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2 ZIRCONIUM AND HAFNIUM

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CONTENTS

INTRODUCTION

Following previous practice in this series, this review attempts comprehensive treatment of the coordination chemistry of zirconium and hafnium. The solid-state chemistry of these elements is treated selectively, and organometallic compounds are included only when the compounds contain

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bonds to elements other than carbon.

The present review covers the major journals for the 1983 calendar year and the lesser known and/or foreign journals for the period covered by *Chemical Abstracts*, Volume 97, Number 21 through Volume 99, Number 21.

2.1 ZIRCONIUM(IV) AND HAFNIUM(IV) COMPOUNDS

2.1.1 Halide complexes

The reaction of hafnium(IV) fluoride and caesium fluoride in anhydrous acetic acid yields two solid compounds, either $CsHfF_5$ or $Cs_2[HfF_6]$, depending on the molar ratio of the components. This approach to synthesis of anhydrous $CsHfF_5$ is convenient since aqueous preparations yield the hydrate, $CsHfF_5 \cdot H_2O$ [1]. Heating of K_2HfF_6 reveals complex polymorphism; six different phases have been identified by X-ray powder diffraction [2].

The thermal properties and coordination environment of the zirconium atom in crystalline and vitreous $M''ZrF_6$ (M'' = Ba, Sr, or Pb) have been studied by differential thermal analysis and Raman spectroscopy, respectively. The DTA data suggest that low- and high-temperature modifications are present for $PbZrF_6$, as well as for $BaZrF_6$ and $SrZrF_6$. Comparison of Raman symmetric stretching frequencies ν_s(Zr-F) and available structural data for metal florozirconates indicates that ν_s(Zr-F) cannot be utilized as a reliable guide for identifying the coordination number of the zirconium atom in fluorozirconate complexes of unknown structure. However, the Raman spectra of vitreous $M''ZrF_6$ (M'' = Ba, Sr, or Pb) exhibit similar features to those found for the crystalline form of $M''ZrF_6$ that contains chains of *a*-edge-shared ZrF_8 dodecahedra [3]. An eight-coordinate environment for zirconium in $BaZrF_6$ and $PbZrF_6$ glasses is also consistent with X-ray radial distribution analyses [4].

Time differential perturbed angular correlation measurements (15-580 K) on $NH_4Hf_2F_9$ indicate that the hafnium atoms occupy two inequivalent sites [5].

Following an earlier X-ray study [6], a neutron diffraction study [7] of $Cu_3(ZrF_7)_2 \cdot 16H_2O$ has identified the location of the protons. The structure contains $[Cu(H_2O)_6]^{2+}$, $[Cu_2(H_2O)_{10}]^{4+}$, and $[Zr_2F_{14}]^{6-}$ ions that are linked by a dense network of hydrogen bonds. The $[Zr_2F_{14}]^{6-}$ ion is a centrosymmetric dimer in which two ZrF_8 square antiprisms share a common *s* polyhedral edge {*r*(Zr-F terminal) = 2.048-2.107 Å; *r*(Zr-F bridging) = 2.171, 2.185 Å}.

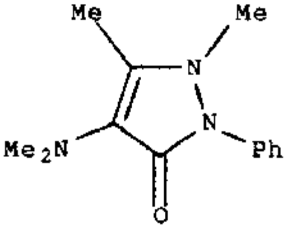
The oxide fluoride $PbZr_6F_{22}O_2$ consists of a three-dimensional framework of ZrF_7O square antiprisms, which enclose two kinds of cavities. The smaller, cuboctahedral cavities contain one 'extra' fluorine atom, while the larger cavities contain [12 + 6]-coordinated lead atoms [8].

Equilibrium decomposition pressures of Cs_2MCl_6 (M = Zr or Hf) {equation (1)} have been measured, and thermodynamic parameters for decomposition of the

$$Cs_2MCl_6(\text{s or l}) \rightleftharpoons 2CsCl(\text{s or l}) + MCl_4(\text{g}) \qquad (1)$$

solid compounds have been derived from the temperature dependence of the vapour pressures. X-ray powder patterns of M'_2HfCl_6 (M' = Na, K, or Cs) have been reported. K_2HfCl_6 and Cs_2HfCl_6 are cubic (a = 10.036(3) and 10.394(4) Å, respectively), but Na_2HfCl_6 is tetragonal (a = 15.99, c = 13.21 Å) [9]. The reaction of gaseous $ZrCl_4$ with ammonia yields $ZrCl_4 \cdot 2NH_3$ at 300 °C; $ZrCl_4 \cdot 2NH_3$, ZrClN, and NH_4Cl at 350-700 °C; $ZrCl_4 \cdot 2NH_3$, ZrClN, ZrN_x, Zr_3N_4, and NH_4Cl at 750 °C; ZrClN, ZrN_x, Zr_3N_4, and NH_4Cl at 800-950 °C; ZrN_x, Zr_3N_4, and NH_4Cl at 1000-1050 °C; and ZrN_x (x = 1.28-1.12), NH_4Cl, and HCl at 1100-1400 °C. $ZrCl_4 \cdot 2NH_3$ has a cubic unit cell with a = 10.13 Å [10].

Zirconium(IV) chloride forms solid 1:1 adducts with aminopyrine **(1)** and acetone thiosemicarbazone, $Me_2C{=}NNHCSNH_2$. Infrared spectra indicate that both ligands are bidentate. Aminopyrine coordinates to zirconium through the carbonyl oxygen atom and the dimethylamino-nitrogen atom [11], while thiosemicarbazone coordinates through sulfur and the azomethine nitrogen atom [12].



(1)

2.1.2 *Complexes with O-donor ligands*

Vibrational spectra of $ZrOCl_2 \cdot 8H_2O$ and its deuteriated analogue have been studied in the solid state and in aqueous solutions. No bands attributable to the zirconyl group $(Zr=O)^{2+}$ were observed in the region 800-1000 cm^{-1}. A characteristic infrared band near 1000 cm^{-1}, which shifts to lower frequency upon deuteriation, has been assigned to a δ(ZrOH) mode of the hydroxo-bridged, tetranuclear $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ ion. Raman spectra of 2.5 *M* $ZrOCl_2$ in 5 *M* HCl exhibit ν(Zr–OH) bands at 580 and 150 cm^{-1}, with a shoulder at *ca.* 420 cm^{-1} tentatively assigned to a $\nu(Zr{-}OH_2)$ vibration. Upon addition of NaOH, the 420 cm^{-1} band decreases in intensity and a new band appears at *ca.* 530 cm^{-1}; the latter band may be due to ν(Zr–OH) vibrations of the terminal hydroxyl groups in a more highly hydrolyzed species such as $[Zr_4(OH)_8(OH)_4(H_2O)_{12}]^{4+}$ [13].

Several dinuclear zirconium compounds that contain oxo-bridges have been reported during the past year. The reaction of zirconium(IV) chloride with excess trichloronitromethane affords $[NO]_2[Zr_2OCl_8]$ in 90 % yield (equation (2)). Infrared spectra of this compound exhibit ν(NO) bands at

$$2ZrCl_4 + 2CCl_3(NO_2) \longrightarrow [NO]_2[Zr_2OCl_8] + CCl_4 + COCl_2 \qquad (2)$$

2198 and 2180 cm^{-1}, ν(ZrOZr) bands at 605 and 584 cm^{-1}, and ν(Zr–Cl) bands at 280-390 cm^{-1} [14]. The reaction of $[\{(Me_3Si)_2N\}_2ZrMe_2]$ with carbon monoxide (equation (3)) yields the oxo-bridged complex **(2)**. In the crystal, compound

$$\begin{array}{c} 3[\{(Me_3Si)_2N\}_2ZrMe_2] + 2CO \\ \Big\downarrow \\ [\{[(Me_3Si)_2N]_2ZrMe\}_2O] + [\{(Me_3Si)_2N\}_2Zr\{OC(Me)=CMe_2\}(Me)] \\ \textbf{(2)} \end{array} \qquad (3)$$

(2) is centrosymmetric with *r*(Zr–O) = 1.950(1) Å, *r*(Zr–C) = 2.225(3) Å, *r*(Zr–N) = 2.081 ± 0.001 Å, and Zr–$\hat{O}$–Zr = 180° [15]. $[\{(cp)_2ZrMe\}_2O]$, obtained by exposing a stirred benzene solution of $[(cp)_2ZrMe_2]$ to the air for sixteen hours, has as oxo-bridged structure with *r*(Zr–O) = 1.948(1) Å and Zr–$\hat{O}$–Zr = 174.1(3)° [16].

Solubility measurements in the $Al(OCHMe_2)_3$–$Zr(OCHMe_2)_4$–L (L = thf or $HOCHMe_2$) systems have confirmed the existence of the bimetallic alkoxide $AlZr(OCHMe_2)_7$, but failed to provide evidence for $Al_2Zr(OCHMe_2)_{10}$ [17].

The volatility and thermal decomposition of the 1,3-diketonate chelates [M(acac)$_4$], [M(tfacac)$_4$], and [M(CF$_3$CF$_2$CF$_2$COCHCOCH$_3$)$_4$] (M = Zr or Hf) have been studied by Volkov *et al.* [18].

A variety of complexes of the type [(cp)$_2$Zr(dik)][S$_2$CNRR'] (dik = acac or bzac; R,R' = alkyl or aryl) have been prepared by mixing aqueous solutions of [(cp)$_2$Zr(dik)]Cl and the appropriate sodium *N,N*-dialkyldithiocarbamate [19,20]. A similar procedure has been used to synthesize the corresponding bis(η^5-indenyl) and (η^5-indenyl)(η^5-pyrrolyl) derivatives, [(η^5-C$_9$H$_7$)$_2$Zr(acac)][S$_2$CNRR'] and [(η^5-C$_9$H$_7$)(η^5-C$_4$H$_4$N)Zr(acac)][S$_2$CNRR'] [21,22], and the alkylxanthate salts, [(cp)$_2$Zr(dik)][S$_2$COR] (dik = acac or bzac; R = Me, Et, or CHMe$_2$) [23]. All of these complexes behave as 1:1 electrolytes in nitrobenzene. Tetrahedral coordination about zirconium has been proposed on the basis of IR and ^{1}H NMR spectra, which show that the 1,3-diketonate ligands are bidentate and the dithiocarbamate and xanthate groups are uncoordinated.

1,3-Diketonate- and nitrate-containing complexes of the types [(cp)M(dik)$_2$(NO$_3$)] and [(cp)M(dik)(NO$_3$)$_2$] (M = Zr or Hf; dik = acac or dbzm) have been prepared by reaction of nitric acid with appropriate zirconium or hafnium 1,3-diketonates in dichloromethane or 1,2-dichloroethane. Typical reactions are given in equations (4) and (5). Reactions of [(cp)M(dik)$_2$Cl]

$$[(cp)M(dbzm)_3] + HNO_3 \xrightarrow{-35\ ^\circ C} [(cp)M(dbzm)_2(NO_3)] + dbzmH \qquad (4)$$

$$[(cp)M(dbzm)_2(NO_3)] + HNO_3 \xrightarrow{20\ ^\circ C} [(cp)M(dbzm)(NO_3)_2] + dbzmH \qquad (5)$$

with nitric acid led to the formation of two or three products (equation (6)

$$[(cp)M(dbzm)_2Cl] \xrightarrow[-35\ ^\circ C]{HNO_3} [(cp)M(dbzm)_2(NO_3)] + (cp)MCl_2(NO_3)\cdot 4H_2O \qquad (6)$$

(M = Zr or Hf)

and (7)). The new compounds (cp)MCl$_2$(NO$_3$)·4H$_2$O (M = Zr or Hf) can be

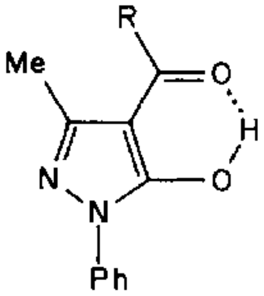
$$[(cp)Zr(acac)_2Cl] \xrightarrow[-35\ ^\circ C]{HNO_3} [(cp)Zr(acac)_2(NO_3)] + [(cp)Zr(acac)(NO_3)_2] + (cp)ZrCl_2(NO_3)\cdot 4H_2O \qquad (7)$$

reconverted to 1,3-diketonate complexes upon treatment with 1,3-diketone (dbzmH or Hbenzac) and triethylamine (equation (8)). The [(cp)M(dik)$_2$(NO$_3$)]

$$(cp)ZrCl_2(NO_3)\cdot 4H_2O + 2dikH + 2Et_3N \longrightarrow [(cp)Zr(dik)_2(NO_3)] + 2[Et_3NH]Cl + 4H_2O \qquad (8)$$

and $[(cp)M(dik)(NO_3)_2]$ complexes are essentially non-electrolytes in tetrahydrofuran. IR spectra indicate that the 1,3-diketonate ligands are bidentate and suggest that the nitrate ligands are probably bidentate as well [24,25].

Heterocyclic tetrakis(1,3-diketonates) of the type $Zr(dik)_n(OCHMe_2)_{4-n}$ {dik is the anion of 4-acyl-3-methyl-1-phenyl-2-pyrazol-5-one (3) and



(3; R = Me, Et, Ph, 3-ClC_6H_4)

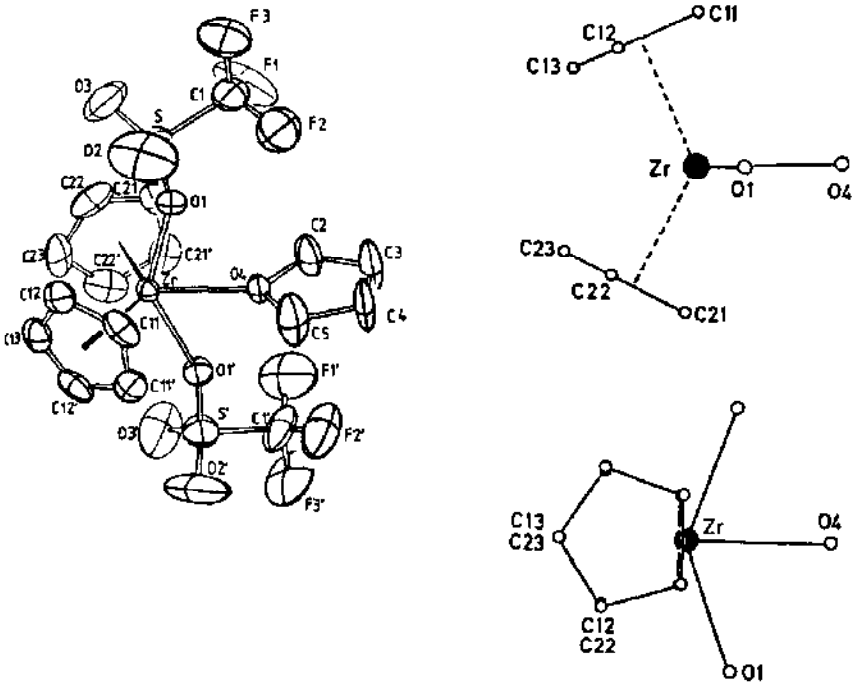
n = 1, 2, 3, or 4} have been prepared by reaction of stoicheiometric amounts of the pyrazolone and $Zr(OCHMe_2)_4\cdot HOCHMe_2$ in benzene at reflux. These complexes are monomeric in boiling benzene, except for the compounds of composition $Zr(dik)(OCHMe_2)_3$, which tend to dimerize. The $Zr(dik)_n(OCHMe_2)_{4-n}$ complexes exchange alkoxide ligands with Me_3COH yielding $Zr(dik)_n(OCMe_3)_{4-n}$ analogues, and they react with phenyl isocyanate giving the insertion products, $Zr(dik)_n\{NPhC(O)OCHMe_2\}_{4-n}$ (n = 1, 2, or 3) [26].

Among the compounds formed in the HfO_2-M_2SO_4-H_2O systems (M = Na, K, Rb, Cs, or NH_4) are complex sulfates of the type $M_2Hf(SO_4)_3(H_2O)_x$, $M_4Hf(SO_4)_4(H_2O)_x$, and $M_6Hf(SO_4)_5(H_2O)_x$ [27]. IR spectra of the sodium hafnium sulfates have been investigated [28], and the X-ray crystal structure of $[NH_4]_4[Hf(SO_4)_4(H_2O)_2]\cdot 2H_2O$ has been determined [29]. This compound contains complex anions in which the hafnium atom is dodecahedrally coordinated by eight oxygen atoms from two bidentate sulfate ligands {r(Hf-O) = 2.223, 2.283 Å}, two monodentate sulfate ligands {r(Hf-O) = 2.067 Å, and two water molecules {r(Hf–O) = 2.196 Å}. The bidentate ligands span the dodecahedral a edges, and the monodentate sulfate ligands and water molecules occupy the B sites.

Standard enthalpies of formation at 298.15 K have been determined by calorimetric measurements for $Hf(SO_4)_2$ ($\Delta H_f^\circ = -2230.1 \pm 3.4$ kJ mol^{-1}) and $Hf(SO_4)_2 \cdot 4H_2O$ ($\Delta H_f^\circ = -3492.8 \pm 3.3$ kJ mol-^{1}) [30].

Zirconium(IV) fluorosulfates, $Zr(SO_3F)_4$, $ZrO(SO_3F)_2$, $Zr(O_2CMe)_2(SO_3F)_2$ and $Zr(O_2CMe)_3(SO_3F)$ have been synthesized by reaction of fluorosulfuric acid with $Zr(O_2CCF_3)_4$, anhydrous $ZrOCl_2$, or $Zr(O_2CMe)_4$. On the basis of IR spectra, the fluorosulfate ligands appear to be bidentate in the first three compounds and tridentate (C_{3v} symmetry) in $Zr(O_2CMe)_3(SO_3F)$. All four compounds are good Lewis acids and form coordination complexes with triphenylphosphine oxide, pyridine, and 2,2'-bipyridine [31].

The trifluoromethane sulfonato-complex $[(cp)_2Zr(CF_3SO_3)_2(thf)]$ has been prepared by the reaction of $[(cp)_2ZrCl_2]$ with $AgCF_3SO_3$ in tetrahydrofuran. This complex has a five-coordinate bent metallocene structure (4) in which



(4)

the oxygen atoms of the two monodentate CF_3SO_3 ligands {r(Zr–O) = 2.219(6) Å} and the thf ligand {r(Zr–O) = 2.278(9) Å} lie nearly in a plane bisecting the (cp)-Zr-(cp) angle {r(Zr-centroid cp) = 2.203 and 2.211 Å; (centroid cp)-$\hat{Z}$r-(centroid cp) = 128.1°}. The thf ligand is symmetrically flanked by the CF_3SO_3 ligands {O(CF_3SO_3)-$\hat{Z}$r-O(thf) = 70.5(2)°} [32].

The temperature dependence of the vapour pressure of [$Zr(ClO_4)_4$] suggests the presence of two crystalline forms of this compound in the temperature range 25.0–95.7 °C. The transition temperature is 49 °C, and the enthalpy for the conversion of the low-temperature form to the high-temperature form is 29 kJ mol^{-1}. [$Zr(ClO_4)_4$] is highly volatile; the vapour pressure varies from 0.8 mm Hg at 25.0 °C to 210.8 mm Hg at 95.7 °C. IR and Raman spectra of gaseous and crystalline [$Zr(ClO_4)_4$] indicate that there is no significant change in the structure upon volatilization [33].

Polymeric, insoluble basic carboxylates of composition $Zr(OH)_3\{O_2C(CH_2)_nCOOH\}$ (n = 1, 2, or 4) have been isolated from aqueous solutions of zirconyl chloride and the dicarboxylic acid at pH 2–3 [34].

IR and pH titration data indicate that carbonato-complexes $[M(OH)_2(CO_3)_2]^{2-}$ (M = Zr or Hf) are formed at pH > 7 in Na_2CO_3/$MOCl_2$ solutions having a Na_2CO_3:$MOCl_2$ molar ratio of 2–6 [35].

Diphenyl sulfoxide complexes of the type [$ZrOX_2(dpso)_2$] (X = Cl, Br, I, NCS, NCSe, or NO_3) have been prepared by treating a methanol solution of the appropriate zirconyl salt with three equivalents of dpso at 10 °C. These complexes are monomeric non-electrolytes in nitrobenzene. IR spectra show that:

(a) the dpso ligands are attached to zirconium through the oxygen atom,
(b) the NCS and NCSe ligands are each coordinated through the nitrogen atom, and
(c) the nitrate ligands are bidentate.

A weak IR band in the region 910–980 cm^{-1} has been assigned to the ν(Zr=O) mode, but the presence of a zirconyl group in these compounds remains to be established [36].

Several TGA and DTA studies of the thermal decomposition of the O-donor ligand complexes have been reported within the past year. Among the compounds studied are:

(a) the above mentioned diphenyl sulfoxide complexes [$ZrOX_2(dpso)_2$] (X = Cl, Br, NCS, or NO_3) [36];

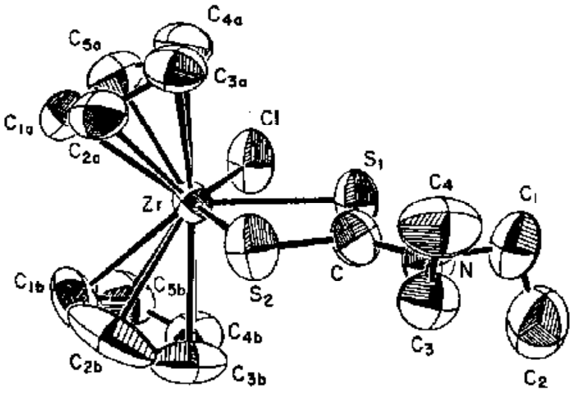
(b) aromatic amine *N*-oxide complexes of the type $[ZrOX_2L_2]$ (X = Cl, Br, NCS, or NO_3) and $[ZrOL_6][ClO_4]_2$ (L = pyridine *N*-oxide, 2,6-dimethylpyridine *N*-oxide, or MephenNO {1,10-phenanthroline mono-*N*-oxide}) [37];

(c) dimethylmethanamide complexes of the type $MOCl_2(dmf)_2(H_2O)_2$, $M(SO_4)_2(dmf)_4$, $MOSO_4(dmf)(H_2O)$, and $MO(OH)(NO_3)(dmf)$ (M = Zr or Hf) [38].

The tetrakis(1-oxo-2-pyridonato)- complex, $[Zr(C_5H_4NO_2)_4]\cdot CHCl_3$, has been reported in connection with an X-ray structural study of the related nine-coordinate thorium compound, $[Th(C_5H_4NO_2)_4(H_2O)]\cdot 2H_2O$ [39].

2.1.3 *Complexes with S-donor ligands*

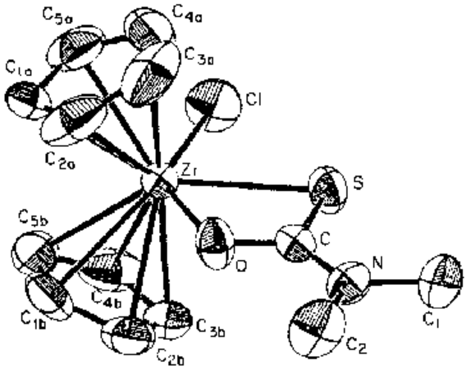
Several papers have appeared during the past year which shed light on the structure and molecular rearrangements of zirconium(IV) dithiocarbamate and monothiocarbamate complexes. An X-ray study has established a five-coordinate bent metallocene structure (5) for $[(cp)_2ZrCl(S_2CNEt_2)]$ {*r*(Zr–centroid cp) = 2.216, 2.222 Å; (centroid cp)–$\hat{Z}$r–centroid cp) = 129.4°}.



(5)

The zirconium atom, chlorine atom, and the two sulfur atoms of the bidentate dithiocarbamate ligand lie in a quasi mirror plane that is nearly perpendicular to the plane defined by the zirconium atom and the centroids of the two symmetrically attached η^5-cyclopentadienyl ligands. Because of crowding in the $ZrClS_2C_{10}$ coordination group, the bonds to the lateral coordination sites are unusually long {r(Zr–Cl) = 2.556(2) Å; r(Zr–S_2) = 2.723(2) Å}; these distances are the longest terminal Zr–Cl and Zr–S bond lengths yet observed for a zirconium(IV) complex. The Zr–S_1 bond length is normal {r(Zr–S_1) = 2.635(2) Å}. A 300 MHz ^{1}H NMR study has afforded the following kinetic data for exchange of methyl groups in the analogous $[(cp)_2ZrCl(S_2CNMe_2)]$ complex: k(25 °C = 8.6 s^{-1}; $\Delta G^{\ddagger}$(25 °C) = 67.7 ± 0.3 kJ mol^{-1}; $\Delta H^{\ddagger}$ = 67 ± 8 kJ mol^{-1}; $\Delta S^{\ddagger}$ = −4 ± 28 J mol^{-1} K^{-1}. The mechanism of this process involves rotation about the C$\overset{\cdots}{=}$N bond in the dithiocarbamate ligand and may involve prior rupture of the Zr–S_2 bond. The equilibrium geometry and the possibility of Zr–S_2 bond rupture have been probed by extended Hückel molecular orbital calculations [40].

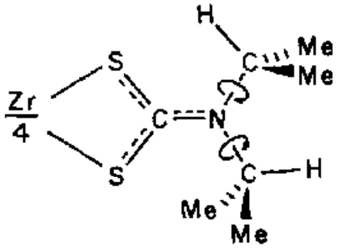
The analogous monothiocarbamato-complex $[(cp)_2ZrCl(SOCNMe_2)]$ has a similar bent metallocene structure (6), with the monothiocarbamate ligand oriented so as to place the smaller oxygen atom in the sterically more congested, lateral coordination site and the larger sulfur atom in the less congested, interior site adjacent to the chlorine atom {r(Zr–Cl) = 2.550(2) Å; r(Zr–O) = 2.249(4) Å; r(Zr–S) = 2.641(2) Å; r(Zr–centroid cp) = 2.230, 2.236 Å; (centroid cp–$\hat{Z}$r–centroid cp) = 128.5°; S–$\hat{Z}$r–O = 62.0°; Cl–$\hat{Z}$r–S = 76.1°; Cl–Zr–O = 138.1°}. $[(cp)_2ZrCl(SOCNMe_2)]$ was prepared by reaction of $[(cp)_2ZrCl_2]$ with anhydrous $Na[SOCNMe_2]$ in boiling dichloromethane [41].



(6)

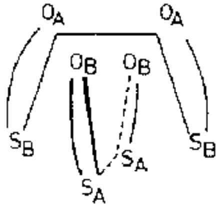
Hafnium(IV) dithiocarbamates of the types $[(cp)_2HfCl(S_2CNRR')]$ and $[(cp)Hf(S_2CNRR')_3]$ (RR' = Et, 3-C_6H_4Me; H, cyclo-C_5H_9; or H, cyclo-C_7H_{13}) have been synthesized by reaction of $[(cp)_2HfCl_2]$ and $Na(S_2CNRR')$ in 1:1 or 1:3 molar ratio. All of these complexes are monomeric non-electrolytes in solution, and IR spectra suggest that the dithiocarbamate ligands are bidentate [42]. Presumably, the $[(cp)_2HfCl(S_2CNRR')$ complexes have five-coordinate bent metallocene structures like $[(cp)_2ZrCl(S_2CNEt_2)]$ [40], and the $[(cp)Hf(S_2CNRR')_3]$ compounds are pentagonal bipyramidal like $[(cp)M(S_2CNMe_2)_3]$ (M = Ti or Zr) [43,44]. Analogous bis(fluorenyl)-*O*-alkylxanthato-complexes, $[(\eta^5\text{-}C_{13}H_9)_2ZrCl(S_2COR)]$ (R = Me, Et, or $CHMe_2$) have been prepared by reaction of equimolar amounts of $[(\eta^5\text{-}C_{13}H_9)_2ZrCl_2]$ and $K[S_2COR]$ in dimethoxyethane [45].

Low-temperature ^1H NMR spectra of $[Zr\{S_2CN(CHMe_2)_2\}_4]$ exhibit two equally intense isopropyl methyl doublets and two equally intense methine septets, attributable to a ligand conformation (7) in which the methine protons of the inequivalent isopropyl groups are located in the plane of the ligand. At higher temperatures, the methyl doublets and methine septets coalesce to a single doublet and a single septet, respectively, due to hindered rotation about the C-N single bonds. Rate constants for this process range from 20 s^{-1} at -25.0 °C to 670 s^{-1} at 21.0 °C; $\Delta H^{\ddagger} = 45 \pm 1$ kJ mol^{-1} and $\Delta S^{\ddagger} = -39 \pm 5$ J mol^{-1} deg^{-1}. $[Zr\{S_2CN(CHMe_2)_2\}_4]$ was prepared by the reaction of $ZrCl_4$ with $Na\{S_2CN(CHMe_2)_2\}$ in the presence of triethyl phosphite [46].



(7)

Low-temperature ^1H NMR spectra of the monothiocarbamato-complex $[Zr(SOCNMe_2)_4]$ can be interpreted in terms of four overlapping methyl peaks, consistent with the spectrum expected for the C_{2v} dodecahedral stereoisomer (8). Variable temperature ^1H NMR spectra indicate the presence of two



(8)

distinct kinetic processes:

(a) a low-temperature process (LTP) involving metal-centered rearrangement, and

(b) a high-temperature process (HTP) involving rotation about the $\mathrm{C}\overset{\text{- - -}}{\text{——}}\mathrm{N}$ partial double bond in the ligand.

Coalescence temperatures (°C) and activation parameters (kJ mol^{-1} or J mol^{-1} deg^{-1}) for the LTP are: T_c = −53.5; $\Delta G^{\ddagger}$(−53.5 °C) = 47.1 ± 0.2; $\Delta H^{\ddagger}$= 40 ± 1; $\Delta S^{\ddagger}$ = −34 ± 5. Corresponding values for the HTP are: T_c = 78.2; $\Delta G^{\ddagger}$(78.2 °C) = 82.7 ± 0.5; $\Delta H^{\ddagger}$ = 99 ± 5; $\Delta S^{\ddagger}$ = 47 ± 15. The greater stereochemical rigidity of $[Zr(SOCNMe_2)_4]$ in comparison with $[Ti(SOCNMe_2)_4]$ and analogous $[M(S_2CNR_2)_4]$ (M = Ti or Zr) complexes suggests a polytopal rearrangement mechanism for the metal-centered process [47].

Moisture-sensitive 1:1 and 2:1 adducts of $ZrCl_4$ and $HfCl_4$ with thiourea have been prepared by mixing stoicheiometric amounts of the metal chloride and thiourea in ethyl acetate. IR spectra indicate that the 1:1 adducts contain *S*-bonded thiourea ligands and both terminal and bridging chlorine atoms; a dimeric structure $[\{(H_2N)_2CS\}Cl_3MCl_2MCl_3\{SC(NH_2)_2\}]$ has been suggested [48]. The IR spectra and calorimetric measurements indicate that only one thiourea molecule is attached to the metal in the 1:2 adducts; the second thiourea molecule appears to interact with the complex via hydrogen bonds [48,49].

2.1.4 Complexes with N-donor ligands

Oxozirconium(IV) complexes with *N*-heterocyclic ligands, $ZrOX_2L_n$ (L = pyridine, 2-methylpyridine, 2-aminopyridine, 2,4-dimethylpyridine, 2,6-dimethylpyridine, quinoline, ½(bipy), or ½(phen); *n* = 4 when X = Cl, Br, I, or ClO_4; n = 2 when X = NO_3, or NCS), have been prepared in methanol. All of these compounds are non-electrolytes in nitrobenzene except for the perchlorate derivatives, which behave as 1:2 electrolytes. Infrared spectra indicate:

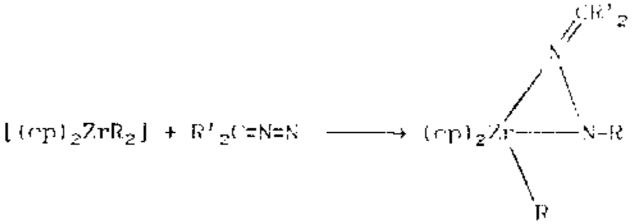
(a) the *N*-heterocyclic ligands are coordinate through the hetero-nitrogen atom, and the amino-nitrogen atom of the 2-aminopyridine is not attached to the metal;
(b) the perchlorate compounds contain uncoordinated ClO_4^- ions;
(c) the nitrate ligands are bidentate;
(d) the NCS^- ligands are coordinated through the nitrogen atom [50,51].

Oxozirconium(IV) selenocyanate reacts with a variety of *O*- and *N*-donor ligands in methanol yielding complexes of the type $ZrO(NCSe)_2L_2$ (L = antipyrine, pyridine *N*-oxide, Ph_3PO, $(Bu_3Sn)_2O$, pyridine, 2,4-dimethylpyridine, hydrazine, or phenylhydrazine) and $ZrO(NCSe)_2L$ (L = 4-aminoantipyrine, 2,2-bipyridine *N*,*N'*-dioxide, bipy, or phen). These complexes are non-electrolytes in ethanenitrile, and IR spectra indicate that they contain *N*-bonded thiocyanate ligands [52].

Substituted-phenylhydrazido(1-) complexes of zirconium(IV), $[XC_6H_4NHNH_3]_2[ZrCl_{6-n}(NHNHC_6H_4X)_n]$ (X = Cl, Br, or I; n = 1, 2, 3, 4, or 6), are obtained from the reaction of $ZrCl_4$ with $XC_6H_4NHNH_2$ or the corresponding hydrazine hydrochloride. The thermal decomposition of these compounds has been studied [53].

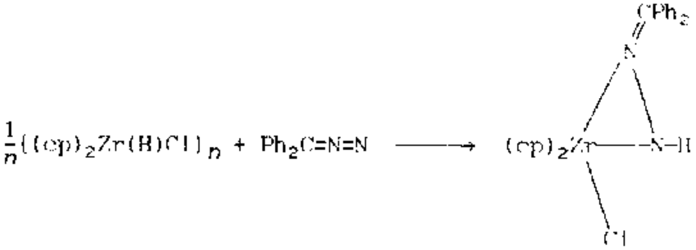
Diazoalkanes $R'_2C{=}N{=}N$ (R' = Ph or CO_2Et) insert into zirconium-carbon and zirconium-hydrogen bonds of $[(cp)_2ZrR_2]$ (R = Me or CH_2Ph) and $\{(cp)_2Zr(H)Cl\}_n$, respectively, yielding five-coordinate bent metallocenes that contain η^2-*N*,*N'*-bonded hydrazonato(1-) ligands (equations (9) and (10)). X-ray crystal structures of compounds **(10)**, **(11)**, and **(12)** indicate that the lateral Zr–N bond is longer than the interior Zr–N bond {r(Zr–NCR_2) = 2.25–2.283 Å; r(Zr–NR) = 2.103(3) Å in **(10)**, 2.21(1) Å in **(11)**, and 2.12(2) Å in **(12)**}. The bond to the other lateral coordination site {r(Zr–Me) = 2.357(6) Å in **(10)**, r(Zr–CH_2Ph) = 2.37(1) Å in **(11)**, and r(Zr–Cl) = 2.549(5) Å in **(12)**} is also significantly lengthened because of the η^2-attachment of the hydrazonato(1-) ligand. The X-ray results and the IR studies indicate π-electronic delocalization over the C–N–N unit [54].

Spirocyclic silylamides, $[M\{(NSiMe_3)_2SiMe_2\}_2]$ (M = Zr or Hf), have been prepared in good yield by reaction of the metal tetrachloride with the lithium-substituted bis(amido)silane, $Me_2Si\{N(Li)SiMe_3\}_2$. These volatile,



(9)

(9; R = Bz, R' = Ph)
(10; R = Me, R' = Ph)
(11; R = Bz, R' = COOEt)



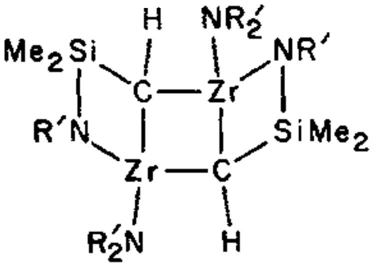
(10)

(12)

moisture-sensitive compounds have been characterized by mass spectra, IR and Raman spectra, and ^1H and ^{29}Si NMR spectra. The spirocyclic complexes are cleaved by MCl_4 (M = Zr or Hf), yielding amorphous polymeric dichloro-monocyclic compounds (equation (11)), which appear to contain chlorine-bridges on the basis of the IR spectra [55].

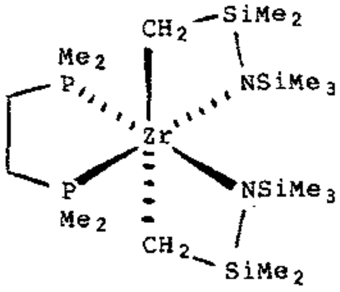
$$[M\{(NSiMe_3)_2SiMe_2\}_2] + MCl_4 \longrightarrow 2MCl_2\{(NSiMe_3)_2SiMe_2\} \qquad (11)$$

Thermal decomposition of $[R_2Zr\{N(SiMe_3)_2\}_2]$ (R = Me, Et, or CH_2SiMe_3) at 60 °C and 10^{-2} mm Hg yields a bridging carbene compound, $[\{\overline{ZrCHSiMe_2N}SiMe_3\{N(SiMe_3)_2\}\}_2]$, having a structure (13) in which three fused, planar, four-membered rings adopt a "tub" conformation [r(Zr–C) = 2.16 and 2.19 Å; r(Zr–N) = 2.04–2.09 Å]; the dihedral angles between the two ZrNSiC rings and the central Zr_2C_2 ring are 111° and 124°. In the case of the analogous hafnium complexes, $[R_2Hf\{N(SiMe_3)_2\}_2]$ (R = Me, Et, or CH_2SiMe_3), the decomposition product was isolated as the pyridine adduct, $[\{\overline{HfCHSiMe_2N}SiMe_3[N(SiMe_3)_2](py)\}_2]$ [56].

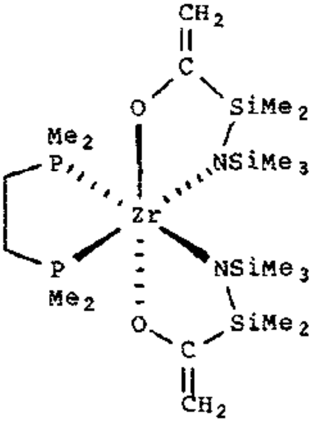


(13; R' = $SiMe_3$)

Reaction of 1,2-bis(dimethylphosphino)ethane (dmpe) with $\{[\overline{MCH_2SiMe_2N}SiMe_3\{N(SiMe_3)_2\}]_2\}$ (M = Zr or Hf) at room temperature or with $[R_2M\{N(SiMe_3)_2\}_2]$ (M = Zr or Hf; R = Me, Et, or CH_2SiMe_3) at 60 °C affords the bis(metallacycle) $[\overline{M(CH_2SiMe_2N}SiMe_3)_2(dmpe)]$. The zirconium complex has an octahedral tris(chelate) structure of idealized C_2 symmetry **(14)** [r(Zr–C) = 2.316 Å; r(Zr–N) = 2.088 Å; r(Zr–P) = 2.852 Å]. Compound (14) reacts with carbon monoxide (20 atm, 20 °C) in pentane yielding compound **(15)**; the proposed structure of (15) is based on ^1H NMR and ^{13}C NMR spectra [57].

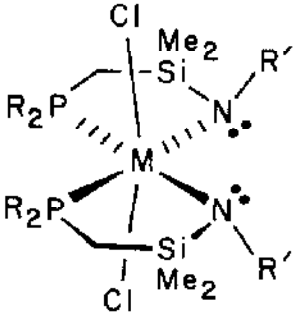


(14)



(15)

Reaction of the phosphorus containing disilylamide $LiN(SiMe_2CH_2PR_2)_2$ (R = Me or Ph) with MCl_4 (M = Zr or Hf) yields $[MCl_2\{N(SiMe_2CH_2PR_2)_2\}_2]$ complexes as colourless, air- and moisture- sensitive crystalline solids. ^1H NMR and $^{31}P\{^1H\}$ NMR spectra of these compounds are consistent with structure **(16)**, which has been established by X-ray diffraction for



(16; R' = $SiMe_2CH_2PR_2$)

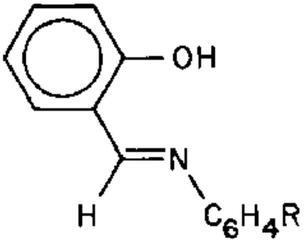
$[ZrCl_2\{N(SiMe_2CH_2PMe_2)_2\}_2]$. The bulky $N(SiMe_2CH_2PR_2)_2$ ligands are bidentate, with the two uncoordinated $SiMe_2CH_2PR_2$ groups being located on opposite sides of the equatorial plane. The resulting distorted octahedral structure has approximate C_2 symmetry and is chiral {$\bar{r}$(Zr–P) = 2.798, $\bar{r}$(Zr–N) = 2.096, $\bar{r}$(Zr–Cl) = 2.460 Å; Cl–$\hat{\text{Zr}}$–Cl = 155.42(4), N–$\hat{\text{Zr}}$–N = 119.1(1)°} [58].

$[HfCl_2\{N(SiMe_2CH_2PMe_2)_2\}_2]$ disproportionates in the presence of excess $HfCl_4$, yielding the "mono" amide complex $[HfCl_3\{N(SiMe_2CH_2PMe_2)_2\}_2HfCl_4]_x$, which can be converted to the monomeric complex $[Hf(BH_4)_3\{N(SiMe_2CH_2PMe_2)_2\}]$ and $[Hf(BH_4)_4]$ by reaction with an excess of $Li[BH_4]$. Treatment of $[Hf(BH_4)_3\{N(SiMe_2CH_2PMe_2)_2\}]$ with Lewis bases (NEt_3 or PMe_3) gives the dinuclear trihydride $[\{Hf[N(SiMe_2CH_2PMe_2)_2]\}_2(H)_3(BH_4)_3]$ [59].

Poly(pyrazolyl)borate *tert*-butoxide complexes of zirconium(IV) of the type $[ZrCl_2(OCMe_3)(RBPz_3)]$ (R = H, $CHMe_2$, Bu, or Pz) and $[ZrCl_2(OCMe_3)\{HB(3,5\text{-}Me_2Pz)_3\}]$ have been prepared by reaction of the corresponding $[ZrCl_3(RBPz_3)]$ or $[ZrCl_3\{HB(3,5\text{-}Me_2Pz)_3\}]$ complexes with one equivalent of $KOCMe_3$ in toluene. The $[ZrCl_2(OCMe_3)(RBPz_3)]$ complexes are fluxional on the NMR time scale ($\Delta G^\ddagger$ = 56 ± 2 kJ mol^{-1} for R = Bu), while the more sterically hindered $[ZrCl_2(OCMe_3)\{HB(3,5\text{-}Me_2Pz)_3\}]$ is stereochemically rigid at temperatures up to 140 °C. The preferred rearrangement mechanism is a trigonal twist [60]. $[ZrCl_2(OCMe_3)\{HB(3,5\text{-}Me_2Pz)_3\}]$ serves as a useful starting material for the synthesis of stable alkyl derivatives $[Zr(OCMe_3)R_2\{HB(3,5\text{-}Me_2Pz)_3\}]$ (R = Me, CH_2Ph, or C≡CMe) [61]. Di- and tri-*tert*-butoxide derivatives $[ZrCl_{3-n}(OCMe_3)_n\{HB(3,5\text{-}Me_2Pz)_3\}]$ (n = 2 or 3) have also been prepared [60,61].

The 8-quinolinolato-complexes $[(cp)_2Zr(8\text{-}O\text{-}quin)][S_2CNRR']$ (RR' = alkyl or aryl) and $[(cp)_2Zr(8\text{-}O\text{-}quin)][S_2COR]$ (R = Me, Et, or $CHMe_2$) have been prepared by mixing aqueous solutions of $[(cp)_2Zr(8\text{-}O\text{-}quin)]Cl$ and the appropriate sodium *N,N*-dialkyldithiocarbamate [19,62] or potassium *O*-alkylxanthate [23]. These compounds are 1:1 electrolytes in nitrobenzene, and are analogous to the 1,3-diketonato-derivatives $[(cp)_2Zr(dik)]Y$ (Y = S_2CNRR' or S_2COR) mentioned in Section 2.1.2.

Dichlorobis(indenyl)zirconium(IV) reacts with salicylaldimine Schiff bases **(17; HL)** in the presence of triethylamine yielding complexes of the type

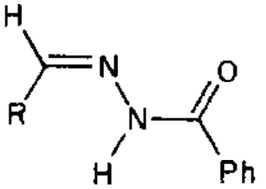


(17; HL; R = H, 2-Me, 3-Me, 4-Me)

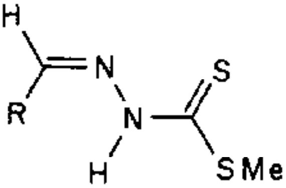
$[(\eta^5\text{-}C_9H_7)_2ZrLCl]$, which are non-electrolytes in nitrobenzene. IR spectra indicate that the Schiff bases behave as *NO*-donor bidentate ligands [63].

N-(2-pyridyl)salicylaldimine (HL) complexes of the type $[Zr(OCHMe_2)_{4-n}(L)_n]$ (n = 1, 2, or 3) have been prepared by the reaction of $Zr(OCHMe_2)_4\cdot HOCHMe_2$ with stoicheiometric amounts of the Schiff base in benzene at reflux. These complexes are monomeric in boiling benzene, and IR spectra suggest that the salicylaldimine behaves as an *NO*-bidentate ligand, coordinating through the azomethine nitrogen atom and the phenolate oxygen atom. Therefore, the coordination number of the zirconium atom is 5, 6, or 7 for n = 1, 2, or 3, respectively. It was not possible to replace the fourth isopropoxide ligand; reaction of $Zr(OCHMe_2)_4\cdot HOCHMe_2$ with four equivalents of *N*-(2-pyridyl)salicylaldimine gave $Zr(OCHMe_2)(L)_3\cdot HL$ [64].

$Hf(OCHMe_2)_4\cdot HOCHMe_2$ reacts in benzene at reflux with stoicheiometric amounts of the monobasic, *NO*-bidentate benzoyl hydrazones **(18; HL)** and *NS*-bidentate Schiff bases derived from *S*-methyl dithiocarbazate **(19; HL)** yielding complexes of the type $Hf(OCHMe_2)_{4-n}(L)_n$ (n = 1, 2, 3 or 4). The

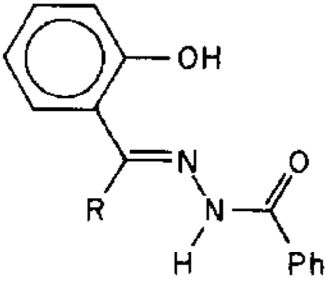


(18; HL; R = Ph, $\overline{C_4H_3O}$)

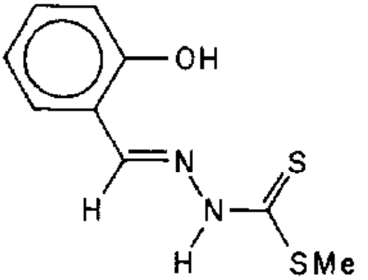


(19; HL; R = Ph, $\overline{C_4H_3O}$)

corresponding dibasic *ONO*- and *ONS*-tridentate ligands (20 and 21; H_2L') give products of the type $Hf(OCHMe_2)_2(L')$ and $Hf(L')_2$. These complexes are moisture sensitive, soluble in organic solvents, and non-electrolytes in dimethylmethanamide. A tridentate mode of attachment of the ligands was assigned on the basis of IR spectroscopy [65,66]. Only mono- and di-substitution products could be obtained from reactions of $HfCl_4$ with (18)–(21). The resulting $HfCl_3(L)$, $HfCl_2(L)_2$, and $HfCl_2(L')$ complexes are insoluble in common organic solvents and are probably polymeric [67,68].

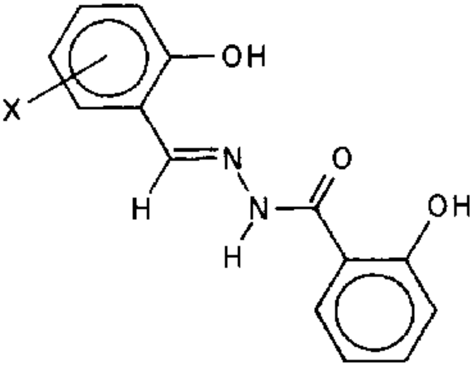


(20; H_2L'; R = H, Me)



(21; H_2L')

Zirconyl acetate reacts in methanol at reflux with Schiff bases **(22; H_2L')** derived from substituted salicylaldehydes and salicylhydrazide to



(22; H_2L'; X = H, 5-Cl, 5-Br, 5-NO_2, 3-OEt, 5-OMe, 3,5-Cl_2, 5,6-benzo) give monomeric 1:2 complexes of the type $[ZrO(HL')_2]$. IR spectra indicate that the Schiff bases behave as monobasic *ONO*-tridentate ligands, coordinating to zirconium through the carbonyl oxygen, azomethine nitrogen, and phenolate oxygen atoms. The complexes exhibit an IR band in the region 905–915 cm^{-1}, which has been assigned to $\nu(Zr{=}O)$. If these compounds do contain a Zr=O group, the zirconium atom would be seven coordinate [69].

2.1.5 Complexes with P-donor ligands

The bis(diorganophosphide) complexes $[(cp)_2M(PR_2)_2]$ (M = Zr or Hf; R = Et, cych, or Ph) have been prepared by reaction of $[(cp)_2MCl_2]$ with two equivalents of $LiPR_2$ in tetrahydrofuran. An X-ray structural study has shown that $[(cp)_2Hf(PEt_2)_2]$ is an eighteen-electron complex; the hafnium atom is attached *via* an Hf–P single bond to a pyramidal (sp^3) phosphorus atom and is attached *via* an Hf=P double bond to a trigonal planar phosphine atom {*r*(Hf–P) = 2.682(1) Å; *r*(Hf=P) = 2.488(1) Å. ^{31}P NMR spectra indicate that interconversion of the Hf–P and Hf=P bonds is fast on the NMR time scale; for $[(cp)_2M\{P(cych)_2\}_2]$ (M = Zr or Hf), the barrier to exchange is 25 ± 1 kJ mol^{-1} [70].

In a parallel study Wade et al. [71] have reported that $[(cp)_2MCl_2]$ reacts with $LiPR_2$ to give $[(cp)_2M(PR_2)_2]$ (M = Zr, R = Ph; M = Hf, R = Ph or cych), but when R = Me, the reaction products are the dimeric zirconium(III) and hafnium(III) complexes $[\{(cp)_2M(PMe_2)\}_2]$. Treatment of $[(cp)_2Zr(PPh_2)_2]$ with one equivalent of PPh_2Cl gives the mixed-ligand complex $[(cp)_2ZrCl(PPh_2)]$. The reactions of the $[(cp)_2M(PR_2)_2]$ complexes with a variety of protic and halogen-containing species result in cleavage of the metal-phosphorus bonds.

The 1,2-bis(dimethylphosphino)ethane-containing complexes $[\overline{M(CH_2SiMe_2N}SiMe_3)_2(dmpe)]$ (M = Zr or Hf) [57] were discussed in Section 2.1.4.

2.1.6 Hydride and borohydride complexes

^{1}H NMR spectra of sparingly soluble $(cp)_2ZrH_2$ in extremely dilute C_6D_6 and $CD_3C_6D_5$ solutions at ambient temperature exhibit the expected C_5H_5 resonance at δ 5.75 and two triplets at δ 3.85 and δ −3.45, both with

J = 7.3 Hz; the spin coupling was collapsed by irradiation of either triplet. These data are consistent with a dimeric structure [$\{(cp)_2ZrH(\mu\text{-}H)\}_2$], with two bridging and two terminal hydride ligands. Collapse of the hydride triplets and intensity changes at elevated temperatures were interpreted in terms of:

(a) rapid bridge-terminal hydride exchange and

(b) a dimer-monomer equilibrium.

The reaction of [$\{(cp)_2ZrH(\mu\text{-}H)\}_2$] with diphenylacetylene yields H_2 and the zirconacyclopentadiene complex [$(cp)_2Zr(C_4Ph_4)$] [72]. [$\{(Mecp)_2ZrH(\mu\text{-}H)\}_2$] reacts with diphenylacetylene or phenylacetylene yielding H_2 and analogous zirconacyclopentadiene complexes; however, if the reactions are carried out without the removal of H_2, appreciable hydrogenation of acetylene occurs [73].

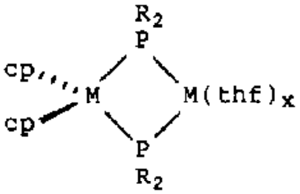
The dinuclear trihydride [$\{Hf[N(SiMe_2CH_2PMe_2)_2]\}_2(H)_3(BH_4)_3$] and its precursor [$Hf(BH_4)_3\{N(SiMe_2CH_2PMe_2)_2\}$] [59] were discussed in Section 2.1.1.

A neutron diffraction study of $Hf(BH_4)_4$ has shown that the crystal contains regular tetrahedral molecules, which occupy sites of crystallographic $\bar{4}3m$ (T_d) symmetry. The $[BH_4]^-$ ligands are tridentate and adopt the conformation in which the three Hf–H bonds to one $[BH_4]^-$ ligand are staggered with respect to the Hf–B bonds to the other three $[BH_4]^-$ ligands {r(Hf–B) = 2.281(8), r(Hf–H_b) = 2.130(9), r(B–H_b) = 1.235(10), r(B–H_t) = 1.150(19) Å, where H_b and H_t denote the bridging and terminal hydrogen atoms respectively} [74].

The methyltrihydroborato-complex [$Zr(BH_3Me)_4$] has been synthesised by reaction of $ZrCl_4$ and $LiBH_3Me$ in chlorobenzene. It also has a tetrahedral structure, with tridentate attachment of the $[BH_3Me]^-$ ligands. The following bond lengths have been determined by X-ray diffraction: $\bar{r}$(Zr–B) = 2.335(3), $\bar{r}$(Zr–H_b) = 2.06, $\bar{r}$(B–H_b) = 1.14 Å [75].

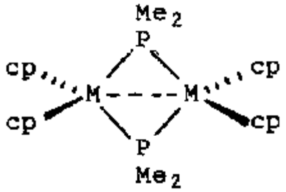
2.2 ZIRCONIUM(III) AND HAFNIUM(III) COMPOUNDS

Reduction of [$(cp)_2M(PR_2)_2$] (M = Zr or Hf; R = Et, cyhx, or Ph) with sodium naphthalenide in thf at 25 °C yields thermally stable zirconium(III) and hafnium(III) complexes, [$(cp)_2M(PR_2)_2Na(thf)_x$]. ^{23}Na hyperfine splittings have been observed in EPR spectra of [$(cp)_2Zr(PR_2)_2Na(thf)_x$] (R = Et or cyhx), which suggests that these complexes have a phosphide-bridged structure (23) [70].



(23)

The red-brown $[\{(cp)_2M(PMe_2)\}_2]$ (M = Zr or Hf) complexes, obtained by reaction of $[(cp)_2MCl_2]$ with two equivalents of $LiPMe_2$, are diamagnetic in solution. ^1H NMR spectra of these complexes exhibit a sharp singlet due to the equivalent C_5H_5 protons and a triplet due to virtual coupling of the PMe_2 protons to two ^{31}P nuclei. The spectra are consistent with a phosphido-bridged structure **(24)**, with significant Zr···Zr interaction.



(24)

Reactions of the $[\{(cp)_2M(PMe_2)\}_2]$ complexes with halogen-containing species result in cleavage of the metal-phosphorus bonds and oxidation of the metal to give $[(cp)_2MX_2]$ (X = halogen) [71].

Photolysis or prolonged heating at 75 °C of a benzene slurry of $[\{(Mecp)_2ZrH(\mu-H)\}_2]$ results in evolution of H_2 and formation of dark purple solutions. EPR spectra of these solutions indicate the presence of a paramagnetic zirconium(III)-hydride complex, which reacts with diphenylacetylene to give another zirconium(III)-hydride species, perhaps $[(Mecp)_2Zr(H)(PhC{\equiv}CPh)]$ [73].

Paramagnetic zirconium(III)-hydride complexes are also produced when thf solutions of $[(cp)_2ZrCl_2]$ are reduced with magnesium. A ^1H hyperfine splitting of 7.4 G, which is not observed when the experiment is repeated with $[(\eta^5-C_5D_5)_2ZrCl_2]$, indicates that the zirconium(III)-hydride is produced by hydrogen abstraction from a cyclopentadienyl ring. Additional zirconium(III)-hydride complexes were observed by EPR when $[(cp)_2ZrCl_2]$ was reduced by magnesium in the presence of alkenes or alkynes [76].

Low-temperature photolysis studies in toluene or methyl cyclohexane of $[(cp)_2ZrR_2]$ (R = alkyl or aryl) or $[(cp)_2Zr(R)Cl]$ (R = H, Me, cp, or Cl) have led to EPR characterization of a number of zirconium(III) species, including $[(cp)_2ZrR]$, $[(cp)_2ZrCl]$, and a zirconium(III) hydride. The EPR spectra suggest that the solutions contain $[(cp)_2Zr(PEt_3)R]$ adducts when the $[(cp)_2ZrR_2]$ complexes are photolyzed in the presence of PEt_3 [77].

2.3 ZIRCONIUM(I) COMPOUNDS

The layer structure of ZrCl and ZrBr can be intercalated with oxygen and hydrogen atoms yielding interstitial derivatives of the monohalides. ZrX (X = Cl or Br) reacts with ZrO_2 at *ca.* 980 °C according to equation (12), where x

$$ZrX + nZrO_2 \longrightarrow ZrXO_y + nZrO_x \qquad (12)$$

and y can take on values up to *ca.* 0.4. The pure monohalides have a structure consisting of four-layer slabs with stacking sequence X–Zr–Zr–X. X-ray studies have shown that in $ZrXO_y$ the oxygen atoms are randomly distributed in tetrahedral interstices between the double zirconium layers of an expanded ZrX structure. Reactions analogous to equation (12) do not occur between ZrCl and ZrC, ZrN, ZrF_4, or $Zr_{1+x}S$, and attempts to intercalate ZrCl with several small molecules were unsuccessful [78].

Guinier X-ray powder data indicate that the monohalide hydrides $ZrBrH_{0.5}$, ZrBrH, and ZrClH also have expanded ZrX structures. Hydride formation is accompanied by a progressive increase in the distance between the adjacent zirconium layers; the hydrogen atoms are presumed to occupy the tetrahedral interstices between the zirconium atoms [79]. X-ray and UV photoelectron spectra of $ZrXH_{0.5}$, ZrXH (X = Cl or Br), and $ZrH_{1.90}$ indicate an appreciable amount of Zr–H covalency [80].

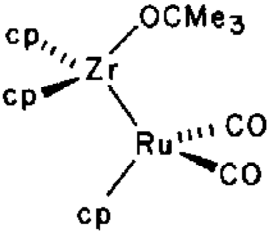
Trends in XPES data for zirconium, $ZrCl_n$ (n = 1–4), ZrBr, $ZrXH_x$ (X = Cl or Br; x = 0.5 or 1), and $ZrClO_{0.4}$ have been reviewed. The binding energy of the zirconium $3d_{5/2}$ level exhibits a regular increase with increasing formal oxidation state except for $ZrCl_3$ and $ZrCl_4$, where the binding energies are displaced to higher binding energy by *ca.* 1.3 eV. The break in the trend, between oxidation state +2 and +3, occurs in the region where metal-metal bonding and valence-electron delocalization disappear [81].

2.4 ZIRCONIUM(0) AND HAFNIUM(0) COMPOUNDS

The tris(2,2'-bipyridine) and tris(1,10-phenanthroline) complexes, $[M(bipy)_3]$ and $[M(phen)_3]$ (M = Zr or Hf), have been prepared in *ca.* 80% yield by reduction of $ZrCl_4$ or $HfCl_4$ with sodium amalgam in thf solutions that contain a stoicheiometric amount of the ligand. These complexes are dark coloured, extremely air sensitive, monomeric, and diamagnetic [82].

2.5 COMPOUNDS WITH METAL-METAL BONDS

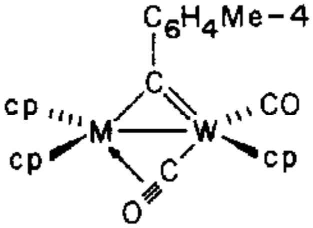
Heterobimetallic complexes of the type $[(cp)_2XZrM(CO)_2(cp)]$ (X = Cl, $OCMe_3$, or Me, when M = Ru; X = $OCMe_3$ or Me, when M = Fe) have been synthesized by reaction of $[(cp)_2ZrClX]$ with one equivalent of $K[(cp)M(CO)_2]$ in thf. The presence of a metal-metal bond in these compounds was confirmed by the X-ray structure of $[(cp)_2(Me_3CO)ZrRu(CO)_2(cp)]$ **(25)** {r(Zr-Ru) = 2.910(1) Å; r(Zr-O) = 1.910(4) Å; $Zr\text{-}\hat{O}\text{-}C = 169.6^\circ$} [83].



(25)

The complexes $[(cp)_2M(CO)_2]$ (M = Ti or Zr) react with $[(cp)W(\equiv CC_6H_4Me\text{-}4)(CO)_2]$ in toluene at 55–70 °C to give the thermally stable and relatively inert bimetallic compounds $[(cp)_2M(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)W(CO)(cp)]$

(26). The structure of the titanium compound, which features a Ti-W bond bridged by the CC_6H_4Me-4 ligand and an η^1,η^2-carbonyl group, has been established by X-ray diffraction [84].



(26)

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