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3. ZIRCONIUM AND HAFNIUM

R.C. FAY

CONTENTS

INTRODUCTION

The 1980 literature on zirconium and hafnium covers a broad spectrum of research ranging from organic chemistry at one extreme to solid state physics at the other. This review attempts comprehensive coverage of the coordination chemistry of zirconium and hafnium; organometallic and solid-state aspects of the chemistry of these elements are treated selectively. For a comprehensive treatment of the organometallic chemistry, the reader is referred to the annual reviews by Labinger in the Journal of Organometallic Chemistry; a review of the literature for 1979 has appeared during the past year [1]. On the solid state side, Corbett has reviewed the structural chemistry of reduced binary halides of early transition metals, including such compounds as ZrCl, $ZrCl_2$, Zr_6Cl_{12} and $ZrCl_3$ [2]. Other reviews that have appeared during 1980 deal with metal atom synthesis of zerovalent arene compounds [3], the chemistry of organoimido (NR) compounds [4], and the mechanisms of reduction of carbon monoxide by zirconium hydrides [5].

The present review covers the major journals for the 1980 calendar year and the lesser known and/or foreign journals for the period covered by Chemical Abstracts, Volume 91, Number 21 through Volume 93, Number 18.

3.1 ZIRCONIUM(IV) AND HAFNIUM(IV)

3.1.1 Halide complexes

The ethylenediammonium fluorozirconates $[enH_2](ZrF_5)_2.H_2O$, $[enH_2](ZrF_6)$ and $[enH_2]_3[ZrF_7]_2.2H_2O$ have been prepared in aqueous solution by reaction of various molar ratios of $[enH_2]F_2.HF$ and $H_2ZrF_6.2H_2O$. These compounds have been characterised by chemical analysis, X-ray diffraction, IR spectroscopy and TGA. On the basis of the IR and X-ray studies, the authors believe that $[enH_2](ZrF_5)_2.H_2O$ probably has a polymeric structure in which the zirconium atoms are bridged by fluorine atoms, $[enH_2](ZrF_6)$ contains dinuclear $[Zr_2F_{12}]^{4-}$ anions in which two pentagonal bipyramidal $\{ZrF_7\}^{3-}$ groups share a common edge, and $[enH_2]_3[ZrF_7]_2.2H_2O$ contains discrete mononuclear $[ZrF_7]^{3-}$ anions [6].

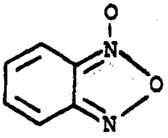
Solid state reactions of BaF_2 with ZrF_4 at 400-860 °C afford several new phases in addition to the already known polymorphic forms (α and β) of $BaZrF_6$. The new phases include α- and β-$BaZr_2F_{10}$, Ba_3ZrF_{10}, $Ba_{0.65}Zr_{0.35}F_{2.70}$, and two non-stoicheiometric phases, $Ba_{1-x}Zr_xF_{2+2x}$ $(0 \le x \le 0.10)$ and $Ba_{4-z}Zr_{2+z/2}F_{16}$ $(0 \le z \le 0.232)$ [7]. The latter phase has a structure in which the Zr^{4+} ions are surrounded by eight fluoride ions at the vertices of a distorted bicapped trigonal prism. The Zr-F distance to one of the capping sites (2.288 Å) is appreciably longer than the other seven Zr-F distances (2.00-2.09 Å) [8]. In the SrF_2-MF_4 (M = Zr or Hf) systems, the following compounds have been identified: α- and β-$SrMF_6$, α- and β-Sr_2MF_8, and Sr_3MF_{10} [9].

X-ray diffraction studies have shown that lanthanide fluorides react with HfF_4 at 800 °C (150-200 h annealing time) to give compounds having composition $LnF_3.nHfF_4$ (n = 1,2 or 3). 1:1 compounds, $LnHfF_7$, are obtained for all of the lanthanides. The lighter lanthanides (Ln = La-Nd) form, in addition, compounds of composition $LnHf_2F_{11}$, while the heavier lanthanides (Ln = Sm-Lu) and yttrium give compounds of the type $Ln(HfF_5)_3$. Lattice parameters have been reported for $LnHfF_7$ and $Ln(MF_5)_3$ (M = Zr or Hf) [10].

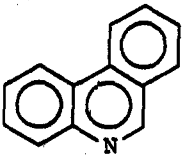
The crystal structure of $MnZrF_6.5H_2O$ has been refined from neutron and X-ray data in order to locate the hydrogen atoms and define the system of O-H...F and O-H...O hydrogen bonds. The zirconium atoms are surrounded by a triangular (D_{2d}) dodecahedron of eight fluorine atoms with the $\{ZrF_8\}$ groups being linked into infinite chains by sharing of the dodecahedral a edges. The Zr-F bonds to the dodecahedral A sites ($\bar{r}$ = 2.21 Å) are appreciably longer than those to the B sites ($\bar{r}$ = 2.03 Å) [11].

A mass spectrometric study has shown that the saturated vapour in the NaF-ZrF_4 system contains not only the pure components but also the complex molecules Na_2ZrF_6, $NaZrF_5$, $(NaZrF_5)_2$, and $NaZr_2F_9$[12]. The negative ions $[HfF_5]^-$ and $[Hf_2F_9]^-$ have been detected in a mass spectrometric study of the saturated vapour of the KF-HfF_4 system [13].

Zirconium(IV) chloride reacts with benzofuroxane (1) and 3,4-benzoquinoline (2)

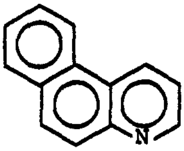


(1)



(2)

to give solid $[ZrCl_4L_2]$ adducts that have been assigned octahedral *cis* and *trans* structures, respectively, on the basis of the number of ν(Zr-L) or ν(Zr-Cl) bands in their IR spectra [14,15]. The benzofuroxane ligand is attached to the metal through the acyclic oxygen atom [14]. With 5,6-benzoquinoline (3), an insoluble $ZrCl_4L$



(3)

adduct has been obtained; the IR spectrum of this 1:1 complex suggests a chlorine-bridged polymeric structure [16]. The reaction of $ZrCl_4$ with triphenylphosphine sulphide in benzene at reflux also affords a 1:1 adduct; this compound has been assigned a dimeric μ_2-Cl bridged structure, $[(Ph_3PS)Cl_3Zr(\mu\text{-}Cl)_2ZrCl_3(SPPh_3)]$, on the basis of molecular weight, conductance and IR data [17].

Raman spectra of $ZrCl_4$-PCl_5 mixtures reveal the presence of at least one chlorozirconate(IV) species in addition to $[ZrCl_6]^{2-}$. The new Raman frequencies have been attributed to $[ZrCl_5]^-$, which is formed as a result of equilibrium (1) [18].

$$[ZrCl_6]^{2-} + [PCl_4]^+ \rightleftharpoons [ZrCl_5]^- + PCl_5 \qquad (1)$$

The electrochemical reduction of $ZrCl_4$ in $AlCl_3$-KCl, $AlCl_3$-NaCl, and $AlCl_3$-KCl-NaCl eutectics has been studied by Basile *et al.* [19].

Hafnium(IV) bromide and iodide react with excess trimethylamine in a sealed system to give $[HfX_4(NMe_3)_2]$ adducts that have been assigned a *trans*-octahedral structure on the basis of single, intense ν(Hf-Br) and ν(Hf-I) IR bands at 290 and 165 cm^{-1}, respectively. Benzene solutions of $[HfX_4(NMe_3)_2]$ (X = Cl, Br or I) are useful precursors of other $[HfX_4L_2]$ complexes which are difficult to prepare by direct reaction. For example, addition of thf to a benzene solution of $[HfCl_4(NMe_3)_2]$ gives immediate precipitation of *trans*-$[HfCl_4(thf)_2]$ [20].

Organozirconium and organohafnium halides can be synthesised by electrochemical oxidation of the metals in a cell containing an organic halide RX (R = alkyl or aryl; X = Cl, Br or I). The products are conveniently isolated as MeCN or 2,2'-bipyridine adducts; the most commonly isolated products are [$R_2MX_2L_2$] (M = Zr or Hf; L = MeCN or ½bipy) [21].

Several spectroscopic studies of [$(cp)_2MCl_2$] compounds have appeared during the past year. Far IR and Raman spectra of solid and gaseous [$(cp)_2MCl_2$] (M = Zr or Hf) have been reported; ring and skeletal vibrations have been assigned, and barriers to restricted rotation about the M-cp bonds have been determined [22,23]. ^1H and ^{13}C chemical shifts have been published for a series of bis(alkyl-substituted cyclopentadienyl)zirconium(IV) dichlorides, [$(\eta^5\text{-}RC_5H_4)_2ZrCl_2$] and [$(\eta^5\text{-}RR'C_5H_3)_2ZrCl_2$]; the ^{13}C chemical shifts can be predicted on the basis of additive contributions from the alkyl groups [24]. He-I and He-II photoelectron spectra have been reported for [$(C_5Me_5)_2ZrCl_2$]; the spectra exhibit two low-energy bands assignable to ionisations from MO's with dominant cp(π) character and a group of higher energy bands assignable to ionisations from MO's with dominant Cl 3p character [25].

The cyclic voltammogram of [$(cp)_2ZrCl_2$] in thf-[Bu_4N][PF_6] at a carbon electrode provides evidence for reversible electrochemical reduction to [$(cp)_2ZrCl_2$]$^-$ [26].

3.1.2 Complexes with O-donor ligands

In this section, compounds are discussed in order of increasing complexity of the *O*-donor ligand. Oxometal complexes are considered first, complexes with monodentate ligands next, and complexes with polydentate ligands last. Discussion of complexes with polydentate ligands that contain other donor atoms in addition to oxygen is deferred to later sections dealing with the other element.

Oxozirconium(IV) triphenylphosphine oxide and tetramethylene sulphoxide complexes of the type [$ZrOL_2X_2$] (L = Ph_3PO or tmso; X = Cl, Br or NO_3), [$ZrOL_4$]I_2, and [$ZrOL_6$][ClO_4]$_2$ have been prepared by reaction of Ph_3PO or tmso with a methanol solution of the appropriate zirconyl salt. Molecular weight and conductance measurements in nitrobenzene indicate that the [$ZrOL_2X_2$] complexes are monomeric nonelectrolytes, while the [$ZrOL_4$]I_2 and [$ZrOL_6$][ClO_4]$_2$ complexes are 1:2 electrolytes. The thiocyanate complex [$ZrOL_2(NCS)_2$] is a monomeric nonelectrolyte when L = Ph_3PO, but appears to have the more complex formulation [$\{ZrOL_2(NCS)\}_2$][NCS]$_2$ when L = tmso. IR spectra of these compounds indicate that (i) Ph_3PO and tmso are attached to zirconium *via* the oxygen atom, (ii) nitrate behaves as a bidentate ligand, (iii) perchlorate is ionic, and (iv) when thiocyanate is attached to zirconium, it is coordinated through the *N* atom. A weak IR band at 900-960 cm^{-1} has been attributed to ν(Zr=O), and the coordination number of zirconium in these compounds has been assigned as five or seven [27,28]. In view of the rarity of both five-coordinate zirconium and the Zr=O group, the structures of these compounds should be investigated by X-ray crystallographic techniques.

$ZrOCl(OCHMe_2).2CHMe_2OH$ reacts with nitrogen and oxygen bases (L = py, quin, bipy, dmf, dma or phthalimide) to give adducts of the type $ZrOCl(OCHMe_2).L$; with L = dmso, the product is $2ZrOCl(OCHMe_2).3dmso$. The corresponding dialkoxides $ZrO(OR)_2.ROH$ (R = Me, Et or $CHMe_2$) fail to react with these bases. The $ZrOCl(OCHMe_2).L$ adducts are nonelectrolytes in nitrobenzene. They exhibit a fairly intense IR band at 650-660 cm^{-1} that is probably due to bridging Zr-O-Zr groups [29].

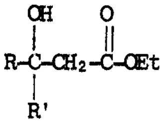
Bis(benzeneseleninato)oxozirconium(IV) complexes, $ZrO(O_2SeC_6H_4X)_2$ (X = 4-Cl, 3-Cl or 3-Br) and $ZrO(O_2SeC_6H_4\text{-}3\text{-}NO_2)_2.2H_2O$, have been synthesised in aqueous solution by reaction of a 1:4 molar ratio of $Zr(NO_3)_4$ and the sodium salt of the ligand. IR spectra indicate an *O,O'*-bidentate attachment of the $O_2SeC_6H_4X$ ligands and an oxo-bridged polymeric structure. The presence of just one ν(Zr-O-Zr) IR band (739-750 cm^{-1}) and two ν(Zr-O) bands for the bonds to the $O_2SeC_6H_4X$ ligands (405-504 cm^{-1}) suggests a *trans*-octahedral environment for the zirconium atom [30].

Thiomalic acid, $HOOCCH_2CH(SH)COOH$ reacts with $MOCl_2$ (M = Zr or Hf) in aqueous solution to give insoluble 1:1 complexes of composition $MO(C_4H_4O_4S).4H_2O$. IR spectra suggest bidentate coordination of the carboxylate groups and indicate that the SH group remains intact and relatively unperturbed by complex formation. The $MO(C_4H_4O_4S).4H_2O$ complexes are believed to be polymeric, but no unambiguous assignment of ν(M-O-M) frequencies could be made [31].

Two forms (liquid and crystalline) of zirconium isopropoxide have been shown to exist, and their physicochemical properties have been investigated. Upon desolvation of solid $Zr(OCHMe_2)_4.CHMe_2OH$ at 90-120 °C and 1 Torr, $Zr(OCHMe_2)_4$ is obtained as a viscous, slightly yellowish, extremely hygroscopic liquid, b.p. 160 °C/0.1 Torr. This liquid does not solidify on standing for one year. However, when liquid $Zr(OCHMe_2)_4$ is treated with $CHMe_2OH$, heat is evolved and a powder is deposited, which also analyses for $Zr(OCHMe_2)_4$. Upon recrystallisation from CS_2 , the $Zr(OCHMe_2)_4$ is obtained as fairly large crystals, m.p. 135 °C; the crystals and the powder have identical X-ray powder patterns. When solid $Zr(OCHMe_2)_4$ melts, a non-crystallisable liquid is formed which has an IR spectrum identical to that of the liquid $Zr(OCHMe_2)_4$ obtained by desolvation of $Zr(OCHMe_2)_4.CHMe_2OH$. IR spectra of the liquid and crystalline forms of $Zr(OCHMe_2)_4$ differ only slightly in the ν(Zr-O) region. The existence of two forms of $Zr(OCHMe_2)_4$ is presumably due to a difference in molecular composition; attempts to determine the degree of association by cryoscopic measurements were unsuccessful owing to the extremely high hygroscopicity of $Zr(OCHMe_2)_4$ solutions [32].

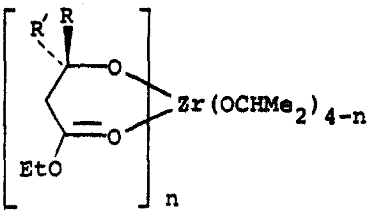
Conductometric titration of $ZrCl_4$ with K[OPh] in nitrobenzene has indicated the formation of $Zr(OPh)_4$, $ZrCl_3(OPh)$, and $ZrCl_2(OPh)_2$, which have been isolated and characterised by chemical analysis. The Lewis acidity of $Zr(OPh)_4$ and $ZrCl_2(OPh)_2$ has been established by isolation of adducts with py, bipy, phen, and their *N*-oxides [33].

The reactions of $Zr(OCHMe_2)_4.CHMe_2OH$ with hydroxy esters **(4)**-**(6)** in 1:1, 1:2, 1:3 or 1:4 molar ratios in benzene at reflux afford light yellow to brown, viscous liquid complexes of the type **(7)**, where the value of *n* depends on the stoicheiometry of the reaction mixture.



$R\text{-}C(OH)(R')\text{-}CH_2\text{-}C(=O)\text{-}OEt$

(4; R = C_6H_{11}, R' = H**)**
(5; R = Ph, R' = H**)**
(6; R = Ph, R' = Me**)**



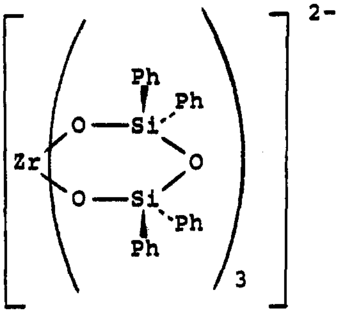
(7; *n* = 1,2,3 or 4**)**

These compounds have been characterised by chemical analysis , IR and ^1H NMR spectroscopy. They are monomeric in boiling benzene, which indicates that the zirconium atom has a coordination number of five, six, seven or eight when *n* is 1, 2, 3 or 4, respectively. The complexes that contain $OCHMe_2$ groups can be converted to the corresponding *tert*-butoxide derivatives by reaction of **(7)** (n = 1, 2 or 3) with Me_3COH in benzene at reflux [34].

Zirconium(IV) complexes with the potentially tridentate 3-cyanopentane-2,4-dionate ligand have been prepared by reaction of $ZrCl_4$ with 3-cyanopentane-2,4-dione in dichloromethane. Di-, tri-, and tetra-substituted products, ZrL_nCl_{4-n} (L = 3-CNacac; n = 2, 3 or 4), were isolated depending on the stoicheiometry of the reaction mixture. The cyclopentadienyl derivative $[(cp)ZrL_3]$ was obtained from the reaction of $[(cp)_2ZrCl_2]$ with a benzene solution of 3-cyanopentane-2,4-dione and triethylamine. IR spectra of these complexes show that the 3-CNacac ligands are coordinated to the metal through both oxygen atoms. However, in ZrL_2Cl_2 and ZrL_3Cl, the cyano group of one 3-CNacac ligand appears to be coordinated as well; this ligand bridges to a second zirconium centre. ^1H NMR spectra of ZrL_2Cl_2, ZrL_3Cl and $[ZrL_4]$ at 35 °C in $CDCl_3$ exhibit a single methyl resonance, indicative of stereochemical non-rigidity. In contrast, $[(cp)ZrL_3]$ shows three methyl resonances, consistent with a pentagonal bipyramidal structure in which the methyl groups of the equatorial ligands are undergoing rapid exchange [35]. Similar kinetic behaviour has been observed for the corresponding $[Zr(acac)_nCl_{4-n}]$ and $[(cp)Zr(acac)_3]$ complexes [36-38].

Benzoylacetonate, dibenzoylmethanate and 8-quinolinolate complexes of the type $(cp)_2ZrLX$ (L = benzac, dbzm or 8-O-quin; X = Br or OPh) have been synthesised by reaction of the acid form of the ligand HL with the dizirconoxanes $[\{(cp)_2ZrX\}_2O]$ [39].

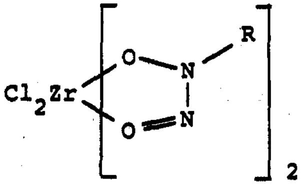
The diethylammonium salt of the tris(tetraphenyldisiloxanediolato)zirconate(IV) anion (8) has been obtained in very low yield from the reaction of $Zr(NEt_2)_4$ with diphenylsilanediol in thf. The ligand results, under the basic reaction conditions, from condensation of two $Ph_2Si(OH)_2$ molecules. Anion (8) has an octahedral tris-chelate structure with a twist angle (46.9 °) that indicates some distortion towards a trigonal prismatic geometry [40].



(8)

Zirconium(IV) trichloroethanoate, $Zr(CCl_3CO_2)_4$, has been prepared by reaction of $ZrCl_4$ with an excess of hot trichloroethanoic acid. With py, pyNO or Ph_3PO, $Zr(CCl_3CO_2)_4$ behaves as a Lewis acid, forming $Zr(CCl_3CO_2)_4L_2$ adducts. The IR spectra and the low solubility of $Zr(CCl_3CO_2)_4$ and its adducts suggest that these complexes may be polymeric [41].

Zirconium(IV) alkyls of the type ZrR_2Cl_2 ($R = CH_2SiMe_3$) or ZrR_4 ($R = CH_2SiMe_3$ or CH_2CMe_3) react with nitrogen oxide, NO, to give the six- or eight-coordinate *N*-alkyl-*N*-nitrosohydroxylaminate complexes (9) or (10), respectively [42].



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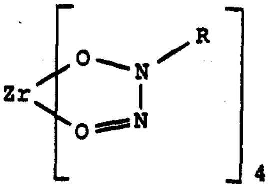
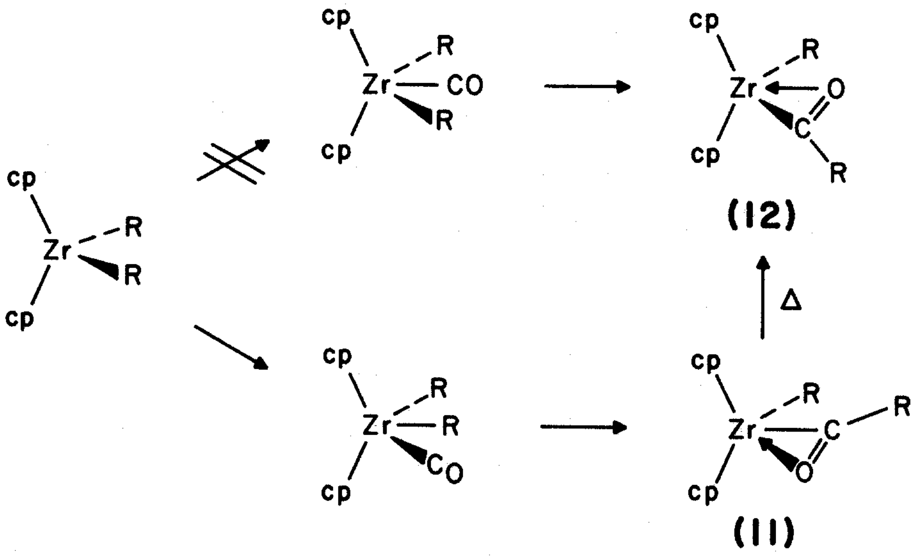


(10)

Carbonylation of $[(cp)_2ZrR_2]$ complexes at low temperatures evidently involves CO attack at a lateral, rather than an interior, coordination site since the kinetic insertion product is the η^2-acyl complex (11) that has the oxygen atom in a lateral site {equation (2)}. Subsequent isomerisation of (11) gives the thermodynamically favoured isomer (12), which has the oxygen atom in the interior coordination site.



(2)

Isomers **(11)** and **(12)** are separated by a substantial energy barrier when R = aryl ($\Delta G^{\ddagger} \simeq$ 65 kJ mol^{-1} at *ca.* -60 °C), but a smaller barrier when R = Me ($\Delta G^{\ddagger} \simeq$ 47.7 kJ mol^{-1} at -123 °C) [43]. Equilibrium constants for insertion of CO into $[(cp)_2ZrMeX]$ {equation (3)} decrease in the order X = Me > Cl > OEt. This result can

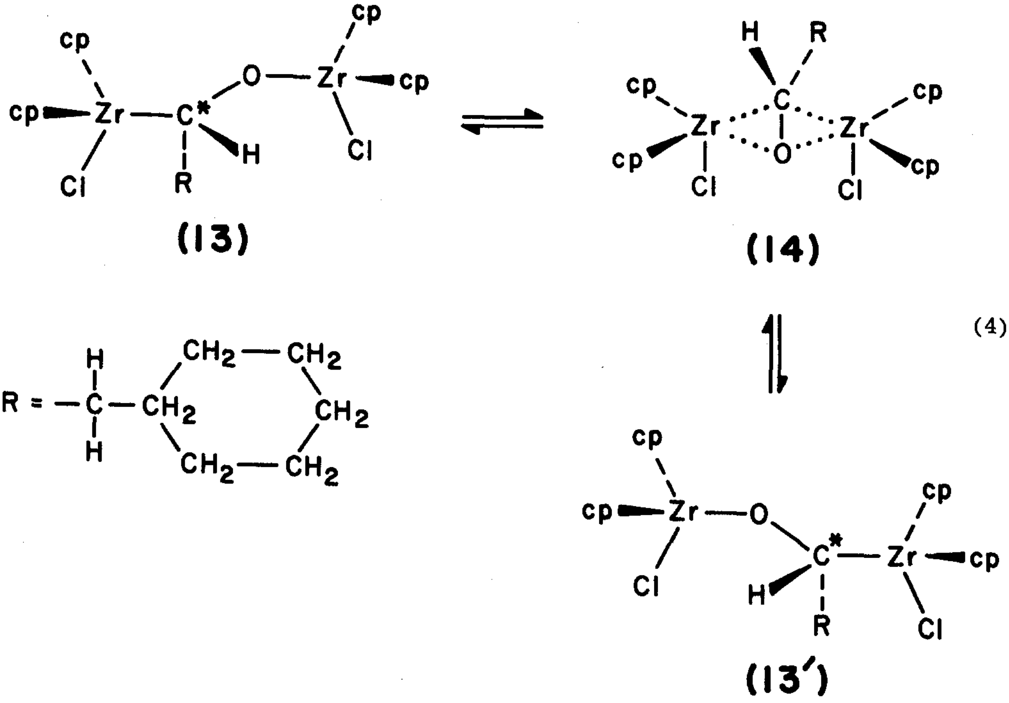
$$[(cp)_2ZrMeX] \;+\; CO \;\rightleftharpoons\; [(cp)_2Zr\{C(O)Me\}X] \qquad (3)$$

be understood in terms of competition between the π-donor orbitals on X and the oxygen donor orbital of the η^2-ethanoyl group [44].

A new type of fluxional process {equation (4)} has been reported for the dinuclear zirconium complex $[(cp)_2ClZrOCHRZrCl(cp)_2]$ (**13**; R = $CH_2C_6H_{11}$). ^1H and ^{13}C NMR studies indicate that the rearrangement involves simultaneous exchange of (i) the inequivalent $(cp)_2Zr$ groups, (ii) the diastereotopic methylene protons of the cyclohexylmethyl group, and (iii) the diastereotopic carbon atoms in the cyclohexyl ring. The proposed mechanism features a C_s transition state, (**14**), with a bonding pattern which resembles that of the η^2-carbonyl unit in mononuclear acylzirconium(IV) complexes. Passage through this transition state effects simultaneous exchange of the O- and C-bonds to the two zirconium atoms and inversion of configuration at the asymmetric carbon atom [45].

3.1.3 Oxides, mixed-metal oxides and oxyanion salts

Phase transformations in ZrO_2 and HfO_2 have been investigated in the pressure range 80–300 kbar at *ca.* 1000 °C. ZrO_2 and HfO_2 transform to a cotunnite-type structure (orthorhombic, space group *Pmnb*) at pressures greater than 100 and 150 kbar,



(13) (14) (13′) (4)

respectively, and are the first oxides known to adopt this structure. At 1000 ° C or below, it is suggested that the sequence of high-pressure polymorphism in both ZrO_2 and HfO_2 is baddeleyite (monoclinic) → tetragonal → cotunnite with increasing pressure; the coordination number of the metal ion in these polymorphs increases from seven to eight to nine [46].

The X-ray crystal structures of several mixed-metal oxides have been published during the past year. The structure of $K_4Zr_5O_{12}$ contains zirconium(IV) both octahedrally and trigonal prismatically coordinated by oxygen. It consists of perovskite-like layers (three octahedra deep) with sheets of hexagonal rings of edge-shared trigonal prismatically coordinated zirconium ions inserted between every third and fourth layer of the perovskite-like structure. The trigonal prisms are face-shared to octahedra above and below [47]. $Ba_2Zr_{\frac{3}{4}}\square_{\frac{1}{4}}SbO_6$ has a tetragonal perovskite structure with an ordered distribution of the vacancies [48]. UZr_6FO_{14} crystallises in an ordered excess-anion fluorite-related structure [49].

The standard enthalpy of formation of anhydrous $Zr(ClO_4)_4$ at 25 °C (ΔH_f° = -723.1 ± 1.7 kJ mol^{-1}) has been determined by calorimetric measurements [50]. Alekseeva *et al.* have reported equilibrium constants for the formation of outer-sphere and inner-sphere complexes of zirconium(IV) and hafnium(IV) with sulphate at 25 °C, pH 1–2, and metal ion concentrations of 10^{-5} –10^{-6} *M*; under these conditions hafnium(IV) forms 1:1 and 1:2 inner-sphere complexes, $[Hf(OH)_2(SO_4)]$ and

$[\mathrm{Hf(OH)(SO_4)_2}]^-$, while zirconium(IV) forms only a 1:1 complex [51]. A thermal study (TGA, DTGA and DTA) of crystalline hydrates of zirconium sulphate, $\mathrm{Zr(SO_4)_2}.n\mathrm{H_2O}$ (n = 3.5, 4.0, 4.5 or 5.5), suggests that these compounds should be formulated as monohydroxo complexes, $\mathrm{Zr(OH)(HSO_4)(SO_4)}.(n-1)\mathrm{H_2O}$, and that they decompose thermally according to the scheme set out in equation (5) [52]. An X-ray

$$\mathrm{Zr(OH)(HSO_4)(SO_4)}.(n-1)\mathrm{H_2O} \xrightarrow{-(n-1)\mathrm{H_2O}} \mathrm{Zr(OH)(HSO_4)(SO_4)}$$
$$\xrightarrow{-\frac{1}{2}\mathrm{H_2O}} \tfrac{1}{2}\mathrm{Zr_2O(HSO_4)_2(SO_4)_2} \xrightarrow{-\frac{1}{2}\mathrm{H_2O}} \tfrac{1}{2}\mathrm{Zr_2O(S_2O_7)(SO_4)_2}$$
$$\xrightarrow{-\mathrm{SO_3}} \mathrm{ZrO(SO_4)} \xrightarrow{-\mathrm{SO_3}} \mathrm{ZrO_2} \qquad (5)$$

diffraction study of the double sulphate $\mathrm{Hf(SO_4)_2.3Na_2SO_4.H_2O}$ shows that the structure contains $[\mathrm{Hf(SO_4)_5(OH_2)}]^{6-}$ anions connected by $\mathrm{Na^+}$ cations and hydrogen bonds. The hafnium atom is surrounded by eight oxygen atoms from two bidentate sulphate groups, three monodentate sulphate groups, and the water molecule; r(Hf-O) = 2.10-2.33 Å. The geometry of the $\{\mathrm{HfO_8}\}$ coordination group does not closely approximate to any of the common eight-coordination polyhedra [53].

IR and Raman spectra have been reported for $\mathrm{ZrP_2O_7}$, and a normal coordinate analysis has been carried out assuming that the $[\mathrm{P_2O_7}]^{4-}$ ion has D_{3d} symmetry. The exclusion rule applies, indicating that $[\mathrm{P_2O_7}]^{4-}$ is centrosymmetric; agreement between the observed and calculated frequencies is satisfactory [54].

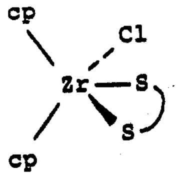
Crystalline zirconium(IV) phosphates continue to be of interest as inorganic ion exchangers. This area is beyond the scope of the present review; however, several leading references to the synthesis [55,56] , reactivity [57,58], dehydration [59], thermodynamic properties [60], and ion exchange behaviour [61-64] of these materials are noted.

$\mathrm{ZrO(CO_3).2H_2O}$ has been synthesised under high pressure by reaction of hydrous $\mathrm{ZrO_2}$ with $\mathrm{CO_2}$ (4000 atm) at 150 °C [65]. The formation of zirconium-carbonate complexes in aqueous solutions of zirconium(IV) sulphate and sodium carbonate has been studied by pH titration and IR spectroscopy. Evidence is presented for the formation of $[\mathrm{Zr(OH)_2(CO_3)_2}]^{2-}$, $[\mathrm{Zr(OH)(CO_3)_3}]^{3-}$ and $[\mathrm{Zr(CO_3)_4}]^{4-}$ [66].

3.1.4 Complexes with S-donor ligands

$\mathrm{ZrX_4}$ (X = F or Cl) reacts with the sodium salt of piperazine-1,4-dicarbodithioate to give complexes of composition $\mathrm{ZrF_2\{S_2CN(CH_2CH_2)_2NC(S)SH\}_2}$ and $\mathrm{Zr_2Cl_6\{S_2CN(CH_2CH_2)_2NCS_2\}}$, respectively [67,68]. On the basis of IR evidence, the fluoride complex has been assigned a *trans*-octahedral structure in which one $\mathrm{CS_2^-}$ group of each piperazine-1,4-dicarbodithioate acts as a bidentate ligand while the other $\mathrm{CS_2^-}$ group is attached to a proton [67]. IR spectra indicate that the piperazine-1,4-dicarbodithioate behaves as a tetradentate ligand in the chloride complex [68]. Aqueous solutions of $MOCl_2$ (M = Zr or Hf) react with dithiocarbamate ligands to give compounds of composition $MO(S_2CNR_2)_2.2H_2O$; these complexes appear to contain bidentate dithiocarbamate ligands, but their structures are unknown [69].

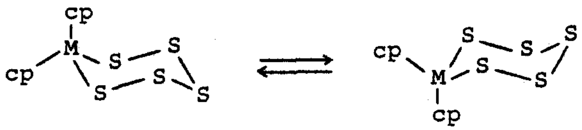
Five-coordinate cyclopentadienyl *N*-aryl-substituted dithiocarbamato complexes of the type $[(cp)_2Zr(S_2CNHAr)Cl]$ have been prepared by reaction of equimolar amounts of $[(cp)_2ZrCl_2]$ and anhydrous $[NH_4][S_2CNHAr]$ in dichloromethane at reflux. These complexes are monomeric nonelectrolytes in solution, and IR spectra indicate bidentate attachment of the dithiocarbamate ligands. A trigonal bipyramidal structure with the two cyclopentadienyl ligands in *trans* positions has been suggested on the basis of a single cyclopentadienyl ^1H NMR resonance [70]. However, such a structure is unlikely; a single-crystal X-ray study has established that the corresponding $[(cp)_2Zr(S_2CNEt_2)Cl]$ complex has the expected bent metallocene structure **(15)** [71].



(15)

Seven-coordinate $[(cp)Hf(S_2CNR_2)_3]$ (R = Me or Et) complexes have been synthesised in boiling CH_2Cl_2 or thf by reaction of $[(cp)_2HfCl_2]$ with three equivalents of anhydrous $Na[S_2CNR_2]$. These complexes have been assigned a capped octahedral geometry on the basis of two equally intense methyl ^1H NMR resonances for $[(cp)Hf(S_2CNMe_2)_3]$ [72]. A capped octahedral structure is unlikely in view of the steric bulk of the cp ligand and the established pentagonal bipyramidal structures of the analogous $[(cp)Ti(S_2CNMe_2)_3]$ and $[(cp)Zr(S_2CNMe_2)_3]$ complexes [73,74]. In support of a pentagonal bipyramidal structure for $[(cp)Hf(S_2CNMe_2)_3]$, we note an unpublished report [75] of a higher resolution ^1H NMR spectrum which exhibits three methyl resonances of relative intensity 2:1:3. Moreover, the resonance of relative intensity three exhibits some asymmetry, in accord with the 2:1:2:1 intensity pattern expected for a pentagonal bipyramidal structure.

New $[(cp)_2MS_5]$ (M = Zr or Hf) complexes have a six-membered chair conformation similar to that reported previously for M = Ti. ^1H NMR studies show that the barriers to MS_5 ring inversion {equation (6)} decrease as M varies in the order Ti > Zr > Hf. The $[(cp)_2MS_5]$ complexes are best prepared by reaction of $[(cp)_2MCl_2]$ with Li_2S_2 and sulphur [76].



(6)

HfOS has a cubic structure in which the hafnium atom is attached to three oxygen atoms {r(Hf-O) = 2.078 Å} and four sulphur atoms {r(Hf-S) = 2.706 Å (3x) and 2.593 Å (1x)}. The {HfO_3S_4} coordination polyhedron is a monocapped octahedron with one of the sulphur atoms capping a face bounded by three oxygen atoms [77]. Binding energies of the metal and sulphur core electrons in ZrS_2, $NbS_{1.6}$ and MoS_2 have been measured by X-ray photoelectron spectroscopy. The results indicate that the ionic character of the metal-sulphur bond decreases in the order $ZrS_2 > NbS_{1.6} > MoS_2$ [78].

3.1.5 Complexes with N-donor ligands

The chlorotris(silylamido)- complexes [$MCl\{N(SiMe_3)_2\}_3$] (M = Zr or Hf) have been prepared by reaction of MCl_4 with an excess of Li[$N(SiMe_3)_2$]. X-ray and NMR studies indicate the presence of considerable steric crowding in these compounds due to the bulky $N(SiMe_3)_2$ ligands. In the solid state, the [$MCl\{N(SiMe_3)_2\}_3$] complexes have crystallographically imposed C_3 symmetry and a distorted tetrahedral geometry {r(Zr-Cl) = 2.394 Å; r(Zr-N) = 2.070 Å; r(Hf-Cl) = 2.436 Å; r(Hf-N) = 2.040 Å}. Crowding is evidenced by $\text{Cl-}\hat{\text{M}}\text{-N}$ being 10-13° less than $\text{N-}\hat{\text{M}}\text{-N}$ and by $\text{M-}\hat{\text{N}}\text{-Si}$ proximal to Cl being 8-10° less than $\text{M-}\hat{\text{N}}\text{-Si}$ distal to Cl. ^1H NMR spectra, which exhibit two equally intense resonances below the coalescence temperature of 4-5 °C, are interpreted in terms of restricted rotation about the M-N bonds. A higher coalescence temperature in [$TiCl\{N(SiMe_3)_2\}_3$] (34 °C) is consistent with less congestion in the zirconium and hafnium complexes than in the titanium compound [79]. A convenient method for the preparation of analogous halo- and pseudohalo- hafnium complexes [$HfX\{N(SiMe_3)_2\}_3$] (X = Br, I, [N_3] or [CN]) utilises the reaction of [$HfCl\{N(SiMe_3)_2\}_3$] with trimethylsilyl halides or pseudohalides {equation (7)}.

$$[HfCl\{N(SiMe_3)_2\}_3] + Me_3SiX \longrightarrow [HfX\{N(SiMe_3)_2\}_3] + Me_3SiCl \qquad (7)$$

Isolation of the product is trivial since Me_3SiCl can be removed in vacuum and the product crystallised from toluene or dichloromethane [80].

The alkylchlorobis(silylamido) complexes [$HfRCl\{N(SiMe_3)_2\}_2$] (R = Me_3CCH_2 or Me_3SiCH_2) and unsymmetrical dialkylbis(silylamido) complexes [$HfRR'\{N(SiMe_3)_2\}_2$] (R' = Me or Et) have been synthesised in pentane-diethyl ether solution {equations (8) and (9)}. The trimethylsiloxo derivative [$Hf(OSiMe_3)Cl\{N(SiMe_3)_2\}_2$] has been obtained by reaction of [$HfCl_2\{N(SiMe_3)_2\}_2$] with Na[$OSiMe_3$], and has been converted

$$[\mathrm{HfCl_2\{N(SiMe_3)_2\}_2}] + \tfrac{1}{2}\mathrm{MgR_2} \longrightarrow [\mathrm{HfRCl\{N(SiMe_3)_2\}_2}] + \tfrac{1}{2}\mathrm{MgCl_2} \quad (8)$$

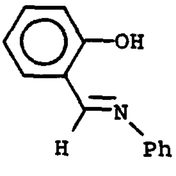
$$[\mathrm{HfRCl\{N(SiMe_3)_2\}_2}] + \tfrac{1}{2}\mathrm{MgR'_2} \longrightarrow [\mathrm{HfRR'\{N(SiMe_3)_2\}_2}] + \tfrac{1}{2}\mathrm{MgCl_2} \quad (9)$$

to $[\mathrm{Hf(OSiMe_3)R'\{N(SiMe_3)_2\}_2}]$ by reaction with $\mathrm{MgR'_2}$ (R' = Me or Et) [81].

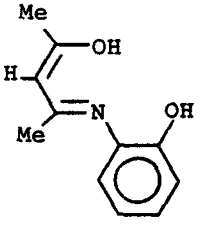
Imido complexes of the type $\mathrm{Zr(OCHMe_2)_{4-\mathit{n}}(NHCOR)_{\mathit{n}}}$ (n = 1, 2, 3 or 4; R = Me, Ph or $\mathrm{C_5H_4N}$) have been prepared in quantitative yield by reaction of $\mathrm{Zr(OCHMe_2)_4.CHMe_2OH}$ with stoicheiometric amounts of acetamide, benzamide or nicotinamide. These compounds are insoluble in common organic solvents, nonvolatile, and probably polymeric. IR spectra show unperturbed ν(C=O) vibrations, indicating that the NHCOR ligands coordinate through the nitrogen atom [82]. An X-ray study of $[\mathrm{Zr\{(NCMe_3)_2SiMe_2\}_2}]$ has established a spirocyclic structure of approximate D_{2d} symmetry with planar $\{\mathrm{Zr\mathit{N_2Si}}\}$ rings $\{r(\mathrm{Zr\text{-}N}) = 2.053$ Å; N-$\hat{\mathrm{Zr}}$-N = 77.9°} [83].

The pyrrolyl complexes $[(\mathrm{cp})_2\mathrm{Zr}(\eta^1\text{-}\mathrm{NC_4H_4})_2]$ and $[\mathrm{Na(thf)_6}]_2[\mathrm{Zr}(\eta^1\text{-}\mathrm{NC_4H_4})_6]$ have been prepared by reaction of $[(\mathrm{cp})_2\mathrm{ZrCl_2}]$ with (pyrrolyl)sodium in thf at room temperature and at reflux temperature, respectively. These compounds have short Zr-N bond lengths (2.169 and 2.198 Å, respectively) and Zr-$\hat{\mathrm{N}}$-(centroid η^1-$\mathrm{NC_4H_4}$) angles near 180° (~164° and 179°, respectively). Both features point to considerable d_π-p_π character in the Zr-N bonds. $[(\mathrm{cp})_2\mathrm{Zr}(\eta^1\text{-}\mathrm{NC_4H_4})_2]$ exhibits distorted tetrahedral geometry about the zirconium atom (N-$\hat{\mathrm{Zr}}$-N = 95.7°; (centroid cp)-$\hat{\mathrm{Zr}}$-(centroid cp) = 128.5°), while the $[\mathrm{Zr}(\eta^1\text{-}\mathrm{NC_4H_4})_6]^{2-}$ ion is octahedral with N-$\hat{\mathrm{Zr}}$-N angles near 90° [84].

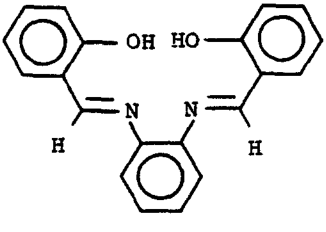
Schiff base complexes of the type $[(\mathrm{cp})_2\mathrm{ZrCl(L)}]$, $[(\mathrm{cp})_2\mathrm{Zr(L)_2}]$, $[(\mathrm{cp})_2\mathrm{Zr(L')}]$, $[(\mathrm{cp})_2\mathrm{Zr(L'')}]$ and $[\{(\mathrm{cp})_2\mathrm{ZrCl}\}_2\mathrm{(L'')}]$ have been synthesised in thf by reaction of stoicheiometric amounts of $[(\mathrm{cp})_2\mathrm{ZrCl_2}]$, triethylamine, and any one of several bidentate (HL), tridentate ($\mathrm{H_2L'}$) or tetradentate ($\mathrm{H_2L''}$) Schiff bases; an example of each type of Schiff base is shown in **(16)**-**(18)**. On the basis of elemental



(16; HL)

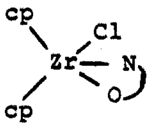


(17; $\mathrm{H_2L'}$)



(18; $\mathrm{H_2L''}$)

analysis, molecular weight and conductance measurements, and IR spectra, these compounds have been assigned the five- and six- coordinate structures **(19)-(23)** in



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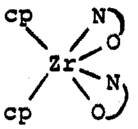

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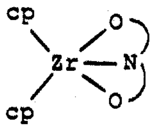

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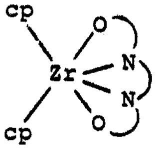

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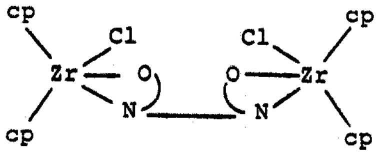
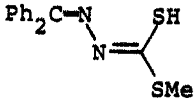
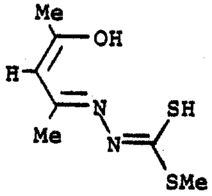


(23)

which all of the oxygen and nitrogen atoms are coordinated to the metal [85]. Analogous $[(cp)_2ZrCl(L)]$, $[(cp)_2Zr(L)_2]$ and $[(cp)_2Zr(L')]$ complexes containing *NS*-donor bidentate and *ONS*-donor tridentate Schiff base ligands derived from *S*-methyl-dithiocarbazate, for example **(24)** and **(25)**, have been prepared by the same



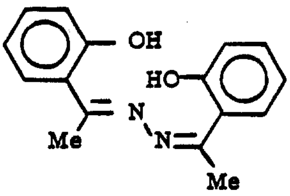
(24; HL)



(25; H_2L')

procedure [86]. X-ray structures of the $[(cp)_2Zr(L)_2]$ and $[(cp)_2Zr(L'')]$ complexes would be of interest since these compounds have been formulated [85] as twenty-electron complexes.

$Zr(OCHMe_2).CHMe_2OH$ reacts in benzene at reflux with a variety of dibasic tridentate Schiff bases H_2L in 1:1 and 1:2 mole ratios to give complexes of the type $[\{Zr(OCHMe_2)_2(L)\}_2]$ and $[Zr(L)_2]$, respectively. The Schiff bases that undergo these reactions include azines **(26)** [87], semicarbazones **(27)** [88], thiosemicarbazones **(28)** [89], and other *S*-containing tridentate Schiff bases **(29)** [90]; one example of each type of ligand is shown in **(26)-(29)**. Molecular weight measurements indicate that the $[Zr(L)_2]$ complexes are monomeric in solution, while the $[\{Zr(OCHMe_2)_2(L)\}_2]$ analogues are dimeric. Six-coordinate structures have been proposed in which $[L]^{2-}$ behaves as an *ONO*- or *ONS*- tridentate ligand, for example **(30)** and **(31)** for the azine



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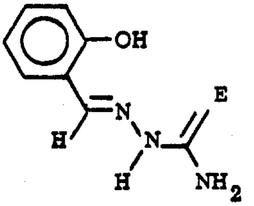
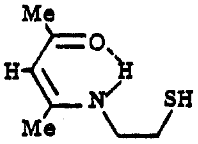


(27; E = O)

(28; E = S)



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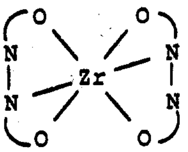

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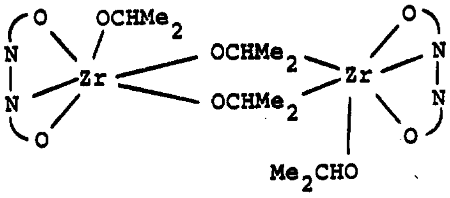
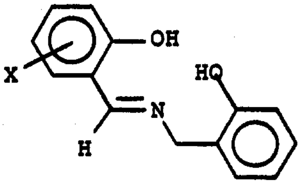


(31)

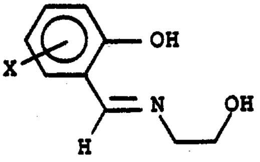
complexes. Alkoxide exchange reactions of the $[\{Zr(OCHMe_2)_2(L)\}_2]$ complexes with alcohols such as Me_3COH, 2-methylpentane-2,4-diol ($C_6H_{14}O_2$), or benzene-1,2-diol ($C_6H_6O_2$) afford the $Zr(OCMe_3)_2(L)$, $Zr(C_6H_{12}O_2)(L)$ or $Zr(C_6H_4O_2)(L)$ derivatives, respectively [87-90].

Mixed-ligand complexes $[Zr(L)(L')]$ that contain dinegative anions of two different *ONO*-tridentate Schiff bases have been prepared in benzene at reflux by reaction of a 1:1:1 mole ratio of $Zr(OCHMe_2)_4.CHMe_2OH$, H_2L and H_2L' [91]. A variety of complexes that contain the dinegative anions of *ONS*-tridentate Schiff bases and *SNNS*-tetradentate Schiff bases have been synthesised by reaction of $Zr(OCHMe_2)_4.CHMe_2OH$ with benzthiazolines [92].

Zirconyl chloride (or ethanoate) reacts in methanol at reflux with tridentate Schiff bases H_2L (32) or (33) to give 1:2 metal:ligand complexes that have been

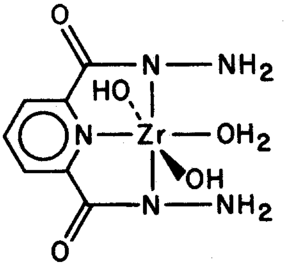


(32; H_2L)



(33; H_2L)

formulated on the basis of elemental analysis, molecular weight and conductance measurements, and IR spectra as seven-coordinate $ZrO(HL)_2$ complexes in which the Schiff base behaves as a monobasic *ONO*-tridentate ligand [93,94]. Formulation as $Zr(OH_2)(L)_2$ complexes seems not to have been considered. In view of the lack of evidence for the existence of the Zr=O moiety in zirconyl compounds, the structures of these complexes should be investigated. Zirconyl chloride reacts with 2,6-dipicolinyl dihydrazine (H_2dpdh) yielding a 1:1 complex that has been formulated as $ZrO(OH_2)_2$(dpdh) or $Zr(OH)_2(OH_2)$(dpdh) **(34)**. The free NH_2 groups of compound **(34)** condense with the carbonyl groups of β-diketones affording compounds **(35)** that are believed to contain twelve-membered macrocyclic ligands [95].



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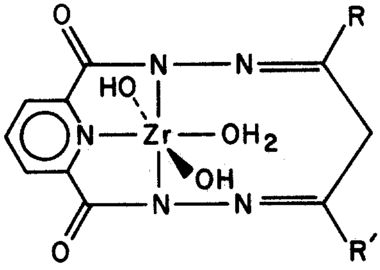


(35)

3.1.6 *Complexes with P-containing ligands*

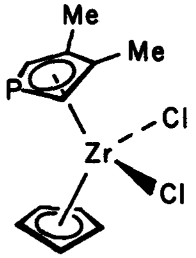
$ZrCl_4$ reacts with $P(NCO)_3$ in benzene and with $P(CN)_3$ in benzene-diethyl ether to give $ZrCl_3\{P(NCO)_2\}$ and $ZrCl_3\{P(CN)_2\}$, respectively {equation (10)}. These compounds have been obtained as somewhat impure, very hygroscopic solids. On the basis of IR evidence, the $P(NCO)_2$ and $P(CN)_2$ ligands are believed to be coordinated through the phosphorus atom [96].

$$ZrCl_4 + PX_3 \xrightarrow[\text{or NCO}]{X = CN} ZrCl_3(PX_2) + ClX \qquad (10)$$

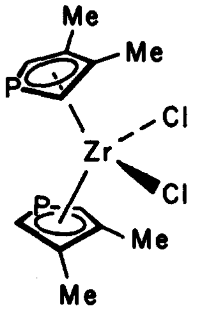
The phospha- and diphospha-zirconocene dichlorides, **(36)** and **(37)**, have been prepared as air-sensitive solids by reaction of the corresponding 1-phospholylmagnesium bromide with (cp)$ZrCl_3$ and $ZrCl_4$, respectively [97].

Trimethylmethylene phosphorane reacts with $[(cp)_2Zr(R)(H)]$ (R = cyclohexylmethyl) in toluene to give methylcyclohexane and a green, thermally unstable, air- and moisture sensitive zirconium(IV) ylide hydride complex $[(cp)_2Zr\{(CH_2)_2PMe_2\}H]$ {equation (11)}. Deuterium labeling experiments suggest that the mechanism of this

$$[(cp)_2Zr(R)(H)] + Me_3\overset{+}{P}\text{-}\overset{-}{C}H_2 \longrightarrow [(cp)_2Zr\{(CH_2)_2PMe_2\}H] + RH \qquad (11)$$

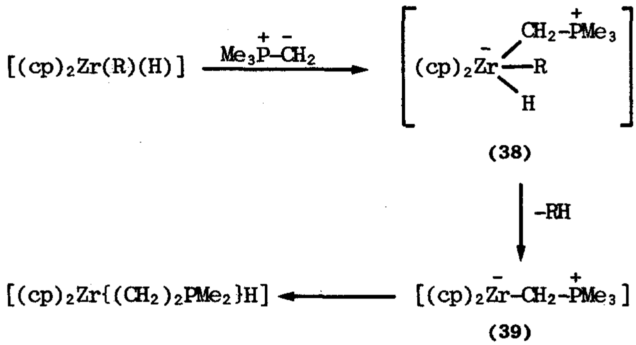


(36)



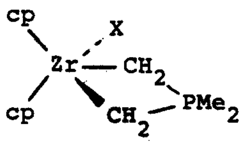
(37)

reaction {equation (12)} involves formation of an unstable eighteen-electron complex (38) which collapses to a zirconium(II) intermediate (39) *via* reductive elimination



(12)

of methylcyclohexane; the zirconium(II) centre then inserts into the C-H bond of a methyl group on phosphorus. $[(cp)_2Zr\{(CH_2)_2PMe_2\}H]$ reacts with methyl chloride yielding methane and the analogous ylide chloride complex $[(cp)_2Zr\{(CH_2)_2PMe_2\}Cl]$. NMR data for the hydride and chloride complexes suggest structure (40), which



(40; X = H or Cl)

contains bidentate phosphonium dimethylide ligands and inequivalent methylene groups. The hydride complex is stereochemically rigid up to 85 °C, where thermal decomposition is rapid, but the chloride complex is fluxional, with equivalencing of the methylene groups at *ca.* 50 °C ($\Delta G^{\ddagger} \simeq 65$ kJ mol^{-1}). A mechanism involving Zr–C bond rupture has been suggested. In a slower process, $[(cp)_2Zr\{(CH_2)_2PMe_2\}Cl]$ isomerises at 50 °C to $[(cp)_2Zr(CHPMe_3)Cl]$ [98].

The sixteen-electron complex $[(cp)_2Zr(CH_2PPh_2)Cl]$ has been prepared as a pale yellow, crystalline solid by reaction of $[(cp)_2ZrCl_2]$ with $Ph_2PCH_2Li.tmen$ in thf at −78 °C. The structure of this complex is remarkable in that the formally open-shell zirconium atom and the phosphorus atom avoid interacting with each other; the Zr–C–P angle is unusually open (130.1°), and the Zr...P distance is 3.75 Å. $[(cp)_2Zr(CH_2PPh_2)Cl]$ reacts with $[Cr(CO)_5(thf)]$ and with $[Fe_2(CO)_9]$ to give $[(cp)_2Zr(Cl)CH_2PPh_2Cr(CO)_5]$ and $[(cp)_2Zr(Cl)CH_2PPh_2Fe(CO)_4]$, respectively, in which the phosphorus atom complexes to a second transition metal. Analogous alkyl- and alkenyl- complexes, $[(cp)_2Zr(CH_2PPh_2)(R)]$ (R = C_8H_{17} or $(CH_2)_4CH{=}CH_2$), have been obtained as impure, thermally unstable oils. The bis(phosphinomethyl) complex $[(cp)_2Zr(CH_2PPh_2)_2]$ has been isolated as a stable light brown crystalline solid [99].

3.1.7 Complexes with Si-donor ligands

$[(cp)_2ZrCl(SiMe_3)]$ and $[(cp)_2Zr(SiMe_3)_2]$ have been prepared by the reaction of $[(cp)_2ZrCl_2]$ with $[Hg(SiMe_3)_2]$ in boiling benzene. $[(cp)_2ZrCl(SiMe_3)]$ is unreactive toward hex-1-yne (55–60 °C) and CO (350 psi), but the Zr–Cl bond is cleaved by electrophiles such as Cl_2, $HgCl_2$ and $AlCl_3$ [100].

3.1.8 Hydride and borohydride complexes

Hydrogenolysis of the $M{-}CH_3$ bonds of $[(Rcp)_2MMe_2]$ (M = Zr or Hf; R = Me, $CHMe_2$, CMe_3 or CH_2Ph), $[(R^*cp)_2MMe_2]$ (M = Zr or Hf; R* = $MeCHEtCH_2$ or $PhCHEtCH_2$) and $[(R^*cp)(cp)HfMe_2]$ (R* = PhCHMe) gives the corresponding achiral and chiral dihydrides $[(Rcp)_2MH_2]$, $[(R^*cp)_2MH_2]$ and $[(R^*cp)(cp)HfH_2]$. The hydride ligands of $[(Rcp)_2HfH_2]$ can be substituted by a variety of other ligands, including halides, alkoxides, carboxylates and SPh. The dihydride complexes are good catalysts for the hydrogenation of alkenes, but the chiral dihydrides give only poor asymmetric induction in the catalytic reduction of prochiral alkenes [101].

Low-temperature (−70 °C) IR measurements have revealed that the carbonyl stretching frequencies of $[(C_5Me_5)_2ZrH_2(CO)]$ (2044 cm^{-1}), $[\{C_5(CD_3)_5\}_2ZrD_2(CO)]$ (2044 cm^{-1}) and $[(C_5Me_5)_2HfH_2(CO)]$ (2036 cm^{-1}) are *ca.* 100 cm^{-1} lower than $\nu(CO)$ in carbon monoxide. The unanticipated reduction of $\nu(CO)$ upon coordination to a d^0 metal centre has been rationalised in terms of π-backbonding from the filled MH_2 bonding orbital of b_2 symmetry [102].

The vibrational spectrum of $Zr(BH_4)_4$ supported on an alumina surface has been studied by the technique of inelastic electron tunneling spectroscopy. This technique has also been applied to investigate interactions of the supported zirconium complex with D_2, D_2O, H_2O, ethene, propene and ethyne [103-105].

3.2 ZIRCONIUM(III) AND HAFNIUM(III)

Ultraviolet and X-ray photoelectron emission spectra of solid ZrCl, $ZrCl_2$, Zr_6Cl_{12} and $ZrCl_3$ exhibit a metal-rich valence band at 1.1-1.5 eV which moves away from the Fermi level as the oxidation state of zirconium increases. These results are in accord with decreasing metallic character on going from ZrCl to $ZrCl_3$. On the basis of Zr-Zr distances alone, one might have expected strong metal-metal bonding in $ZrCl_3$ [106].

The Zr(III)/Zr(IV) mixed valence compound $Zr_{12}Al_4Cl_{51}$ has been synthesised as blue-black crystals from a $ZrCl_4$-Al_2Cl_6-Zr reaction system at 200 °C. The chemical properties of $Zr_{12}Al_4Cl_{51}$ parallel those of $ZrCl_3$. A partial determination of the structure by X-ray diffraction reveals a monoclinic unit cell of composition $\{Zr_{12}Cl_{36}\}^{n+}$. Each zirconium ion is located at the centre of a trigonal prism of chloride ions. and the zirconium ions are associated in triangles, each edge of which is doubly bridged by chloride ions. The Zr_3 triangles are joined by two chloride ion bridges at each vertex to form a ring of six Zr_3 units which encloses an 11 Å diameter hole. In the three-dimensional structure the holes stack so as to give an unbroken channel parallel to the *c* direction. The holes have more than enough volume to accommodate the remaining fifteen chloride ions and four aluminium(III) ions per unit cell, but unfortunately attempts to fix the position of these ions in the channels were unsuccessful owing to their disorder. The stoicheiometry requires that the $\{Zr_{12}Cl_{36}\}^{n+}$ (n = 3) units contain nine zirconium(III) (d^1) ions and three zirconium(IV) (d^0) ions. Since the zirconium ions occupy two different crystallographic sites in the ratio 2:1, there is no way to rationally distribute identifiable Zr(III) and Zr(IV) ions in the unit cell. Thus the $\{Zr_{12}Cl_{36}\}^{3+}$ unit must be viewed as a mixed-oxidation state species with nine d electrons delocalised over the twelve zirconium ions, which have an average formal oxidation state of 3.25. Although the Zr-Zr distances (the shortest is 3.354 Å) are considered to be too long for direct metal-metal bonding, magnetic susceptibility measurements indicate the presence of cooperative interactions which decrease the susceptibility far below that expected for a compound containing magnetically dilute zirconium(III) ions [107].

The disproportionations of solid $HfCl_3$ (to $HfCl_2$ (s) and $HfCl_4$ (g)) and solid $HfBr_3$ (to HfBr (s) and $HfBr_4$ (g)) have been studied by thermal analysis (TGA, DTGA and DTA) and by vapour pressure measurements. Values of ΔH° and ΔS° for the disproportionation reactions have been determined, and standard heats of formation and entropies of the trihalides have been calculated [108,109].

ZrI_3 has been synthesised in a steel or quartz reaction vessel by reaction of

ZrI_4 with metallic zirconium at 360-520 °C. Thermal analysis, vapour pressure and X-ray diffraction measurements indicate that zirconium(III) iodide forms a phase of variable composition with a broad homogeneity range. Lattice parameters of $ZrI_{3.0}$ and $ZrI_{2.64}$ (space group $P6_3/mcm$) have been determined, and the structure of $ZrI_{3.0}$ has been refined from a two-dimensional projection. The iodine atoms are in slightly distorted hexagonal close packing; the zirconium atoms occupy one-third of the octahedral holes, forming chains of zirconium atoms which extend along the c direction of the hexagonal crystal [110].

Reduction of a thf solution of $[(cp)_2Zr(CH_2PPh_2)Cl]$ with sodium amalgam gives a zirconium(III) species that exhibits an intense EPR signal at $g \simeq 1.98$ with hyperfine splitting by one ^{91}Zr nucleus (a = 13.5 G) and one ^{31}P nucleus (a = 19.5 G). The ^{31}P hyperfine splitting is consistent with a zirconium(III) complex that contains a Zr-P bond, probably $[(cp)_2Zr(CH_2PPh_2)Cl_n]^n$ (n = 0 or 1) [99]. The *meso*-metallocycles $[(cp)_2M\{CH(SiMe_3)C_6H_4CH(SiMe_3)\text{-}2\}]$ (M = Zr or Hf) can be reduced in thf with sodium naphthalenide or electrochemically (in a quasi-reversible one-electron process) to give M(III) complexes of probable formula $[(cp)_2M\{CH(SiMe_3)C_6H_4CH(SiMe_3)\text{-}2\}]^-$. The M(III) species have been characterised by their EPR spectra (g = 1.979 for M = Zr; g = 1.943 for M = Hf) [111].

3.3 ZIRCONIUM(II) AND HAFNIUM(II)

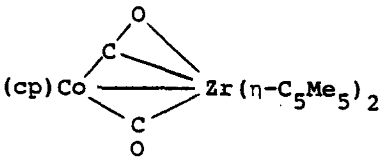
Solid hafnium dihalides HfX_2 (X = Cl or Br) disproportionate at 620 °C or 470-480 °C, respectively, to give solid HfX and gaseous HfX_4. Thermodynamic parameters for the disproportionations have been determined from vapour pressure measurements, and the standard heats of formation and entropies for the dihalides have been calculated [108,109]. $HfBr_2$ was prepared as a fine, crystalline, almost black powder by reaction of $HfBr_4$ with hafnium metal at 460-530 °C. The X-ray powder pattern of $HfBr_2$ indicates that the crystals are tetragonal with unit cell parameters a = 7.556 Å and c = 18.20 Å [109].

Zirconium(II) iodide has been synthesised by reaction of ZrI_4 vapour at a pressure of one atmosphere with metallic zirconium foil at 760-780 °C. An X-ray diffraction study of single crystals of ZrI_2 showed the existence of polytypes of a layer structure with orthorhombic cell parameters: a = 3.74 Å, b = 6.93 Å and $c = n \times 14.85$ Å. For the polytype studied in most detail, n = 24 and Z = 96 [110].

The electronic structure of ZrS, with the NaCl- and WC-type structures, has been investigated theoretically by band calculations and experimentally by photoelectron spectroscopy and low-temperature heat capacity measurements [112].

The red, air-sensitive zirconium(II) complex $[(cp)_2Zr\{P(OMe)_3\}_2]$ has been prepared by condensing sodium atoms at -100 °C into a thf solution containing $[(cp)_2ZrCl_2]$ and excess trimethyl phosphite. $[(cp)_2Zr\{P(OMe)_3\}_2]$ reacts cleanly with carbon monoxide in pentane solution at 25 °C/ 1 atmosphere to give $[(cp)_2Zr(CO)_2]$ [113]. $[(cp)_2Zr(PPh_2Me)_2]$ reacts with $CH_2{=}PPh_3$ to give $[(cp)_2Zr(CH_2)(PPh_2Me)]$, the first example of a Group IV metal carbene complex. $[(cp)_2Zr(CH_2)(PPh_2Me)]$ has been characterised in solution by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy [114]. $[(cp)_2ZrL_2]$ (L = PPh_2Me or PMe_2Ph) complexes are oxidised by alkyl halides yielding the formal oxidative addition product $[(cp)_2ZrRX]$ and/or $[(cp)_2ZrX_2]$. Experimental evidence has been adduced in support of an oxidation mechanism involving formation of alkyl radicals [115].

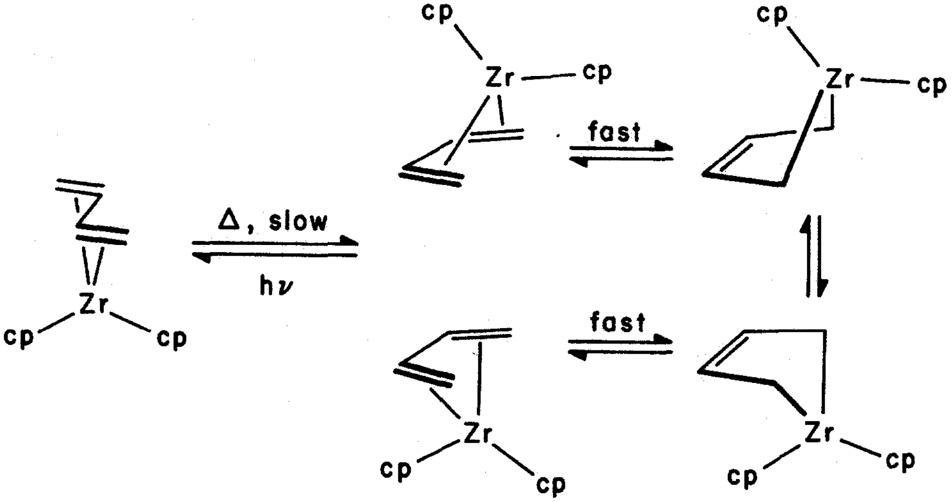
An X-ray crystallographic study of $[(cp)_2Zr(CO)_2]$ confirms the expected distorted tetrahedral geometry; OC-$\hat{\mathrm{Zr}}$-CO = 89.2°, (centroid cp)-$\hat{\mathrm{Zr}}$-(centroid cp) = 143.4°. The Zr-CO bond length, 2.187(4) Å, is slightly longer than expected on the basis of the Ti-CO bond length, 2.030(11) Å, in $[(cp)_2Ti(CO)_2]$ [116]. The dinuclear complex $[(cp)Co(CO)_2Zr(\eta\text{-}C_5Me_5)_2]$, prepared by reaction of $[(cp)Co(CO)_2]$ with $[(\eta\text{-}C_5Me_5)_2ZrH_2]$ or $[\{(\eta\text{-}C_5Me_5)_2ZrN_2\}_2N_2]$, has an interesting structure **(41)** in



(41)

which the two carbonyl groups exhibit different bonding modes. One bridges the two metal atoms in a standard μ_2 manner, while the other bridges in a μ_2-η^1,η^2 fashion *via* a σ-bond to cobalt and an interaction of the CO π-bond with zirconium. The unsymmetrical bridging arrangement and the presence of a Co-Zr single bond {*r*(Co-Zr) = 2.926 Å} allow both metals to achieve closed-shell, eighteen-electron configurations [117].

Photolysis of $[(cp)_2ZrPh_2]$ at -30 °C in toluene solution in the presence of suitable conjugated dienes affords the corresponding monomeric $[(cp)_2Zr(\eta^4\text{-diene})]$ complexes. Some of these complexes were isolated as mixtures of two isomers that differ in the conformation adopted by the η^4-diene ligand, *viz.* *s-cis* **(42)** or *s-trans* **(43)**; others were isolated as the *s-cis* **(42)** or *s-trans* **(43)** isomer, depending on the diene. $\Delta G^{\ddagger}$ for *s-trans* to *s-cis* isomerisation {equation (13)} is 76-95 kJ mol^{-1}, and in most cases the *s-cis* isomer is more stable thermodynamically. However, the *s-cis* isomer **(42)** can be converted to the *s-trans* isomer **(43)** photochemically. The two isomers are readily distinguished by NMR spectroscopy. The two inequivalent cp ligands of the *s-cis* complexes **(42)**, as well as the syn and anti hydrogens on the terminal carbon atoms of the diene, undergo rapid exchange ($\Delta G^{\ddagger}$ = 33-53 kJ mol^{-1}) by a process that is believed to involve rapid migration of



(13)

(43) (42) (44)

the $(cp)_2Zr$ unit from one face of the diene to the other *via* a metallacyclopentane intermediate **(44)**. This mechanism is supported by the crystal structure of $[(cp)_2Zr(\eta^4$-*s*-*cis*-2,3-dimethylbutadiene)] which shows considerably stronger bonding to the diene terminal carbon atoms $\{r(Zr–C) = 2.300$ Å$\}$ than to the diene interior carbon atoms $\{r(Zr–C) = 2.597$ Å$\}$. Thus, relatively little motion is required to form the metallacyclopentane intermediate **(44)**. The structure of the *s*-*trans*-butadiene complex $[(cp)_2Zr(s\text{-}trans\text{-}C_4H_6)]$ has been confirmed by X-ray crystallography. This work demonstrates, among other things, that coordination of a conjugated diene in an *s*-*trans* geometry does not necessarily require two metal centres, as has been stressed in the literature [118].

Following an earlier communication [119], a full paper [120] has been published describing the preparation and properties of the hydrido(η^5-dienyl)bis{1,2-bis(dimethylphosphino)ethane}zirconium(II) complexes $[ZrH(\eta^5$-cyclohexadienyl)(dmpe)$_2]$ and $[ZrH(\eta^5$-cyclooctadienyl)(dmpe)$_2]$. The latter compound has a distorted octahedral geometry with the hydride ligand *trans* to the C_8H_{11} group. Five carbon atoms of the C_8H_{11} group are coplanar and approximately the same distance (2.43–2.47 Å) from the zirconium atom. $[ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2]$ catalyses the disproportionation of 1,3-cyclohexadiene to benzene and cyclohexene, as well as a number of related hydrogen transfer reactions.

The reaction of $[(cp)_2ZrMe_2]$ with PhLi (or $[(cp)_2ZrPh_2]$ with MeLi) in diethyl ether at 20 °C yields methane, benzene, cyclopentadienyllithium and $MeZrPh.3Et_2O$.

The zirconium compound was isolated as brown, pyrophoric crystals, slightly soluble in organic solvents, suggesting a polymeric structure. Some of the reactions of $MeZrPh.3Et_2O$ are summarised in equations (14) - (16) [121].

$$MeZrPh.3Et_2O + 4HX \xrightarrow[20°C]{PhMe} MeH + PhH + 3Et_2O + H_2 + ZrX_4 \quad (14)$$

(X = OH, Cl or MeCOO)

$$MeZrPh.3Et_2O + 4HgCl_2 \xrightarrow[80°C]{thf} MeHgCl + PhHgCl + Hg_2Cl_2 + ZrCl_4.3Et_2O \quad (15)$$

$$MeZrPh.3Et_2O + 2CO_2 \xrightarrow{PhMe} (MeCOO)Zr(OOCPh).3Et_2O \quad (16)$$

3.4 ZIRCONIUM(I) AND HAFNIUM(I)

Zirconium monochloride has a layer structure in which four-layer Cl-Zr-Zr-Cl sandwiches stack along the hexagonal *c* direction. The zirconium atoms are surrounded by three zirconium and three chlorine neighbours in trigonal antiprismatic coordination [122]. Electronic band calculations on ZrCl indicate the presence, within the sandwiches, of strong covalent metal-metal bonding involving zirconium 4d orbitals. The Fermi level falls in a deep (but nonzero) trough in the density of states, consistent with the d-band metallic properties of ZrCl [123,124].

The disproportionation of solid HfCl to gaseous $HfCl_4$ and hafnium metal has been studied by thermal analysis (TGA, DTGA and DTA) and by the Knudsen effusion method [108].

3.5 ZIRCONIUM(0) AND HAFNIUM(0)

The η-cycloheptatrienyl-η-cycloheptadienyl complexes $[M(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ (M = Zr or Hf) have been prepared by cocondensation of cycloheptatriene with zirconium or hafnium vapours followed by vacuum pyrolysis of the products at 120-160 °C [125].

The butadiene-containing complex $[\{Zr(\eta\text{-}C_4H_6)_2(dmpe)\}_2(dmpe)]$ catalyses the dimerisation of alkenes. On the basis of product distributions, a mechanism involving formation of a metallacyclopentane complex has been proposed [126].

Finally, a new zirconium phosphide ZrNiP is noted, which is not easily classified in terms of formal oxidation states. This compound has a hexagonal structure, space group $P6_3/mmc$, in which the zirconium atoms are hexagonal close packed with the nickel atoms in octahedral interstices and the phosphorus atoms in paired tetrahedral interstices. Each zirconium atom is surrounded by six nickel atoms and three phosphorus atoms {r(Zr-Ni) = 2.82 Å; r(Zr-P) = 2.18 Å} [127].

REFERENCES

1 J.A. Labinger, *J. Organomet. Chem.*, 196 (1980) 37.
2 J.D. Corbett, in "Adv. Chem. Ser., No. 186, Solid State Chemistry: A Contemporary Overview," (S.L. Holt, J.B. Milstein and M. Robbins, Eds.), 1980 pp. 329-347.
3 M.L.H. Green, *J. Organomet. Chem.*, 200 (1980) 119.
4 W.A. Nugent and B.L. Haymore, *Coord. Chem. Rev.*, 31 (1980) 123.
5 P.T. Wolczanski and J.E. Bercaw, *Acc. Chem. Res.*, 13 (1980) 121.
6 M.A. Medkov, M.D. Davidovich, M.D. Rizaeva, I.P. Kondratyuk and B.V. Bukvetskii, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 29 (1980) 1185.
7 J.P. Laval, B. Frit and B. Gaudreau, *Rev. Chim. Miner.*, 16 (1979) 509.
8 J.P. Laval and B. Frit, *Acta Crystallogr. Sect. B*, 36 (1980) 2533.
9 I.D. Ratnikova, Yu.M. Korenev and A.V. Novoselova, *Russ. J. Inorg. Chem.*, 25 (1980) 452.
10 Yu.M. Korenev, P.I. Antipov and A.V. Novoselova, *Russ. J. Inorg. Chem.*, 25 (1980) 698.
11 L.P. Otroshchenko, V.I. Simonov, R.L. Davidovich, L.E. Fykin, V. Ya. Duderov and S.P. Solov'ev, *Sov. Phys. Crystallogr.*, 25 (1980) 416.
12 Yu.M. Korenev, L.N. Sidorov, A.N. Tykov and A.V. Novoselova, *Russ. J. Inorg. Chem.*, 25 (1980) 154.
13 M.I. Nikitin, I.D. Sorokin, E.V. Skokan and L.N. Sidorov, *Russ. J. Phys. Chem.*, 54 (1980) 770.
14 V. Fernandez and C. Muro, *Z. Anorg. Allg. Chem.*, 466 (1980) 209.
15 S.A.A. Zaidi, T.A. Khan and N.S. Neelam, *Indian J. Chem., Sect. A*, 18 (1979) 461.
16 S.A.A. Zaidi, T.A. Khan and N.S. Neelam, *Indian J. Chem., Sect. A*, 19 (1980) 169.
17 K.C. Malhotra, G. Mehrotra and S.C. Chaudhry, *Indian J. Chem., Sect. A*, 17 (1979) 421.
18 A.F. Demiray and W. Brockner, *Monatsch. Chem.*, 111 (1980) 21.
19 F. Basile, E. Chassaing and G. Lorthioir, *Ann. Chim. Fr.*, 5 (1980) 553.
20 S.R. Wade and G.R. Willey, *J. Less-Common Met.*, 68 (1979) 105.
21 F.F. Said and D.G. Tuck, *Can. J. Chem.*, 58 (1980) 1673.
22 G. Balducci, L. Bencivenni, G. De Rosa, R. Gigli, B. Martini and S.N. Cesaro, *J. Mol. Struct.*, 64 (1980) 163.
23 M. Spoliti, L. Bencivenni, A. Farina, B. Martini and S.N. Cesaro, *J. Mol. Struct.*, 65 (1980) 105.
24 J.H. Davis, H.-N. Sun, D. Redfield and G.D. Stucky, *J. Magn. Reson.*, 37 (1980) 441.
25 I. Fragala, T.J. Marks, P.J. Fagan and J.M. Manriquez, *J. Electron Spectrosc. Relat. Phenom.*, 20 (1980) 249.
26 N.E. Murr, A. Chaloyard and J. Tirouflet, *J. Chem. Soc., Chem. Commun.*, (1980) 446.
27 R.K. Agarwal, A.K. Srivastava and T.N. Srivastava, *Indian J. Chem., Sect. A*, 18 (1979) 459.
28 R.K. Agarwal and A.K. Srivastava, *Inorg. Nucl. Chem. Lett.*, 16 (1980) 311.
29 S.K. Vasisht and S.K. Gupta, *Monatsh. Chem.*, 110 (1979) 1197.
30 C. Preti, G. Tosi and P. Zannini, *Transition Met. Chem.,(Weinheim Ger.)*, 5 (1980) 200.
31 P.R. Patil and V. Krishnan, *Indian J. Chem., Sect. A*, 19 (1980) 555.
32 N.I. Kozlova and N.Ya. Turova, *Russ. J. Inorg. Chem.*, 25 (1980) 1188.
33 K.C. Malhotra, G. Mehrotra and S.C. Chaudhry, *Natl. Acad. Sci. Lett. (India)*, 3 (1980) 21; [*Chem. Abstr.*, 93 (1980) 160480].
34 M. Pal and R.N. Kapoor, *Inorg. Chim. Acta*, 40 (1980) 99.
35 G.A. Lock and D.W. Thompson, *J. Chem. Soc., Dalton Trans.*, (1980) 1265.
36 T.J. Pinnavaia and R.C. Fay, *Inorg. Chem.*, 7 (1968) 502.
37 R.C. Fay and J.K. Howie, *J. Am. Chem. Soc.*, 101 (1979) 1115.
38 T.J. Pinnavaia, J.J. Howe and R.E. Teets, *Inorg. Chem.*, 13 (1974) 1074.

39 E.M. Brainina and M.Kh. Minacheva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1980) 410.
40 A. Hossain and M.B. Hursthouse, *Inorg. Chim. Acta*, 44 (1980) L259.
41 K.C. Malhotra, A. Kumar and S.C. Chaudhry, *Indian J. Chem., Sect. A*, 18 (1979) 423.
42 A.R. Middleton and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1980) 1888.
43 G. Erker and F. Rosenfeldt, *J. Organomet. Chem.*, 188 (1980) C1.
44 J.A. Marsella, K.G. Moloy and K.G. Caulton, *J. Organomet. Chem.*, 201 (1980) 389.
45 K.I. Gell, G.M. Williams and J. Schwartz, *J. Chem. Soc., Chem. Commun.*, (1980) 550.
46 L.-G. Lin, *J. Phys. Chem. Solids*, 41 (1980) 331.
47 B.M. Gatehouse and M.C. Nesbit, *J. Solid State Chem.*, 31 (1980) 53.
48 U. Treiber and S. Kemmler-Sack, *Z. Anorg. Allg. Chem.*, 470 (1980) 103.
49 R. Papiernik, D. Mercurio and B. Frit, *Acta Crystallogr., Sect. B*, 36 (1980) 1769.
50 V.P. Vasil'ev, V.A. Borodin, A.I. Lytkin, V.P. Babaeva and V.Ya. Rosolovskii, *Russ. J. Inorg. Chem.*, 25 (1980) 363.
51 I.I. Alekseeva, V.V. Borisova, I.I. Nemzer and L.I. Yuranova, *Russ. J. Inorg. Chem.*, 24 (1979) 1467.
52 T.P. Spasibenko, *Russ. J. Inorg. Chem.*, 24 (1979) 1815.
53 D.L. Rogachev, V.Ya. Kuznetsov, L.M. Dikareva, G.G. Sadikov and M.A. Porai-Koshits, *J. Struct. Chem.*, 21 (1980) 118.
54 Y. Inomata, T. Inomata and T. Moriwaki, *Spectrochim. Acta, Part A*, 36 (1980) 839.
55 Y. Inoue and Y. Yamada, *Bull. Chem. Soc. Japan*, 52 (1979) 3528.
56 G. Alberti, U. Costantino and R. Giulietti, *J. Inorg. Nucl. Chem.*, 42 (1980) 1062.
57 J.W. Johnson, *J. Chem. Soc., Chem. Commun.*, (1980) 263.
58 B.W. Levitt, *Chem. Ind. (London)*, (1980) 289.
59 A. Clearfield and S.P. Pack, *J. Inorg. Nucl. Chem.*, 42 (1980) 771.
60 S. Allulli, M.A. Massucci and N. Tomassini, *J. Chem. Thermodyn.*, 11 (1979) 613.
61 G. Alberti, M.G. Bernasconi, M. Casciola and U. Costantino, *J. Inorg. Nucl. Chem.*, 42 (1980) 1631.
62 L. Kullberg and A. Clearfield, *J. Phys. Chem.*, 84 (1980) 165.
63 U. Costantino, A. Isernia and G. De Meo, *Bull. Chem. Soc. Jpn.*, 53 (1980) 2384.
64 Y. Yazawa, T. Eguchi, K. Takaguchi and I. Tomita, *Bull. Chem. Soc. Jpn.*, 52 (1979) 2923.
65 H. Ehrhardt, H. Schweer and H. Seidel, *Z. Anorg. Allg. Chem.*, 462 (1980) 185.
66 L.A. Malinko, L.S. Chumakova, K.I. Arsenin, K.F. Karlysheva and I.A. Sheka, *Russ. J. Inorg. Chem.*, 25 (1980) 1184.
67 S.A.A. Zaidi, T.A. Khan and B.S. Neelam, *J. Inorg. Nucl. Chem.*, 42 (1980) 1525.
68 S.A.A. Zaidi, T.A. Khan and N.S. Neelam, *Indian J. Chem., Sect. A*, 17 (1979) 419.
69 S. Kumar and N.K. Kaushik, *Inorg. Nucl. Chem. Lett.*, 16 (1980) 389.
70 N.K. Kaushik, B. Bhushan and G.R. Chhatwal, *J. Inorg. Nucl. Chem.*, 42 (1980) 457.
71 M.E. Silver and R.C. Fay, unpublished results.
72 R.K. Tuli, P. Soni, K. Chandra, R.K. Sharma and B.S. Garg, *Transition Met. Chem., (Weinheim Ger.)*, 5 (1980) 145.
73 W.L. Steffen, H.K. Chun and R.C. Fay, *Inorg. Chem.*, 17 (1978) 3498.
74 A.H. Bruder, R.C. Fay, D.F. Lewis and A.A. Sayler, *J. Am. Chem. Soc.*, 98 (1976) 6932.
75 J.R. Weir Ph.D. Thesis, Cornell University, 1981; J.R. Weir and R.C. Fay, to be published.
76 J.M. McCall and A. Shaver, *J. Organomet. Chem.*, 193 (1980) C37.
77 K. Stocks, G. Eulenberger and H. Hahn, *Z. Anorg. Allg. Chem.*, 463 (1980) 105.
78 V.G. Aleshin and A.I. Kharlamov, *Russ. J. Inorg. Chem.*, 25 (1980) 1128.
79 C. Airoldi, D.C. Bradley, H. Chudzynska, M.B. Hursthouse, K.M. Abdul Malik and P.R. Raithby, *J. Chem. Soc., Dalton Trans.*, (1980) 2010.
80 R.A. Andersen, *Inorg. Nucl. Chem. Lett.*, 16 (1980) 31.
81 R.A. Andersen, *J. Organomet. Chem.*, 192 (1980) 189.
82 K.R. Nahar, A.K. Solanki and A.M. Bhandari, *Indian J. Chem., Sect. A*, 19 (1980) 69.

83 D.J. Brauer, H. Burger, E. Essig and W. Geschwandtner, *J. Organomet. Chem.*, 190 (1980) 343.

84 R.V. Bynum, W.E. Hunter, R.D. Rogers and J.L. Atwood, *Inorg. Chem.*, 19 (1980) 2368.

85 G. Gupta, R. Sharan and R.N. Kapoor, *Bull. Chem. Soc. Jpn.*, 52 (1979) 3088.

86 G. Gupta. R. Sharan and R.N. Kapoor, *Indian J. Chem., Sect. A*, 18 (1979) 56.

87 R.K. Sharma and J.P. Tandon, *J. Prakt. Chem.*, 322 (1980) 161.

88 R.K. Sharma, R.V. Singh and J.P. Tandon, *J. Prakt. Chem.*, 322 (1980) 508.

89 R.K. Sharma, R.V. Singh and J.P. Tandon, *J. Inorg. Nucl. Chem.*, 42 (1980) 463.

90 R.K. Sharma, R.V. Singh and J.P. Tandon, *Curr. Sci.*, 49 (1980) 89.

91 R.K. Sharma, R.V. Singh and J.P. Tandon, *Indian J. Chem., Sect. A*, 18 (1979) 360.

92 R.K. Sharma, R.V. Singh and J.P. Tandon, *J. Inorg. Nucl. Chem.*, 42 (1980) 1267.

93 A. Syamal and D. Kumar, *Synth. React. Inorg. Met.-Org. Chem.*, 10 (1980) 63.

94 A. Syamal and D. Kumar, *J. Less-Common Met.*, 71 (1980) 113.

95 S. Kher, S.K. Sahni, V. Kumari and R.N. Kapoor, *Synth. React. Inorg. Met.-Org. Chem.*, 10 (1980) 431.

96 M.S. Delgado and V. Fernandez, *Z. Anorg. Allg. Chem.*, 467 (1980) 225.

97 P. Meunier and B. Gautheron, *J. Organomet. Chem.*, 193 (1980) C13.

98 K.I. Gell and J. Schwartz, *Inorg. Chem.*, 19 (1980) 3207.

99 N.E. Schore and H. Hope, *J. Am. Chem. Soc.*, 102 (1980) 4251.

100 A.J. Blakeney and J.A. Gladysz, *J. Organomet. Chem.*, 202 (1980) 263.

101 S. Couturier, G. Tainturier and B. Gautheron, *J. Organomet. Chem.*, 195 (1980) 291.

102 J.A. Marsella, C.J. Curtiss, J.E. Bercaw and K.G. Caulton, *J. Am. Chem. Soc.*, 102 (1980) 7244.

103 H.E. Evans and W.H. Weinberg, *J. Am. Chem. Soc.*, 102 (1980) 872.

104 H.E. Evans and W.H. Weinberg, *J. Am. Chem. Soc.*, 102 (1980) 2548.

105 H.E. Evans and W.H. Weinberg, *J. Am. Chem. Soc.*, 102 (1980) 2554.

106 J.D. Corbett and J.W. Anderegg, *Inorg. Chem.*, 19 (1980) 3822.

107 J. Kleppinger, J. Wrazel, J.C. Calabrese and E.M. Larsen, *Inorg. Chem.*, 19 (1980) 3172.

108 A.S. Izmailovich,V.I. Tsirel'nikov and L.N. Komissarova, *Russ. J. Inorg. Chem.*, 24 (1979) 1309.

109 G.S. Marek, S.I. Troyanov and V.I. Tsirel'nikov, *Russ. J. Inorg. Chem.*, 24 (1979) 1303.

110 Kh.S. Lopis, S.I. Troyanov and V.I. Tsirel'nikov, *Russ. J. Inorg. Chem.*, 24 (1979) 1306.

111 M.F. Lappert and C.L. Raston, *J. Chem. Soc., Chem. Commun.*, (1980) 1284.

112 T.-H. Nguyen, H. Franzen and B.N. Harmon, *J. Chem. Phys.*, 73 (1980) 425.

113 M. Chang, P.L. Timms and R.B. King, *J. Organomet. Chem.*, 199 (1980) C3.

114 J. Schwartz and K.I. Gell, *J. Organomet. Chem.*, 184 (1980) C1.

115 G.M. Williams, K.I. Gell and J. Schwartz, *J. Am. Chem. Soc.*, 102 (1980) 3660.

116 J.L. Atwood, R.D. Rogers, W.E. Hunter, C. Floriani, G. Fachinetti and A. Chiesi-Villa, *Inorg. Chem.*, 19 (1980) 3812.

117 P.T. Barger and J.E. Bercaw, *J. Organomet. Chem.*, 201 (1980) C39.

118 G. Erker, J. Wicher, K. Engel, F. Rosenfeldt, W. Dietrich and C. Kruger, *J. Am. Chem. Soc.*, 102 (1980) 6344.

119 S. Datta, S.S. Wreford, R.P. Beatty and T.J. McNeese, *J. Am. Chem. Soc.*, 101 (1979) 1053.

120 M.B. Fischer, E.J. James, T.J. McNeese, S.C. Nyburg, B. Posin, W. Wong-Ng and S.S. Wreford, *J. Am. Chem. Soc.*, 102 (1980) 4941.

121 G.A. Razuvaev, L.I. Vyshinskaya, G.A. Vasil'eva, A.V. Malysheva and V.P Mar'in, *Inorg. Chim. Acta*, 44 (1980) L285.

122 D.G. Adolphson and J.D. Corbett, *Inorg. Chem.*, 15 (1976) 1820.

123 D.W. Bullett, *Inorg. Chem.*, 19 (1980) 1780.

124 J.F. Marchiando, B.N. Harmon and S.H. Liu, *Physica, B+C*, 99B (1980) 259.

125 F.G.N. Cloke, M.L.H. Green and P.J. Lennon, *J. Organomet. Chem.*, 188 (1980) C25.

126 S. Datta, M.B. Fischer and S.S. Wreford, *J. Organomet. Chem.*, 188 (1980) 353.

127 Yu.B. Kuz'ma and Ya.F. Palfii, *Russ. J. Inorg. Chem.*, 24 (1979) 1421.