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3. ZIRCONIUM AND HAFNIUM

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CONTENTS

INTRODUCTION

The 1979 literature on zirconium and hafnium is extensive and diverse, including reports of compounds in which the metal exhibits all possible integral oxidation states from +4 to zero. The chemistry of these metals in their lower oxidation states is a subject of expanding interest and importance. Among the more significant developments in this area during the past year are: (1) synthesis and characterization of the first Zr(0) and Hf(0) compounds; (2) preparation and spectroscopic characterization of $[(\eta\text{-}C_5H_4R)_2Zr(N_2)\text{-}\{CH(SiMe_3)_2\}]$ (R = H or Me), the first compounds that contain a "side-on" attached dinitrogen ligand; and (3) X-ray structural studies of $ZrCl_2$, a layer compound in which Zr exhibits trigonal prismatic coordination, and $[(\eta\text{-}C_5H_5)_2Hf(CO)_2]$, the first hafnium carbonyl. The stereochemistry of eight-coordinate Zr(IV) and Hf(IV) chelates continues to attract attention. Several X-ray structures have been reported, and the first NMR studies yielding information about the stereochemistry and rearrangement kinetics of eight-coordinate Zr(IV) and Hf(IV) complexes in solution have been carried out. An especially interesting development in the area of Zr hydride complexes is the synthesis of hydrido "zirconoxy" carbenes, $[(\eta\text{-}C_5H_5)_2M{=}CHOZr(H)(\eta\text{-}C_5Me_5)_2]$ (M = Cr, Mo, W or Nb(H)).

This review covers the major journals for the 1979 calendar year and the

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lesser known and/or foreign journals for the period covered by Chemical Abstracts, Volume 90, No. 1 to Volume 91, No. 20. Comprehensive coverage of the coordination chemistry of Zr and Hf is attempted, but organometallic and solid-state aspects of the chemistry of these elements are treated selectively and, usually, in connection with some other theme. For a comprehensive treatment of the organometallic chemistry, the reader is referred to the annual reviews by Labinger in the Journal of Organometallic Chemistry; reviews of the literature for 1977 [1] and 1978 [2] have appeared during the past year and a review of the 1979 literature is forthcoming. On the solid state side, Whittingham has reviewed the chemistry of intercalation compounds of transition metal chalcogenides, including the sulphides and selenides of Zr and Hf [3].

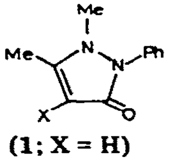
3.1 ZIRCONIUM(IV) AND HAFNIUM(IV) COMPOUNDS

3.1.1 Halide and pseudo-halide complexes

The structures of gaseous [ZrF_4] and [HfF_4] have been determined by electron diffraction at 975 and 1025 K, respectively. These molecules have regular tetrahedral structures with bond distances $\bar{r}$(Zr—F) = 1.902(4) Å and $\bar{r}$(Hf—F) = 1.909(5) Å [4]. The complex fluorides $[Et_4N]_2[MF_6] \cdot 2\,H_2O$ (M = Zr or Hf) have been prepared by direct electrochemical oxidation of zirconium or hafnium anodes in PhCN solutions that contain $[Et_4N]F \cdot 3\,HF$ [5]. The hydrolyses of $K_2[ZrF_6]$ and $K_2[HfF_6]$ in the pH range 1—4 have been studied by paper chromatography [6].

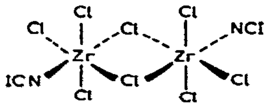
Tuck has reviewed methods for direct electrochemical synthesis of a large number of inorganic and organometallic compounds including MX_4, $[MX_4(MeCN)_2]$ and $[Et_4N]_2[MX_6]$ (M = Zr or Hf; X = Cl or Br) [7]. The ^{35}Cl nuclear quadrupole resonance spectra of $ZrCl_4$ and $HfCl_4$ exhibit two equally intense lines of widely different frequency [8], consistent with the crystal structure of $ZrCl_4$, which shows the presence of bridging and terminal chlorine atoms [9,10].

$ZrCl_4$ reacts with Lewis bases to give solid adducts of the type $ZrCl_4L$ and $ZrCl_4L_2$. Mixtures of $ZrCl_4$ and the pyrazolone ligands antipyrene (1) and 4-aminoantipyrene (2) afford insoluble [$ZrCl_4L_2$] complexes that have been assigned an octahedral *trans* structure on the basis of IR spectra; the pyrazolone ligands are coordinated through the carbonyl oxygen atom [11].



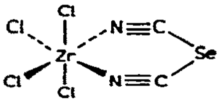
(1; X = H)
(2; X = NH_2)

The pseudo-halogen ICN adds to $ZrCl_4$ to give a 1 : 1 adduct in which ICN is attached to Zr through the N atom; a dimeric C_{2h} structure (3) has been



(3)

proposed on the basis of IR and Raman spectral evidence [12]. Vibrational spectra indicate that $ZrCl_4$ adducts with $S(CN)_2$ and $Se(CN)_2$ adopt rather different structures. $[ZrCl_4\{S(CN)_2\}_2]$ has been assigned an octahedral *cis* structure in which the $S(CN)_2$ ligands are bonded to Zr through the S atoms. $[ZrCl_4\{Se(CN)_2\}]$, a 1 : 1 adduct, appears to contain an *N*-bonded $Se(CN)_2$ ligand, and a chelate structure (4) has been suggested [13]. However, oligomeric structures in which $Se(CN)_2$ acts as an *N*-bonded bridging ligand may be more likely in view of the geometry of $Se(CN)_2$ [14]. The pseudo-halogen IOCN reacts with $ZrCl_4$ in dichloromethane at —30°C (eqn. (1)) to give $ZrCl_3(NCO)$ as a white solid; IR spectra indicate that the cyanate ligand is



(4)

$$ZrCl_4 + IOCN \rightarrow ZrCl_3(NCO) + ICl \qquad (1)$$

attached to Zr through the N atom [15].

t-Butylisonitrile inserts into a Hf—Cl bond of $HfCl_4$ yielding $[\{HfCl_3(C(Cl)NCMe_3)(CNCMe_3)\}_2]$, which is believed to be dimeric on the basis of a molecular weight measurement on the more soluble titanium analogue. The inserted isonitrile probably bridges to the second Hf atom through the imino-nitrogen atom; IR spectra show the presence of inserted ($\nu(C{=}N)$ = 1600—1750 cm^{-1}) and terminal ($\nu(C{\equiv}N)$ = 2225 cm^{-1}) isonitrile ligands. Attempts to induce further isonitrile insertion by reaction of $[\{HfCl_3(C(Cl)\cdot NCMe_3)(CNCMe_3)\}_2]$ with chelating ligands such as bis(diphenylphosphino)ethane (dppe), 8-quinolinolate (8-*O*-quin), and *N,N*-diethyldithiocarbamate led to displacement of isonitrile ligands; dppe and 8-*O*-quin displace the terminal isonitrile ligands yielding $[HfCl_3\{C(Cl)NCMe_3\}(dppe)]$ and $[HfCl_2\{C(Cl)NCMe_3\}(8\text{-}O\text{-quin})]$, respectively, while $[Et_2NCS_2]^-$ displaces all of the isonitrile affording $[Hf(Et_2NCS_2)_4]$ [16].

^{79}Br and ^{127}I NQR spectra have been reported for MBr_4 and MI_4 (M = Zr or Hf) [8]. The tetrabromides exhibit two intense resonances having frequencies in good agreement with a previous report [17]; however, the spectra are complicated by the presence of additional weak resonance lines. Spectra of the tetraiodides are even more complex and suggest the presence of several crystalline modifications. X-ray diffraction studies of ZrI_4 crystals obtained by condensation of ZrI_4 vapour revealed the presence of at least two kinds of crystals (orthorhombic and tetragonal) [8]. Monoclinic crystals of ZrI_4 have been grown by annealing a sample of ZrI_4 at 503 K in an evacuated glass ampoule. The structure of this modification consists of infinite chains of $\{ZrI_6\}$ octahedra that share non-opposite edges so as to give a helical arrangement with an identity period of six octahedra along the chain. This structure is different from the α-NbI_4, $ZrCl_4$ and β-$ReCl_4$ chain structures, and it appears to be the first AB_4 structure of its type. Zr—I bond lengths vary from 2.692(1) to 3.030(1) Å; Zr ··· Zr distances along the chain are quite uniform (4.394(1) and 4.416(1) Å) [18].

^{35}Cl and ^{79}Br NQR resonance frequencies for $[(\eta\text{-}C_5H_5)_2ZrCl_2]$ and $[(\eta\text{-}C_5H_5)_2ZrBr_2]$ are 25—30% lower than for the analogous Ti compounds; this result has been interpreted in terms of more metal—halogen π bonding in the Zr complexes than in the Ti analogues [19]. $[(\eta\text{-}C_5H_5)_2Zr(NCO)_2]$ has a distorted tetrahedral structure that contains approximately linear Zr—N—C—O moieties, with $\bar{r}$(Zr—N) = 2.110 Å; $\bar{r}$\{Zr—(centroid C_5H_5)\} = 2.194 Å; N—$\widehat{Zr}$—N = 96.4°; and (centroid C_5H_5)—$\widehat{Zr}$—(centroid C_5H_5) = 130.9°. The IR spectrum of $[(\eta\text{-}C_5H_5)_2Hf(NCO)_2]$ is very similar to spectra of the isostructural Zr and Ti analogues, and therefore it seems likely that the Hf compound also contains *N*-bonded cyanate ligands [20].

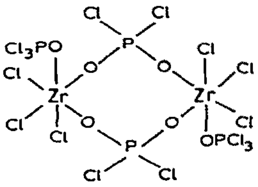
3.1.2 Complexes with O-donor ligands

Dichlorophosphates of the type $ZrCl_3(O_2PCl_2) \cdot POCl_3$ and $MOCl(O_2PCl_2) \cdot POCl_3$ (M = Zr or Hf) have been prepared by reaction of the metal tetrachlorides with Cl_2O in $POCl_3$ (eqns. (2) and (3)). IR and Raman spectral studies suggest that $ZrCl_3(O_2PCl_2) \cdot POCl_3$ has a centrosymmetric dimeric

$$ZrCl_4 + 2\ POCl_3 + Cl_2O \rightarrow ZrCl_3(O_2PCl_2) \cdot POCl_3 + 2\ Cl_2 \qquad (2)$$

$$MCl_4 + 2\ POCl_3 + 2\ Cl_2O \rightarrow MOCl(O_2PCl_2) \cdot POCl_3 + 4\ Cl_2 \qquad (3)$$

structure (5), while the very insoluble $MOCl(O_2PCl_2) \cdot POCl_3$ compounds are assumed to have an oxo-bridged polymeric structure, (6) [21].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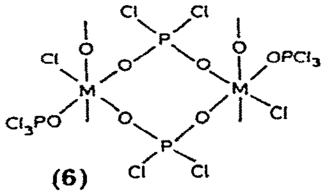

(6)

The structures of two interesting oxo-bridged organometallic zirconium complexes have been determined by X-ray diffraction. The molecular structure of $[\{(\eta\text{-}C_5H_5)_2Zr(SPh)\}_2O]$, the hydrolysis product of $[(\eta\text{-}C_5H_5)_2Zr(SPh)_2]$, consists of two $\{(\eta\text{-}C_5H_5)_2Zr(SPh)\}$ units linked by a non-linear oxo bridge ($Zr—\hat{O}—Zr = 165.8(2)°$). Relatively short Zr—O bond distances (1.968(3) and 1.964(3) Å) and a dihedral angle of 61.7° between the two S—Zr—O planes are in accord with a significant amount of oxygen $p_\pi \rightarrow$ zirconium d_π bonding [22]. The unprecedented cyclic trimer $[\{(\eta\text{-}C_5H_5)_2ZrO\}_3]$ has been obtained by reaction of $[(\eta\text{-}C_5H_5)_2Zr(CO)_2]$ with CO_2 in hot toluene (eqn. (4)). It contains a nearly planar six-membered Zr_3O_3 ring with quite uniform Zr—O—Zr and O—Zr—O bond angles (averaged values 142.5 and 97.5°, respectively) and with a mean Zr—O bond length (1.959(3) Å) indicative of an appreciable amount of zirconium—oxygen double bonding [23].

$$3[(\eta\text{-}C_5H_5)_2Zr(CO)_2] + 3\ CO_2 \rightarrow [\{(\eta\text{-}C_5H_5)_2ZrO\}_3] + 9\ CO \qquad (4)$$

The polymorphism of ZrO_2 at temperatures of 25, 300, 400 and 450°C has been studied as a function of pressure up to 130 kbar. The monoclinic modification, which is the stable form of ZrO_2 under ordinary conditions, converts to an orthorhombic modification at higher pressures [24].

Most of the papers concerning complexes with *O*-donor ligands report studies of compounds that contain bidentate chelating ligands. Using the Freon solvent $CHClF_2$, ^1H and ^{19}F NMR spectra of Zr(IV) and Hf(IV) tetrakis(β-diketonates) have been investigated at temperatures down to −170°C, and several complexes have been identified which become stereochemically rigid on the NMR time scale at temperatures in the range −115 to −170°C [25]. Spectra of $[Zr(acac)_4]$ and $[Hf(acac)_4]$ exhibit two methyl proton resonances of equal intensity in the slow-exchange limit, consistent with the square antiprismatic *ssss*-D_2 stereoisomer found in the solid state for $[Zr(acac)_4]$ [26]. Similarly, the limiting slow-exchange ^1H NMR spectrum of $[Zr(acac)_2(NO_3)_2]$ is in accord with the *mmmm*-C_2 dodecahedral structure found in crystalline $[Zr(acac)_2(NO_3)_2]$ [27]. ^{19}F spectra of $[Zr(tfacac)_4]$ (tfacacH = CF_3COCH_2COMe) show that more than one geometric isomer is present in solution. The kinetics of the intramolecular rearrangement processes which exchange the ligands between the two inequivalent sites of $[Zr(acac)_4]$, $[Zr(acac)_2(NO_3)_2]$, or $[Zr(dmh)_4]$ (dmhH = Me_3CCOCH_2COMe) have been studied by NMR line-shape analysis; kinetic data are summarized in Table 1. A detailed line-shape analysis was not performed for $[Hf(acac)_4]$, but the methyl line shapes are similar to those for $[Zr(acac)_4]$ and the coalescence temperatures (T_c) for the Zr and Hf compounds are almost identical (−145 and −149°C, respectively). The dynamic properties of these β-diketonate complexes can be rationalized in terms of a polytopal rearrangement mechanism; however, one-bond rupture mechanisms cannot be ruled out [25].

$[Zr(dbzm)_4]$ (dbzmH = $PhCOCH_2COPh$) has a slightly distorted square antiprismatic structure in which the bidentate ligands span the *s* edges to give the *ssss*-D_2 stereoisomer. Distortions of the coordination polyhedron are in

TABLE 1

Kinetic data for methyl or *t*-butyl group exchange in Zr(IV) β-diketonate complexes [a]

	$[Zr(acac)_4]$ [b]	$[Zr(acac)_2(NO_3)_2]$ [b]	$[Zr(dmh)_4]$ [c]
T_c (°C)	−145	−144	−116
$k_{25°C}$ (s^{-1})	4.7×10^5	1.4×10^6	1.7×10^5
$k_{-125°C}$ (s^{-1})	2.0×10^2	2.9×10^2	6.8
$\Delta G^\ddagger$ (−125°C) (kJ mol^{-1})	28.9 ± 0.3	28.5 ± 0.2	33.1 ± 0.1
$\Delta H^\ddagger$ (kJ mol^{-1})	17.2 ± 1.3	18.8 ± 1.3	23.0 ± 2.1
$\Delta S^\ddagger$ (J mol^{-1} K^{-1})	−78.2 ± 10.5	−63.6 ± 10.5	−67.8 ± 12.1
E_a (kJ mol^{-1})	18.4 ± 1.3	20.1 ± 1.3	24.3 ± 2.1
log *A*	8.8 ± 0.6	9.5 ± 0.5	9.4 ± 0.6

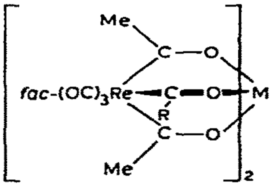
[a] In $CHClF_2$ solution. All errors are random errors estimated at the 95% confidence level.
[b] Methyl group exchange.
[c] *t*-Butyl group exchange.

the direction of a bicapped trigonal prism. The Zr—O bonds fall into two symmetry-inequivalent sets having averaged lengths 2.153(7) and 2.192(9) Å. The C_3O_2 portions of the chelate rings are planar, but the rings are appreciably folded (by 21.7 ± 2.2°) about the edges (O ··· O) of the antiprism; all four rings are bent away from the quasi-$\bar{8}$ axis of the antiprism [28].

Several new cyclopentadienyl zirconium β-diketonate complexes have been prepared by reaction of β-diketones with dizirconoxanes. Reaction of $[\{(\eta\text{-}C_5H_5)_2ZrCl\}_2O]$ with two equivalents of dibenzoylmethane (dbzmH) cleaves the dizirconoxane bond giving the formally five-coordinate complex $[(\eta\text{-}C_5H_5)_2Zr(dbzm)Cl]$, while reaction with an excess of dbzmH cleaves, in addition, the bond to one $\eta\text{-}C_5H_5$ group, affording $[(\eta\text{-}C_5H_5)Zr(dbzm)_2Cl]$. $[(\eta\text{-}C_5H_5)_2Zr(dbzm)Cl]$ hydrolyses in the presence of triethylamine to form the dizirconoxane $[\{(\eta\text{-}C_5H_5)_2Zr(dbzm)\}_2O]$, which can be converted to the presumably seven-coordinate $[(\eta\text{-}C_5H_5)Zr(dbzm)_3]$ by reaction with four equivalents of dbzmH. Preliminary ^1H and ^{13}C NMR spectra of $[(\eta\text{-}C_5H_5)_2Zr(dbzm)Cl]$ are said to indicate the presence of at least three stereoisomers in solution, but the nature of the isomerism is not at all clear [29].

Tetrakis(3-mesitylpentane-2,4-dionato)zirconium(IV) has been prepared and its ^1H NMR spectrum reported in connection with a study of the magnetic anisotropy in metal β-diketonate chelate rings [30].

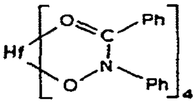
Neutral bis-chelate complexes of the type $[\{fac\text{-}(OC)_3Re(CH_3CO)_3\}_2Zr]$ and $[\{fac\text{-}(OC)_3Re(CH_3CO)_2(RCO)\}_2Hf]$ (R = Me, CMe_2H or $PhCH_2$) have been prepared by reaction of $[RC(O)Re(CO)_5]$ with MeLi in tetrahydrofuran (thf), followed by addition of a thf solution of $ZrCl_4$ or $HfCl_4$. The $[fac\text{-}(OC)_3Re(CH_3CO)_3]^{2-}$ dianion is the formal, metalla analogue of the triethanoylmethanate anion. The Zr and Hf complexes were obtained in rather poor yields as pale yellow, air-sensitive solids. IR and ^1H NMR spectra are consistent with tridentate coordination (7) of the triacetylmetallate ligands [31].

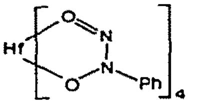


(7)

The tetrakis(catecholato)hafnate(IV) anion in crystalline $Na_4[Hf(O_2C_6H_4)_4] \cdot 21\ H_2O$ occupies a site of $\bar{4}$ symmetry and has a dodecahedral structure in which the bidentate catecholate ligands span the *m* edges of the coordination polyhedron. A 0.026 Å difference between the two inequivalent Hf—O bond distances (Hf—O_A = 2.220(3) Å; Hf—O_B = 2.194(3) Å) is attributed to non-bonded repulsions along the short (2.554(5) Å) *a* edges of the dodecahedron. The isostructural $[M(O_2C_6H_4)_4]^{4-}$ complexes of the larger Ce(IV) and Th(IV) ions exhibit no significant differences between the M—O_A and M—O_B bond lengths, but the U—O_A bond distance in $[U(O_2C_6H_4)_4]^{4-}$ is longer than the U—O_B distance by 0.027 Å; the latter difference is attributed to a ligand field effect of the f electrons in the f^2 U(IV) ion [32]. Equilibrium constants for formation of 1 : 1 complexes between zirconium and azo-derivatives of pyrocatechol have been measured in aqueous dioxane [33].

Measurement of the hyperfine quadrupole coupling parameters in a series of Hf(IV) chelates having a dodecahedral $\{HfO_8\}$ coordination group has provided evidence for metal—ligand π bonding. π bonding arises from charge-transfer from the ligand π orbitals to the metal $d_{x^2-y^2}$ orbital and involves primarily the ligand atoms in the dodecahedral B sites. The charge transferred into $d_{x^2-y^2}$ has been estimated at ~20% of the overall charge donated by the ligands in tetrakis(*N*-benzoyl-*N*-phenylhydroxylaminato)hafnium(IV) (8) and ~16% in tetrakis(*N*-nitroso-*N*-phenylhydroxylaminato)hafnium(IV) (9).





(8) (9)

The overall charge donated by the ligands into the metal valence orbitals is in the range —0.7 to —1.2 e; thus the Hf—O bonds are still quite highly ionic [34].

The stepwise thermal decomposition of several zirconium and hafnium carboxylates has been studied by thermogravimetric and differential thermal analysis. $SrZrO(C_2O_4)_2 \cdot 6\ H_2O$ and $BaZrO(C_2O_4)_2 \cdot 4.5\ H_2O$ undergo stepwise loss of water followed by conversion to carbonates and then zirconates, $SrZrO_3$ and $BaZrO_3$ [35,36]. Hafnium compounds with hydroxycarboxylic acids (e.g. hafnium mandelates and salicylates) decompose in a stepwise manner to monoclinic HfO_2 [37].

Several solvent extraction studies have been reported in which Zr(IV) or Hf(IV) was extracted from an aqueous phase into an organic phase owing to complex formation with the anions of β-diketones [38,39], salicylic acid [40], or dinonylnaphthalene sulphonic acid [41]. A new solvent extraction method for clean separation of Hf from Zr employs pure mesityl oxide (4-methyl-3-pentane-2-one) as the organic phase [42].

3.1.3 Zirconates(IV), hafnates(IV) and oxyanion salts

Alkaline earth and rare earth zirconates(IV) and hafnates(IV) are of interest as high-temperature refractory materials. They are generally prepared by high-temperature solid-phase reaction of ZrO_2 or HfO_2 with the appropriate metal oxide or carbonate. Syntheses of $MZrO_3$ (M = Ca, Sr or Ba) are appreciably accelerated when the reactions are carried out in the presence of $Na_2[CO_3]/K_2[CO_3]$ melts [43]. The crystalline hydrated zirconate $BaZrO_3 \cdot 1.8$—$2.3\ H_2O$ has been prepared in aqueous solution by absorption of $Ba(OH)_2$ on zirconium(IV) hydroxide followed by ageing the mixture at 100°C [44]. The rare earth zirconates and hafnates $Ln_2M_2O_7$ (Ln = La or Nd; M = Zr or Hf) have been synthesized from the oxides and have been characterized by X-ray diffraction, electron microscopy and IR spectroscopy. These compounds are very high melting (m.p. 2230—2550°C), and they have cubic pyrochlore structures with lattice parameters $a = 10.808$ Å ($La_2Zr_2O_7$), 10.774 Å ($La_2Hf_2O_7$), 10.668 Å ($Nd_2Zr_2O_7$) and 10.635 Å ($Nd_2Hf_2O_7$) [45,46].

Anhydrous hafnium(IV) perchlorate has been prepared by reaction of $HfCl_4$ with a solution of Cl_2O_7 in anhydrous perchloric acid at —10°C. $[Hf(ClO_4)_4]$ sublimes in vacuo above 70°C, melts at 105°C and decomposes to $HfO(ClO_4)_2$ in the range 130—160°C. IR and Raman spectra have been interpreted in terms of an eight-coordinate structure that contains bidentate perchlorate ligands; the low melting point and high volatility suggest that the hafnium—perchlorate bonds have an appreciable degree of covalent character [47].

Lattice parameters and space groups have been determined by X-ray diffraction for alkali hafnium and ammonium hafnium double sulphates of the types $Hf(SO_4)_2 \cdot M_2SO_4 \cdot n\ H_2O$, $Hf(SO_4)_2 \cdot 2\ M_2SO_4 \cdot n\ H_2O$, $Hf_2O(SO_4)_3 \cdot M_2SO_4 \cdot n\ H_2O$, and $2\ HfO(SO_4) \cdot M_2SO_4 \cdot 6\ H_2O$ (M = Rb, Cs or NH_4) [48,49]. The thermal decomposition and characteristic features of the structures of hydrated zirconium and hafnium oxide nitrates, $MO(NO_3)_2 \cdot n\ H_2O$ (M = Zr or Hf; $n = 2$ or 6), have been studied by Erokhina et al. [50,51]. IR and broad-line ^1H NMR spectra indicate that the nitrate groups and the water molecules occupy both coordinated and uncoordinated sites; in addition, these compounds contain one hydroxide group per metal ion. Procedures have been reported for synthesis of $PbZr(PO_4)_3$ [52], $LiNaZrSi_6O_{15}$ [53] and $Hf(OH)_2Mo_2O_7 \cdot 2\ H_2O$ [54], and the lattice parameters of these oxyanion salts have been characterized by X-ray diffraction.

3.1.4 Zirconium(IV) phosphates as ion exchangers

Zirconium(IV) phosphates are of great interest as inorganic ion exchangers [55,56]; they have layered structures which are capable of adjustment to incorporate a wide variety of hydrated and non-hydrated cations. Because of their thermal stability and their stability in the presence of high doses of radiation, they offer advantages over organic ion exchange resins. Zirconium(IV) phosphates are already used in renal dialysis [57] and in the treatment of radioactive wastes [58], and further applications in removing cations from industrial waste solutions are likely [59]. In addition, the intercalation properties of zirconium(IV) phosphates make them possible supports for catalytic processes [60].

The two most important forms of crystalline zirconium(IV) phosphate are the alpha phase, $Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP), which has a small (7.55 Å) interlayer spacing [61], and the gamma phase, $Zr(HPO_4)_2 \cdot 2\ H_2O$ (γ-ZrP), which has a larger (12.2 Å) interlayer spacing [62]. During this past year the ion exchange properties of α-ZrP [63—67] and its alkali metal exchanged forms [68,69] have been extensively investigated. One of the more interesting developments is the intercalation of amines [59,70], alkynols and glycols [60] into the interlayer spaces of α-ZrP; the amine intercalated α-ZrP has relatively large interlayer spacings and readily exchanges with large cations which do not ordinarily exchange with α-ZrP [59]. The ion exchange properties of the isomorphous zirconium(IV) arsenate, $Zr(HAsO_4)_2 \cdot H_2O$ (α-ZrAs) and its alkali metal exchanged forms have also been studied [70,71]. The conditions for formation of γ-ZrP have been determined, and a structural model for this phase has been proposed in which the $\{ZrO_6\}$ octahedra and $\{PO_3(OH)\}$ tetrahedra are more densely linked than in the known structure of α-ZrP [72]. γ-ZrP promotes ring cleavage of 1,2-epoxyethane to give the layered phosphate ester, $Zr(HOC_2H_4OPO_3)_2 \cdot H_2O$, from which $[HOC_2H_4OPO_3]^{2-}$ anions can be removed by exchange with phosphate ions [73]. The exchange of alkali metal ions on γ-ZrP [74] and the thermal behaviour of γ-ZrP [75] have also been investigated.

3.1.5 Complexes with S-donor ligands

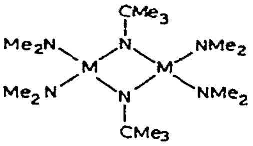
Alkyl thioglycolate complexes of the type $Zr(OCHMe_2)_2G$ and ZrG_2 ($G = [SCH{=}C(OR)O]^{2-}$; R = Me or Et) have been synthesised by reaction of $Zr(OCHMe_2)_4$ with stoicheiometric amounts of the alkyl thioglycolate, H_2G. The isopropoxy groups of $Zr(OCHMe_2)_2G$ are replaced by *t*-butoxy groups when the isopropoxy complex is heated under reflux with an excess of Me_3COH in benzene. IR spectra and molecular weight measurements indicate that the $Zr(OR)_2G$ complexes have alkoxy-bridged dimeric structures. In both the $Zr(OR)_2G$ and the ZrG_2 complexes, the alkyl thioglycolates act as dinegative, bidentate ligands [76].

Russian workers have reported the melting point, density, microhardness, magnetic susceptibility, and electrical properties of rare earth thiohafnates(IV) of composition Ln_2HfS_5 (where Ln is La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er or Y); these compounds are stable toward organic solvents, boiling water and aqueous base, but they are converted to rare earth hafnates(IV) when treated with HCl or H_2SO_4 [77]. Europium(II) thiozirconate(IV) $EuZrS_3$ has been synthesised by heating EuS and ZrS_2 in vacuo at 1050—1250°C; this compound has an orthorhombic unit cell and is isostructural with $SrZrS_3$ [78].

The cubic spinel phases $Ag_{2x}(M_{2x}Zr_{2-2x})S_4$ (where M = In or Y) have been prepared by heating mixtures of ZrS_2 and $AgMS_2$ at 850°C. These phases have a range of composition $0.40 < x < 0.50$ (for M = In) and $0.37 < x < 0.50$ (for M = Y). The Ag^+ ions occupy the tetrahedral sites of the spinel structure, while the M^{3+} and Zr^{4+} ions take the octahedral sites. Activation energies for ionic conductivity in these materials have been determined by complex impedence measurements [79].

3.1.6 Complexes with N-donor ligands

Bis{μ-(*N*-*t*-butylimido)}tetrakis(dimethylamido)dizirconium(IV) and -dihafnium(IV) (**10**) have been prepared by heating a hexane solution of $M(NMe_2)_4$

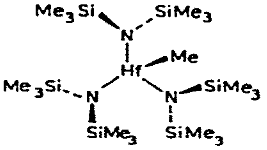


(**10**)

(M = Zr or Hf) under reflux with 1 equivalent of Me_3CNH_2, followed by removing the solvent and subliming the residue at 150°C in vacuo. The dimeric structure of (**10**) has been confirmed by an X-ray study of the Zr complex. The geometry about Zr is roughly tetrahedral, with the Zr—N bonds to the nearly planar dimethylamide ligands and the symmetrically bridging *t*-butylimide ligands being nearly identical ($\bar{r}$(ZrN) = 2.060 and 2.066 Å, respectively). The molecule is centrosymmetric, and the Zr_2N_2 ring is planar [80].

Reaction of sodium bis(trimethylsilyl)amide with $ZrCl_4$ or $HfCl_4$ affords the chloro silylamides $[ClM\{N(SiMe_3)_2\}_3]$ (M = Zr or Hf). These compounds are surprisingly inert to substitution reactions; they do not react with dioxygen, water, dilute mineral acids, aqueous $AgNO_3$, $LiCH_2SiMe_3$, $Li[BH_4]$ or excess $Na[N(SiMe_3)_2]$. However, they do react with methyllithium, giving $[MeM\{N(SiMe_3)_2\}_3]$. The methyl compounds are similarly stable toward dioxygen and water, and they are unreactive when treated with methanol, tetrafluoroboric acid or CO_2. The unusual stability of these compounds is attributed to the steric bulk of the silylamide ligands, which protect the metal atom from attack by potential reactants. The ^1H NMR spectrum of $[MeHf\{N(SiMe_3)_2\}_3]$ at —40°C is consistent with a chiral structure of C_3

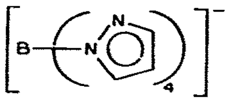
symmetry (11) [81]. The corresponding $[Cl_2M\{N(SiMe_3)_2\}_2]$ (M = Zr of Hf)



(11)

complexes are considerably more reactive than the $[ClM\{N(SiMe_3)_2\}_3]$ analogues. The dichlorobis(silylamides) are air and moisture sensitive. They yield a precipitate of AgCl upon contact with acidic aqueous $AgNO_3$, and they react with $Li[BH_4]$ in diethyl ether to give $[ClM(BH_4)\{N(SiMe_3)_2\}_2]$. The latter complexes contain a tridentate $[BH_4]^-$ ligand which is fluxional on the NMR time scale at —80°C. Reaction of $[Cl_2M\{N(SiMe_3)_2\}_2]$ with $MgMe_2$ in diethyl ether affords the dimethyl derivatives $[Me_2M\{N(SiMe_3)_2\}_2]$; $[Et_2Hf\{N(SiMe_3)_2\}_2]$ and $[(Me_3SiCH_2)_2Hf\{N(SiMe_3)_2\}_2]$ were prepared similarly. The diethyl complex is stable to β-hydrogen elimination, evidently because of the steric bulk of the silylamide ligands. The $[R_2Hf\{N(SiMe_3)_2\}_2]$ (R = Me, Et or CH_2SiMe_3) complexes take up CO_2, yielding the corresponding carbamates $[R_2Hf\{O_2CN(SiMe_3)_2\}_2]$. *t*-Butyl isocyanide inserts into the Hf—C bond of $[R_2Hf\{N(SiMe_3)_2\}_2]$ (R = Me or Et, but not CH_2SiMe_3), giving the iminoacyl complexes $[Hf\{C(R)NCMe_3\}_2\{N(SiMe_3)_2\}_2]$ [82].

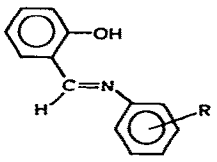
The tetrakis(pyrazol-1-yl)borate complexes of zirconium $[ZrCl_2(BPz_4)_2]$, $[ZrBr_2(BPz_4)_2]$ and $[Zr(BPz_4)_4]$ have been synthesized by reaction of $ZrCl_4$ or $ZrBr_4$ with stoicheiometric amounts of $K[BPz_4]$ in dichloromethane. ^1H NMR spectra indicate that the tetrakis(pyrazol-1-yl)borate ligand (12) behaves



(12; $[BPz_4]^-$)

as a tridentate ligand in the $[ZrX_2(BPz_4)_2]$ complexes, and therefore the Zr atom has coordination number eight. Presumably, $[Zr(BPz_4)_4]$ also has an eight-coordinate structure, with BPz_4 acting as a bidentate ligand; however, this complex is stereochemically nonrigid and gives a time-averaged NMR spectrum [83].

Reactions of $Zr(OCHMe_2)_4$ with the bidentate Schiff bases (13) and (14)



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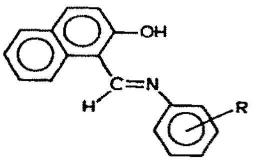
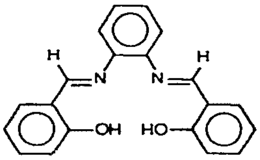


(14)

(R = 2-Me or 4-Me) in 1 : 1 and 1 : 2 mole ratios in benzene at reflux afford the complexes $Zr(OCHMe_2)_3(SB)$ and $Zr(OCHMe_2)_2(SB)_2$, where SB^- is the anion of the Schiff base. Replacement of more than two $OCHMe_2$ groups does not occur, even on prolonged heating with 3 or 4 equivalents of Schiff base. Molecular weight measurements in boiling benzene indicate that the complexes which contain the anion of (**13**; R = 2-Me) are dimeric while those that contain the anion of (**14**; R = 2-Me) are monomeric. The dimeric complexes probably have bridging $OCHMe_2$ groups [84].

The eight-coordinate chelate $[Zr(dsp)_2]$, where $[dsp]^{2-}$ is the dianion of the tetradentate Schiff base (**15**), has been prepared by condensation of

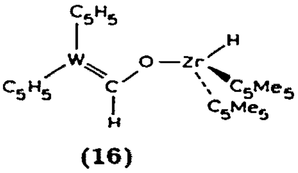


(**15**)

tetrakis(salicylaldehydato)zirconium(IV) and *o*-phenylenediamine. The complex has a dodecahedral coordination polyhedron with nitrogen atoms in the dodecahedral A sites and oxygen atoms in the B sites, in accord with theoretical predictions based on π-bonding considerations. The tetradentate ligands span the *mmmm* polyhedral edges, and the trapezoidal planes are very nearly perpendicular (dihedral angle = 89.2°). The Zr—O bonds (mean 2.10 Å) are appreciably shorter than the Zr—N bonds (mean 2.43 Å) [85].

3.1.7 Hydride complexes

Detailed procedures for synthesis of $[(\eta\text{-}C_5H_5)_2ZrH_2]$ and $[(\eta\text{-}C_5H_5)_2Zr(H)Cl]$ have appeared [86]. The pentamethylcyclopentadienyl complex $[(\eta\text{-}C_5Me_5)_2ZrH_2]$ transfers hydride to the coordinated CO of $[(\eta\text{-}C_5H_5)_2M(CO)]$ (M = Cr, Mo or W) affording the "zirconoxy" carbenes $[(\eta\text{-}C_5H_5)_2M{=}CHOZr(H)(\eta\text{-}C_5Me_5)_2]$. An analogous reaction of $[(\eta\text{-}C_5Me_5)_2ZrH_2]$ with $[(\eta\text{-}C_5H_5)_2Nb(H)CO]$ gives $[(\eta\text{-}C_5H_5)_2(H)Nb{=}CHOZr(H)(\eta\text{-}C_5Me_5)_2]$. The X-ray structure of the tungsten compound (**16**) displays roughly trigonal



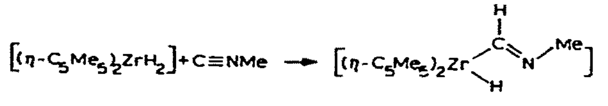
(**16**)

coordination at W and the usual pseudotetrahedral geometry about Zr. Because of the W=C multiple bond (2.005 Å), the two $\eta\text{-}C_5H_5$ ligands are inequivalent (^{1}H NMR 4.38 δ and 4.98 δ). Compound (**16**) is remarkably stable at 150°C in toluene. It reacts with 1 atm. of H_2 at 170°C yielding $[(\eta\text{-}C_5Me_5)_2Zr(H)(OCH_3)]$ (eqn. (5)) and reacts with ethene at 70°C to give the corresponding ethyl derivative (eqn. (6)) [87].

$$[(\eta\text{-}C_5H_5)_2W{=}CHOZr(H)(\eta\text{-}C_5Me_5)_2] + 2\,H_2 \rightarrow [(\eta\text{-}C_5H_5)_2WH_2] + [(\eta\text{-}C_5Me_5)_2Zr(H)(OCH_3)] \qquad (5)$$

$$[(\eta\text{-}C_5H_5)_2W{=}CHOZr(H)(\eta\text{-}C_5Me_5)_2] + C_2H_4 \rightarrow [(\eta\text{-}C_5H_5)_2W{=}CHOZr(C_2H_5)(\eta\text{-}C_5Me_5)_2] \qquad (6)$$

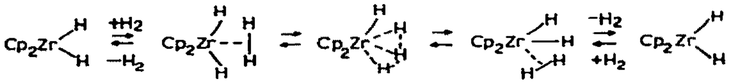
$[(\eta\text{-}C_5Me_5)_2ZrH_2]$ reacts rapidly with methyl isocyanide at —65°C affording the formimidoyl hydride (17) (eqn. (7)), which can be converted to the dimethylamide $[(\eta\text{-}C_5Me_5)_2Zr(H)(NMe_2)]$ by allowing a solution of (17) to warm from —80°C to room temperature under 1 atm. of H_2. 2,6-Dimethylphenyl isocyanide also inserts into a Zr—H bond of $[(\eta\text{-}C_5Me_5)_2ZrH_2]$ to give the corresponding formimidoyl hydride. The implications of these results have been discussed in connection with the possibility of *intra*-molecular migratory insertion of CO into a Zr—H bond in the carbon monoxide adduct $[(\eta\text{-}C_5Me_5)_2ZrH_2(CO)]$ [88].



(7)

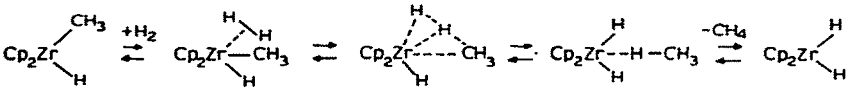
(17)

A low-energy path for hydrogen isotope exchange in $[(\eta\text{-}C_5R_5)_2ZrH_2]$ (R = H or Me) (eqn. (8)) has been suggested on the basis of EHMO calculations.



(8)

This mechanism has been termed "direct hydrogen transfer", and it features a transition state that has an allyl-like $(H \cdots H \cdots H)^-$ ligand configuration. MO calculations suggest an analogous path for H_2-induced alkane elimination (eqn. (9)) [89].



(9)

The molecular vibrations of $[Zr(BH_4)_4]$ have been analysed on the basis of models having T_d symmetry [90] and T symmetry [91].

3.2 ZIRCONIUM(III) AND HAFNIUM(III) COMPOUNDS

Published work on the preparation and disproportionation of the lower chlorides of zirconium has been reviewed, and a scheme has been proposed for the stepwise disproportionation of $ZrCl_3$ (eqns. (10)—(13)).

$$12\,ZrCl_3(s) \xrightarrow{110^\circ C} 10\,ZrCl_{2.8}(s) + 2\,ZrCl_4(g) \qquad (10)$$

$$10\ ZrCl_{2.8}(s) \xrightarrow{300^\circ C} 5\ ZrCl_{1.6}(s) + 5\ ZrCl_4(g) \tag{11}$$

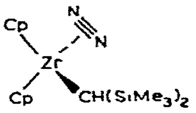
$$5\ ZrCl_{1.6}(s) \rightarrow 4\ ZrCl(s) + ZrCl_4(g) \tag{12}$$

$$4\ ZrCl(s) \xrightarrow{610^\circ C} 3\ Zr(s) + ZrCl_4(g) \tag{13}$$

Enthalpies of formation of the lower chlorides have been derived from the temperature dependence of the disproportionation pressure of $ZrCl_4(g)$ [92].

The IR spectra of gaseous ZrN and HfN have been observed, affording values for the ground state vibrational frequencies (936.6(20) cm^{-1} for ZrN and 919.5(20) cm^{-1} for HfN) and the rotational constants; both molecules have a $^2\Sigma$ ground state [93]. The preparation of single crystals of ZrN has been described; the crystals were grown on a tungsten filament at 2000—2200°C from a gas mixture of $ZrCl_4$, N_2, H_2 and Ar [94].

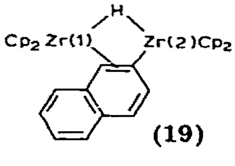
The Zr(III) dinitrogen complexes $[(\eta\text{-}C_5H_4R)_2Zr(N_2)\{CH(SiMe_3)_2\}]$ (R = H or Me) have been prepared by sodium-amalgam reduction of $[(\eta\text{-}C_5H_4R)_2ZrCl\{CH(SiMe_3)_2\}]$ under an N_2 atmosphere. These compounds have been assigned a structure (18) that contains a "side-on" η^2-dinitrogen ligand on



(18)

the basis of: (1) EPR spectra down to −80°C that exhibit a 1 : 2 : 3 : 2 : 1 quintet due to coupling to two equivalent ^{14}N atoms, or a 1 : 2 : 1 triplet for the $^{15}N_2$ isotopomers; (2) the absence of a triplet signal in the frozen (−140°C) solid Q-band EPR spectra, which rules out a bis(dinitrogen)-bridged dimeric structure; and (3) the absence of an IR band in the 2400—1500 cm^{-1} region, the region characteristic of $\nu(N{\equiv}N)$ in complexes that contain "end-on" dinitrogen ligands. The *g* values and the ^{91}Zr and ^{14}N hyperfine coupling constants suggest that a significant amount of unpaired electron density is delocalized onto the N_2 ligand; the presence of negative charge on the N_2 ligand is confirmed by its protonation to yield N_2H_4 upon treatment with concentrated HCl or HBr. Recrystallization of $[(\eta\text{-}C_5H_5)_2Zr(N_2)\{CH(SiMe_3)_2\}]$ from toluene affords the violet, diamagnetic complex $[\{(\eta\text{-}C_5H_5)_2Zr[CH(SiMe_3)_2]\}_2(N_2)]$, which has been assigned a dinitrogen-bridged structure ($\gtrless Zr{-}N{\equiv}N{-}Zr\lessgtr$) on the basis of the absence of a $\nu(N{\equiv}N)$ band in its IR spectrum [95].

Reduction of $[(\eta\text{-}C_5H_5)_2ZrCl_2]$ with potassium naphthalenide at low temperatures in thf under argon gives the dinuclear Zr(III) complex $[\{(\eta\text{-}C_5H_5)_2Zr\}_2(C_{10}H_7)H]$ (19) in which two $(\eta\text{-}C_5H_5)_2Zr$ moieties are joined by a



(19)

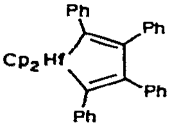
bridging $\eta^1 : \eta^2$ naphthyl group $\{r(Zr(1)—C) = 2.459$ and 2.662 Å; $r(Zr(2)—C) = 2.29$ Å; $r(Zr(1)—Zr(2)) = 3.307$ Å$\}$. The bridging hydride ligand was not definitely located in the X-ray structural determination, but its presence was inferred from the ^1H NMR spectrum and the reaction of **(19)** with excess CH_3I, which yields 1 equivalent of CH_4 [96]. Reduction of $[(\eta\text{-}C_5H_4R)_2MR'_2]$ (M = Zr or Hf; R = H, Me, or $CHMe_2$; R' = Me, CH_2Ph, CH_2CMe_3, CH_2SiMe_3 or $CHPh_2$) with sodium naphthalenide in thf affords the corresponding d^1 anions $[(\eta\text{-}C_5H_4R)_2MR'_2]^-$, which have been characterized by EPR spectroscopy [97].

3.3 ZIRCONIUM(II) AND HAFNIUM(II) COMPOUNDS

The crystal structure of $ZrCl_2$ consists of homoatomic layers of Zr and Cl atoms, sequenced Cl—Zr—Cl, with D_{3h} trigonal prismatic coordination of Zr by Cl; $ZrCl_2$ is isoelectronic and isostructural with $3R$-MoS_2. Several substoicheiometric dichloride phases having composition between $ZrCl_{1.5}$ (i.e. $Zr_{1.3}Cl_2$) and $ZrCl_2$ have been prepared, and the structure of one of these, $6T$-$Zr_{1.05}Cl_2$, has been determined by X-ray diffraction. It has an ordered superstructure derived from the basic three-layer Cl—Zr—Cl slabs of $3R$-$ZrCl_2$, but has an extra Zr atom every six slabs in an interslab octahedral hole with a partial occupancy of 0.28. The X-ray photoelectron spectrum of $ZrCl_2$ exhibits a narrow metal $4d$ band 1.2 eV below the Fermi level. Attempts to intercalate $ZrCl_2$ were unsuccessful [98].

Zirconium and hafnium polonides, ZrPo and HfPo, have been synthesised from the elements at 380—600°C. They are isostructural with TiPo and have a hexagonal structure of the NiAs type [99].

An X-ray structural study of the first hafnium carbonyl, $[(\eta\text{-}C_5H_5)_2Hf(CO)_2]$, has revealed the expected tetrahedral disposition of ligands with $OC—\widehat{Hf}—CO$ and $(\text{centroid } C_5H_5)—\widehat{Hf}—(\text{centroid } C_5H_5)$ angles of 89.3 and 141°, respectively, and $\bar{r}(Hf—CO)$ and $\bar{r}\{Hf—(\text{centroid } C_5H_5)\}$ distances of 2.16 Å. $[(\eta\text{-}C_5H_5)_2Hf(CO)_2]$ undergoes photochemically induced substitution reactions with L (= PPh_3, PMe_3, PF_3 or dppe) to give $[(\eta\text{-}C_5H_5)_2Hf(CO)L]$. Attempts to replace both carbonyl groups with the chelating diphosphine dppe have thus far been unsuccessful. Photolysis of $[(\eta\text{-}C_5H_5)_2Hf(CO)_2]$ in benzene in the presence of 2 equivalents of diphenylacetylene yields the metallocycle (20)



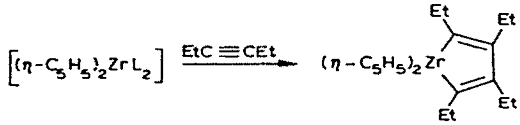
(20)

as the sole organometallic product. $[(\eta\text{-}C_5H_5)_2Zr(CO)_2]$ undergoes an analogous series of photochemical reactions [100].

Reactive di(cyclopentadienyl)bis(phosphine)zirconium(II) complexes

$[(\eta\text{-}C_5H_5)_2ZrL_2]$ (L_2 = $(Ph_2PMe)_2$, $(PhPMe_2)_2$, dppe or dmpe) have been prepared by phosphine-induced reductive elimination of methylcyclohexane from the alkyl zirconium hydride $[(\eta\text{-}C_5H_5)_2Zr(CH_2C_6H_{11})H]$. The $[(\eta\text{-}C_5H_5)_2ZrL_2]$ complexes react with CO (eqn. (14)) and diethylacetylene (eqn. (15)), and they undergo very rapid oxidative addition of MeX (X = OSO_2F, Cl or I) (eqn. (16)). They reversibly metallate aromatic solvents to give arylzirconium hydrides, which are not directly observable but can be trapped by reaction with propanone (eqn. (17)). Thermal decomposition of $[(\eta\text{-}C_5H_5)_2ZrL_2]$ (L = Ph_2PMe or $PhPMe_2$) involves loss of 1 equivalent of phosphine and 0.5 equivalents of H_2 and results in formation of the diamagnetic, dinuclear Zr(III) complex (21) [101].

$$[(\eta\text{-}C_5H_5)_2ZrL_2] \xrightarrow[1\,atm]{CO} [(\eta\text{-}C_5H_5)_2Zr(CO)_2] + [(\eta\text{-}C_5H_5)_2Zr(CO)L] \qquad (14)$$



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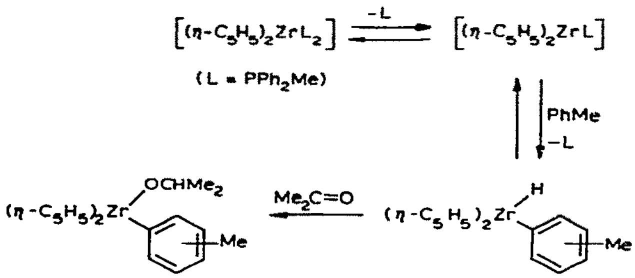
$$[(\eta\text{-}C_5H_5)_2ZrL_2] \xrightarrow{MeX} [(\eta\text{-}C_5H_5)_2Zr(Me)X] \qquad (16)$$



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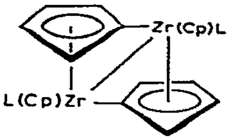

(21)

Reduction of $[ZrCl_4(dmpe)_2]$ with sodium amalgam in thf in the presence of excess 1,3-cyclohexadiene affords the Zr(II) complex $[ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2]$. This compound is thought to result from reduction of $[ZrCl_4(dmpe)_2]$ to the Zr(0) fragment $[Zr(dmpe)_2]$, followed by insertion of Zr into the C—H bond of an allylic methylene group of cyclohexadiene. $[ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2]$ is an efficient catalyst for the disproportionation of cyclohexadiene to benzene and cyclohexene [102].

TABLE 2

Thermodynamic data for ZrBr and HfBr

	ZrBr	HfBr
(1) Disproportionation (eqn. (18))		
ΔH^0 (kJ mol^{-1}) (temp. (K))	113 ± 8 (850)	142 ± 9 (830)
ΔS^0 (J mol^{-1} K^{-1}) (temp. (K))	115 ± 13 (850)	156 ± 13 (830)
(2) Formation		
ΔH_f^0 (kJ mol^{-1}) (temp. (K))	—204 ± 4 (850) —193 ± 4 (298)	—214 ± 6 (830) —204 ± 6 (298)
ΔS^0 (J mol^{-1} K^{-1}) (temp. (K))	154 ± 6 (850) 96 ± 6 (298)	148 ± 8 (830) 90 ± 8 (298)

3.4 ZIRCONIUM(I) AND HAFNIUM(I) COMPOUNDS

Pure hafnium(I) bromide has been prepared by reduction of $HfBr_4$ vapour (30—40 atm.) with hafnium metal foil at 480—580°C for 1000 h, followed by heating the product at 500°C in ~1 atm. of $HfBr_4$ vapour for 24 h. HfBr is an extremely soft, graphite-like black powder and, like ZrBr and ZrCl, it is useful as a high-temperature lubricant. Crystalline HfBr has a rhombohedral unit cell with a = 9.620(3) Å and α = 20.80(1)°; it is isostructural with ZrBr. At elevated temperatures, ZrBr and HfBr disproportionate according to eqn. (18). The temperature dependence of the vapour pressure of MBr_4 has afforded

$$4\ MBr(s) \rightleftharpoons 3\ M(s) + MBr_4(g) \qquad (18)$$

values of the enthalpies and entropies of disproportionation, and the derived values of the enthalpies of formation and entropies of the crystalline monobromides (see Table 2) [103].

3.5 ZIRCONIUM(0) AND HAFNIUM(0) COMPOUNDS

Several papers have appeared during the past year which report the first examples of zerovalent zirconium and hafnium. Co-condensation of Zr or Hf vapour from an electron-gun furnace with arenes and trimethylphosphine at —196°C gives good yields of $[M(\eta\text{-arene})_2(PMe_3)]$ (M = Zr, arene = C_6H_5Me; M = Hf, arene = C_6H_6 or C_6H_5Me). These compounds have been characterised by microanalysis, mass spectra, and ^1H NMR spectra. They decompose upon exposure to air, water or dinitrogen, but appear to be stable indefinitely under argon. Bent sandwich structures have been suggested [104].

Reduction of $[ZrCl_4(dmpe)_2]$ with sodium amalgam in thf in the presence of butadiene affords the brown dmpe-bridged dimer $[\{Zr(\eta\text{-}C_4H_6)_2(dmpe)\}_2(\mu\text{-dmpe})]$, which is in equilibrium, in solution, with the violet, coordinatively unsaturated [Zr(η-C_4H_6)$_2$(dmpe)] and free dmpe. The dimer reacts with CO at −45°C in toluene to give the yellow, thermally unstable [Zr(η-C_4H_6)$_2$(dmpe)(CO)], which loses CO on warming in vacuo. The resulting [Zr(η-C_4H_6)$_2$(dmpe)], isolated as a violet crystalline solid, forms (in solution at low temperatures) brown adducts [Zr(η-C_4H_6)$_2$(dmpe)L] with L (= PMe_3, PMe_2Ph or $P(OMe)_3$). Equilibrium constants and thermodynamic parameters for adduct formation have been determined by NMR. In arene solvents, [{Zr(η-C_4H_6)$_2$(dmpe)}$_2$(μ-dmpe)] is a catalyst for the hydrogenation of alkenes and alkynes [102,105].

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