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4. Zirconium 1991

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CONTENTS

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 coordiantion 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.

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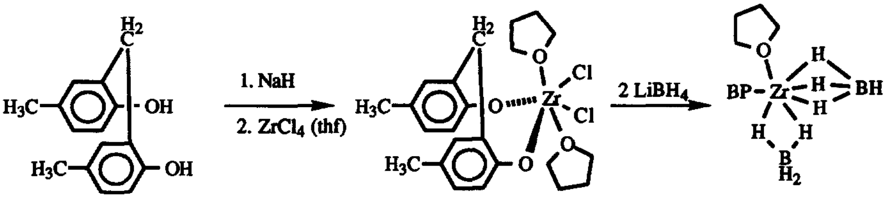
4.1 ZIRCONIUM(IV)

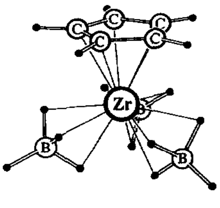
4.1.1 Complexes with ligands containing boron

Tetrahydroborate derivatives of zirconium(IV) and titanium(IV) bonded to the bisphenoxo dianion (BP) (scheme 1) have been synthesised. Results of ^1H and ^{11}B NMR spectroscopy showed the complex to undergo rapid dynamic behaviour even at 193K. The solid state IR spectrum indicated the presence of one didentate and one tridentate 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].



Scheme 1

The complex $(C_5H_5)Zr(BH_4)_3$ (1) was successfully synthesised from $(C_5H_5)ZrBr_3$ and $LiBH_4$. Electron diffraction studies on similar organometallic derivatives of tetrahydroborates $L_xM(BH_4)_y$ 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].



(1)

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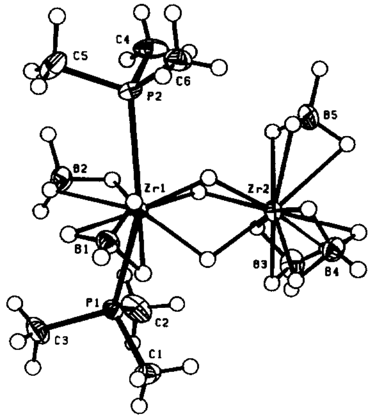
Treatment of $Zr(BH_4)_4$ with PMe_3 yields amber crystals of the new polyhydride $Zr_2H_3(BH_4)_5(PMe_3)_2$ (2), which has been extensively studied in the solid state by X-ray diffraction and in solution by ^1H, $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. In contrast, treatment of the tetrahydroborate complex with a didentate phosphine, 1,2-bis(dimethylphosphino)ethane, dmpe, gives the mononuclear hydride, $ZrH(BH_4)_3(dmpe)$ or $ZrH_2(BH_4)_2(dmpe)$ 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_4^- groups are exchanging and the dihydride having a trigonal dodecahedral ligand arrangement with C_2 symmetry. Above 25°C the dihydride was fluxional, but the exchange barrier of 15.6 kcal mol^{-1} was unusually high for a complex with such a high coordination number [3].



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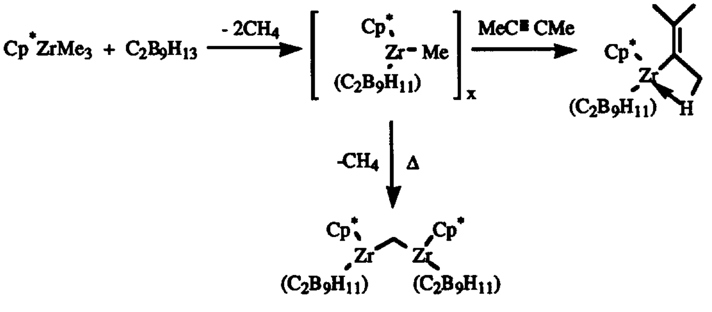
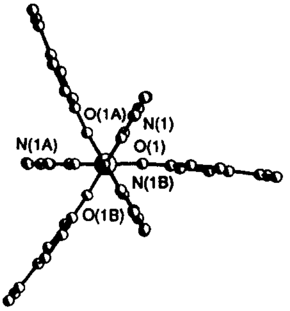


Scheme 2

The reaction of equimolar amounts of $C_2B_9H_{13}$ and $Cp^*Zr(Me)_3$ results in Zr-C bond cleavage and reformation to give $\{(Cp^*)(C_2B_9H_{11})Zr(Me)\}_x$ 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 $(Cp^*)(C_2B_9H_{11})Zr(C(Me){=}CMe_2)$. 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 $[(C_5R_5)_2Zr(R)]^{n+}$ complexes. The alkenyl group lies in the plane between the two η^5 ligands and is distorted by an agostic interaction involving one of the β-CH_3 hydrogens. This complex has olefin and acetylene insertion reactivity and will polymerise ethyne and propylene. Thermolysis results in quantitative yields of $(Cp^*)(C_2B_9H_{11})Zr]_2(\mu-CH_2)$ and methane. The X-ray crystallographic structure shows this methylidene-bridged complex to possess close B-H-Zr contacts involving a B-H bond of each dicarbollide ligand and the non η^5-bonded zirconium metal atom [4].

The tripodal ligand hydrotris(3,5-dimethylpyrazol-1-yl)borate, L^-, $[HB(3,5\text{-}Me_2C_3N_2H)_3]^-$, forms six coordinate complexes of the type $ZrLCl_3$. Replacement of the chloride ligands with phenol derivatives gives only the tris(aryloxo) complexes $ZrL(OC_6H_4X)_3$ when X is sterically undemanding (X = H, 2-F, 3-F, 4-F, 3-NO_2, 4-NO_2, or 4-^tBu) but the mixed chloroaryloxo zirconium complexes when X is sterically demanding *e.g.* $ZrL(Cl)(OC_6H_4Ph\text{-}2)_2$, $ZrLCl_2(OC_6H_3Me_2\text{-}2,6)$ and $ZrLCl_2(OC_6H_3Ph_2\text{-}2,6)$. X-ray single crystal structures of $ZrL(OC_6H_4NO_2\text{-}4)_3$, $ZrL(OC_6H_3Me_2\text{-}2,6)_3$ and $ZrLCl(OC_6H_3Me_2\text{-}2,6)_2$ show that in each case the aryl group is found to be oriented towards the borate ligand and interdisposed between adjacent $3,5\text{-}Me_2C_3N_2H$ moieties. With increasing steric crowding, deviation in the ideal octahedral coordination geometry at the zirconium metal occurs, along with a gradual twist of the phenyl rings out of the plane bisecting the two adjacent pyrazolyl groups of the ligand L^- as shown in structures (3a)-(3c) [5].



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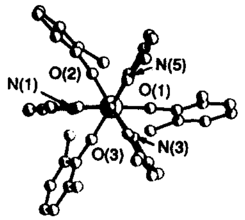

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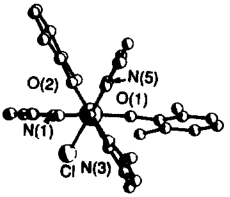

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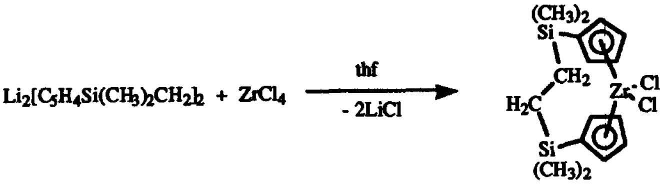
The protonated form of the hydridotris(pyrazol-1-yl)borate ligand, HL, reacts with zirconocene dichloride to give $Zr(C_5H_5)\{HB(C_3N_2H_3)_3\}Cl_2$. This novel complex has a reduction potential comparable to that of zirconocene dichloride (–1.59V *v* SCE), and reacts with phenols to give more moisture stable complexes of general formula $Zr(C_5H_5)\{HB(C_3N_2H_3)_3\}(OC_6H_4R)_2$ (R = H, 4-OMe, 4-NO_2, 2-Ph). The solid state structure of $Zr(C_5H_5)\{HB(C_3N_2H_3)_3\}(OC_6H_4Ph\text{-}2)_2$ obtained from X-ray crystallography shows the two phenoxide ligands to be inequivalent [6].

4.1.2 Complexes with carbon-based ligands

Potential energy barrier calculations and packing analysis have been used along with ^{13}C MAS-NMR spectroscopy to investigate the reorientational ring process that occurs in $(C_5H_5)_2ZrCl_2$ and $(C_5H_5)_2ZrC_4H_4Me_2$ and the diene flip observed in the latter and in $(C_5H_4{}^tBu)_2ZrC_4H_6$ [7].

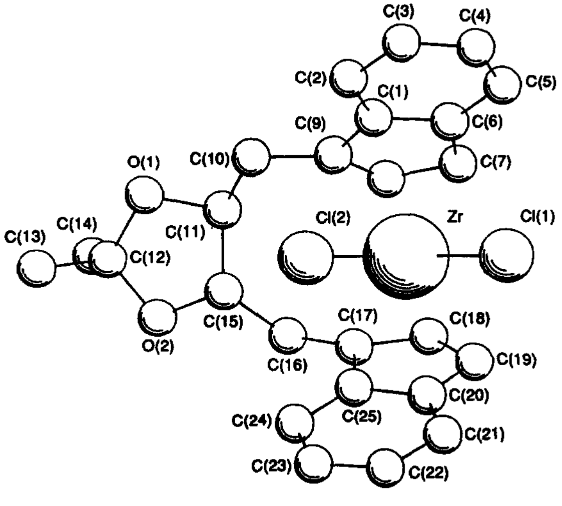
Reaction of two equivalents of 1,2,4-tris(trimethylsilyl)cyclopentadienyllithium with $ZrCl_4$ in refluxing toluene yields 1,1',2,2',4,4'-hexakis(trimethylsilyl) zirconocene dichloride, 53% after chromatography. The temperature dependence of the ^1H NMR spectra of this complex were explained in terms of full rotation of the substituted cyclopentadienyl ligands with a barrier to rotation of 11.0 ± 0.02 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 $[C_5H_4Si(CH_3)_2CH_2]_2^{2-}$ and $ZrCl_4$ (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 $[(C_5H_4)CHR(Cp')]^{2-}$ (R = Me or ^{t}Bu; Cp' = C_5H_4, C_9H_6, or $C_{13}H_8$) react with $ZrCl_4$ in thf to give the complexes $(C_5H_4)CHR(Cp')MCl_2$ which were characterised by ^1H and ^{13}C NMR spectroscopy [10].



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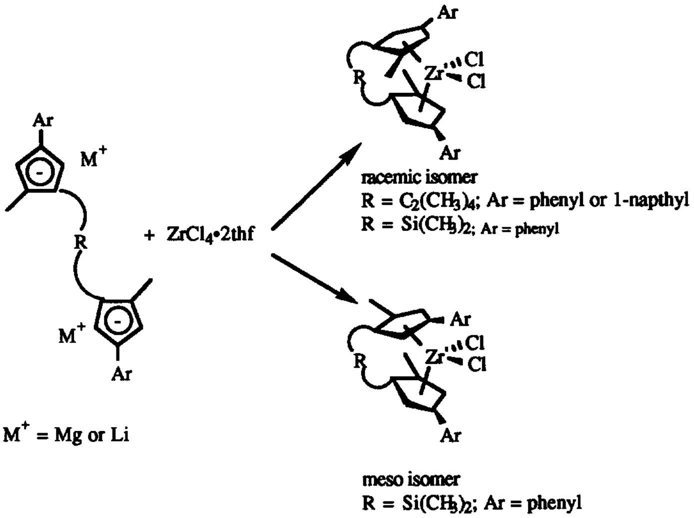
The chiral indene derivative (4*S*,5*S*)-*trans*-4,5-bis(1*H*-inden-3-ylmethyl)-2,2-dimethyl-1,3-dioxolane (H_2L) has been prepared after purification from optically pure 2,2-dimethyl-4,5-

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 $ZrCl_4$ to yield $ZrLCl_2$. The molecular structure of this chiral zirconium derivative (4) shows the dihedral angle between the indene rings to be 37° as a result of the bridging unit twisting one of the indene rings to one side. Hydrogenation of this complex with PtO_2 as catalyst gives the bis(4,5,6,7-tetrahydroinden-1-ylmethyl) derivative ZrL'_2Cl_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 β-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 ^1H NMR spectroscopy and X-ray crystallography. In contrast to other ansa-metallocenes bearing bulkier tertiary alkyl β-substituents, the interannular bridges were found to lie close to the rear extension of the $ZrCl_2$ bisector axes, and possess a much more accessible coordination site. In accord with this, very high activities as α-alkene polymerisation catalysts were observed for these aryl-substituted complexes [12].

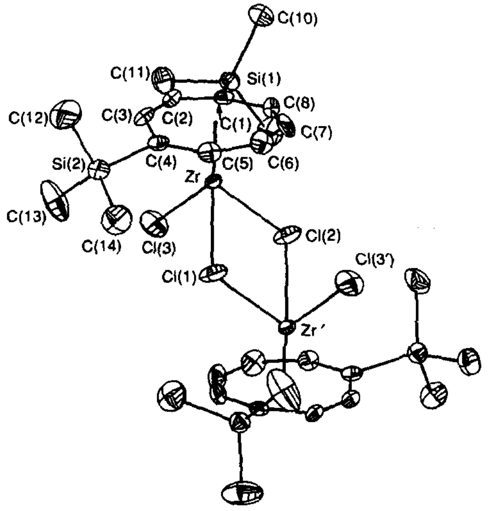


Scheme 4

The complex $Zr\{\eta^8\text{-}C_8H_6(SiMe_3)_2\}\{\eta^4\text{-}C_8H_6(SiMe_3)_2\}$ was prepared from reducing $C_8H_8(SiMe_3)_2$-1,4 with two equivalents of BuLi and then reacting with $[ZrCl_4(thf)_2]$. 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 C_8H_8 environment was observed in the ^1H NMR spectrum of $Zr(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)$. The zirconium metal centres act as Lewis acids and readily form adducts with thf, NH_3 and Bu^tNC; (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 η^8 and η^4 coordination mode of the cyclooctatetraene ligands although the distribution of the C-C bond lengths is not consistent with those found in $Fe(\eta^4-C_8H_8)(CO)_3$ or $Ru(\eta^4-C_8H_8)(CO)_3$. The zirconium-to-ring-carbon bond lengths in these structures increase on coordination of NH_3 or Bu^tCN indicating a weakening of the metal-to-C_8H_8 interaction [13].

An alternative to the study of $Zr(\eta^5-C_5H_5)X_2$ complexes is that of the half-sandwich monocyclooctatetraene zirconium derivatives $Zr(\eta^8-C_8H_8)Cl_2$. Both the solvated and non solvated forms are now readily synthesised from the reaction of $Zr(\eta^8-C_8H_8)(\eta^4-C_8H_8)$ with $ZrCl_4(thf)_2$. The bistrimethylsilylated derivative gave the structurally characterised complex $\{Zr(\eta^8-C_8H_6(SiMe_3)_2)Cl\}(\mu-Cl)_2$ which possesses a plane of symmetry that bisects the two bridging chlorine atoms as shown in structure (5) [14].



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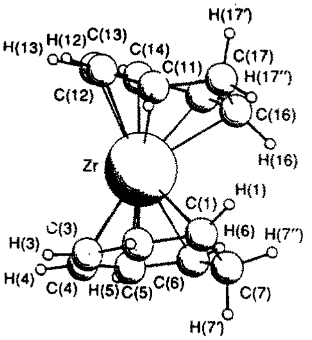
The structure of $Zr(C_8H_8)_2$ has been investigated using variable temperature solution and solid state NMR spectroscopy and X-ray crystallography. The X-ray crystal structure unequivocally shows that one C_8H_8 ring is η^8- and the other η^4-coordinated to the zirconium atom. The ^{13}C and ^1H NMR 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 kcal mol^{-1} in solution and >13.5 kcal mol^{-1} in the solid state. A second fluxional process involves 1,2-shifts of the $\eta^4-C_8H_8$ ring [15].

Reduction of $ZrCl_4$ with sodium amalgam in the presence of cycloheptatriene gives the complex $Zr(\eta^6-C_7H_8)_2$ (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°. On reaction with carbon monoxide, Sn_2Me_6 or *N,N,N',N'*-tetramethylethylenediamine, the compound $Zr(\eta^7-C_7H_7)(\eta^5-C_7H_9)$ was produced. The electronic structure of this complex has been investigated by PES and extended Hückel molecular orbital calculations. The complex $Zr(\eta^6\text{-}C_7H_8)_2$ reacts with PMe_3 or the didentate phosphine 1,2-bis(dimethylphosphino)ethane (dmpe) to give $Zr(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)(PMe_3)$ and $\{Zr(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)\}_2(dmpe)]$, respectively. These compounds have been extensively studied using ^{31}P, ^{13}C and ^{1}H NMR spectroscopies. Reaction of $Zr(\eta^6\text{-}C_7H_8)_2$ with the Lewis acid $(AlEt_2Cl)_2$ in thf for 1 week gave a compound proposed to be the zirconium dimer $(Zr(\eta^7\text{-}C_7H_7)(thf)(\mu\text{-}Cl)_2$ which acts as a good source of the $\{Zr(\eta^7\text{-}C_7H_7)\}$-fragment in subsequent reactions [16].



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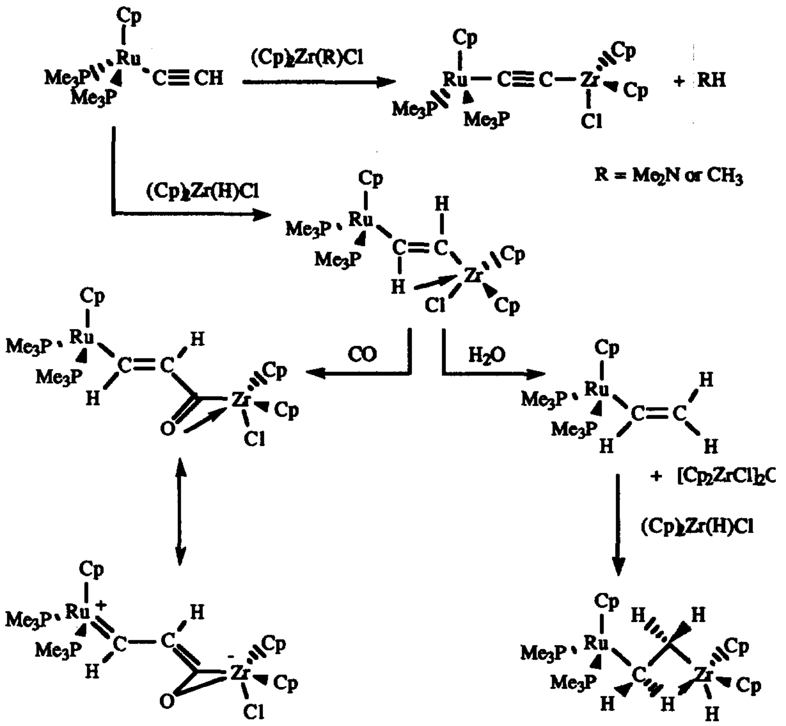
(6)

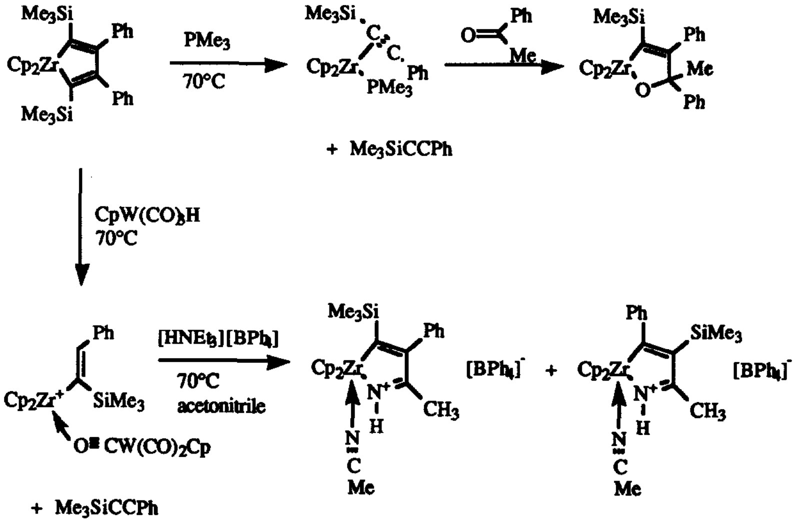
A series of dimetallic ruthenium/zirconium complexes of general formula $Cp(PMe_3)_2RuCH_nCH_nZrClCp_2$ (n = 0,1,2) have been prepared from $Cp(PMe_3)_2RuC{\equiv}CH$ (see scheme 5). Two of the products are $Cp(PMe_3)_2RuCH{=}CHZrClCp_2$ and $Cp(PMe_3)_2RuCH_2CH_2ZrClCp$ and each exhibits a three-centre two-electron agostic interaction between the zirconium and a CH that is β to zirconium atom. These complexes are important as they represent a rare example of a C_2-unit bridging an electron rich metal atom and an electron deficient metal centre. The spectroscopic and structural data on an η^2-acyl complex obtained on carbonylation of $Cp(PMe_3)_2RuCH{=}CHZrClCp_2$ 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 $Cp_2\overline{Zr(CSiMe_3CPhCSiMe_3C}Ph)$ 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 $Cp_2Zr(\eta^2\text{-}C(SiMe_3)C(Ph)$. This was evident from the spectroscopic characterisation of the products and the systematic loss of free $Me_3SiCCPh$ in each case. Reactions are summarised in scheme 6 [18].

When a slurry of $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZrCl_2]_2$ in thf is treated with an excess of $(\eta^3\text{-}C_3H_5)MgCl$ at room temperature, the dinuclear fulvalene zirconium allyl derivative *anti*-$[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\eta^1\text{-}CH_2CHCH_2)(\eta^3\text{-}CH_2CHCH_2)]_2$ is formed. The solid state structure of this complex shows the fulvalene to be planar and each zirconium atom to be coordinated to one η^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 η^1-η^3-allyl rearrangement. Attempts to prepare the complex $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZrR_2]_2$ (where R = tolyl) failed, spectroscopic data indicating the presence of $\eta^1{:}\eta^5\text{-}C_5H_4$ rings [19].

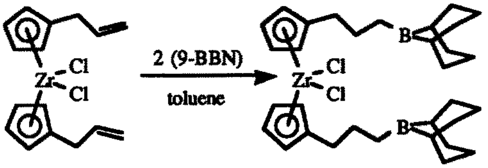


Scheme 5



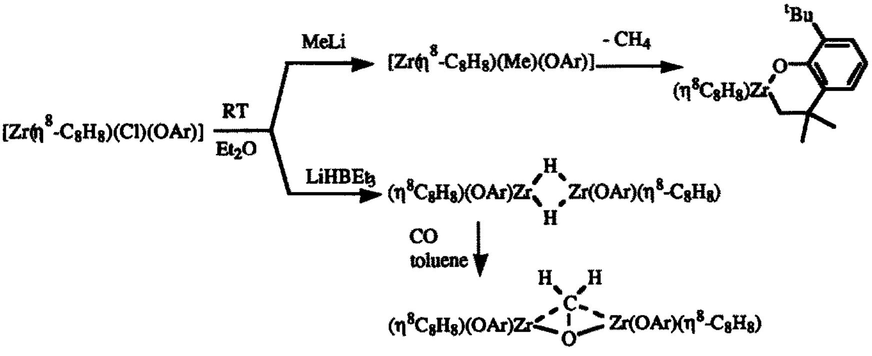
Scheme 6

The addition of 9-borabicyclo[3.3.1]nonane (9-BBN) to $(\eta^5\text{-}C_5H_4CH_2CH{=}CH_2)_2ZrCl_2$ yields $(\eta^5\text{-}C_5H_4(CH_2)_3(9\text{-BBN}))_2ZrCl_2$ (scheme 7). One of the Cp-bonded allyl ligands of this allyl cyclopentadienylzirconium dichloride couples with butadiene. Similar zirconium systems $[(\eta^5\text{-}C_5H_4CH{=}C(CH_3)R]_2ZrCl_2$ (R = CH_3, Ph) also undergo addition reactions with 9-BBN to give $[(\eta^5\text{-}C_5H_4CH(9\text{-BBN})CH(CH_3)R]_2ZrCl_2$ (R = CH_3 *rac/meso* ~ 1:1) (R = Ph, *threo/erythro* ~ 1:1). The mixtures of diastereoisomers were separated by fractional crystallisation [20].



Scheme 7

The yield of the complexes $Cp^*(R)ZrX_2$ ($Cp^* = (CH_3)_5C_5$, R = C_3H_5, X = Cl; R = 1,1,2-trimethylallyl, X = Br; R = 1,2,3-trimethylallyl, X = 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 Cp^*ZrCl_3 and their reactivity towards $[MCp(CO)_2]^-$ (M = Fe, Ru) and $LiCH_2PPh_2$ were investigated. The X-ray crystal structures of $Cp^*(\eta3\text{-}C_3H_5)ZrCl_2$ and $Cp^*(R')(\eta^2\text{-}CH_2PPh_2)Zr$ (R' = 1,2-dimethylbutadiene) are reported and the dynamic behaviour of the latter was examined by variable temperature ^1H NMR spectroscopy [21].

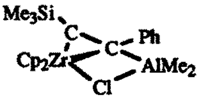


Scheme 8

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 C_5Me_4H exhibits an electron-donor effect greater than C_5H_5 and slightly weaker than C_5Me_5. A structural examination of the complex $(C_5Me_4H)_2Zr(Ph)Cl$ and the study of the ^1H and ^{13}C dynamic NMR properties of the compounds $(C_5Me_4H)_2MR^1R^2$ (M= Ti, Zr; $R^1 = R^2$ = Ph, $p\text{-}C_6H_4Me$; R^1 = Cl, Br; R^2 = Ph, $p\text{-}C_6H_4Me$) show that C_5Me_4H has a steric effect intermediate between C_5H_5 and C_5Me_5. The steric and electronic effects of C_5Me_4H 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 β-agostic complex $Cp_2ZrCl[C(SiMe_3)=CHPh$ reacts with trimethylaluminium to give a mixture of (η^2-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].



(7)

4.1.3 Complexes with ligands containing silicon

The complex $Cp_2Zr(\eta^2$-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-butylisocyanide 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].

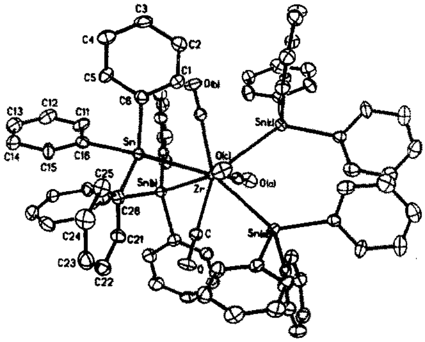
The first example of a metal silanimine complex has been prepared $Cp_2Zr(\eta^2$-$SiMe_2=N^tBu)(PMe_3)$. The single crystal X-ray structure of this complex shows the Zr-Si distance to be 2.654 (1)Å. This short bond length and correspondingly long Si-N distance of 1.687 (3)Å imply that the bonding of silanimine to the metal centre is best described as a metallacycle rather than a π-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 (η^2-$Me_2Si=N^tBu)(CO)$ 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-stannylene 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 π-donation from zirconium to tin. The room temperature ^1H NMR spectrum is consistent with the solid-state structure with two equivalent stannylene units. However at −30°C, the $SiMe_3$ resonance splits into three signals and this observation is interpreted in terms of rotation of one stannylene ligand into the Sn-Zr-Sn plane [27].

$$ZrCl_4{\cdot}2thf + 2NaC_{10}H_8 \xrightarrow{4PMe_3,\ 4Ph_3SnNa,\ CO} Na_2[(Ph_3Sn)_4Zr(CO)_4] + 2C_{10}H_8 \qquad (i)$$

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, ^1H, ^{13}C and ^{119}Sn NMR spectroscopy and single crystal X-ray crystallography [28].



(8)
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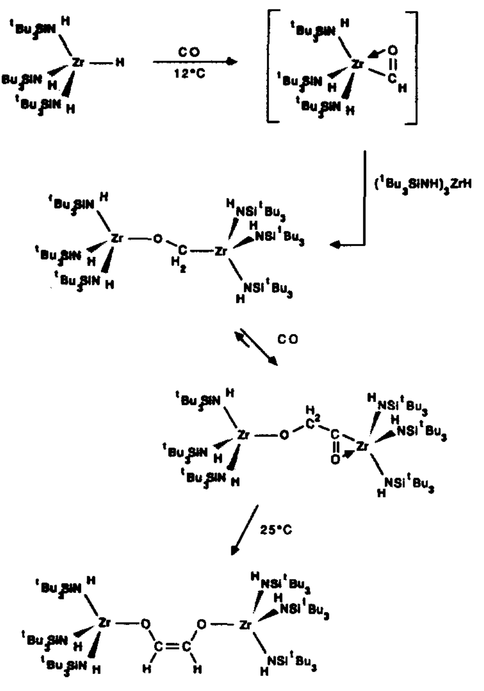
4.1.5 Complexes with nitrogen donor ligands

The zirconium(III) bridged chloride $(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\mu\text{-}Cl)Zr(\eta^5\text{-}C_5H_5)]_2$ readily absorbs atmospheric oxygen to give $(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\mu\text{-}O)(\eta^5\text{-}C_5H_5)ZrCl]_2$. This led to investigations into the reaction of this complex with diazo compounds $N_2{=}C(C_6H_5)_2$ (scheme 9), and isocyanides $[C{\equiv}NC(CH_3)_3]$ and organic azides $(Me_3Si)N_3$. 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-$CNC(CH_3)_3$ bond length (2.180 (2)Å) is similar to that observed in $[(\eta^5\text{-}C_5H_4CH_3)_2Zr(\mu_2\text{-}\eta^1{:}\eta^2\text{-}CC(C_6H_5)]_2$ (2.187Å) 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 $C{\equiv}NC(CH_3)_3$ yields the cyano complex $(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)(\mu\text{-}\eta^1{:}\eta^2\text{-}CN)Zr(\eta^5\text{-}C_5H_5)_2$ which was characterised from spectroscopic data [29].

Treatment of $ZrCl_4$ with 3 equivalents of ${}^tBu_3SiNHLi$ gives $({}^tBu_3SiNH)_3ZrCl$ which on methylation affords $({}^tBu_3SiNH)_3ZrCH_3$. 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 $(^tBu_3SiNH)_2Zr{=}NSi^tBu_3$ which rapidly adds H_2 across the imido linkage to give $(^tBu_3SiNH)_3ZrH$. The hydride resonance is downfield at δ 9.60 (C_6D_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}C and ^1H NMR spectroscopy (scheme 10) [30].

Scheme 9



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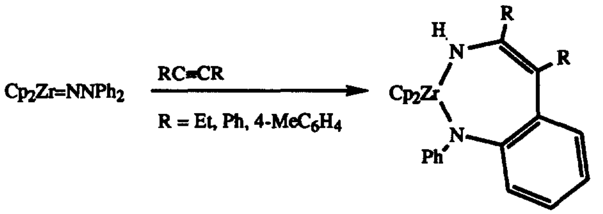
Scheme 10

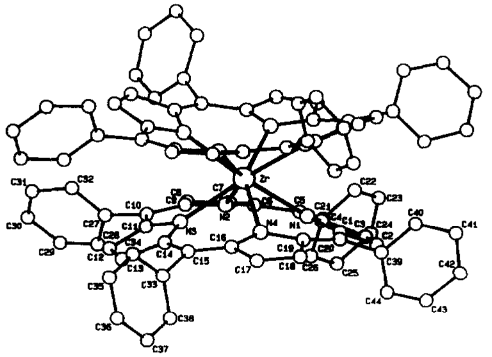
The first η^1-hydrazidozirconocene complex $Cp_2Zr{=}NNPh_2$ can be trapped with alkynes (scheme 11) or CO to give an unprecedented rearrangement which involves N-N bond cleavage. In the absence of any trap, this complex forms a bridging hydrazido dimer which has been crystallographically characterised. When the six-donor 4-(*N,N*-dimethylamino)pyridine (DMAP) is present, a monomeric hydrazido (2−) complex $Cp_2Zr(NNPh_2)(DMAP)$ is formed [31].



Scheme 11

Phosphine derivatives of zirconium complexes have been successfully synthesised and studied in which the hybrid chelating ligand $-N(SiMe_2CH_2PR_2)_2$ (R = Me, ^iPr, Ph) as a hard amide donor has been incorporated. The reactions of similar species of general formula $ZrCl_3[N(SiMe_2CH_2PR_2)_2$ 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 $\{[^iPr_2PCH_2SiMe_2)_2N]ZrCl\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$. This novel dinuclear dinitrogen complex is prepared from the addition of two equivalents of Na/Hg to $ZrCl_3[N(SiMe_2CH_2P^iPr_2)_2$ under an atmosphere of N_2 [32].

$$ZrCp_2Cl_2 + 2\,Li_2(P) \xrightarrow[200°C]{\text{trichlorobenzene}} Zr(P)_2 + 2\,LiCl + 2\,LiCp \qquad \text{(ii)}$$



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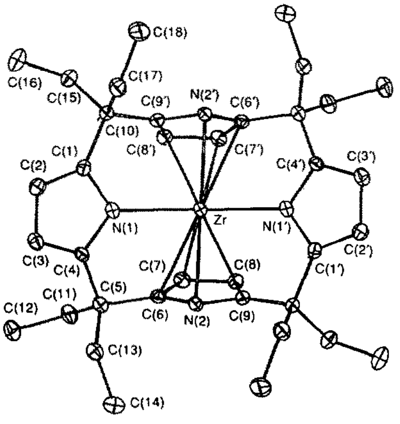
(9)

Two new zirconium bisporphyrinate double decker complexes $Zr(P)_2$ (PH_2 = $OEPH_2$ or $TPPH_2$) were synthesised according to equation (ii). The complexes were characterised by UV-VIS, near IR and ^1H NMR spectroscopies and cyclic voltammetry. These data indicate that there is a strong π-π interaction between the porphyrin ligands and the small zirconium(IV) centre. This is confirmed crystallographically by the solid state structure of $\mathrm{Zr(TPP)_2}$ (**9**) which has a sandwich-like structure with an average Zr-N distance of 2.4(1)Å and a porphyrin interplanar spacing (2.561Å) that is the shortest ever recorded for similar $\mathrm{M(porphyrinato)_2}$ complexes [33]. Both systems undergo two oxidations and two reductions, and can be chemically oxidised with phenoxathiinylium hexachloroantimonate to give the π-radical-cation complexes $\mathrm{[Zr(TPP)_2]^+[SbCl_6]^-}$ and $\mathrm{[Zr(OEP)_2]^+[SbCl_6]^-}$. The cationic species were spectroscopically characterised and the data for these, like their neutral parent compounds, indicate significantly strong overlap between the π-systems of the two porphyrin rings [34].

The synthesis and solid state structure of a meso-octaethylporphyrinogen zirconium(IV) complex (**10**) have been attained. The solid state structure shows that two of the pyrrolyl anions are η^5-bonded and two are σ-bonded *via* their nitrogen atoms to the zirconium metal centre. At room temperature two distinct signala are observed for the σ and η^5-pyrrolic protons in the ^{1}H NMR spectrum, but at 320K these collapse to a singlet suggesting fast exchange of the σ and η^5 forms of the pyrrolyl anion [35].



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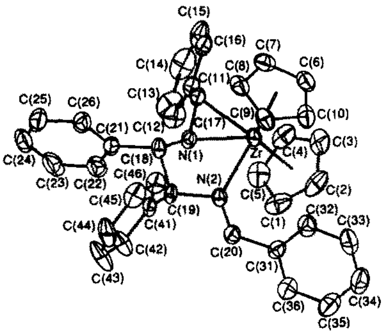
(10)

Deprotonation of $\mathrm{PhCH{=}NCH_2Ph}$ by KH in thf in the presence of 18-crown-6 led to the isolation of the 2-azaallyl anion-potassium ion pair $\mathrm{[PhCH{=}N{=}CHPh]^-\,[K(18\text{-}crown\text{-}6)]^+}$ which was oxidatively coupled to a diamino ligand by $\mathrm{Cp_2ZrCl_2}$ to form $\mathrm{Cp_2Zr(\eta^2\text{-}PhCH\text{-}N\text{-}CH(Ph)CH(Ph)\text{-}N{=}CHPh\text{-}\eta^1)}$ (**11**). The η^1-N bonded and η^2-C,N bonded imino groups are confirmed in the solid state structure of the complex [36].

Cationic molybdenum complexes readily undergo nucleophilic attack by zirconium amides to give π-allyl complexes. The mechanism is thought to involve nucleophilic attack by the polar Zr-N bond on the terminal carbon of the coordinated diene. The resulting cationic zirconocene amido complex then abstracts a fluoride from its $\mathrm{BF_4^-}$ counterion to give $\mathrm{Cp_2Zr(NRPh)F}$ or $\mathrm{Cp_2ZrMoF}$ and $\mathrm{BF_3}$. The reaction does not always involve the formation of Zr-F bonds however as illustrated in the example in scheme 12, from which the first zirconium complex with a primary amido ligand to be characterised crystallographically was obtained [37].



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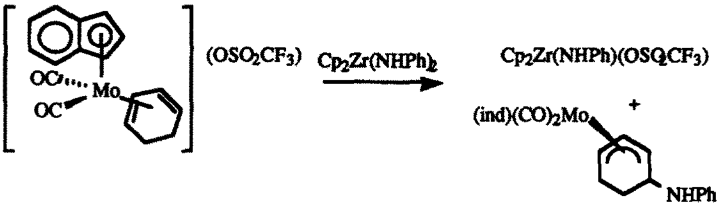
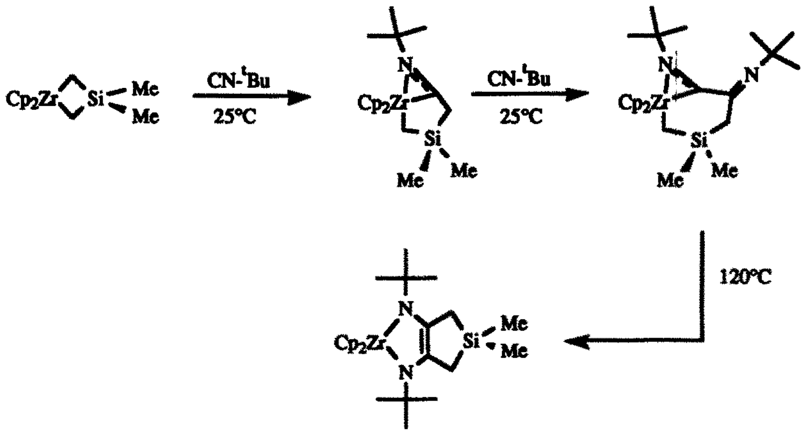


Scheme 12

The preparation, structure, spectroscopic and electrochromic properties of bis(phthalocyaninato)zirconium(IV) $Zr(Pc)_2$, have been reported. The attempted synthesis of this species from $Zr(OAc)_4$ instead of $ZrCl_4$ seemed to produce $Zr(Pc)(OAc)_2$ from comparison of its electronic spectrum with that of $Lu(Pc)(OAc)(H_2O)_2.H_2O.CH_2Cl_2$. The solid state structure of $Zr(Pc)_2$ 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 2.30Å) 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].

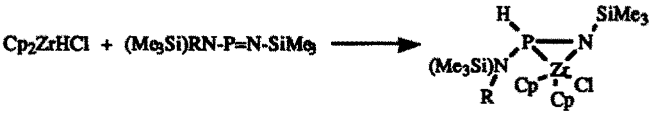
Insertion of one equivalent of CN^tBu into the complex $Cp_2Zr(CH_2SiMe_2CH_2)$ gives the thermodynamically stable η^2-iminoacyl complex $Cp_2Zr(N(CMe_3)CCH_2SiMe_2CH_2)$ (scheme 13). Addition of a second equivalent of CN^tBu proceeds by reductive coupling of the two CN^tBu *via* nucleophilic displacement of the original η^2-iminoacyl and not *via* breakage of the C(η^2-iminoacyl)-C(methylene) bond. The resulting complex $Cp_2Zr(N(CMe_3)C\text{-}C(=NCMe_3)(CH_2SiMe_2CH_2)$ 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 Cp_2ZrHCl 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.* $Me_3SiSO_3CF_3$ or $NaBPh_4$), 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 Cp_2MR^+ (M = Zr, Ti). In contrast, loss of cyclisation occurs on the addition of $Fe_2(CO)_9$, S_8, or 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].



(R = Me_3Si single crystal structure)

Scheme 14

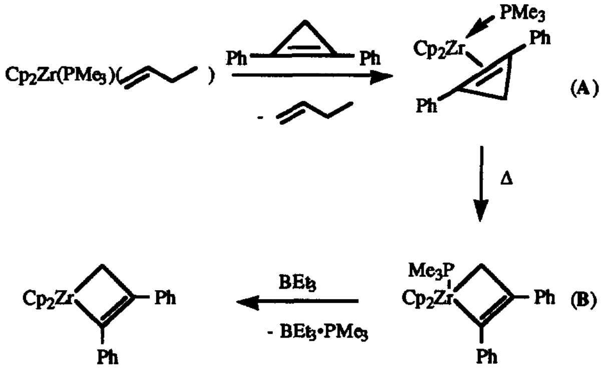
4.1.7 Complexes with phosphorus donor ligands

The reaction of methyl allyl Grignard or lithium reagents with Cp^*ZrX_3 gives increased yields of compounds of the type $Cp^*(allyl)ZrX_2$ (allyl = C_3H_5, 1,1,2-trimethylallyl, 1,2,3-trimethylallyl, X = Cl, Br) compared to the unsubstituted species. Cp^*(1,1,2-trimethylallyl)$ZrBr_2$ 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 ^1H NMR spectroscopy and revealed a η^3-η' allyl mechanism ($\Delta G^\ddagger = 66.2 \pm 1.0$ kJ mol^{-1}). Both 1,1,2- and 1,2,3-trimethylallyl zirconium complexes can be reduced by $K^+[CpM(CO)_2]^-$ (M = Fe, Ru) giving the Group 8 dimer $[CpM(CO)_2]_2$ and uncharacterised oils, and react with 2 equivalents of $LiCH_2PPh_2$ to give $Cp^*(\eta^4\text{-}2,3\text{-}Me_2(butadiene))(\eta^2\text{-}CH_2PPh_2)Zr$ and $Cp^*(\eta^4\text{-}1,2\text{-}Me_2(butadiene))(\eta^2\text{-}CH_2PPh_2)Zr$ respectively. The butadiene results from abstraction of an allyl terminal methyl proton by $PPh_2\text{-}CH_2$; free $MePPh_2$ is observed by NMR spectroscopy. Variable temperature ^1H NMR spectroscopy indicated that a dynamic process occurs in solution involving Zr-P bond rupture ($\Delta G^{\ddagger}$ = 38.9 ± 1.0 kJ mol^{-1}). The novel η^2-coordination mode of the CH_2PPh_2 ligand was confirmed in the solid state by X-ray crystallography, the bond lengths being Zr-CH_2 2.346(8)Å and Zr-PPh_2 2.66(2)Å respectively in the strained Zr-C-P ring [41].

$$2\ Cp_2ZrCl_2 + 1\ Mg(s) + (2,4,6\text{-}Me_3C_6H_2)PH_2 \xrightarrow{\text{thf, } 25^{\circ}C} \begin{array}{l}(Cp_2ZrCl)_2(\mu\text{-}P(2,4,6\text{-}Me_3C_6H_2))\\ +\ H_2(g)\ +\ MgCl_2(s)\end{array} \qquad (iv)$$

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 Zr_2P-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 $Cp_2Zr(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$. A similar reaction using $PCyH_2$ as the phosphine produces a tetranuclear ring system in which two zirconium atoms are bridged by two phosphide groups ($PCyH^-$), the Zr_2P_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 Cp^*ZrCl_2 and $CyPH_2$ appears from ^{31}P NMR spectroscopy to yield $Cp^*_2Zr(PHCy)H$ as well as $Cp^*_2Zr{=}PCy$ *via* H_2 loss [42].

The synthesis and crystal structure determination of $[Cp_2Ti(\mu\text{-}PEt_3)]_2$ 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 Cp_2Ti 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 ≤ 340 K is observed for the zirconium analogue [43].



Scheme 15

A (η^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}P, ^1H, and ^{13}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 metallocyclobutene derivative (B) [44].

The reaction of $(Me_3Si)_2NPPh_2NSiMe_3$ with $ZrCl_4$ yields $[ZrCl_3(Me_3SiNPPh_2NSiMe_3$-N,N')]•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].

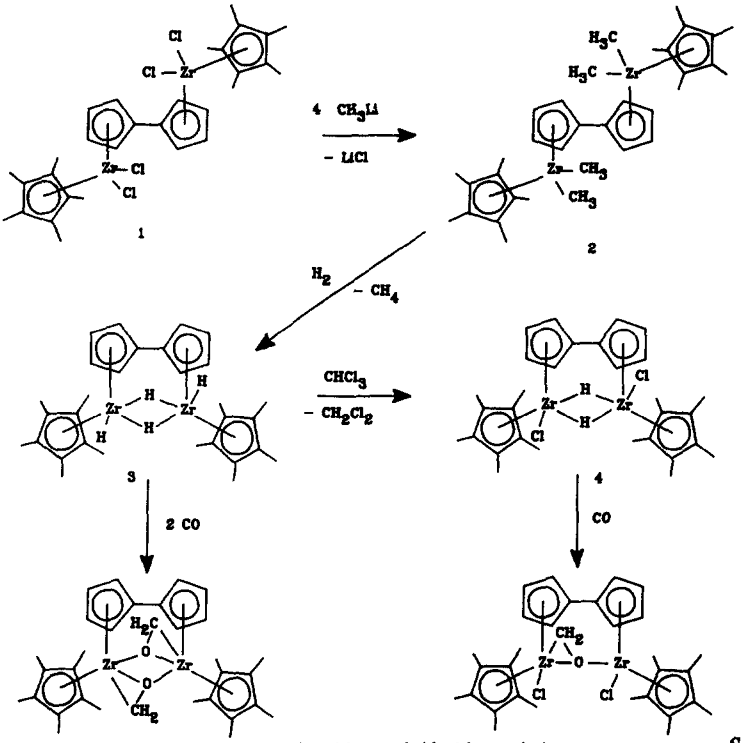
4.1.8 *Complexes with oxygen donor ligands*

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 Haltiwanger synthesised several hydride formaldehyde bridged fulvalene complexes $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[Cp^*ZrH_2]_2$, $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[Cp^*Zr(H)Cl]_2$, and $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[Cp^*ZrCl]_2(OCH_2)$ (scheme 16) which were examined by variable temperature ^1H NMR spectroscopy. At high temperature the latter complex appears to undergo rapid rotation bout the C-O bond, this is in contrast to the results obtained for $(Cp_2ZrCl)_2(\mu\text{–}OCHR)$ 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 $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[Cp^*Zr(OCH_2)]_2$ have been reported and show that the bond distances in this species are analogous to those of $[Cp_2Zr(OCH_2)]_2$ [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 $Na^+[CpM(CO)_2CO_2]^-$ (M = Fe, Ru) with zirconocene dichloride at low temperatures (scheme 17). The $(\eta^5\text{-}C_5H_5)(CO)_2RuCO_2Zr(Cl)(\eta^5\text{-}C_5H_5)_2$ adduct was more stable in benzene solution than was its iron equivalent, but both decomposed slowly to give the species $Cp_2M(CO)_4$ and $[Cp(Cl)Zr]_2(\mu\text{-}O)$. According to the infrared and ^1H and ^{13}C NMR spectroscopic results, protonation of the species with HBF_4 deoxygenates the coordinated carbon dioxide moiety and yields the complexes $[CpM(CO)_3](BF_4)$ and $[Cp_2(Cl)Zr]_2(\mu\text{-}O)$ [47].

The heterodimetallic ruthenium complex $Cp(CO)_2Ru(CO)_2Zr(Cl)Cp_2$ undergoes reduction to its $\mu\text{–}\eta^1(C){:}\eta^1(O)$ formaldehyde derivative $Cp(CO)_2Ru(CH_2O)Zr(Cl)Cp_2$ on reaction with two equivalents of $Cp_2Zr(H)Cl$ (scheme 18). A ^{13}C NMR spectroscopic study of this reaction shows that hydride transfer occurs at a ligated carbonyl ligand and not at the carboxylate (CO_2) ligand [48].

The volatile compound $ZrF_3(C_3F_7COO)$ can be prepared in a two step process from zirconium tetrachloride and C_3F_7COOH. Interest in this complex stems from its possible use as a precursor to ZrF_4 [49].



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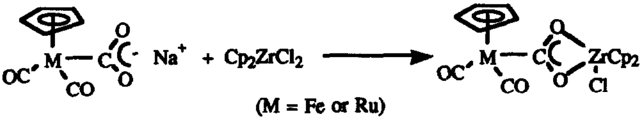
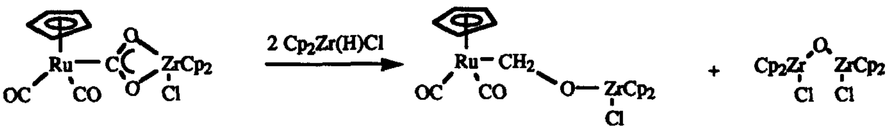
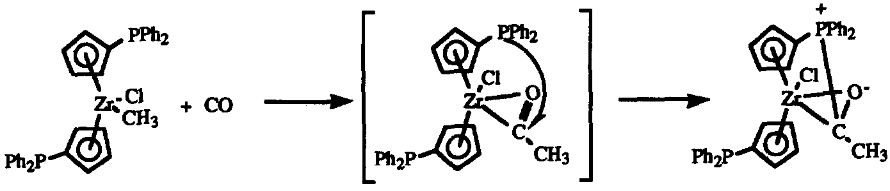
Scheme 16



Scheme 17



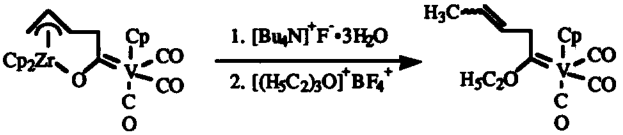
Scheme 18



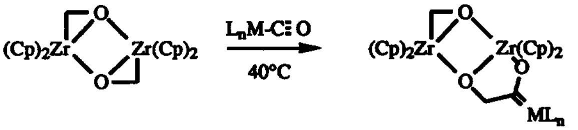
Scheme 19

The compound $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]_2ZrCl_2$ reacts with a 10% excess of methyl Grignard reagent to give $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]_2Zr(CH_3)_2$, which can be converted to its mono methyl analogue by $PbCl_2$ The carbonylation of these species does not give simple CO insertion into the Zr-CH_3 bond; a fluxional "acyl-phosphonium" moiety is formed due to the intramolecular attack of one of the ring bound phosphines on a transient acyl complex as shown in scheme 19. Neither phosphine is preferred and an associative interchange occurs at 30°C in dichloromethane-d^2 (activation energy = 61 kJ mol^{-1}). A single crystal structure determination of the "acyl-phosphonium" compound ($[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2][(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]Zr[\eta^2\text{-}(OC)CH_3]Cl$), shows several features of note. Firstly, the Zr-O bond is relatively long(2.065 (2)Å) suggesting that there is less $O_{p\pi}\text{-}Zr_{d\pi}$ back bonding than observed in comparable systems. Secondly, the tetrahedral geometry of the carbon atom derived from the CO molecule is distorted. The former feature is thought to be due to the presence of other donor atoms, the latter is a result of the η^2-binding of the CO-unit and the Zr-C-P-Cp ring geometry [50].

The compound (*S*-*trans*–η^4-butadiene)zirconocene adds to a carbonyl ligand of $CpV(CO)_4$ to give the [(π-allyl)-zirconoxycarbene]vanadium complex $Cp_2ZrOC[{=}VCp(CO)_3]C_4H_6$ which contains a seven-membered metallacyclic ring. Spectroscopic evidence suggests that in subsequent reaction with ketones, (*i.e.* acetone, acetophenone, methyl(vinyl ketone), acrolein or pivalonitrile), nine membered metalloxycarbene vanadium complexes such as $Cp_2ZrOC[{=}VCp(CO)_3]CH_2CH{=}CHCH_2C(CH_3)_2O$ containing a chiral trans-cycloalkene dioxametalla-*trans*-cyclonene framework are produced. The extrusion of the zirconium atom can be achieved by reaction with tetrabutylammonium fluoride trihydrate in thf (scheme 20) [51].



Scheme 20

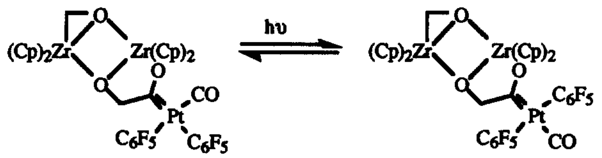


ML_n = $Mo(CO)_5$, $W(CO)_5$, $CpCo(CO)$, $CpRh(CO)$, $CpV(CO)_3$, $(C_6F_5)_2Pt(CO)$

Scheme 21

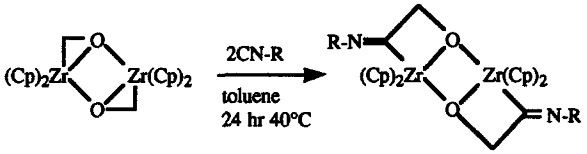
Having established a convenient two step synthesis for the formation of a metallacyclicoxirane dimer $[Cp_2ZrOCH_2]_2$ from Cp_2ZrHCl, Erker *et al.* have been able to produce a variety of metallacyclic heteroatom-stabilised carbene complexes in which one of the two Cp_2ZrOCH_2 metallaoxirane units react *via* insertion into the zirconium-carbon bond (scheme 21).

In most cases identical products were formed on photolysis and thermolysis, but two exceptions were found. Photolysis with $W(CO)_6$ 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].

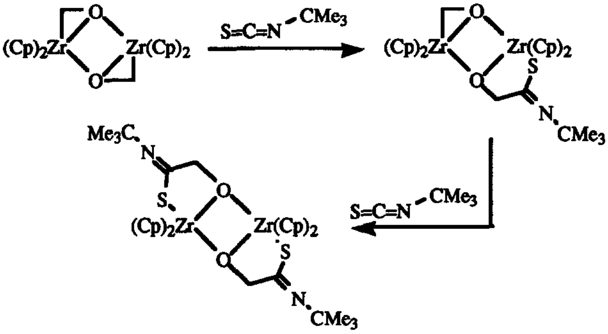


Scheme 22

In contrast to the formation of the metallaoxiranes, the reaction of $[Cp_2ZrOCH_2]_2$ with alkyl isocyanides (CN-R) (where R = CH_2SiMe_3, CH_2CMe_3, $CMe_2CH_2CMe_3$) results in double insertion to form C_{2h}-symmetric metallatricyclic complexes containing two (η^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 (η^2-formaldehyde)zirconocene dimer $[Cp_2ZrOCH_2]_2$ reacts with ^{t}butylisothiocyanate at 120°C by sequential insertion of the heterocumulene S=C bond into the metallaoxirane Zr-C linkages (scheme 24). The intermediate product of mono-insertion was detected by ^1H and ^{13}C NMR spectroscopies but the final product (a metallatricyclic dimer containing a Zr_2O_2 four membered ring system) was characterised by single crystal X-ray diffraction [54]. The same dimer $[Cp_2ZrOCH_2]_2$ reacts with less than stoichiometric quantities of BEt_3 to give an insoluble oligomeric zirconocene oxide $\{Cp_2ZrO\}_x$ 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 $(CH_2O)(ZrCp_2Cl)_2$. This proved a useful building block in preparation of the mixed metal dimer $Cp_2ZrCl(\mu\text{-}CH_2O)(Cp_2HfCl)$ 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 La^{3+} ion is coordinatively saturated by isoporpoxy bridges and/or internal chlorides [57].

$$\mathrm{LaCl_3{\cdot}3Pr^iOH + nK^+[Zr_2(OPr^i)_9]^- \longrightarrow [Cl_{3-n}La\{Zr_2(OPr^i)_9\}_n]_{(s)} + 3KCl_{(s)} + 3Pr^iOH}$$

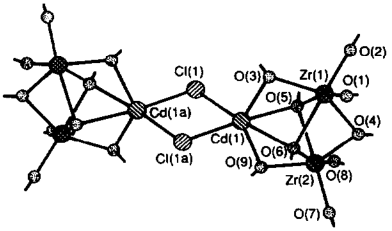
(where n = 1-3)

$$\mathrm{[Cl_nLa\{Zr_2(OPr^i)_9\}_{3-n}] + 2KOR \longrightarrow [(OR)_nLa\{Zr_2(OPr^i)_9\}_{3-n}] + 2KCL_{(s)}}$$

(where R = Pr^i, Bu^i, n = 1,2)

Scheme 25

The product of the reaction between equimolar amounts of $CdCl_2$ and $K[Zr_2(OPr^i)_9]$ in benzene is the dimeric species $\{Cd[Zr_2(OPr^i)_9(\mu\text{-}Cl)\}_2$ (**12**). The molecular structure of this complex was confirmed crystallographically and shows the dimer to consist of two triangular $[CdZr_2(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_3(OPr^i)_4]^+$ units linked by two chloride bridges, such that both metals have distorted octahedral geometry [58].



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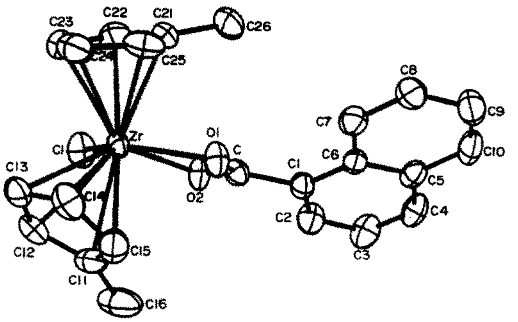
(12)

A new five-coordinate 18-electron complex $(CH_3C_5H_4)_2ZrCl(\alpha\text{-}C_{10}H_7COO)$ (**13**) was synthesised by reacting equimolar amounts of $(MeCp)_2ZrCl_2$ and sodium α-naphthoate. The solid state structure of this complex shows the α-naphthoxy ligand is didentate (Zr-O, 2.317 (2)Å, 2.260 (2)Å) [59].



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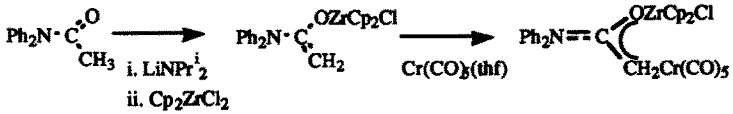
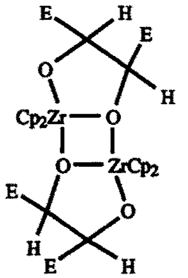
(13)

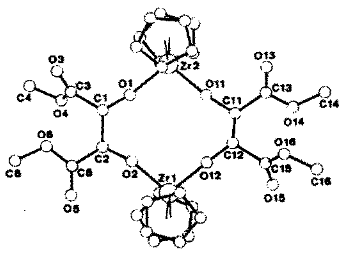
The zirconium amide enolate Ph_2N-$C(CH_2)OZr$-$(\eta^5C_5H_5)_2Cl$ has been synthesised (scheme 26) and structural characterisation shows that the oxygen atom of the enolato anion is bonded to the zirconium centre. The Zr-O bond (1.976(3)Å) lengthens on reaction of the methylene carbon centre with $Cr(CO)_5(thf)$. The resulting complex has the amide enolato *O*-bonded to zirconium centre (Zr-O 2.045(3)Å) and *C*-bonded to chromium centre (Cr-C 2.329(5)Å) [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 ^1H NMR spectroscopic evidence for exchange involving the CH(E)CH(E)-units (E = CO_2CHMe_2) (activation barrier = 12±1 kcal mol^{-1} at 255 K). The dynamic behaviour of racemic chiral and mesomeric achiral diastereomeric (tartrato)zirconocene dimers was shown to be quite different. The NMR spectra of the meso compounds were consistent with a ten membered dimetallocyclic structure. In solution, the -CO_2CH_3 derivative possesses the C_2-symmetric dimetallotricyclic structure but the solid state structure is that of the ten membered dimetallomonocycle (**15**) [61].





(14)

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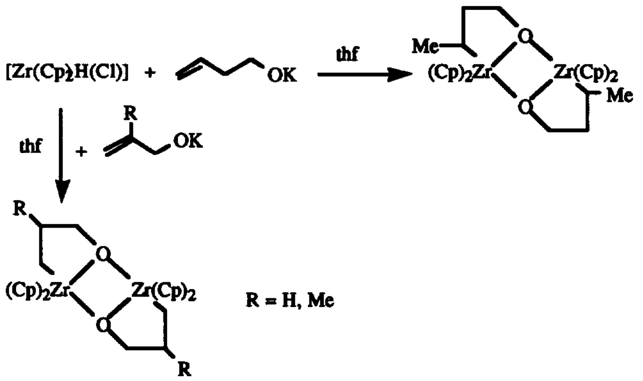
(15)

The reaction of $(Me_3C)_2Si(OH)_2$ with $ZrCl_4$ 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 $Zr_2Co_4(\mu_6\text{-}O)(\mu_2\text{-}OC_3H_7)_8(OC_3H_7)_2(acac)_4$ have been reported. The complex crystallises as discrete hexanuclear molecules with the oxygen atoms of the $Zr_2Co_4O_{19}$ 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 μ_6-O atom is located [63].

The reaction of $ZrCl_4$, CO_2 and NHR_2 in toluene resulted in the formation of the *N,N*-dialkylcarbamato zirconium complex $[Zr(O_2CNR_2)_4]$ (R = Et, isopropyl). Reaction of this complex with hydrogen halides resulted in salts of general formula $[Et_2H_2N]_2{}^+[ZrX_6]^{2-}$ (X = Cl, Br, I) [64].

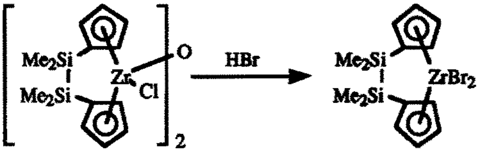
The dimeric five coordinate zirconacycles $[\{ZrCp_2(OCH_2CHRCH_2)\}_2]$ (R = H, Me) and $[\{ZrCp_2(OCH_2CH_2CHMe)\}_2]$ were formed from the intramolecular hydrozirconation of $ZrCp_2HCl$ with potassium allyl or homoallyl alcoholates (scheme 27). The solid state structures of the latter and the monomeric complex $[Zr(C_6Me_5)_2(OCH_2(CH_2)_2CH_2)]$ were obtained. This monomeric zirconacycle 1-oxa-2-zirconacyclohexane, and its analogue 1-oxa-2-zirconacyclopentane were prepared from reacting $Zr(C_5Me_5)_2Cl_2$ with the Normant Grignard reagents $ClMg(CH_2)_xOMgCl$ (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 μ-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-η^5-dicyclopentadienylzirconium dibromide has been synthesised by bromination of zirconocenophane with HBr (scheme 28), and characterised by X-ray crystallography [67].

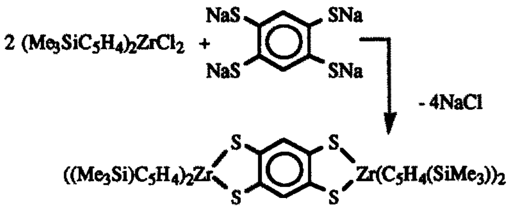


Scheme 28

Bis(η^5-pentamethylcyclopentadienyl)zirconium dialkyls of general formula $Cp^*{}_2Zr(R)(R')$ ($R = CH_3$, CH_2Ph, $CH_2C(CH_3)_3$, $R' = R$, 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(η^5-cyclopentadienyl)zirconocenes [68].

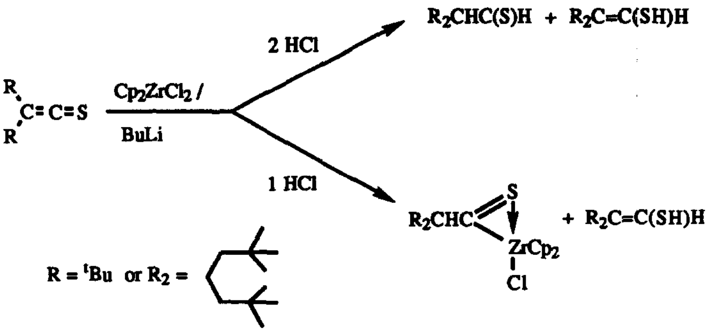
4.1.9 Complexes with sulfur donor ligands

The dinuclear chelate-bridged complex formed in the reaction shown in scheme 29 was characterised from IR and ^1H NMR spectroscopies and mass spectrometry. A single crystal X-ray structure of the hafnium analogue was obtained and showed the bridging $HfS_2C_6H_2S_2Hf$ moiety to have a chair-like conformation with the HfS_2 planes inclined by 47° with respect to the $S_2C_6S_2$ plane [69].



Scheme 29

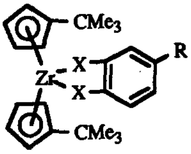
The addition of zirconocene reagents to thioketenes followed by acidolysis offers a novel route to thioaldehydes and their enethiol isomers in conjunction with η^2-thioacyl complexes of zirconium (scheme 30). The thioacyl group was confirmed to be η^2-CS-bonded to the zirconium centre from an X-ray crystallographic study of the metallacycle with $R_2 = (^tBuCH_2)_2CH$. Interestingly, although the solid-state structure shows the thioacyl to be bonded in the *S*-outside configuration in this complex, the ^{13}C NMR spectrum of the t-butyl analogue implies the presence of both the *S*-outside and *S*-inside conformers with two low field η^2-acyl resonances at δ 369.91 and δ 380.75 [70].



Scheme 30

A tetradentate Schiff's base $C_{30}H_{26}N_4S_4$ formed from the condensation of benzyldithiocarbazate and benzil was reacted with $Zr(NO_3)_4.4H_2O$ in a basic solution of H_2O_2 to give the comple $Zr(O_2)(C_{30}H_{24}N_4S_4)$. 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 ν(O-O) modes of the $M(O_2)$ unit shows that this decreases with an increase in metal atomic number (M = Zr, Th, Mo, W, V) [71]. Other complexes of zirconium containing the tetradentate Schiff's bases have also been studied [72].

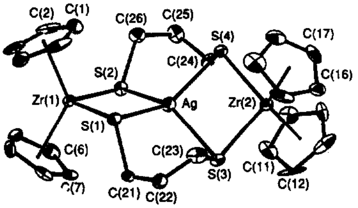
The reaction of the appropriate organolithium reagent with bis(tert-butylcyclopentadienyl)zirconium dichloride gives *para*-substituted diphenylzirconocenes $(^tBuCp)_2Zr(p\text{-}C_6H_4R)_2$ (R = Br or NMe_2). Heating these complexes results in the elimination of bromobenzene or N,N-dimethylaminobenzene to give aryneziroconocenes into which two chalcogen atoms can be inserted *e.g.* $(^tBuCp)_2ZrX_2(C_6H_4R)$ (**16**) (X = S or Se). When attacked by electrophiles, these dichalcogenated zirconacycles result in the formation of new functionalised dichalcogenated benzenic compounds e.g. $3,4\text{-}(NCCH_2)_2C_6H_3NMe_2$ [73].



(16)

Powder X-ray diffraction has been used to study the complex barium zirconium sulfides, Ba_2ZrS_4 and $Ba_3Zr_2S_7$, produced from the reaction of CS_2 with a mixture of $BaCO_3$ and $BaZrO_3$ [74].

The bridged zirconocene pentasulfide chelate $((CH_3)_2SiC_5H_4)ZrS_5$ has been synthesised and its structure postulated from ^1H NMR spectroscopy [75]. The sulfur coordinated bimetallic macrocycle $Cp_2Zr(\mu\text{-}SCH_2CH_2CH_2S)_2ZrCp_2$ is formed on reaction of Cp_2ZrMe_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)Å apart. Further reaction of this macrocyclic compound with $AgBPh_4$ produces the novel silver bound species $[Cp_2Zr(\mu\text{-}SCH_2CH_2CH_2S)_2ZrCp_2Ag](BPh_4)$ (**17**) in which the silver atom has flattened tetrahedral symmetry, and the zirconium atoms are 6.613(1)Å apart [76].



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(17)

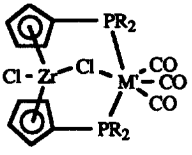
The reaction of $Me_2NC(S)SN(SiMe_3)_2$ with $ZrCl_4$ yields the dithiocarbamate complex $ZrCl_3\{Me_2NC(S)S\}$. The solid state structure of this complex has been confirmed crystallographically [77]. The preparation of $\{Cp_2ZrCl\}_2(dto)$ ($dtoH_2$ = dithiooxalic acid) was achieved by reacting Cp_2ZrCl_2 with potassium dithiooxalate in CH_2Cl_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 $[CpZrCl_3]$ with $S(SiMe_3)_2$. The solid state structure of this complex shows that each discrete $[Cp_6Zr_6S_9]$ molecule consists of a Zr_6 octahedron coordinated by μ_3-S ligands. In the centre of this metal octahedron is an additional μ_6-S atom [79].

The structure of bis(η^5-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 2.789Å). 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 $MM'Cl(\mu\text{-}Cl)(\mu\text{-}C_5H_4PR_2)_2(CO)_3$ (**18**), (M= Ti, Zr; M' = Cr, Mo, W; R = C_6H_5, $4\text{-}C_6H_4CH_3$) was synthesised from the reaction of $MCl_2(C_5H_4PR_2)_2$ and $M'(CO)_3L_3$ (L = acetonitrile, CO, $P(OMe)_3$). Methyl sulfide (MeS^-) ligands substitute both for terminal and bridging chloride ligands to give the complexes $MM'(SMe)(\mu\text{-}SMe)(\mu\text{-}C_5H_4PR_2)_2(CO)_3$ which are inert towards CO or $P(OMe)_3$ [81].



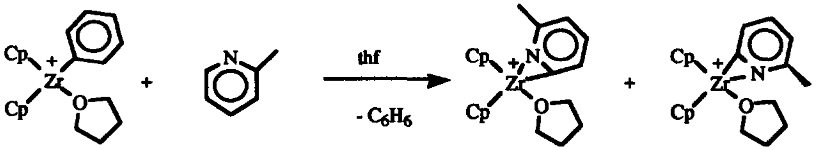
(**18**)

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 3.649Å) 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_3 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

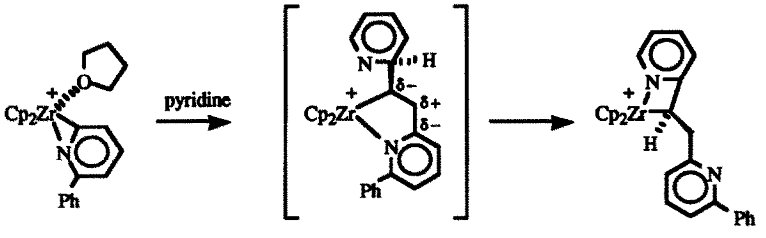
The reactions of isolable $[Cp_2Zr(R)(L)]^+$ compounds with unsaturated substrates are of interest firstly, for comprehension of the factors that influence the rates of insertion and β-H elimination reactions, and therefore chain propagation and chain transfer reactions in polymerisation processes and secondly, for development of other related stoichiometric and catalytic C-C bond forming reactions.

Current interest in the chemistry of $[Cp_2Zr(R)(L)]^+$ complexes is motivated by the proposed role of closely related 14-electron $[Cp_2Zr(R)]^+$ ions in Cp_2ZrX_2-based Ziegler-Natta alkene polymerisation catalyst systems. The reactivity of the neutral species $Cp_2Zr(R)_2$ (R = CH_3, CH_2Ph, Ph) with $[Cp^*{}_2Fe](BPh_4)$ has been explored showing oxidative Zr-R bond cleavage for the CH_3 and CH_2Ph derivatives to give $[Cp_2Zr(R)(thf)](BPh_4)$. The diphenyl neutral complex forms $[Cp_2Zr(Ph)(thf)]^+$ on reaction with $[HN(CH_3)_3Ph](BPh_4)$ and undergoes nucleophilic thf ring opening on reaction with $[HN(CH_3)_3](BPh_4)$. 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 $[Cp_2Zr(Ph)(thf)]^+$ reacts rapidly with a variety of reagents such as 2-methylpyridine (scheme 31) and PMe_3 [83].

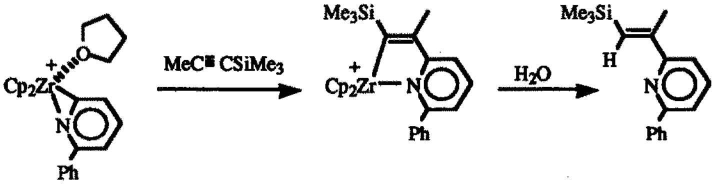


Scheme 31

The cationic zirconium(IV) complex $[Cp_2Zr(Me)(thf)]^+$ reacts selectively with a variety of pyridines, pyrazines and related substrates *via* ortho C-H activation to yield new three membered azametallacycles *e.g.* $[Cp_2Zr(\eta^2\text{-(CN)-\{6-phenyl-pyrid-2-yl\}})(thf)]^+$ (scheme 32). Once formed this cationic complex undergoes 1,2-insertion with α-olefins $H_2C{=}CHR$ (where R is an electron donating substituent R = allyl, CH_2SiMe_3, CH_2OR) to afford β-substituted five-membered metallacycles. 2,1-Insertion however, leading to α-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 α negative charge on the polar transition states and the products. Symmetric terminal alkenes also insert regioselectively to yield α-substituted unsaturated five membered metallacycles, but the unsymmetrical 2-hexyne affords a mixture of regioisomers, and silylacetylene $MeCCSiMe_3$ yields an α-$SiMe_3$ substituted metallacycle (scheme 33) [84].



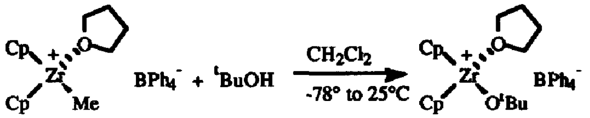
Scheme 32



Scheme 33

Interest in the synthesis of thf adducts of $[Cp_2ZrMe]^+$ stems from the fact that the isolated cations participate as catalysts in Ziegler-Natta alkene polymerisation. In order to synthesise such species, the ring opening of $L_nZr(CH_2SiMe_2CH_2)$ ($L_n = (C_6H_5)_2$, $SiMe_2(C_5H_4)_2$, $(C_5Me_5)_2$) by protonation of a methylene group using $[NEt_3H](BPh_4)$ was investigated. The resulting (trimethylsilyl)methyl substituted metal alkyl tetraphenylborate salts $[L_nZr(CH_2SiMe_3)(thf)](BPh_4)$ were characterised using ^1H and ^{13}C NMR spectroscopy. The α-CH_2 resonances of the perpendicularly coordinated thf molecules are shifted upfield for all these complexes except $[Cp^*_2Zr(CH_2SiMe_3)(thf)]^+$, and is thought to be due to the shielding provided by the π-electrons of the Cp rings. The exception is verified by the molecular structure of $[Cp^*_2Zr(CH_2SiMe_3)(thf)]^+$ obtained using X-ray diffraction methods. Here the Cp* ligands have a significant stereoelectronic influence resulting in the weak binding of the thf ligand, the Zr-O bond (2.243(3)Å) and its parallel orientation with respect to the equatorial plane of the metallocene wedge. The preparation of the isolated thf-free cation $[Cp^*_2Zr(CH_2SiMe_3)]^+$ was attempted by using a bulkier protonating agent $[N(n\text{-butyl})_3H](BPh_4)$ in toluene. This reaction however led instead to the formation of the Zwitterionic complex $Cp^*_2Zr(+)$-(μ-C_6H_4)-B(−)PPh_3. The catalytic behaviour of all these species towards ethylene polymerisation is reported [85].

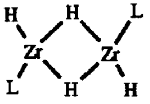
A cationic alkoxyzirconocene complex can be synthesised in high yield (scheme 34) and it can act as a Lewis acid catalyst for the regioselective Diels-Alder reaction of methyl acrylate with isoprene or cyclopentadiene. The structural data on this cationic complex indicate significant *pπ-dπ* back donation to the electron deficient metal centre as the oxygen of the tert-butoxide ligand is approximately sp hybridised and the Zr-O bond distance is only 1.899(3)Å. Further evidence is obtained from the rate of exchange of free and bound thf, deduced from variable temperature ^{13}C and ^{1}H NMR spectroscopic data and the 'in-plane' conformation of the thf ligand [86].



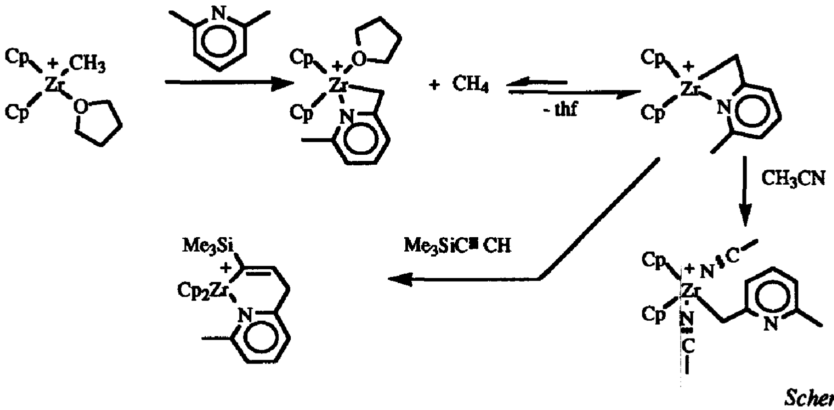
Scheme 34

The cationic complexes $[Cp_2Zr(R)(CH_3CN)_n]^+$ (R = H, Ph, CH_3, η^2-CH_2Ph) undergo single irreversible insertion of CH_3CN to yield the azaalkenylidene complexes $[Cp_2Zr\{N{=}C(R)(CH_3)\}(CH_3CN)]^+$ in which the qualitative trend in R migration as determined from kinetic and NMR spectroscopic studies is H, Ph (rapid at 23°C) >> CH_3>> η^2-CH_2Ph (no reaction at 60°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(η^5-4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride ($LZrCl_2$). This complex reacts with two equivalents of $Na[Et_3BH]$ in benzene to give the hydride complex $\{LZrH\}_2(\mu\text{-}H)_2$ (**19**) which has a characteristic room temperature ^1H NMR spectrum exhibiting two distinct triplet resonances for the bridging and terminal hydride ligands (δ 5.16 and −1.29). Reaction of this hydride with a weak acid (here $PhMe_2NH^+$) gives a soluble hydride cation $[LZr(H)(NPhMe_2)]^+$ 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].



(19)



Scheme 35

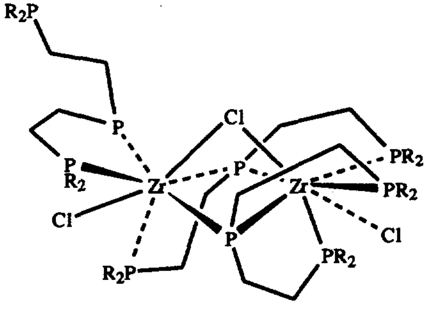
The four membered cationic azazirconacycle $[Cp_2Zr(\eta^2\text{-N,C-CH}_2\{6\text{-Me-pyrid-2-yl}\})]^+$, which exists in solution in its predominantly thf dissociated form (scheme 35), undergoes facile 1,2-insertion reactions with alkenes and alkynes to afford six-membered metallacycles. These reactions provide the basis for the Zr-mediated functionalisation of the methyl C-H bands of 2,6-lutidine. Treatment of the cation with CH_3CN however yields a thermally sensitive bis-CH_3CN 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 $[Cp'_2ZrMe](BPh_4)$ (Cp'_2 = *rac*-$C_2H_4(\text{indenyl})_2$, *rac*-$C_2H_4(\text{tetrahydroindenyl})_2$, or Cp' = $(Me_3C)C_5H_4$, $(Me_3Si)C_5H_4$) have been prepared. In all cases the low temperature ^1H 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 ^1H and ^{13}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 $Zr_2Cl_3\{(P(CH_2CH_2PMe_2)_2\}_3$ (**20**), ($Zr_2Cl_3(ppp)_3$), has been synthesised from the reaction of $ZrCl_4$ with three equivalents of the lithium salt Li[ppp] of the multidentate phosphido ligand. The diamagnetic nature of the compound is thought to be due to interaction between the zirconium atoms (Zr-Zr distance 3.361(2)Å) or spin pairing *via* the phosphido bridges. The $^{31}P\{^1H\}$ 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

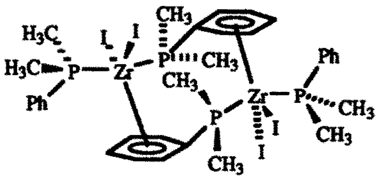
Recent studies show zirconium(III) to be unstable with respect to disproportionation into zirconium(IV) and zirconium(II). This process depends on the nature of the substituents and in some cases whether stable zirconium(III) derivatives can be isolated.

The diamagnetic zirconium(III) chloro complex $(Me_2SiCp_2)ZrCl)_2$ was synthesised in 65-75% yield by reduction of the metal dichloro derivative $(Me_2SiCp_2)ZrCl_2$ with one equivalent of Na/Hg. The presence of two cyclopentadienyl rings bridged by an interannular Me_2Si 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 $[(Me_2SiCp_2)ZrCl]_2(\mu\text{-}O)$ that disproportionates to Cp_2ZrCl_2 and uncharacterised oxozirconium(IV) species [92].

4.3 Zirconium(II)

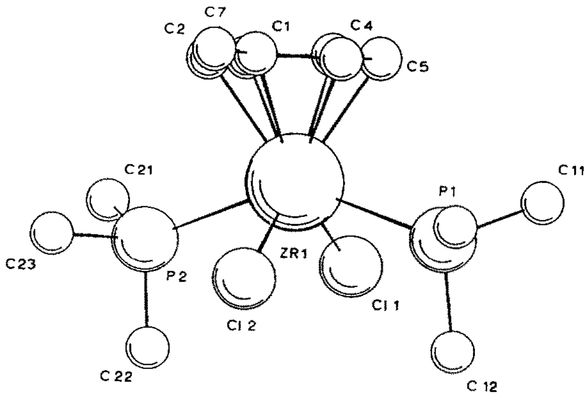
4.3.1 Complexes with phosphorus donor ligands

The reduction of ZrI_4 with Na/Hg amalgam and subsequent addition of 2 equivalents of PMe_2Ph yields a novel zirconium(II) dimer $Zr_2I_4(\eta 6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$ (**21**) in which the central ZrI_2P_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} σ-type orbital on the zirconium and a formerly $e_2\pi^*$ orbital on the arene. A single crystal X-ray structure of the $Hf_2Br_4(\eta 6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$ 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].



(21)

When a solution of $ZrCl_4$ in toluene at −78°C is treated with one equivalent of $Me_2NCH_2CH_2NMe_2$, two equivalents of sodium amalgam and an excess of cycloheptatriene, the novel η-arene complex $Zr(\eta^7\text{-}C_7H_7)(Me_2NCH_2CH_2NMe_2)Cl$ was formed. The complex $Zr(\eta^6\text{-}C_6H_5Me)(PMe_3)_2Cl_2$ (**22**) was prepared in a similar one-pot synthesis and its molecular structure was obtained. Reaction of the latter with $Li[BH_4]$ gave a bis(borohydrido) derivative which appeared to be fluxional in solution; only one signal was observed in the ^1H NMR spectrum for the eight hydrogen atoms even at 183K [94].



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(22)

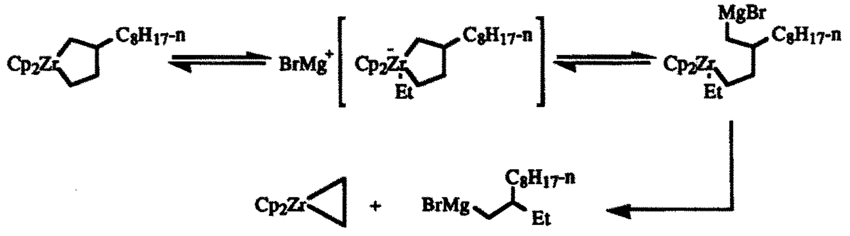
4.3.2 Complexes with chloride ligands

The compound $Zr(\eta^6\text{-benzene})(AlCl_4)_2$ 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 $AlCl_3$. The HMDB formed undergoes isomerisation to hexamethylbenzene. In contrast the reaction of the zirconium(II) arene species with diphenylacetylene forms a seven membered metallocycle $[\overline{\text{ZrCPh(CPh)}_4\text{CPh}}][(\mu\text{-Cl})_2\text{AlCl}_2]_2$ 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].

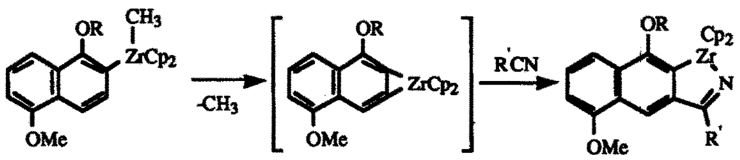
4.4 Zirconium complexes as catalysts

The catalytic addition of ethylmagnesium chloride to simple alkenes using Cp_2ZrCl_2, Cp_2ZrBu_2 or Cp_2ZrEt_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 $Cp_2Zr(CH_2CH_2)$ (scheme 36) has been isolated as its 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 napthalynes are trapped *in situ* with nitriles (scheme 37). These compounds can be converted into ketones, α-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].

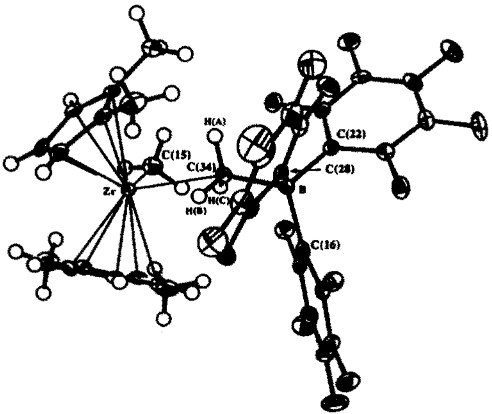


Scheme 36



Scheme 37

A crystallographically characterised "cation-like" zirconocene polymerisation catalyst has been synthesised in which a $[(1,2\text{-}(CH_3)_2C_5H_3)_2ZrCH_3]^+$ cation coordinates to the anion $[CH_3B(C_6F_3)_3]^-$ *via* a non-linear, highly unsymmetrical, Zr(μ–CH_3)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].



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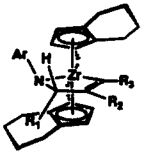
(23)

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].



Ar = Ph
R_1 = n-Bu; $R_2 = R_3 = CH_3$
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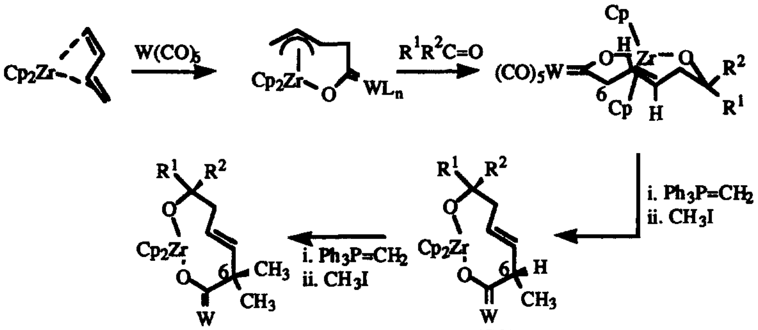
(24)

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.* $Cp_2ZrOC[=W(CO)_5]CH_2CH=CHCH_2CR^1R^2O$ ($R^1 = R^2 = CH_3$, or $R^1 = CH_3$, $R^2 = C(CH_3)_3$), which possess a *trans* C=C bond in the ring. Deprotonation of these systems by the ylide $Ph_3P=CH_2$ at the α-position to the carbene carbon centre gives a chiral unconjugated metallic carbene complex anion which on alkylation stereoselectively at C_6 yields the predominately (2*R**, 6*S**)(4,5,6-p*S**) configurated 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 ($R^1 = CH_3$, $R^2 = C(CH_3)_3$) in the presence of diazomethane gives an enol ether with conservation of the stereochemistry introduced at the metallacyclic starting material [105].



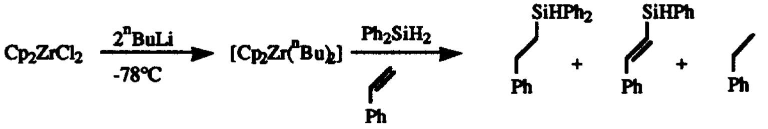
Scheme 38

The non-stereospecific catalysis of the polymerisation of propene using Cp_2ZrCl_2/methylaluminoxane 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 ^1H and ^{13}C NMR spectroscopy and size exclusion chromatography. The polypropene 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 = ^{t}Bu, 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, ^{n}Bu) 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].

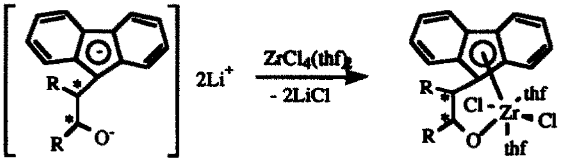
There has been increasing interest in the applications of bimetallic catalytic systems with differing electron densities on the two metal centres *e.g.* d^0-d^8 Zr(IV)-Rh(I). In these systems it is thought both metallic centres can activate carbon monoxide and that a hydrogen atom can migrate from the 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 hydrosilation 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 hydrosilation 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 β-methylstyrene are converted to the corresponding silated 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 $Cp_2ZrSi(\mu\text{-}H)_2(Ph_2Si)ZrCp_2$. This species was structurally characterised and proved inert to 1-octene and therefore not an intermediate in the hydrosilation process. In contrast, treatment of a second cyrstallographically characterised species, $Cp_2Zr(PMe_3)(H)(SiHPh_2)$ isolated from the reaction of $Cp_2Zr(n\text{-}Bu)_2$, 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°C [111].

Investigations into the reactions of chiral bridged mono(η^5-fluorenyl)zirconium(IV) complexes of general type $[C_{13}H_8\text{-}CHR\text{-}CHR\text{-}O]ZrCl_2(thf)_2$ (CHR-CHR = cyclohexyl, cyclopentyl, 1,2-diphenylethyl) have shown these complexes to catalyse the polymerisation of ethene in the presence of $Al(CH_3)_3$. They were prepared from the reaction of symmetrically substituted epoxides with fluorenyllithium and then subsequent reaction with $ZrCl_4(thf)_2$ as shown in scheme 40 [112].



Scheme 40

Four chiral bent metallocene complexes of general formula $(Cp\text{-}CHR^1R^2)_2ZrCl_2$ 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 β-hydride transfer from alkyllithium reagents $LiCH_2CHRR'$ (R,R' = H, alkyl, aryl) gave $[CpCH(CH_3)Cy]Li$ which on subsequent reaction with $ZrCl_4$ resulted in a 1:1 mixture of the $[Cp\text{-}CH(CH_3)Cy]_2ZrCl_2$ diastereomers. The chiral complex *rac*-$[CpCH(CH_3)Cy]_2ZrCl_2$ was obtained >98% isomerically pure by fractional crystallisation. From a similar process starting with 6-methyl-6-phenylfulvene *rac*-$[CpCH(CH_3)Ph]_2ZrCl_2$ was obtained. The regioselective a-deprotonation of 6-cyclohexyl-6-methylfulvene and subsequent reaction with $ZrCl_4$ gave $[CpC(Cy){=}CH_2]_2ZrCl_2$ which was characterised by X-ray crystallography. Hydroboration of this complex gave a 1:1 mixture of the $[CpCH(Cy)CH_2(9\text{-}BBN)]_2ZrCl_2$ 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 $-CH_2(9\text{-}BBN)$ 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 ($CuBr.SMe_2$, CuI, 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-annelated 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 tetraneopentylzirconium, $ZrNp_4$, 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 homoallyllic 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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