temperature  $^1\text{H}$  NMR spectroscopy [21].



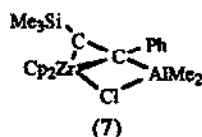
Scheme 8

The electronic and steric effects of the tetramethylcyclopentadienyl ligand on the physical properties of its titanium and zirconium complexes have been examined and the NMR and IR spectra indicated that  $\text{C}_5\text{Me}_4\text{H}$  exhibits an electron-donor effect greater than  $\text{C}_5\text{H}_5$  and slightly weaker than  $\text{C}_5\text{Me}_5$ . A structural examination of the complex  $(\text{C}_5\text{Me}_4\text{H})_2\text{Zr}(\text{Ph})\text{Cl}$  and the study of the  $^1\text{H}$  and  $^{13}\text{C}$  dynamic NMR properties of the compounds  $(\text{C}_5\text{Me}_4\text{H})_2\text{MR}^1\text{R}^2$  ( $\text{M} = \text{Ti}, \text{Zr}$ ;  $\text{R}^1 = \text{R}^2 = \text{Ph}$ , *p*- $\text{C}_6\text{H}_4\text{Me}$ ;  $\text{R}^1 = \text{Cl}, \text{Br}$ ;  $\text{R}^2 = \text{Ph}$ , *p*- $\text{C}_6\text{H}_4\text{Me}$ ) show that  $\text{C}_5\text{Me}_4\text{H}$  has a steric effect intermediate between  $\text{C}_5\text{H}_5$  and  $\text{C}_5\text{Me}_5$ . The steric and electronic effects of  $\text{C}_5\text{Me}_4\text{H}$  have also been

used to induce specific isomerisation reactions of various alkenes by using  $(C_5Me_4H)_2TiMe_2$  as a catalyst [22].

Several novel cyclooctatetraene derivatives of zirconium have been synthesised and structurally characterised. A summary is given in scheme 8. [23].

The  $\beta$ -agostic complex  $Cp_2ZrCl[C(SiMe_3)=CHPh]$  reacts with trimethylaluminium to give a mixture of  $(\eta^2\text{-alkyne})zirconocene$  and  $Cl-AlMe_2$ . These reagents react to give a doubly acetylene/chloride bridged bimetallic Zr/Al complex (7), which uniquely features a planar tetracoordinate carbon atom in the centre [24].



#### 4.1.3 Complexes with ligands containing silicon

The complex  $Cp_2Zr(\eta^2\text{-1-butene})PMe_3$  reacts in thf solution with one equivalent of triphenylsilane by what is thought to be an addition-elimination pathway. The molecular structure of the silyl hydride complex was determined from single crystal X-ray diffraction to be  $Cp_2Zr(H)(SiPh_3)(PMe_3)$ . The reactivity of this species with acetone, pivalonitrile, or tert-butylnitrile gave insertion products in which the hydride ligand participates in new bond-forming reactions. In contrast, the reaction with 2-butyne gives elimination of the silane and the formation of a 5-membered metallacycle [25].

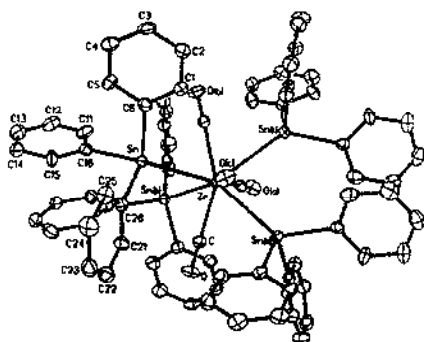
The first example of a metal silanimine complex has been prepared  $Cp_2Zr(\eta^2\text{-}SiMe_2=N^tBu)(PMe_3)$ . The single crystal X-ray structure of this complex shows the Zr-Si distance to be 2.654 (1) Å. This short bond length and correspondingly long Si-N distance of 1.687 (3) Å imply that the bonding of silanimine to the metal centre is best described as a metallacycle rather than a  $\pi$ -donor complex. From  $^1H$  and  $^{31}P\{^1H\}$  NMR data it appears that the  $PMe_3$  ligand is labile in solution, a fact that is borne out on reaction with CO to give the ligand substitution product  $(\eta^2\text{-}Me_2Si=N^tBu)(CO)$  which does not exist as the silaacyl form. The complex readily undergoes Zr-Si bond insertion reactions with ethene or formaldehyde to give five-membered metallacycles [26].

#### 4.1.4 Complexes with ligands containing tin

The synthesis of a novel bis-stannylenes adduct of zirconocene has been achieved by reacting two carbene like fragments  $R_2Zr(n\text{-Bu})_2$  ( $R = Cp, C_5H_4Me$ ) and  $Sn\{CH(SiMe_3)_2\}_2$ . An X-ray crystal structure of this complex  $(C_5H_4Me)_2Zr\{Sn[CH(SiMe_3)_2]_2\}_2$  shows the Zr-Sn distance to be 2.8715 (11) Å; this is only slightly greater than the sum of the covalent radii and implies significant  $\pi$ -donation from zirconium to tin. The room temperature  $^1H$  NMR spectrum is consistent with the solid-state structure with two equivalent stannylenes units. However at  $-30^\circ C$ , the  $SiMe_3$  resonance splits into three signals and this observation is interpreted in terms of rotation of one stannylenes ligand into the Sn-Zr-Sn plane [27].



An unprecedented carbonyl zirconium anion stabilised by four triphenylstannyl ligands has been synthesised (8) which contains an eight coordinate zirconium centre. The synthetic procedure requires that trimethylphosphine must be present to avoid the failure of the carbonylation step (equation (i)). The molecular structure of this complex was confirmed from IR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectroscopy and single crystal X-ray crystallography [28].



(8)

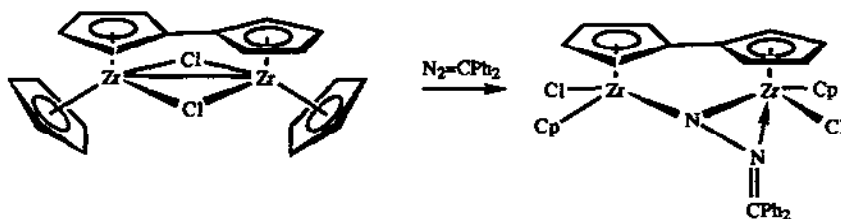
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#### 4.1.5 Complexes with nitrogen donor ligands

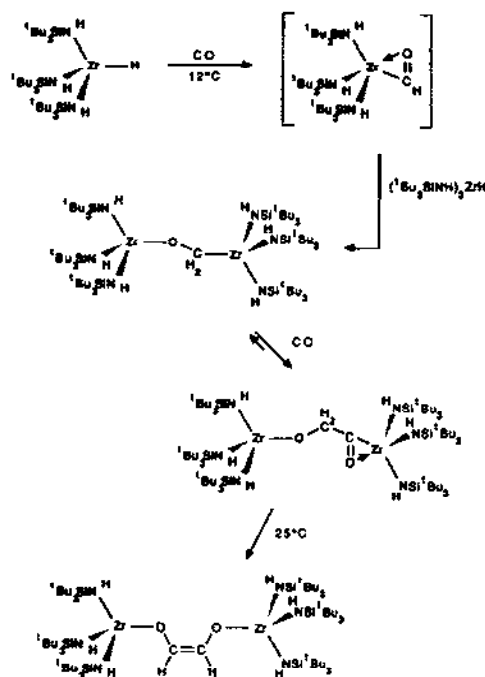
The zirconium(III) bridged chloride  $(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)[(\mu\text{-Cl})\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2]_2$  readily absorbs atmospheric oxygen to give  $(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)[(\mu\text{-O})(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2$ . This led to investigations into the reaction of this complex with diazo compounds  $\text{N}_2=\text{C}(\text{C}_6\text{H}_5)_2$  (scheme 9), and isocyanides  $[\text{C}^1\text{NC}(\text{CH}_3)_3]$  and organic azides  $(\text{Me}_3\text{Si})\text{N}_3$ . Single crystal X-ray structures of the diphenyldiazomethane and tert-butyl isocyanide complexes show that these groups insert into the Zr-Zr bond with concomitant opening of the chloride bridges of the starting material. The unsaturated organic molecules act as bridging ligands coordinated in a  $(\sigma + \pi)$  fashion. The Zr-CNC(CH<sub>3</sub>)<sub>3</sub> bond length (2.180 (2) Å) is similar to that observed in  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Zr}(\mu\text{-}\eta^1\text{-}\eta^2\text{-CC}(\text{C}_6\text{H}_5)_2)]_2$  (2.187 Å) implying some degree of multiple bonding in this interaction. In conjunction with this the IR spectrum (KBr) indicates a decrease in the CN bond order. The reduction of this compound in the presence of  $\text{C}^1\text{NC}(\text{CH}_3)_3$  yields the cyano complex  $(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)(\mu\text{-}\eta^1\text{-}\eta^2\text{-CN})\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2$  which was characterised from spectroscopic data [29].

Treatment of  $\text{ZrCl}_4$  with 3 equivalents of  $^t\text{Bu}_3\text{SiNHLi}$  gives  $(^t\text{Bu}_3\text{SiNH})_3\text{ZrCl}$  which on methylation affords  $(^t\text{Bu}_3\text{SiNH})_3\text{ZrCH}_3$ . The molecular structure of this methyl derivative was determined from X-ray crystallography and shows the zirconium to have near tetrahedral geometry and the Zr-C distance to be in the expected range (2.231 (7) Å). Thermolysis of this species yields a

transient bis(amido)imido complex  $(^t\text{Bu}_3\text{SiNH})_2\text{Zr}=\text{NSi}^t\text{Bu}_3$  which rapidly adds  $\text{H}_2$  across the imido linkage to give  $(^t\text{Bu}_3\text{SiNH})_3\text{ZrH}$ . The hydride resonance is downfield at  $\delta$  9.60 ( $\text{C}_6\text{D}_6$ ) due to the highly electrophilic nature of the zirconium centre. On exposure to CO, a *cis* enediolate compound is formed as the sole product. Several intermediates were observed and detected by  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopy (scheme 10) [30].



Scheme 9

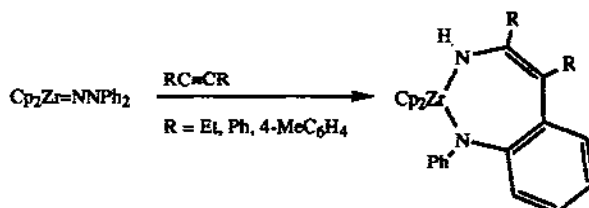


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Scheme 10

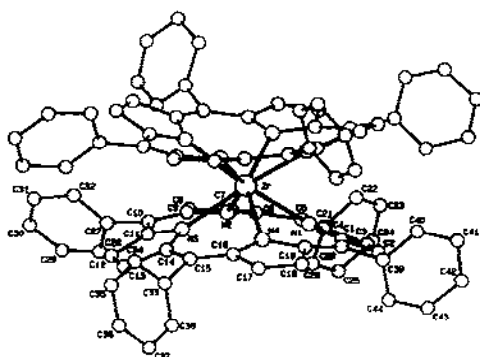
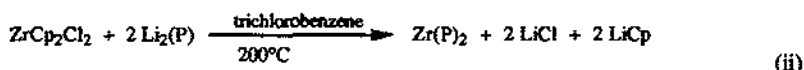
The first  $\eta^1$ -hydrazidozirconocene complex  $\text{Cp}_2\text{Zr}=\text{NNPh}_2$  can be trapped with alkynes (scheme 11) or CO to give an unprecedented rearrangement which involves N-N bond cleavage. In the absence of any trap, this complex forms a bridging hydrazido dimer which has been

crystallographically characterised. When the six-donor 4-(*N,N*-dimethylamino)pyridine (DMAP) is present, a monomeric hydrazido (2-) complex  $\text{Cp}_2\text{Zr}(\text{NNPh}_2)(\text{DMAP})$  is formed [31].



Scheme 11

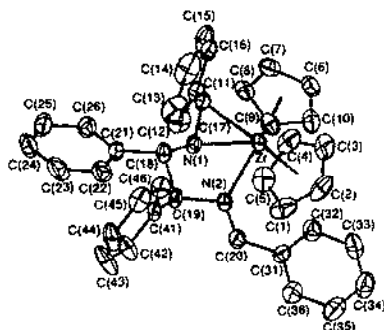
Phosphine derivatives of zirconium complexes have been successfully synthesised and studied in which the hybrid chelating ligand  $\text{-N}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2$  ( $\text{R} = \text{Me, } i\text{Pr, Ph}$ ) as a hard amide donor has been incorporated. The reactions of similar species of general formula  $\text{ZrCl}_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2]$  formally involve the replacement of all or some of the chloride ligands. Many of the resulting complexes undergo fluxional processes in solution, particularly when butadiene or allyl ligands are coordinated. One interesting complex which illustrates the change in reactivity that results from this tridentate ancillary ligand is  $\{[i\text{Pr}_2\text{PCH}_2\text{SiMe}_2]_2\text{N}\}[\text{ZrCl}]_2(\mu\text{-}\eta^2\text{-N}_2)$ . This novel dinuclear dinitrogen complex is prepared from the addition of two equivalents of  $\text{Na/Hg}$  to  $\text{ZrCl}_3[\text{N}(\text{SiMe}_2\text{CH}_2i\text{Pr}_2)_2]$  under an atmosphere of  $\text{N}_2$  [32].



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(9)

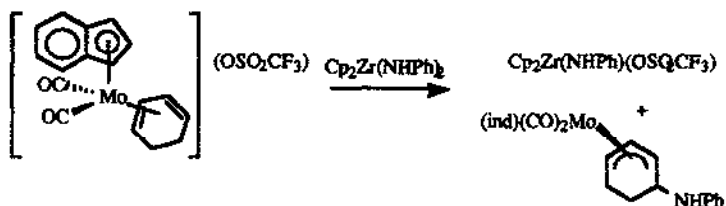
Two new zirconium bisporphyrinate double decker complexes  $\text{Zr}(\text{P})_2$  ( $\text{PH}_2 = \text{OEPH}_2$  or  $\text{TPPH}_2$ ) were synthesised according to equation (ii). The complexes were characterised by UV-VIS, near IR and  $^1\text{H}$  NMR spectroscopies and cyclic voltammetry. These data indicate that there is a





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(11)

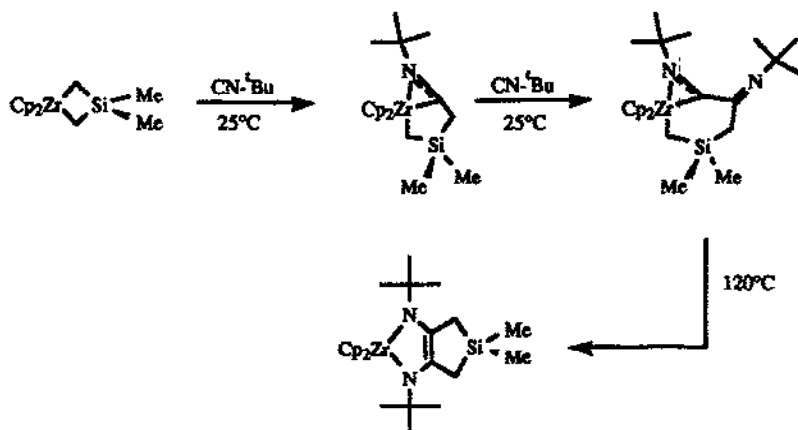


Scheme 12

The preparation, structure, spectroscopic and electrochromic properties of bis(phthalocyaninato)zirconium(IV)  $\text{Zr}(\text{Pc})_2$ , have been reported. The attempted synthesis of this species from  $\text{Zr}(\text{OAc})_4$  instead of  $\text{ZrCl}_4$  seemed to produce  $\text{Zr}(\text{Pc})(\text{OAc})_2$  from comparison of its electronic spectrum with that of  $\text{Lu}(\text{Pc})(\text{OAc})(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_2\text{Cl}_2$ . The solid state structure of  $\text{Zr}(\text{Pc})_2$  indicates that this complex has the most distorted ring system of any metal bisphthalocyanine yet reported. This distortion is primarily caused by the short Zr-N distances (average 2.30 Å) in this complex compared to other similar metal species and has a detrimental effect on the electrochromic properties of the molecule as it aids decomposition during oxidation [38].

Insertion of one equivalent of  $\text{CN}^t\text{Bu}$  into the complex  $\text{Cp}_2\text{Zr}(\text{CH}_2\text{SiMe}_2\text{CH}_2)$  gives the thermodynamically stable  $\eta^2$ -iminoacyl complex  $\text{Cp}_2\text{Zr}(\text{N}(\text{CMe}_3)\text{CCH}_2\text{SiMe}_2\text{CH}_2)$  (scheme 13). Addition of a second equivalent of  $\text{CN}^t\text{Bu}$  proceeds by reductive coupling of the two  $\text{CN}^t\text{Bu}$  via nucleophilic displacement of the original  $\eta^2$ -iminoacyl and not via breakage of the  $\text{C}(\eta^2\text{-iminoacyl})\text{-C}(\text{methylene})$  bond. The resulting complex  $\text{Cp}_2\text{Zr}(\text{N}(\text{CMe}_3)\text{C-C}(\text{=NCMe}_3)(\text{CH}_2\text{SiMe}_2\text{CH}_2))$  undergoes an unusual rearrangement at 120°C to the bicycloenediamido complex. All these complexes were characterised from IR, electronic and variable temperature NMR spectroscopy. The molecular structures of the bicycloenediamido and bicycloenediamidate complexes were established using single crystal X-ray diffraction [39].

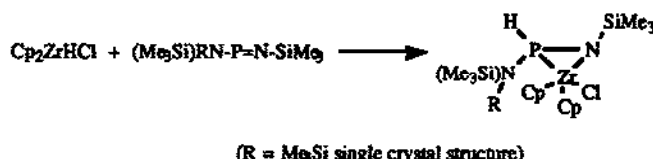




Scheme 13

#### 4.1.6 Complexes with nitrogen and phosphorus donor ligands

Reaction of the hydride  $\text{Cp}_2\text{ZrHCl}$  with dicoordinated phosphorus compounds gives metallocyclic compounds as shown, or example, in scheme 14. These aminozirconaazaphosphiranes undergo reversible halide exchange in the presence of a halide abstractor, (e.g.  $\text{Me}_3\text{SiSO}_3\text{CF}_3$  or  $\text{NaBPh}_4$ ), with the subsequent formation of cationic acetonitrile derivatives. Such species are unique cyclic cationic complexes and of interest due to their analogy to the alkyl complexes  $\text{Cp}_2\text{MR}^+$  ( $\text{M} = \text{Zr}, \text{Ti}$ ). In contrast, loss of cyclisation occurs on the addition of  $\text{Fe}_2(\text{CO})_9$ ,  $\text{S}_8$ , or  $\text{Se}$  to the starting aminozirconaazaphosphiranes via the phosphorus atom of the ligand. Subsequent loss of zirconium then occurs from the intermediate on addition of water [40].

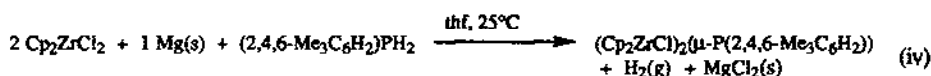


Scheme 14

#### 4.1.7 Complexes with phosphorus donor ligands

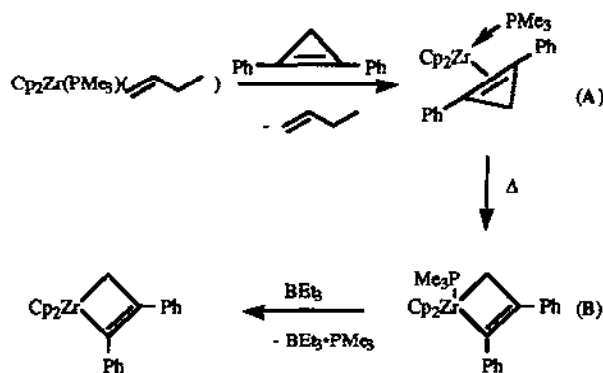
The reaction of methyl allyl Grignard or lithium reagents with  $\text{Cp}^*\text{ZrX}_3$  gives increased yields of compounds of the type  $\text{Cp}^*(\text{allyl})\text{ZrX}_2$  (allyl =  $\text{C}_3\text{H}_5$ , 1,1,2-trimethylallyl, 1,2,3-trimethylallyl,  $\text{X} = \text{Cl}, \text{Br}$ ) compared to the unsubstituted species.  $\text{Cp}^*(1,1,2\text{-trimethylallyl})\text{ZrBr}_2$  exists as two isomers in solution; the major isomer has a structure in which both terminal methyls are in a *syn* orientation and the minor isomer has one of the terminal allyl methyls in an *anti* orientation. The isomer exchange was followed by  $^1\text{H}$  NMR spectroscopy and revealed a  $\eta^3\text{-}\eta^1$  allyl mechanism ( $\Delta G^\ddagger = 66.2 \pm 1.0 \text{ kJ mol}^{-1}$ ). Both 1,1,2- and 1,2,3-trimethylallyl zirconium complexes can be reduced by  $\text{K}^+[\text{CpM}(\text{CO})_2]^-$  ( $\text{M} = \text{Fe}, \text{Ru}$ ) giving the Group 8 dimer  $[\text{CpM}(\text{CO})_2]_2$  and

uncharacterised oils, and react with 2 equivalents of  $\text{LiCH}_2\text{PPh}_2$  to give  $\text{Cp}^*(\eta^4\text{-}2,3\text{-Me}_2\text{(butadiene))}(\eta^2\text{-CH}_2\text{PPh}_2)\text{Zr}$  and  $\text{Cp}^*(\eta^4\text{-}1,2\text{-Me}_2\text{(butadiene))}(\eta^2\text{-CH}_2\text{PPh}_2)\text{Zr}$  respectively. The butadiene results from abstraction of an allyl terminal methyl proton by  $\text{PPh}_2\text{-CH}_2$ ; free  $\text{MePPh}_2$  is observed by NMR spectroscopy. Variable temperature  $^1\text{H}$  NMR spectroscopy indicated that a dynamic process occurs in solution involving Zr-P bond rupture ( $\Delta G^\ddagger = 38.9 \pm 1.0 \text{ kJ mol}^{-1}$ ). The novel  $\eta^2$ -coordination mode of the  $\text{CH}_2\text{PPh}_2$  ligand was confirmed in the solid state by X-ray crystallography, the bond lengths being Zr-CH<sub>2</sub> 2.346(8) Å and Zr-PPh<sub>2</sub> 2.66(2) Å respectively in the strained Zr-C-P ring [41].



A single crystal X-ray structure of the dark green product from the reaction given in equation (iv) shows this compound to be a bridged dimer with the  $\text{Zr}_2\text{P}$ -core and the carbon atom of the mesitylene ligand being coplanar. The Zr-P distances are equivalent and at 2.617(6) Å are shorter than those observed in the analogous complex  $\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)_2\text{RhH}(\text{CO})(\text{PPh}_3)$ . A similar reaction using  $\text{PCyH}_2$  as the phosphine produces a tetranuclear ring system in which two zirconium atoms are bridged by two phosphide groups ( $\text{PCyH}^-$ ), the  $\text{Zr}_2\text{P}_2$  core is coplanar and the Zr-P distances average 2.646 (4) Å. The zirconium atoms are thought to be antiferromagnetically coupled. An equivalent reaction using  $\text{Cp}^*\text{ZrCl}_2$  and  $\text{CyPH}_2$  appears from  $^{31}\text{P}$  NMR spectroscopy to yield  $\text{Cp}^*_2\text{Zr}(\text{PHCy})\text{H}$  as well as  $\text{Cp}^*_2\text{Zr}=\text{PCy}$  via  $\text{H}_2$  loss [42].

The synthesis and crystal structure determination of  $[\text{Cp}_2\text{Ti}(\mu\text{-PEt}_3)]_2$  have been reported. Bulk magnetic susceptibility studies on this solid show it to be diamagnetic over the range 5-340 K. EHMO calculations suggest this results from frontier orbital mixing of the  $\text{Cp}_2\text{Ti}$  and phosphide fragments and hence a pathway for super-exchange through the ligands. The spectroscopic data indicate that at high temperature a paramagnetic monomeric species is generated. No evidence for this or thermal population of the triplet state at  $\leq 340 \text{ K}$  is observed for the zirconium analogue [43].



Scheme 15

A ( $\eta^5$ -cyclopropene)(trimethylphosphane) complex of zirconocene was obtained in good yield by the reaction of 1,2-diphenylcyclopropene with (1-butene)(trimethylphosphane) zirconocene (scheme 15). The complex (A) was characterised in solution by  $^{31}\text{P}$ ,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectroscopy and in the solid state by X-ray diffraction analysis. Above room temperature the compound was found to rearrange to give the metalcyclobutene derivative (B) [44].

The reaction of  $(\text{Me}_3\text{Si})_2\text{NPPH}_2\text{NSiMe}_3$  with  $\text{ZrCl}_4$  yields  $[\text{ZrCl}_3(\text{Me}_3\text{SiNPPH}_2\text{NSiMe}_3\text{-N,N'})]\cdot\text{MeCN}$ . This four membered cyclic phosphazene derivative of zirconium crystallises in a monoclinic space group. The solid state structure determined crystallographically indicates that the cyclic Zr-N interactions are best considered as single bonds [45].

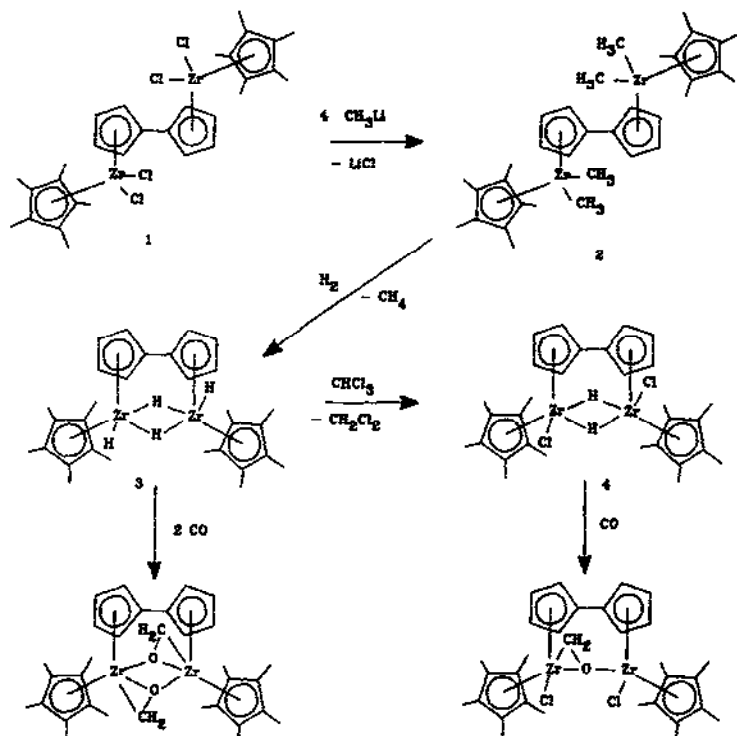
#### 4.1.8 Complexes with oxygen donor ligands

Commonly, reactions of zirconium species use the readily available zirconocene dichloride complex as a precursor. In order to investigate the influence of the rigidity of the Cp ligands on the subsequent reactions of such systems, Curtis and Hiltiwanger synthesised several hydride formaldehyde bridged fulvalene complexes  $(\eta^5\text{:}\eta^5\text{-C}_{10}\text{H}_8)[\text{Cp}^*\text{ZrH}_2]_2$ ,  $(\eta^5\text{:}\eta^5\text{-C}_{10}\text{H}_8)[\text{Cp}^*\text{Zr(H)Cl}]_2$ , and  $(\eta^5\text{:}\eta^5\text{-C}_{10}\text{H}_8)[\text{Cp}^*\text{ZrCl}]_2(\text{OCH}_2)$  (scheme 16) which were examined by variable temperature  $^1\text{H}$  NMR spectroscopy. At high temperature the latter complex appears to undergo rapid rotation about the C-O bond, this is in contrast to the results obtained for  $(\text{Cp}_2\text{ZrCl})_2(\mu\text{-OCHR})$  and is thought to result from the size of the substituents on the aldehyde. The results of a single crystal X-ray structural determination of  $(\eta^5\text{:}\eta^5\text{-C}_{10}\text{H}_8)[\text{Cp}^*\text{Zr}(\text{OCH}_2)]_2$  have been reported and show that the bond distances in this species are analogous to those of  $[\text{Cp}_2\text{Zr}(\text{OCH}_2)]_2$  [46].

Heterodimetallic  $\mu\text{-(}\eta^1\text{-C:}\eta^2\text{-O,O'})$  carbon dioxide complexes of zirconium were prepared by treating the metallocarboxylate complexes  $\text{Na}^+[\text{CpM}(\text{CO})_2\text{CO}_2]^-$  ( $\text{M} = \text{Fe, Ru}$ ) with zirconocene dichloride at low temperatures (scheme 17). The  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{RuCO}_2\text{ZrCl}(\eta^5\text{-C}_5\text{H}_5)_2$  adduct was more stable in benzene solution than was its iron equivalent, but both decomposed slowly to give the species  $\text{Cp}_2\text{M}(\text{CO})_4$  and  $[\text{Cp}(\text{Cl})\text{Zr}]_2(\mu\text{-O})$ . According to the infrared and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic results, protonation of the species with  $\text{HBF}_4$  deoxygenates the coordinated carbon dioxide moiety and yields the complexes  $[\text{CpM}(\text{CO})_3](\text{BF}_4)$  and  $[\text{Cp}_2(\text{Cl})\text{Zr}]_2(\mu\text{-O})$  [47].

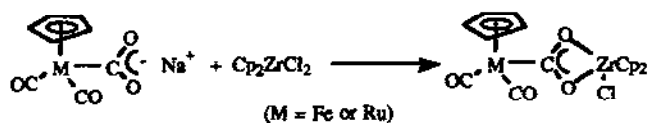
The heterodimetallic ruthenium complex  $\text{Cp}(\text{CO})_2\text{Ru}(\text{CO})_2\text{ZrClCp}_2$  undergoes reduction to its  $\mu\text{-}\eta^1(\text{C}): \eta^1(\text{O})$  formaldehyde derivative  $\text{Cp}(\text{CO})_2\text{Ru}(\text{CH}_2\text{O})\text{ZrClCp}_2$  on reaction with two equivalents of  $\text{Cp}_2\text{Zr(H)Cl}$  (scheme 18). A  $^{13}\text{C}$  NMR spectroscopic study of this reaction shows that hydride transfer occurs at a ligated carbonyl ligand and not at the carboxylate ( $\text{CO}_2$ ) ligand [48].

The volatile compound  $\text{ZrF}_3(\text{C}_3\text{F}_7\text{COO})$  can be prepared in a two step process from zirconium tetrachloride and  $\text{C}_3\text{F}_7\text{COOH}$ . Interest in this complex stems from its possible use as a precursor to  $\text{ZrF}_4$  [49].

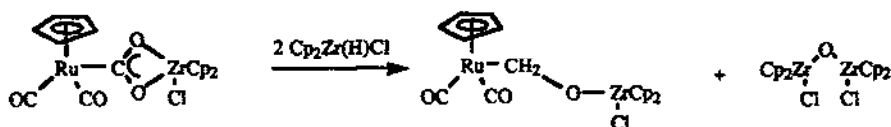


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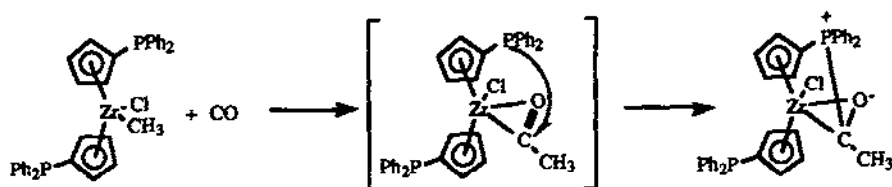
Scheme 16



Scheme 17



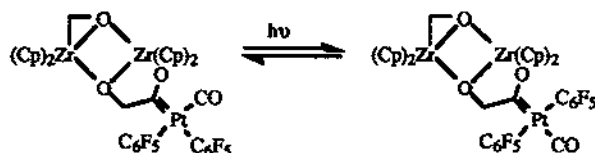
Scheme 18



Scheme 19

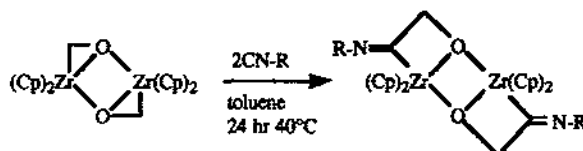


In most cases identical products were formed on photolysis and thermolysis, but two exceptions were found. Photolysis with  $\text{W}(\text{CO})_6$  resulted in the proposed formation of two regio isomers of B, and a second isomeric equilibrium was observed for the analogous zirconoxycarbene platinum complex (scheme 22) [52].

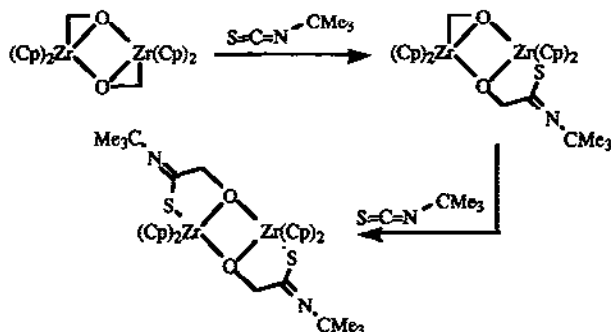


Scheme 22

In contrast to the formation of the metallaoxiranes, the reaction of  $[\text{Cp}_2\text{ZrOCH}_2]_2$  with alkyl isocyanides ( $\text{CN-R}$ ) (where  $\text{R} = \text{CH}_2\text{SiMe}_3$ ,  $\text{CH}_2\text{CMe}_3$ ,  $\text{CMe}_2\text{CH}_2\text{CMe}_3$ ) results in double insertion to form  $\text{C}_{2h}$ -symmetric metallatricyclic complexes containing two ( $\eta^1$ -iminoacyl)zirconocene moieties (scheme 23) as confirmed by a single crystal X-ray determination of the trimethylsilylmethyl derivative [53].



Scheme 23

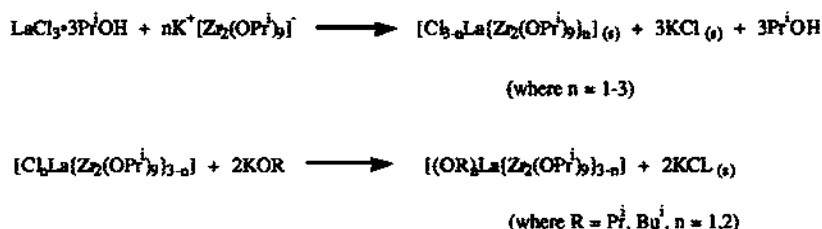


Scheme 24

The ( $\eta^2$ -formaldehyde)zirconocene dimer  $[\text{Cp}_2\text{ZrOCH}_2]_2$  reacts with  $t$ -butylisothiocyanate at  $120^\circ\text{C}$  by sequential insertion of the heterocumulene  $\text{S}=\text{C}$  bond into the metallaoxirane  $\text{Zr}-\text{C}$  linkages (scheme 24). The intermediate product of mono-insertion was detected by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies but the final product (a metallatricyclic dimer containing a  $\text{Zr}_2\text{O}_2$  four membered ring system) was characterised by single crystal X-ray diffraction [54]. The same dimer  $[\text{Cp}_2\text{ZrOCH}_2]_2$  reacts with less than stoichiometric quantities of  $\text{BEt}_3$  to give an insoluble

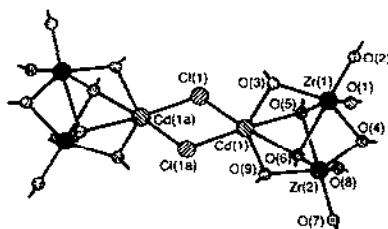
oligomeric zirconocene oxide  $\{\text{Cp}_2\text{ZrO}\}_x$  and trialkyl boron products. The reaction is assumed to take place via methylene insertion into the B-C bond [55]. The dimer undergoes a slow reaction with two equivalents of zirconocene dichloride to give the quantitative formation of  $(\text{CH}_2\text{O})(\text{ZrCp}_2\text{Cl})_2$ . This proved a useful building block in preparation of the mixed metal dimer  $\text{Cp}_2\text{ZrCl}(\mu\text{-CH}_2\text{O})(\text{Cp}_2\text{HfCl})$  in which the methylene unit is exclusively coordinated to the hafnium centre [56].

Seven colourless and hydrocarbon-soluble heterobimetallic isopropoxide derivatives of lanthanum and zirconium have been synthesised in a two step process, dependent on reaction stoichiometry (scheme 25). The products were characterised by elemental analysis and IR and NMR spectroscopy. From these data, structures for these complexes are proposed in which the  $\text{La}^{3+}$  ion is coordinatively saturated by isopropoxy bridges and/or internal chlorides [57].



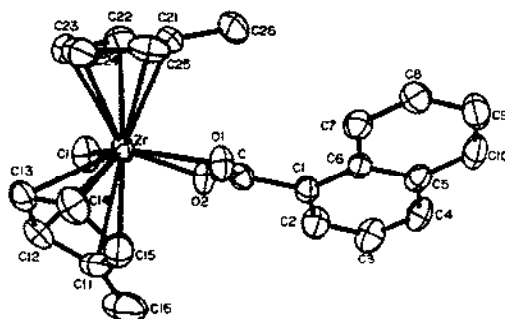
Scheme 25

The product of the reaction between equimolar amounts of  $\text{CdCl}_2$  and  $\text{K}[\text{Zr}_2(\text{OPr}^i)_9]$  in benzene is the dimeric species  $\{\text{Cd}[\text{Zr}_2(\text{OPr}^i)_9(\mu\text{-Cl})]\}_2$  (12). The molecular structure of this complex was confirmed crystallographically and shows the dimer to consist of two triangular  $[\text{CdZr}_2(\mu_3\text{-OPr}^i)_2(\mu\text{-OPr}^i)_3(\text{OPr}^i)_4]^+$  units linked by two chloride bridges, such that both metals have distorted octahedral geometry [58].



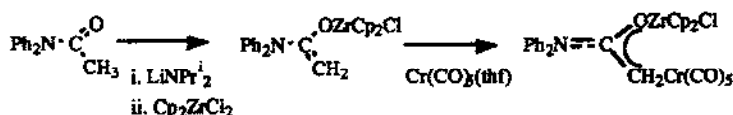
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(12)

A new five-coordinate 18-electron complex  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{ZrCl}(\alpha\text{-C}_{10}\text{H}_7\text{COO})$  (13) was synthesised by reacting equimolar amounts of  $(\text{MeCp})_2\text{ZrCl}_2$  and sodium  $\alpha$ -naphthoate. The solid state structure of this complex shows the  $\alpha$ -naphthoxy ligand is didentate ( $\text{Zr-O}$ , 2.317 (2) Å, 2.260 (2) Å) [59].



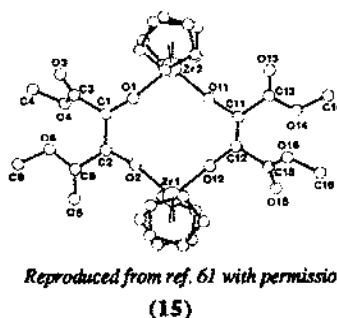
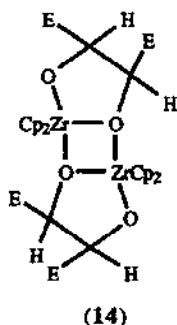
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(13)

The zirconium amide enolate  $\text{Ph}_2\text{N}-\text{C}(\text{CH}_2)\text{OZr}-(\eta^5\text{C}_5\text{H}_5)_2\text{Cl}$  has been synthesised (scheme 26) and structural characterisation shows that the oxygen atom of the enolato anion is bonded to the zirconium centre. The Zr-O bond ( $1.976(3)\text{\AA}$ ) lengthens on reaction of the methylene carbon centre with  $\text{Cr}(\text{CO})_5(\text{thf})$ . The resulting complex has the amide enolato O-bonded to zirconium centre (Zr-O  $2.045(3)\text{\AA}$ ) and C-bonded to chromium centre (Cr-C  $2.329(5)\text{\AA}$ ) [60].



Scheme 26

The reaction of (2*R*, 3*R*)-(+)-diisopropyl tartarate with dimethylzirconocene results in the loss of methane and dimerisation to give a dimetallotricyclic complex (14). In solution there is  $^1\text{H}$  NMR spectroscopic evidence for exchange involving the  $\text{CH}(\text{E})\text{CH}(\text{E})$ -units ( $\text{E} = \text{CO}_2\text{CHMe}_2$ ) (activation barrier =  $12 \pm 1 \text{ kcal mol}^{-1}$  at 255 K). The dynamic behaviour of racemic chiral and mesomeric achiral diastereomeric (tartarate)zirconocene dimers was shown to be quite different. The NMR spectra of the meso compounds were consistent with a ten membered dimetalloctetrahedral structure. In solution, the  $-\text{CO}_2\text{CH}_3$  derivative possesses the  $\text{C}_2$ -symmetric dimetallotricyclic structure but the solid state structure is that of the ten membered dimetallomonocycle (15) [61].



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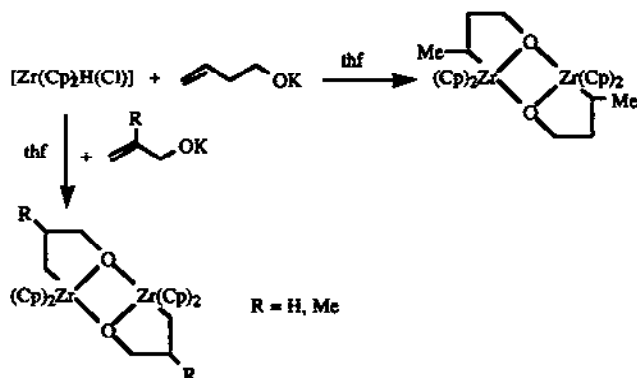


The reaction of  $(\text{Me}_3\text{C})_2\text{Si}(\text{OH})_2$  with  $\text{ZrCl}_4$  affords an eight membered ring complex in which the zirconium metal centre has an octahedral geometry due to the coordination of two thf solvent molecules. The solid state structure of this compound has been confirmed crystallographically [62].

The synthesis and molecular structure of the novel heterometallic alkoxide  $\text{Zr}_2\text{Co}_4(\mu_6\text{-O})(\mu_2\text{-OC}_3\text{H}_7)_8(\text{OC}_3\text{H}_7)_2(\text{acac})_4$  have been reported. The complex crystallises as discrete hexanuclear molecules with the oxygen atoms of the  $\text{Zr}_2\text{Co}_4\text{O}_{19}$  core adopting a cubic close packed arrangement in which the metal atoms occupy the octahedral holes. At the centre of the resulting metal octahedron, a  $\mu_6\text{-O}$  atom is located [63].

The reaction of  $\text{ZrCl}_4$ ,  $\text{CO}_2$  and  $\text{NHR}_2$  in toluene resulted in the formation of the *N,N*-dialkylcarbamato zirconium complex  $[\text{Zr}(\text{O}_2\text{CNR}_2)_4]$  ( $\text{R} = \text{Et}$ , isopropyl). Reaction of this complex with hydrogen halides resulted in salts of general formula  $[\text{Et}_2\text{H}_2\text{N}]_2^+[\text{ZrX}_6]^{2-}$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ) [64].

The dimeric five coordinate zirconacycles  $[\{\text{ZrCp}_2(\text{OCH}_2\text{CHRCH}_2)\}_2]$  ( $\text{R} = \text{H}$ ,  $\text{Me}$ ) and  $[\{\text{ZrCp}_2(\text{OCH}_2\text{CH}_2\text{CHMe})\}_2]$  were formed from the intramolecular hydrozirconation of  $\text{ZrCp}_2\text{HCl}$  with potassium allyl or homoallyl alcoholates (scheme 27). The solid state structures of the latter and the monomeric complex  $[\text{Zr}(\text{C}_6\text{Me}_5)_2(\text{OCH}_2(\text{CH}_2)_2\text{CH}_2)]$  were obtained. This monomeric zirconacycle 1-oxa-2-zirconacyclohexane, and its analogue 1-oxa-2-zirconacyclopentane were prepared from reacting  $\text{Zr}(\text{C}_5\text{Me}_5)_2\text{Cl}_2$  with the Normant Grignard reagents  $\text{ClMg}(\text{CH}_2)_x\text{OMgCl}$  (where  $x = 3$  or 4 respectively). The modes of thermal decomposition of these zirconacycles have been extensively studied and are found to depend on the coordination number (4 or 5) of the zirconium atom and on the size of the metallacycle [65].

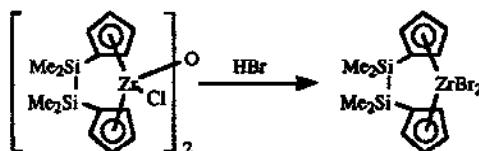


Scheme 27

The structure of  $\mu$ -oxo-bis[*mer*-(1,2-bis(dimethoxy)ethane-*O,O'*) trichlorozirconium(IV)] has been determined by X-ray crystallography. The molecule consists of 2 distorted octahedra sharing an oxygen atom corner. The plane of the molecule, coplanar with the mirror plane, is defined by the zirconium atoms, the bridging oxygen atom, the 1,2-bis(dimethoxy)ethane (dme) ligands, and two of the six chloride ligands. The remaining chloride ligands are located above and below the zirconium atoms. Each zirconium atom is 6-coordinate, bound to 3 chloride ligands and 3 oxygen

atoms in a *mer* configuration. Two of the oxygen atoms come from the dme ligand which forms a 5-membered chelate ring with zirconium [66].

The compound 1,1'-tetramethyldisilyl- $\eta^5$ -dicyclopentadienylzirconium dibromide has been synthesised by bromination of zirconocenophane with HBr (scheme 28), and characterised by X-ray crystallography [67].

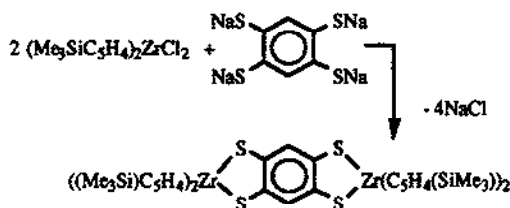


Scheme 28

Bis( $\eta^5$ -pentamethylcyclopentadienyl)zirconium dialkyls of general formula  $\text{Cp}^*_2\text{Zr}(\text{R})(\text{R}')$  ( $\text{R} = \text{CH}_3, \text{CH}_2\text{Ph}, \text{CH}_2\text{C}(\text{CH}_3)_3, \text{R}' = \text{R}, \text{Cl}$ ) absorb oxygen when in hydrocarbon solution. The rates of initiation and the mechanism of this autooxidation have been explored and differ from those of bis( $\eta^5$ -cyclopentadienyl)zirconocenes [68].

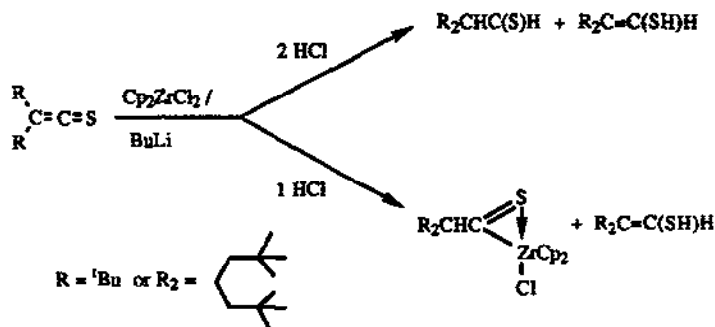
#### 4.1.9 Complexes with sulfur donor ligands

The dinuclear chelate-bridged complex formed in the reaction shown in scheme 29 was characterised from IR and  $^1\text{H}$  NMR spectroscopies and mass spectrometry. A single crystal X-ray structure of the hafnium analogue was obtained and showed the bridging  $\text{HfS}_2\text{C}_6\text{H}_2\text{S}_2\text{Hf}$  moiety to have a chair-like conformation with the  $\text{HfS}_2$  planes inclined by  $47^\circ$  with respect to the  $\text{S}_2\text{C}_6\text{S}_2$  plane [69].



Scheme 29

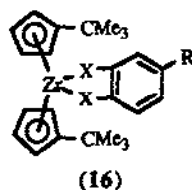
The addition of zirconocene reagents to thioketenes followed by acidolysis offers a novel route to thioaldehydes and their enethiol isomers in conjunction with  $\eta^2$ -thioacyl complexes of zirconium (scheme 30). The thioacyl group was confirmed to be  $\eta^2$ -CS-bonded to the zirconium centre from an X-ray crystallographic study of the metallacycle with  $\text{R}_2 = (\text{tBuCH}_2)_2\text{CH}$ . Interestingly, although the solid-state structure shows the thioacyl to be bonded in the *S*-outside configuration in this complex, the  $^{13}\text{C}$  NMR spectrum of the *t*-butyl analogue implies the presence of both the *S*-outside and *S*-inside conformers with two low field  $\eta^2$ -acyl resonances at  $\delta$  369.91 and  $\delta$  380.75 [70].



Scheme 30

A tetradentate Schiff's base  $\text{C}_{30}\text{H}_{26}\text{N}_4\text{S}_4$  formed from the condensation of benzyldithiocarbamate and benzil was reacted with  $\text{Zr}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  in a basic solution of  $\text{H}_2\text{O}_2$  to give the complex  $\text{Zr}(\text{O}_2)(\text{C}_{30}\text{H}_{24}\text{N}_4\text{S}_4)$ . The IR spectroscopic data suggest that the ligand is deprotonated in the thiol form and that the azomethine nitrogen is coordinated to the metal centre. Comparison of the  $\nu(\text{O}-\text{O})$  modes of the  $\text{M}(\text{O}_2)$  unit shows that this decreases with an increase in metal atomic number ( $\text{M} = \text{Zr}, \text{Th}, \text{Mo}, \text{W}, \text{V}$ ) [71]. Other complexes of zirconium containing the tetradentate Schiff's bases have also been studied [72].

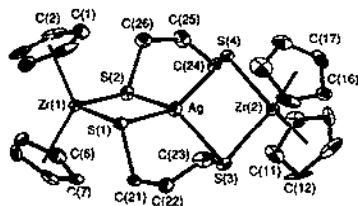
The reaction of the appropriate organolithium reagent with bis(tert-butylcyclopentadienyl)zirconium dichloride gives *para*-substituted diphenylzirconocenes  $(\text{t-BuCp})_2\text{Zr}(p\text{-C}_6\text{H}_4\text{R})_2$  ( $\text{R} = \text{Br}$  or  $\text{NMe}_2$ ). Heating these complexes results in the elimination of bromobenzene or *N,N*-dimethylaminobenzene to give arynezirconocenes into which two chalcogen atoms can be inserted e.g.  $(\text{t-BuCp})_2\text{ZrX}_2(\text{C}_6\text{H}_4\text{R})$  (16) ( $\text{X} = \text{S}$  or  $\text{Se}$ ). When attacked by electrophiles, these dichalcogenated zirconacycles result in the formation of new functionalised dichalcogenated benzenic compounds e.g. 3,4-( $\text{NCCH}_2$ ) $_2\text{C}_6\text{H}_3\text{NMe}_2$  [73].



Powder X-ray diffraction has been used to study the complex barium zirconium sulfides,  $\text{Ba}_2\text{ZrS}_4$  and  $\text{Ba}_3\text{Zr}_2\text{S}_7$ , produced from the reaction of  $\text{CS}_2$  with a mixture of  $\text{BaCO}_3$  and  $\text{BaZrO}_3$  [74].

The bridged zirconocene pentasulfide chelate  $((\text{CH}_3)_2\text{SiC}_5\text{H}_4)\text{ZrS}_5$  has been synthesised and its structure postulated from  $^1\text{H}$  NMR spectroscopy [75]. The sulfur coordinated bimetallic macrocycle  $\text{Cp}_2\text{Zr}(\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{S})_2\text{ZrCp}_2$  is formed on reaction of  $\text{Cp}_2\text{ZrMe}_2$  with propane-1,3-dithiol. The solid state structure of this complex shows that each of the zirconium atoms has a pseudo-tetrahedral geometry and the two zirconium atoms are  $7.570(1)\text{\AA}$  apart. Further reaction of

this macrocyclic compound with  $\text{AgBPh}_4$  produces the novel silver bound species  $[\text{Cp}_2\text{Zr}(\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{S})_2\text{ZrCp}_2\text{Ag}](\text{BPh}_4)$  (17) in which the silver atom has flattened tetrahedral symmetry, and the zirconium atoms are  $6.613(1)\text{\AA}$  apart [76].



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(17)

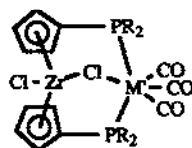
The reaction of  $\text{Me}_2\text{NC(S)SN(SiMe}_3)_2$  with  $\text{ZrCl}_4$  yields the dithiocarbamate complex  $\text{ZrCl}_3\{\text{Me}_2\text{NC(S)S}\}$ . The solid state structure of this complex has been confirmed crystallographically [77]. The preparation of  $[\text{Cp}_2\text{ZrCl}]_2(\text{dto})$  ( $\text{dtoH}_2$  = dithiooxalic acid) was achieved by reacting  $\text{Cp}_2\text{ZrCl}_2$  with potassium dithiooxalate in  $\text{CH}_2\text{Cl}_2$ . A single crystal X-ray diffraction study of this complex shows the zirconium metal centre to be five-coordinate [78].

A novel hexanuclear complex of zirconium was synthesised from the reaction of  $[\text{CpZrCl}_3]$  with  $\text{S(SiMe}_3)_2$ . The solid state structure of this complex shows that each discrete  $[\text{Cp}_6\text{Zr}_6\text{S}_9]$  molecule consists of a  $\text{Zr}_6$  octahedron coordinated by  $\mu_3\text{-S}$  ligands. In the centre of this metal octahedron is an additional  $\mu_6\text{-S}$  atom [79].

The structure of bis( $\eta^5\text{-cyclopentadienyl}$ )( $N,N$ -dimethyldithiocarbamato)phenoxy zirconium(IV) has been examined by X-ray crystallography. The Zr-S bond lengths to the didentate dicarbamate ligand were found to be very long ( $2.656$  and  $2.789\text{\AA}$ ). These unusually long bonds account for the observed rapid rates of N-Me group exchange. The compound crystallises in the monoclinic space group  $P2_1/n$ . The expected bent metallocene geometry is observed [80].

#### 4.1.10 Complexes with halide ligands

A series of ligand-bridged dinuclear complexes  $\text{MM'Cl}(\mu\text{-Cl})(\mu\text{-C}_5\text{H}_4\text{PR}_2)_2(\text{CO})_3$  (18), ( $\text{M} = \text{Ti, Zr}$ ;  $\text{M}' = \text{Cr, Mo, W}$ ;  $\text{R} = \text{C}_6\text{H}_5, 4\text{-C}_6\text{H}_4\text{CH}_3$ ) was synthesised from the reaction of  $\text{MCl}_2(\text{C}_5\text{H}_4\text{PR}_2)_2$  and  $\text{M'CO}_3\text{L}_3$  ( $\text{L} = \text{acetonitrile, CO, P(OMe)}_3$ ). Methyl sulfide ( $\text{MeS}^-$ ) ligands substitute both for terminal and bridging chloride ligands to give the complexes  $\text{MM' (SMe)}(\mu\text{-SMe})(\mu\text{-C}_5\text{H}_4\text{PR}_2)_2(\text{CO})_3$  which are inert towards CO or  $\text{P(OMe)}_3$  [81].



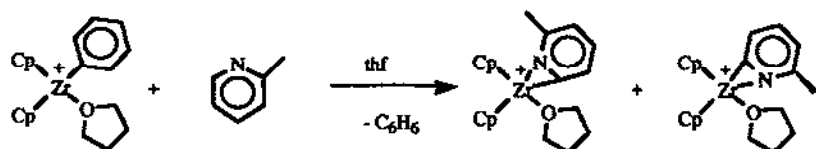
(18)

The molecular structure of octachlorobis(triphenylphosphine) dizirconium has been determined crystallographically. The molecule is confirmed as being dinuclear with the two zirconium atoms (Zr-Zr distance 3.649 Å) bridged by three chlorine atoms that form a triangular face perpendicular to the Zr-Zr axis. The coordination sphere about one zirconium is completed by two chloride and two PPh<sub>3</sub> ligands mutually *trans* to each other. The octahedral coordination sphere about the second zirconium atom is completed by the remaining three chlorine atoms [82].

#### 4.1.11 Cationic complexes

The reactions of isolable  $[\text{Cp}_2\text{Zr}(\text{R})(\text{L})]^+$  compounds with unsaturated substrates are of interest firstly, for comprehension of the factors that influence the rates of insertion and  $\beta$ -H elimination reactions, and therefore chain propagation and chain transfer reactions in polymerisation processes and secondly, for development of other related stoichiometric and catalytic C-C bond forming reactions.

Current interest in the chemistry of  $[\text{Cp}_2\text{Zr}(\text{R})(\text{L})]^+$  complexes is motivated by the proposed role of closely related 14-electron  $[\text{Cp}_2\text{Zr}(\text{R})]^+$  ions in  $\text{Cp}_2\text{ZrX}_2$ -based Ziegler-Natta alkene polymerisation catalyst systems. The reactivity of the neutral species  $\text{Cp}_2\text{Zr}(\text{R})_2$  ( $\text{R} = \text{CH}_3, \text{CH}_2\text{Ph}, \text{Ph}$ ) with  $[\text{Cp}^*_2\text{Fe}](\text{BPh}_4)$  has been explored showing oxidative Zr-R bond cleavage for the  $\text{CH}_3$  and  $\text{CH}_2\text{Ph}$  derivatives to give  $[\text{Cp}_2\text{Zr}(\text{R})(\text{thf})](\text{BPh}_4)$ . The diphenyl neutral complex forms  $[\text{Cp}_2\text{Zr}(\text{Ph})(\text{thf})]^+$  on reaction with  $[\text{HN}(\text{CH}_3)_3\text{Ph}](\text{BPh}_4)$  and undergoes nucleophilic thf ring opening on reaction with  $[\text{HN}(\text{CH}_3)_3](\text{BPh}_4)$ . The initial step in this process is thought to be selective Zr-Ph protonolysis and qualitative rates of this Zr-C bond protonolysis as a function of the organic ligand have been studied. The cationic species  $[\text{Cp}_2\text{Zr}(\text{Ph})(\text{thf})]^+$  reacts rapidly with a variety of reagents such as 2-methylpyridine (scheme 31) and  $\text{PMe}_3$  [83].

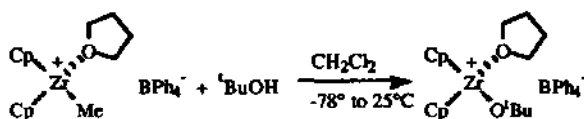


Scheme 31

The cationic zirconium(IV) complex  $[\text{Cp}_2\text{Zr}(\text{Me})(\text{thf})]^+$  reacts selectively with a variety of pyridines, pyrazines and related substrates via ortho C-H activation to yield new three membered azametallacycles e.g.  $[\text{Cp}_2\text{Zr}(\eta^2\text{-}(\text{CN})\text{-}\{6\text{-phenyl-pyrid-2-yl}\})(\text{thf})]^+$  (scheme 32). Once formed this cationic complex undergoes 1,2-insertion with  $\alpha$ -olefins  $\text{H}_2\text{C}=\text{CHR}$  (where R is an electron donating substituent  $\text{R} = \text{allyl}, \text{CH}_2\text{SiMe}_3, \text{CH}_2\text{OR}$ ) to afford  $\beta$ -substituted five-membered metallacycles. 2,1-Insertion however, leading to  $\alpha$ -substituted products, is observed for styrene, 2-vinylpyridine and vinyltrimethylsilane. In these cases the insertion regiochemistry is predominantly controlled by electronic effects rather than steric effects; the substituents on these olefins are electron withdrawing and stabilise the  $\alpha$  negative charge on the polar transition states and the products. Symmetric terminal alkenes also insert regioselectively to yield  $\alpha$ -substituted unsaturated



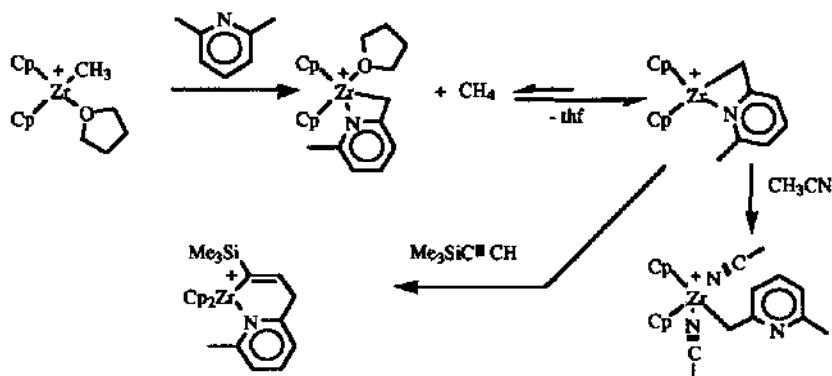
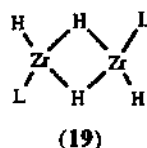
obtained from the rate of exchange of free and bound thf, deduced from variable temperature  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopic data and the 'in-plane' conformation of the thf ligand [86].



Scheme 34

The cationic complexes  $[\text{Cp}_2\text{Zr}(\text{R})(\text{CH}_3\text{CN})_n]^+$  ( $\text{R} = \text{H}, \text{Ph}, \text{CH}_3, \eta^2\text{-CH}_2\text{Ph}$ ) undergo single irreversible insertion of  $\text{CH}_3\text{CN}$  to yield the azaalkenylidene complexes  $[\text{Cp}_2\text{Zr}\{\text{N}=\text{C}(\text{R})(\text{CH}_3)\}(\text{CH}_3\text{CN})]^+$  in which the qualitative trend in R migration as determined from kinetic and NMR spectroscopic studies is  $\text{H}, \text{Ph}$  (rapid at  $23^\circ\text{C}$ )  $\gg \text{CH}_3 \gg \eta^2\text{-CH}_2\text{Ph}$  (no reaction at  $60^\circ\text{C}$ ) [87].

Studies of the chiral enantiomerically pure Group 4 metallocenes have recently attracted much attention as these complexes show promise in effecting asymmetric synthesis e.g. the recently synthesised chiral zirconocene ethylene-1,2-bis( $\eta^5$ -4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride ( $\text{LZrCl}_2$ ). This complex reacts with two equivalents of  $\text{Na}[\text{Et}_3\text{BH}]$  in benzene to give the hydride complex  $[\text{LZrH}]_2(\mu\text{-H})_2$  (**19**) which has a characteristic room temperature  $^1\text{H}$  NMR spectrum exhibiting two distinct triplet resonances for the bridging and terminal hydride ligands ( $\delta$  5.16 and  $-1.29$ ). Reaction of this hydride with a weak acid (here  $\text{PhMe}_2\text{NH}^+$ ) gives a soluble hydride cation  $[\text{LZr}(\text{H})(\text{NPhMe}_2)]^+$  in which the *N,N*-dimethylaniline ligand is weakly coordinated to the metal. This cation efficiently catalysed the reduction of 2-phenyl-1-butene but the enantioselectivity of this complex was low [88].



Scheme 35

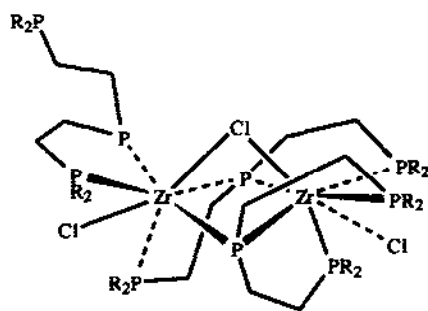
The four membered cationic azazirconacycle  $[\text{Cp}_2\text{Zr}(\eta^2\text{-N,C-CH}_2\{6\text{-Me-pyrid-2-yl}\})]^+$ , which exists in solution in its predominantly thf dissociated form (scheme 35), undergoes facile 1,2-insertion reactions with alkenes and alkynes to afford six-membered metallacycles. These reactions provide the basis for the Zr-mediated functionalisation of the methyl C-H bands of 2,6-lutidine. Treatment of the cation with  $\text{CH}_3\text{CN}$  however yields a thermally sensitive bis- $\text{CH}_3\text{CN}$  complex [89].

In a further study of cationic zirconocene species on aluminoxane as catalysts for alkene polymerisation, a series of Lewis base adducts of the type  $[\text{Cp}'_2\text{ZrMe}](\text{BPh}_4)$  ( $\text{Cp}'_2 = \text{rac-C}_2\text{H}_4(\text{indenyl})_2$ ,  $\text{rac-C}_2\text{H}_4(\text{tetrahydroindenyl})_2$ , or  $\text{Cp}' = (\text{Me}_3\text{C})\text{C}_5\text{H}_4$ ,  $(\text{Me}_3\text{Si})\text{C}_5\text{H}_4$ ) have been prepared. In all cases the low temperature  $^1\text{H}$  NMR spectra in aromatic solvents showed that the tetraphenylborate anion is coordinated *via* one phenyl ring to the zirconium metal centre. An investigation by variable temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy reveals several interesting fluxional processes are occurring, possibly involving enantiomeric or diastereomeric exchange or phenyl ring flipping [90].

## 4.2 Zirconium(III)

### 4.2.1 Complexes with phosphorus donor ligands

The zirconium(III) dimer  $\text{Zr}_2\text{Cl}_3\{(\text{P}(\text{CH}_2\text{CH}_2\text{PMe}_2)_2)_3\}$  (**20**),  $(\text{Zr}_2\text{Cl}_3(\text{ppp})_3)$ , has been synthesised from the reaction of  $\text{ZrCl}_4$  with three equivalents of the lithium salt  $\text{Li}[\text{ppp}]$  of the multidentate phosphido ligand. The diamagnetic nature of the compound is thought to be due to interaction between the zirconium atoms ( $\text{Zr-Zr}$  distance  $3.361(2)\text{\AA}$ ) or spin pairing *via* the phosphido bridges. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of this compound indicates the presence of coordinated and uncoordinated tertiary phosphine and three distinct phosphido functions. This was confirmed in the solid state by single crystal X-ray analysis [91].



(20)



### 4.2.2 Complexes with chloride ligands

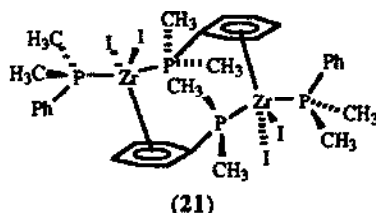
Recent studies show zirconium(III) to be unstable with respect to disproportionation into zirconium(IV) and zirconium(II). This process depends on the nature of the substituents and in some cases whether stable zirconium(III) derivatives can be isolated.

The diamagnetic zirconium(III) chloro complex  $(\text{Me}_2\text{SiCp}_2)\text{ZrCl}_2$  was synthesised in 65–75% yield by reduction of the metal dichloro derivative  $(\text{Me}_2\text{SiCp}_2)_2\text{ZrCl}_2$  with one equivalent of Na/Hg. The presence of two cyclopentadienyl rings bridged by an interannular  $\text{Me}_2\text{Si}$  group seems to be a reasonably successful method for stabilising the zirconium(III) oxidation state. However oxidation does occur to give a spectroscopically characterised complex  $[(\text{Me}_2\text{SiCp}_2)\text{ZrCl}]_2(\mu\text{-O})$  that disproportionates to  $\text{Cp}_2\text{ZrCl}_2$  and uncharacterised oxozirconium(IV) species [92].

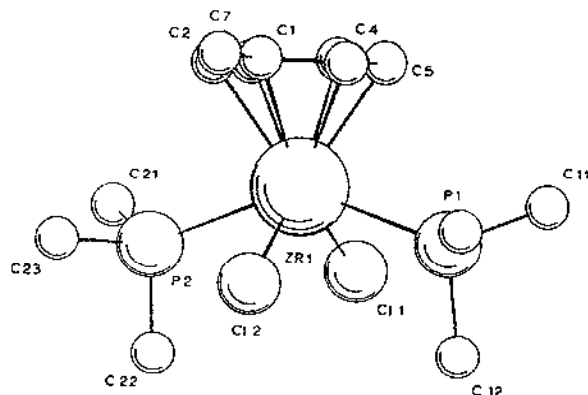
## 4.3 Zirconium(II)

### 4.3.1 Complexes with phosphorus donor ligands

The reduction of  $\text{ZrI}_4$  with Na/Hg amalgam and subsequent addition of 2 equivalents of  $\text{PMe}_2\text{Ph}$  yields a novel zirconium(II) dimer  $\text{Zr}_2\text{I}_4(\eta^6\text{-C}_6\text{H}_5\text{PMe}_2)_2(\text{PMe}_2\text{Ph})_2$  (21) in which the central  $\text{ZrI}_2\text{P}_2$  units are centred over and bound to the phenyl substituent of the phosphine of the adjacent metal centre. The average Zr–I and Zr–P bond lengths are 2.880 (4) and 2.790 (1) Å respectively, and the bound arene rings are puckered. Fenske–Hall molecular orbital calculations suggest the HOMO is composed of a  $d_{xy}$   $\sigma$ -type orbital on the zirconium and a formerly  $e_{2\pi^*}$  orbital on the arene. A single crystal X-ray structure of the  $\text{Hf}_2\text{Br}_4(\eta^6\text{-C}_6\text{H}_5\text{PMe}_2)_2(\text{PMe}_2\text{Ph})_2$  analogue has also been obtained and is in good agreement with the zirconium species, as both contain metal atoms of similar size in similar oxidation states [93].



When a solution of  $\text{ZrCl}_4$  in toluene at  $-78^\circ\text{C}$  is treated with one equivalent of  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ , two equivalents of sodium amalgam and an excess of cycloheptatriene, the novel  $\eta$ -arene complex  $\text{Zr}(\eta^7\text{-C}_7\text{H}_7)(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)\text{Cl}$  was formed. The complex  $\text{Zr}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{PMe}_3)_2\text{Cl}_2$  (22) was prepared in a similar one-pot synthesis and its molecular structure was obtained. Reaction of the latter with  $\text{Li}[\text{BH}_4]$  gave a bis(borohydrido) derivative which appeared to be fluxional in solution; only one signal was observed in the  $^1\text{H}$  NMR spectrum for the eight hydrogen atoms even at 183K [94].



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(22)

#### 4.3.2 Complexes with chloride ligands

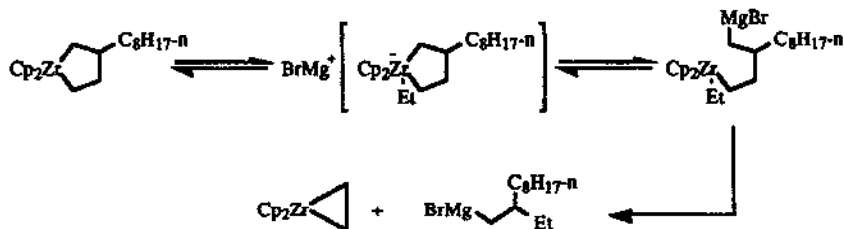
The compound  $\text{Zr}(\eta^6\text{-benzene})(\text{AlCl}_4)_2$  catalyses the cyclotrimerisation of 2-butyne to hexamethylbicyclo[2.2.0]-hexa-2,5-diene (HMDB). Although the cyclotrimerisation of acetylenes is well documented the only other efficient catalysts reported for this specific reaction are the corresponding titanium system and  $\text{AlCl}_3$ . The HMDB formed undergoes isomerisation to hexamethylbenzene. In contrast the reaction of the zirconium(II) arene species with diphenylacetylene forms a seven membered metallocycle  $[\text{ZrCPh}(\text{CPh})_4\text{CPh}][(\mu\text{-Cl})_2\text{AlCl}_2]_2$  in which the zirconium-aluminium interactions are bridged by four chlorine atoms. The compound has been characterised from infrared (nujol mull) spectroscopy and a single crystal X-ray diffraction study [95].

#### 4.4 Zirconium complexes as catalysts

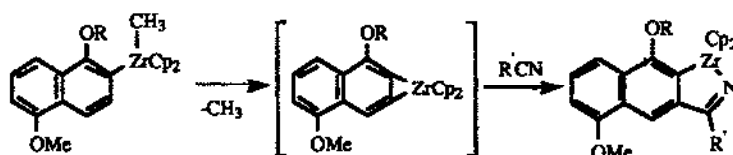
The catalytic addition of ethylmagnesium chloride to simple alkenes using  $\text{Cp}_2\text{ZrCl}_2$ ,  $\text{Cp}_2\text{ZrBu}_2$  or  $\text{Cp}_2\text{ZrEt}_2$  results in the stereoselective formation of C-C bonds. This procedure represents a simple one-pot method for the double alkylation or hydroxyalkylation of an unactivated alkene [96]. In the zirconium-catalysed ethylmagnesations of acyclic or cyclic homoallylic alcohols and ethers, it is the coordination of the heteroatom to the zirconium metal centre that determines the retention of high stereoselectivity in the products. The presence of an internal Lewis base seems to improve the efficiency of the carbometallation [97].

The pair-selective and regioselective formation of 3-alkyl or 2-aryl-1-zirconacyclopentanes *via* the ethyl-alkene (C-C) coupling reactions of zirconocene-alkene complexes and Grignard reagents have been achieved. The by-product  $\text{Cp}_2\text{Zr}(\text{CH}_2\text{CH}_3)_2$  (scheme 36) has been isolated as its  $\text{PMe}_3$  adduct [98]. Such systems rely on a subtle transmetallation equilibrium between the

zirconium and magnesium alkyls [99]. Azametallacycles are formed regioselectively when zirconium complexes with substituted naphthalynes are trapped *in situ* with nitriles (scheme 37). These compounds can be converted into ketones,  $\alpha$ -iodoketones and iodacyl-naphthoquinones by simple experimental procedures [100]. Further work on this methyl zirconocene chloride has shown it to be a successful catalyst in the synthesis of 3,4-disubstituted indoles *via* an intermediate complex with benzyne [101].

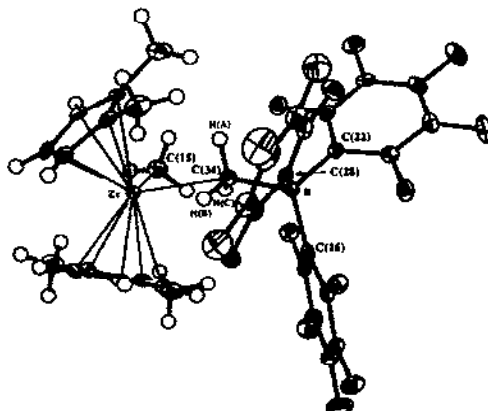


Scheme 36

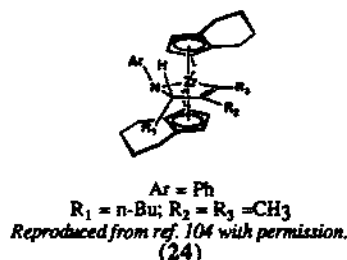


Scheme 37

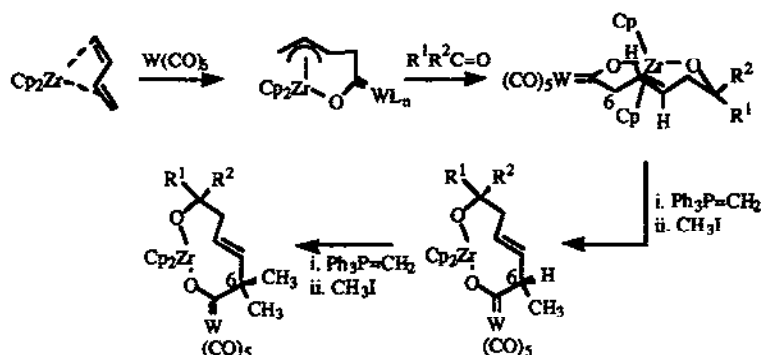
A crystallographically characterised "cation-like" zirconocene polymerisation catalyst has been synthesised in which a  $[(1,2-(\text{CH}_3)_2\text{C}_5\text{H}_3)_2\text{ZrCH}_3]^+$  cation coordinates to the anion  $[\text{CH}_3\text{B}(\text{C}_6\text{F}_3)_3]^-$  *via* a non-linear, highly unsymmetrical,  $\text{Zr}(\mu\text{-CH}_3)\text{B}$  bridge. The overall structure is shown in (23). The synthesis of two other methyl substituted Cp derivatives of this complex were carried out and all were active homogeneous catalysts for alkene polymerisation. Indeed polymerisation of ethene occurs at a rate roughly comparable to typical zirconocene/aluminoxane catalysts [102]. A similar cationic complex was observed to catalyse the isospecific polymerisation of propene [103].



The enantiomerically pure (*S,S*)-dimethyl derivative of (24) has been used for the enantioselective synthesis of allylic amines. An X-ray crystallographic study of one of the racemic metallacycles allowed the assignment of the absolute stereochemistry of the enantiomerically pure amines [104].



Butadiene zirconocene (scheme 38) undergoes Zr-C bond insertion with organic group 4 transition metal carbonyl compounds to yield nine-membered metallacyclic carbene complexes *e.g.* Cp<sub>2</sub>ZrOC[=W(CO)<sub>5</sub>]CH<sub>2</sub>CH=CHCH<sub>2</sub>CR<sup>1</sup>R<sup>2</sup>O (R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub>, or R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = C(CH<sub>3</sub>)<sub>3</sub>), which possess a *trans* C=C bond in the ring. Deprotonation of these systems by the ylide Ph<sub>3</sub>P=CH<sub>2</sub> at the α-position to the carbene carbon centre gives a chiral unconjugated metallic carbene complex anion which on alkylation stereoselectively at C<sub>6</sub> yields the predominately (2*R*\*, 6*S*\*)(4,5,6-*pS*\*) configured carbene. Sequential deprotonation/alkylation reactions yield doubly alkylated complexes which have been structurally characterised by single crystal diffraction studies. Hydrolysis of the mono α-methylated zirconoxycarbene complex (R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = C(CH<sub>3</sub>)<sub>3</sub>) in the presence of diazomethane gives an enol ether with conservation of the stereochemistry introduced at the metallacyclic starting material [105].



Scheme 38

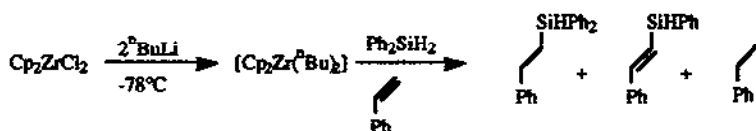
The non-stereospecific catalysis of the polymerisation of propene using Cp<sub>2</sub>ZrCl<sub>2</sub>/methylaluminumoxane was investigated in toluene at constant propene pressure (2 bar) and at 0, 20, 40 and 60°C. Stereo-irregular polypropenes were produced which remain soluble during polymerisation and can be characterised using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and size exclusion

chromatography. The polypropylene molecular weight distribution  $M_w/M_n < 2.4$  indicates the presence of uniform catalytically active sites. The decay of these sites via two second order processes, one reversible and one irreversible successfully predicts the decay of the polymerisation rate with time. At low temperature the deactivation is predominantly reversible [106].

Further investigations into the nature of the active sites on substituted zirconocene compounds with methylaluminoxanes have been made. The complexes  $(C_5H_4R)_2ZrCl_2$  (where  $R = ^iBu, Me_3Si$ ) polymerised ethene, and this catalysis was studied in toluene under argon and ethene atmospheres by IR, and  $^1H, ^{13}C, ^{27}Al$  and  $^{29}Si$  NMR spectroscopies. An increase in the catalytic polymerisation of ethene was observed when  $R = SiMe_3$  and was explained by various electronic effects [107].

The compounds  $Cp_2ZrR_2$  ( $R = Me, ^nBu$ ) have been used for the dehydrogenative polymerisation of disilanes ( $Me_3SiSiHMe_2, Me_2HSiSiHMe_2, Me_2H_2SiSiH_2Me_2$ ) in the absence of solvent to give a mixture of tri, tetra, penta, and higher oligosilanes [108].

There has been increasing interest in the applications of bimetallic catalytic systems with differing electron densities on the two metal centres *e.g.*  $d^0-d^8$  Zr(IV)-Rh(I). In these systems it is thought both metallic centres can activate carbon monoxide and that a hydrogen atom can migrate from the low to high oxidation state metal centres. The catalytic system  $\{[HRh(P(OPh)_3)_4] + Cp_2Zr(CH_2PPh_2)_2\}$  was found to produce selective hydroformylation of hex-1-ene. It is thought that the zirconium diphosphine reacts with the rhodium complex to give  $HRh(P(OPh)_3)_3Cp_2Zr(CH_2PPh_2)_2$  [109].

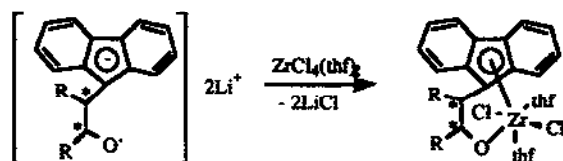


Scheme 39

Alkenes such as styrene, 1-hexene and 2-pentene undergo hydrosilylation with diphenylsilane using  $Cp_2Zr(^nBu)_2$  (scheme 39). The reactions are regioselective giving predominantly terminal organosilicon products. The reaction with styrene produces three compounds, the product distribution depending on the reagent concentrations [110]. Improved hydrosilylation seems to occur if  $Cp_2ZrCl_2$  is added to three equivalents of  $EtMgBr$ . In this case simple 1-alkenes, styrene and internal alkenes such as 1-octene and  $\beta$ -methylstyrene are converted to the corresponding silylated products with a regioselectivity of >99%. The reaction of  $Cp_2Zr(^nBu)_2$  with two equivalents of  $H_2SiPh_2$  produced the unexpected  $n-BuSiHPh_2$  product and a double hydrido-bridged dimer  $Cp_2ZrSi(\mu-H)_2(Ph_2Si)ZrCp_2$ . This species was structurally characterised and proved inert to 1-octene and therefore not an intermediate in the hydrosilylation process. In contrast, treatment of a second crystallographically characterised species,  $Cp_2Zr(PMe_3)(H)(SiHPh_2)$  isolated from the reaction of  $Cp_2Zr(^nBu)_2, H_2SiPh_2$  and  $PMe_3$  with 1-octene did yield the  $(n-oct)SiHPh_2$  product in a slow reaction (6 h) at  $60^\circ C$  [111].

Investigations into the reactions of chiral bridged mono( $\eta^5$ -fluorenyl)zirconium(IV) complexes of general type  $[C_{13}H_8-CHR-CHR-O]ZrCl_2(thf)_2$  ( $CHR-CHR$  = cyclohexyl,

cyclopentyl, 1,2-diphenylethyl) have shown these complexes to catalyse the polymerisation of ethene in the presence of  $\text{Al}(\text{CH}_3)_3$ . They were prepared from the reaction of symmetrically substituted epoxides with fluorenyllithium and then subsequent reaction with  $\text{ZrCl}_4(\text{thf})_2$  as shown in scheme 40 [112].



Scheme 40

Four chiral bent metallocene complexes of general formula  $(\text{Cp}-\text{CHR}^1\text{R}^2)_2\text{ZrCl}_2$  were prepared and used to generate homogeneous Ziegler catalyst systems for the stereoselective polymerisation of propene. The reduction of 6-cyclohexyl-6-methylfulvene by intermolecular  $\beta$ -hydride transfer from alkyl lithium reagents  $\text{LiCH}_2\text{CHRR}'$  ( $\text{R}, \text{R}' = \text{H}$ , alkyl, aryl) gave  $[\text{CpCH}(\text{CH}_3)\text{Cy}]\text{Li}$  which on subsequent reaction with  $\text{ZrCl}_4$  resulted in a 1:1 mixture of the  $[\text{CpCH}(\text{CH}_3)\text{Cy}]_2\text{ZrCl}_2$  diastereomers. The chiral complex *rac*- $[\text{CpCH}(\text{CH}_3)\text{Cy}]_2\text{ZrCl}_2$  was obtained >98% isomerically pure by fractional crystallisation. From a similar process starting with 6-methyl-6-phenylfulvene *rac*- $[\text{CpCH}(\text{CH}_3)\text{Ph}]_2\text{ZrCl}_2$  was obtained. The regioselective  $\alpha$ -deprotonation of 6-cyclohexyl-6-methylfulvene and subsequent reaction with  $\text{ZrCl}_4$  gave  $[\text{CpC}(\text{Cy})=\text{CH}_2]_2\text{ZrCl}_2$  which was characterised by X-ray crystallography. Hydroboration of this complex gave a 1:1 mixture of the  $[\text{CpCH}(\text{Cy})\text{CH}_2(9\text{-BBN})]_2\text{ZrCl}_2$  diastereomers. Variation of the Cp substituents of these metallocene catalysts was found to have a dramatic effect on the asymmetric induction of the C-C coupling process. The presence of phenyl and  $-\text{CH}_2(9\text{-BBN})$  groups was found to improve the efficiency of the metallocene chirality transfer [113].

Commercially available zirconocene hydrochloride has been found to be a suitable reagent for the *in situ* preparation of alkyl cuprates from alkenes. In the presence of one equivalent of an enone and catalytic amounts of Cu(I) salts ( $\text{CuBr}\cdot\text{SMe}_2$ ,  $\text{CuI}$ ,  $\text{CuCN}$ ), moderate to high yields of the corresponding 1,4 addition products are produced [114].

Zirconocene dichloride catalyses the aldol condensation - aromatisation of cyclohexanones. The facile one-step cyclodehydration of these complexes in the presence of the zirconium catalyst readily yields tris-annulated benzene derivatives [115].

A systematic comparison between the dimethylzirconocene and dimethyltitanocene catalysed dehydro-coupling of organosilanes has been reported. It was found that the polymerisation rates for the zirconocene were ten times that of the titanocene. However, in all other aspects of the reaction, both complexes gave essentially identical results. An examination of the catalytic cycle of the zirconocene was performed and several structures isolated. This work and its observations imply that dimethylzirconocene should replace the dimethyltitanocene complex in these catalysed processes [116].

The hydrogenolysis of the reagent from the reaction of tetra-n-pentylzirconium,  $\text{ZrNp}_4$ , with a dehydroxylated silica surface, produces a silica grafted zirconium hydride complex. This is

sufficiently electrophilic to activate the C-H bonds of cyclooctane and methane to subsequently form the corresponding cyclooctyl and methyl-zirconium complexes [117].

Zirconium complexes have long been used as reagents for organic synthesis. One recent example shows zirconocene-3-methoxybenzene to be a useful starting material for the opening of the rings of cyclic allylic ethers to produce homoallylic alcohols and substituted 2,3-dihydrofurans. The mechanism for these reactions are still under dispute [118].

The migration of the hexenyl group of dicyclopentadienyl zirconium-1-hexenyl chloride to a variety of boron containing compounds in the preparation of regio and stereochemically pure 1-alkenylboranes has been examined spectroscopically [119].

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