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8. ZIRCONIUM AND HAFNIUM

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CONTENTS

INTRODUCTION

The 1981 literature on zirconium and hafnium is extensive and diverse. Following previous practice in this series, this review attempts comprehensive coverage of the coordination chemistry of zirconium and hafnium; organometallic and solid-state aspects of the chemistry of these elements are treated selectively. For a comprehensive treatment of the organometallic chemistry, the reader is referred to the annual reviews by Labinger in the Journal of Organometallic Chemistry; the most recent review, for the year 1980, appeared in early 1982 [1]. On the solid state side, Corbett has reviewed structure and metal-metal bonding in halides of early transition metals, including the reduced halides of zirconium [2]. Other reviews that have appeared during the past year are an article on hafnium and hafnium compounds in the Kirk-Othmer Encyclopedia of Chemical Technology [3] and a review of selected aspects of the chemistry of zirconium and hafnium by Chekmarev [4].

This year has seen several new developments, including the preparation of some of the first discrete polynuclear complexes in which zirconium or hafnium is attached to another metal via a metal-metal bond and the first chemical applications of zirconium-91 NMR spectroscopy.

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The present review covers the major journals for the 1981 calendar year and the lesser known and/or foreign journals for the period covered by Chemical Abstracts, Volume 93, Number 19 through Volume 95, Number 18.

8.1 ZIRCONIUM(IV) AND HAFNIUM(IV) COMPOUNDS

8.1.1 Halide and pseudohalide complexes

X-ray crystal structures of a number of fluorozirconates have been published within the past year; the coordination number of zirconium(IV) in these compounds ranges from six to eight. The zirconium(IV) atom is six-coordinate in both high- and low-temperature forms of $FeZrF_6$. The high-temperature, cubic phase is of the ordered ReO_3-type (space group $Fm\bar{3}m$) with r(Zr-F) = 1.991(2) Å. The low-temperature, hexagonal form crystallises in the $LiSbF_6$ structure (space group $R\bar{3}m$) with r(Zr-F) = 1.995(10) Å. The linear Fe-F-Zr bridges of the cubic form are bent (164.4°) in the hexagonal form [5]. Crystals of ethylenediammonium hexafluorozirconate $[enH_2]ZrF_6$ contain centrosymmetric $[Zr_2F_{12}]^{4-}$ ions in which two distorted pentagonal bipyramidal $\{ZrF_7\}$ groups share a common equatorial edge. As expected, the terminal Zr-F bonds $\{\bar{r}$(Zr-F) = 2.027 Å$\}$ are appreciably shorter than the bridging Zr-F bonds $\{\bar{r}$(Zr-F) = 2.150 Å$\}$ [6].

Pb_3ZrF_{10} has an anion-excess fluorite-related structure in which $\{ZrF_8\}$ square antiprisms $\{\bar{r}$(Zr-F) = 2.10 Å$\}$ share faces with $\{PbF_{11}\}$ complex polyhedra [7]. The structure of Pb_3ZrF_{10} is one member of a homologous series of anion-excess fluorite-related structures having general formula $A_nB_2X_{2n+8}$: other members of this series are α-$BaZrF_6$ and probably Pb_5ZrF_{14} [8]. The transport properties of the disordered fluorite-type solid solution $Pb_{1-x}Zr_xF_{2+2x}$ ($0 < x < 0.18$) and of the ordered compounds Pb_5ZrF_{14} ($x = 0.167$), Pb_3ZrF_{10}, and $PbZrF_6$ have been investigated. The disordered phase $Pb_{0.90}Zr_{0.10}F_{2.20}$ is a fairly good anionic conductor [9]. A quasi-continuous series of one-dimensional superstructures with composition varying from $(Zr,U)(O,F)_{2.100}$ to $(Zr,U)(O,F)_{2.143}$ has been prepared by solid state reactions of ZrO_2, U_3O_8, and UF_4 at temperatures from 875 to 1200 °C. A structural model for these phases has been proposed [10].

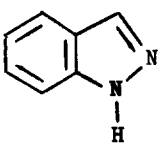
The structure of $Cd_2ZrF_8.6H_2O$ consists of $\{ZrF_8\}$ square antiprisms and $\{CdF_4(OH_2)_3\}$ pentagonal bipyramids which are linked together by sharing of F···F polyhedral edges $\{\bar{r}$(Zr-F) = 2.114 Å$\}$ [11]. $ZrF_4(H_2O)$ has a three-dimensional network structure in which $\{ZrF_6(OH_2)_2\}$ dodecahedra share six corners with six adjacent dodecahedra. The bridging groups are the water molecules $\{r$(Zr-O) = 2.132(1) Å$\}$ and four of the fluorine atoms $\{r$(Zr-F) = 2.058(2) and 2.170(2) Å$\}$; the two terminal Zr-F bond lengths are 2.100(3) Å [12]. It is interesting to note that the better π-donor ligand (F^-) prefers the dodecahedral

B sites, as expected for a complex of a d^0 metal ion [13].

The following peroxofluorides have been isolated from acidic, neutral and basic aqueous solutions: amorphous $Zr(O_2)F_2.2H_2O$ at pH 2-3; crystalline $K_3Zr_2(O_2)_2F_7$, $[NH_4]_3Zr_2(O_2)_2F_7$, $K_2ZrF_5(OOH)$, and $K_2HfF_5(OOH)$ at pH 5-7; and $M_3M'_3(H_2O_2)_4(OH)F_6O_4$ (M = NH_4 or K, M' = Zr or Hf) at pH 9.3. These compounds have been characterized by chemical analysis, vibrational spectroscopy, and X-ray diffraction patterns [14]. A broad-line ^1H and ^{19}F NMR study of $K_2ZrF_5(OOH)$ indicates that this compound contains fluorine-bridged, dimeric $[Zr_2F_{10}(OOH)_2]^{4-}$ ions. Each zirconium(IV) atom is attached to two bridging fluorine atoms, four terminal fluorine atoms, and a bidentate peroxo ligand [15]. $Zr(O_2)F_2.2H_2O$, obtained by reaction of $ZrF_4.3H_2O$ with H_2O_2, has been further characterised by IR and ^1H NMR spectroscopy [16].

The heat of formation of gaseous $[ZrF_5]^-$ has been determined by a mass spectrometric method: $\Delta H^\circ_{f,298} = -2334.7$ kJ mol^{-1} [17].

Several studies of metal tetrachloride adducts with Lewis bases have been reported. Zirconium(IV) chloride reacts with indazole (*1*) to give a solid



(*1*)

$[ZrCl_4L_2]$ adduct that has been assigned an octahedral *trans* structure on the basis of a single ν(Zr-Cl) band at 348 cm^{-1}. A low-frequency shift of the ν(N-H) band of indazole upon complexation and the lack of a shift in the ν(C=N) band indicates that indazole coordinates to zirconium through the pyrrole nitrogen atom [18]. Reaction of equimolar amounts of $ZrCl_4$ and $SiMe_2(NMe_2)_2$ in benzene gives immediate precipitation of a white, moisture-sensitive 1:1 adduct $[ZrCl_4\{(NMe_2)_2SiMe_2\}]$. An octahedral *cis* structure having a $\{ZrN_2Si\}$ chelate ring has been proposed. The presence of two *N*-methyl resonances in ^1H NMR spectra of $[ZrCl_4\{(NMe_2)_2SiMe_2\}]$ suggests the presence of a non-planar $\{ZrN_2Si\}$ ring; the two resonances coalesce to a broad singlet at elevated temperatures (373 K) owing to a rapid ring-inversion process [19].

The complexes $MCl_4.POCl_3$, $MCl_4.2POCl_3$ (M = Ti, Zr, or Hf), and $HfCl_4.3POCl_3$ have been studied by ^{35}Cl NQR spectroscopy. The electron acceptor strength of MCl_4 decreases as the metal varies in the order Hf > Zr > Ti [20].

Zirconium(IV) chloride reacts with freshly prepared $(OCN)_2$ in dichloromethane at -70 °C to give the 1:1 adduct $ZrCl_4\{(NCO)_2\}$. IR spectra of this compound suggest that the NCO-OCN ligand is attached to the metal through the nitrogen

atoms. The nitrogen atoms appear to occupy *cis* positions in the $\{ZrCl_4N_2\}$ coordination group, but it is not known whether this compound is a monomer or a polymer [21]. In contrast, reaction of $ZrCl_4$ with freshly prepared $(SeCN)_2$ in CS_2 at -60 °C yields the substitution product $ZrCl_3(NCSe)$ (equation (1)). IR spectra suggest that the SeCN groups act as ambidentate bridging ligands

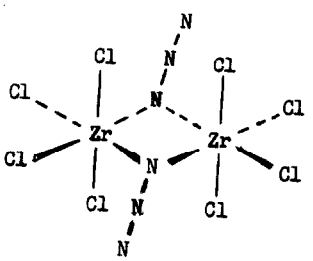
$$ZrCl_4 + (SeCN)_2 \longrightarrow ZrCl_3(NCSe) + ClSeCN \qquad (1)$$

via coordination through the nitrogen and selenium atoms [22].

Highly explosive $ZrCl_3(N_3)$ is obtained from the reaction of $ZrCl_4$ with iodine azide in dichloromethane (equation (2)). IR spectra indicate that this

$$ZrCl_4 + IN_3 \longrightarrow ZrCl_3(N_3) + ICl \qquad (2)$$

compound is polymeric having both azide and chlorine bridges. The reaction of $ZrCl_4$ with one and two moles of $[PPh_4][N_3]$ yields the thermally and mechanically stable complexes $[PPh_4]_2[\{ZrCl_4(N_3)\}_2]$ and $[PPh_4]_2[ZrCl_4(N_3)_2]$. An X-ray study of $[PPh_4]_2[\{ZrCl_4(N_3)\}_2]$ has established that this compound contains centrosymmetric, dimeric $[\{ZrCl_4(N_3)\}_2]^{2-}$ anions (*2*) in which the zirconium atoms are linked by



(2)

the α-nitrogen atoms of the nearly linear azide groups {$\bar{r}$(Zr–Cl) = 2.407 Å; $\bar{r}$(Zr–N) = 2.203 Å; N–$\hat{Z}$r–N = 66.7°; Zr–$\hat{N}$–Zr = 113.3°}. IR spectra indicate that the anion in $[PPh_4]_2[ZrCl_4(N_3)_2]$ has an octahedral *trans* structure [23].

Raman and far IR spectra and normal coordinate analyses have been reported for crystalline zirconium(IV) chloride and bromide [24]. The results are in accord with the X-ray structure of crystalline $ZrCl_4$ which consists of extended chains of distorted $\{ZrCl_6\}$ octahedra with two bridging chlorine atoms between adjacent zirconium atoms [25,26]. The electrochemical reduction of $ZrCl_4$ in molten NaCl, CsCl, and KCl–LiCl has been studied by Basile *et al.* [27].

The compound $[SCl_3]_2[ZrCl_6]$ has been prepared by reaction of stoicheiometric amounts of sulphur and $ZrCl_4$ with a 10% excess of chlorine. The Raman spectrum of the product exhibits the $\nu_1(A_{1g})$, $\nu_2(E_g)$, and $\nu_5(T_{2g})$ bands expected for

$[ZrCl_6]^{2-}$ at 324, 258, and 154 cm^{-1}, respectively [28].

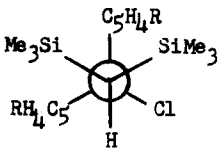
Crystalline HfI_4 has been shown by X-ray diffraction to have a novel AB_4-type structure consisting of folded infinite chains of edge-sharing $\{HfI_6\}$ octahedra with a period of four formula units: none of the shared edges are *trans* to each other. The chain structure differs from those in the α-NbI_4, $ZrCl_4$, and ZrI_4 structure types. As is often found for AB_4-type structures, the terminal Hf-I bonds (2.678 and 2.682 Å) are shorter than the bridging Hf-I bonds that are *trans* to bridging iodine atoms (2.848 and 2.853 Å) which are in turn shorter than the bridging Hf-I bonds that are *trans* to terminal iodine atoms (3.002 and 3.007 Å). Mass spectra show that sublimation gives HfI_4 molecules and that the HfI_4 does not form a gas-phase complex with AlI_3. IR and Raman spectra of crystalline HfI_4 have also been reported [29].

$K_2[ZrI_6]$ has been prepared by reaction of ZrI_4 with KI at 600 °C, and has been characterised by chemical analysis, X-ray powder diffraction, and TGA. When heated above 200 °C, the compound decomposes with loss of gaseous ZrI_4 [30]. The KI-ZrI_4 system has been studied by DTA, chemical analysis and X-ray diffraction, and its equilibrium phase diagram has been constructed. $K_2[ZrI_6]$ is the only congruently melting compound in this system [31].

Several studies of organozirconium and organohafnium halides have been reported. $[(cp)ZrCl_3(dme)]$ has been prepared by reaction of sublimed $ZrCl_4$ and Tl[cp] (2:1 mole ratio) in 1,2-dimethoxyethane at 0 °C. The unsolvated, insoluble and presumably polymeric $(cp)ZrCl_3$ is produced by photolysis of $[(cp)_2ZrCl_2]$ in Me_3CCl. $[(cp)ZrCl_3(dme)]$ has an octahedral structure in which the chelating dme ligand spans axial (*trans* to cp) and equatorial coordination sites [32].

He-I and He-II photoelectron spectra of $[(\eta^5\text{-}C_5Me_5)_2MX_2]$ (M = Zr, Th, or U; X = Cl or Me) have been recorded and compared. The bonding in the zirconium and the actinide complexes is rather similar, the major differences arising from metal-ligand bonding involving metal 5f orbitals in the actinide compounds [33].

The substituted metallocene dihalides $[(\eta^5\text{-}C_5H_4R)_2MCl_2]$ (M = Zr or Hf; R = Me, Et, $CHMe_2$, CMe_3, or $SiMe_3$) have been prepared by reaction of MCl_4 with two equivalents of $Li(C_5H_4R)$ in thf. $[(\eta^5\text{-}C_5H_4CMe_3)_2HfCl_2]$ was converted to the corresponding dibromide upon treatment with BBr_3 in dichloromethane [34]. The chloro-alkyl complexes $[(\eta^5\text{-}C_5H_4R)_2Zr\{CH(SiMe_3)_2\}Cl]$ (R = Me, Et, $CHMe_2$, CMe_3, or $SiMe_3$) have been synthesised by reaction of $[(\eta^5\text{-}C_5H_4R)_2ZrCl_2]$ with an equimolar amount of $Li[CH(SiMe_3)_2]$ in diethyl ether. As illustrated in the Newman projection (*3*), these compounds adopt a conformation in $CDCl_3$ solution in which the $SiMe_3$ and $\eta^5\text{-}C_5H_4R$ groups are diastereotopic. Variable temperature ^1H NMR studies afford values of $\Delta G^{\ddagger}$ for rotation about the Zr-C(σ) bond in the range 59.8 to 65.5 kJ mol^{-1}; in general, $\Delta G^{\ddagger}$ increases with increasing steric



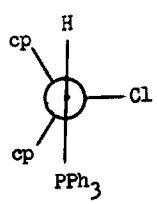
(3)

bulk of the cyclopentadienyl ring-substituent, R. The same conformation (*3*) has been found in the solid-state structures of the isostructural complexes $[(\eta^5\text{-}C_5H_4R)_2Zr\{CH(SiMe_3)_2\}Cl]$ (R = CMe_3 or $SiMe_3$). Steric crowding in these molecules is evidenced by a considerable variation in the Zr-C(π) distances and by a significant displacement of the R group from the plane of the cyclopentadienyl carbon atoms; however, the Zr-Cl and Zr-C(σ) bond lengths are normal {r(Zr-Cl) = 2.452(2) and r(Zr-C) = 2.324(8) Å for R = CMe_3; r(Zr-Cl) = 2.447(1) and r(Zr-C) = 2.327(3) Å for R = $SiMe_3$} [35]. Related complexes $[(cp)_2MRX]$ (M = Zr or Hf; R = CH_2SiMe_3 or CH_2SnMe_3; X = Cl or Br) have been synthesised by reaction of $[(cp)_2MCl_2]$ with RMgCl or RMgBr [36].

The reaction of $[(cp)_2MCl_2]$ (M = Zr or Hf) with excess $\bar{C}H_2\text{-}\overset{+}{P}Ph_3$ in thf yields the chloro-ylide complexes $[(cp)_2MCl(\bar{C}H\text{-}\overset{+}{P}Ph_3)]$ (equation (3)). An X-ray

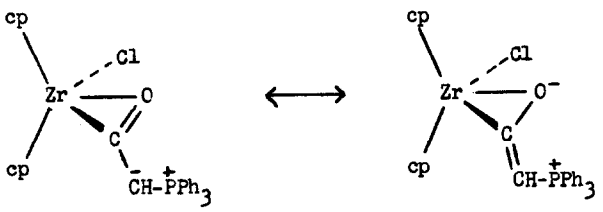
$$[(cp)_2MCl_2] + 2\bar{C}H_2\text{-}\overset{+}{P}Ph_3 \longrightarrow [(cp)_2MCl(\bar{C}H\text{-}\overset{+}{P}Ph_3)] + [MePPh_3]Cl \qquad (3)$$

structure determination on the zirconium compound reveals a long Zr-Cl bond (2.518(3) Å), a very short Zr-C bond to the ylide carbon atom (2.152(8) Å) and a relatively long C-P bond (1.708(6) Å). As shown in Newman projection (*4*),



(4)

the dihedral angle between the ClZrC plane and the ZrCP plane is close to 90° (95.54°). This conformation maximises overlap between the filled ylide carbon p orbital and the empty a_1 LUMO of the $\{(cp)_2Zr\}^{2+}$ fragment. Variable temperature ^{1}H NMR spectra show that there is hindered rotation about the metal-ylide M-C bond; $\Delta G^{\ddagger}$ = 36.0 ± 1.7 kJ mol^{-1} for M = Zr and 34.7 ± 1.7 kJ mol^{-1} for M = Hf. $[(cp)_2ZrCl(\bar{C}H\text{-}\overset{+}{P}Ph_3)]$ reacts with CO yielding a compound, presumably (*5*), that has a strong ν(CO) IR band at 1550 cm^{-1} [37].

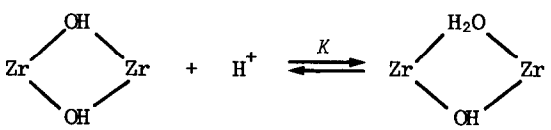


(5)

In the course of attempts to prepare alkylidene zirconium complexes by α-hydrogen atom abstraction, several new neopentyl halides of zirconium have been synthesised. $Zr(CH_2CMe_3)_2X_2$ (X = Cl or Br) complexes were prepared in ether and were isolated as dietherates (yellow-red oils). The ether can be displaced with ligands L (L = PMe_3, PMe_2Ph, NEt_3, ½dmpe, or ½tmen) giving orange to yellow adducts $[Zr(CH_2CMe_3)_2X_2L_2]$. $[Zr(CH_2CMe_3)_3Cl]$ was prepared by reaction of $[Zr(CH_2CMe_3)_2Cl_2(OEt_2)_2]$ with 0.5 equivalents of $Mg(CH_2CMe_3)_2$ and was isolated by sublimation; upon addition of PMe_3 or tmen, it disproportionates to $[Zr(CH_2CMe_3)_4]$ and $[Zr(CH_2CMe_3)_2Cl_2L_2]$. $[(\eta^5\text{-}C_5Me_5)Zr(CH_2CMe_3)Cl_2]$, $(\eta^5\text{-}C_5Me_5)Zr(CH_2CMe_3)_2Cl]$, and $[(\eta^5\text{-}C_5Me_5)Zr(CH_2CMe_3)_3]$ were obtained by reaction of $[(\eta^5\text{-}C_5Me_5)ZrCl_3]$ with $Mg(CH_2CMe_3)_2$ [38].

8.1.2 Complexes with O-donor ligands

The kinetics of the hydrogen ion induced tetramer to monomer conversion $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ $[Zr(H_2O)_8]^{4+}$, abbreviated Zr_4 Zr, in $HClO_4$ solutions follow the simple rate law $k_H[H^+][Zr_4]$; at ionic strength 2.0 *M* ($NaClO_4$): k_H(25 °C) = 0.95 x 10^{-3} M^{-1} s^{-1}, $\Delta H^{\ddagger}$ = 55.2 ± 0.8 kJ mol^{-1}, and $\Delta S^{\ddagger}$ = -117 ± 8 J K^{-1} mol^{-1}. The rate determining step could involve cleavage of the first μ-hydroxo bridge (equations (4)-(5); $k_H = kK$) or cleavage of the second bridge



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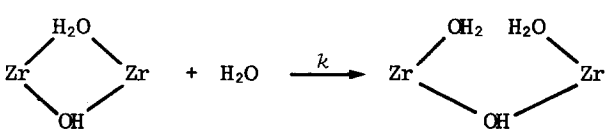
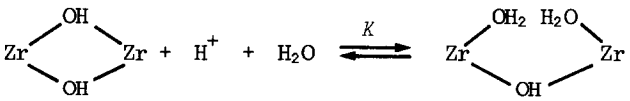


(5)

(equations (6)-(7); $k_H = kK$). Acids, HX, such as H_3PO_4, $H_2C_2O_4$, HF, *etc.*, also



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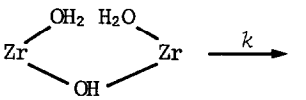


(7)

induce the Zr_4 ⟶ Zr conversion, giving the rate law $k_H[H^+][Zr_4] + k_{HX}[HX][Zr_4]$ [39].

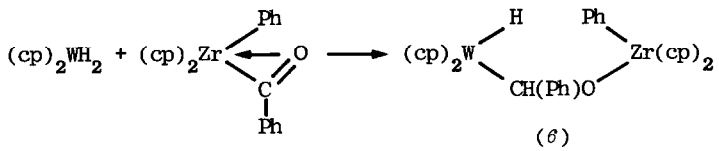
A spectrophotometric method for determination of zirconium(IV) that employs liquid-liquid extraction of zirconium(IV) from nitric acid solutions into molten trioctylphosphine oxide-benzophenone has been developed [40]. The influence of the hydration of zirconium(IV) and hafnium(IV) in nitric acid solutions on their extraction by tributyl phosphate has been studied by Dmitriev *et al.* [41].

Precipitates of composition $Zr(OH)_3(OOCCH{=}CHCOOH)$ and $Zr(OH)_3(OOCC_6H_4COOH)$ have been isolated in a study of complex formation of zirconium(IV) with maleic and phthalic acids. The insolubility of these compounds and their IR spectra suggest that they are polymeric due to bridging by carboxylate and/or hydroxide ligands [42].

The linkage isomers $[R_2Zr(ONO)_2]$ and $[R_2Zr(NO_2)_2]$ (R = cp or η^5-indenyl) have been prepared by reaction of $[(cp)_2ZrCl_2]$ with $AgNO_2$ and $NaNO_2$, respectively, in thf at reflux, and have been characterised by chemical analysis and IR spectra [43]. Di-*tert*-butyl nitroxide reacts with alkyl zirconocenes and hafnocenes, $[(cp)_2MR_2]$, by a rate determining displacement of alkyl radicals, to give the *N*,*N*-di-*tert*-butylhydroxylaminate complexes $[(cp)_2M(R)\{ON(CMe_3)_2\}]$ plus $RON(CMe_3)_2$ [44].

Zirconoxy carbene complexes of niobocene hydride, phenyl, and alkyls, $[(cp)_2(R)Nb{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2]$ {R = H, Me, CH_2Ph, $CH_2C_6H_4OMe$, Ph, $CH_2OZr(H)(\eta^5\text{-}C_5Me_5)_2$}, have been prepared by reaction of the corresponding niobocene carbonyls $[(cp)_2Nb(CO)R]$ with $[(\eta^5\text{-}C_5Me_5)_2ZrH_2]$. The kinetics of hydrogen and alkyl migration from niobium to the carbon atom of the zirconoxy carbene have been studied [45]. Treatment of a solution of $[(cp)_2WH_2]$ and $[(cp)_2ZrMe_2]$ in C_6D_6 with CO (1 atm) leads to formation of the bimetallic complex $[(cp)_2(H)WCH(Me)OZr(Me)(cp)_2]$, which decomposes to $[\{(cp)_2Zr(Me)\}_2O]$, $[(cp)_2W(C_2H_4)]$, plus CH_4 and C_5H_6. The decomposition reaction is believed to proceed *via* an intermediate tungsten-carbene complex $[(cp)_2W{=}C(H)(Me)]$. Reaction of $[(cp)_2WH_2]$ with $[(cp)_2Zr\{C(O)Ph\}Ph]$ yields the analogous bimetallic phenyl

derivative (*6*) {equation (8)}. In the case of compound (*6*), thermolysis affords the carbene complex $[(cp)_2W{=}C(H)(Ph)]$ as an isolable, crystalline solid. The



(8)

(*6*)

X-ray crystal structure of $[(cp)_2W{=}C(H)(Ph)]$ has been determined [46].

β-Diketonate chelates of zirconium and hafnium continue to be the subjects of active investigation. $[Et_4N][ZrF_4(dbzm)]$ (dbzm = dibenzoylmethanate) has been prepared by reaction of $[Zr(dbzm)_4]$ with $[Et_4N]_2[ZrF_6]$ at 140 °C, and has been characterised by IR and NMR spectroscopy and by electrical conductance measurements [47]. $[(cp)Zr(dbzm)_2Cl]$ can be synthesised by ligand-exchange reactions between $[(cp)_2ZrCl_2]$ and either $[Zr(dbzm)_4]$ or $[(cp)_2Zr(dbzm)_2]$ {equations (9) and (10)}: analogous isopropoxy and fluoro complexes have been obtained *via* reactions (11) and (12) [48]. ^1H and $^{13}C\{^1H\}$ NMR spectra of the five-coordinate compounds $[(cp)_2Zr(dbzm)X]$ (X = Cl or OPh) have been interpreted

$$[(cp)_2ZrCl_2] + [Zr(dbzm)_4] \longrightarrow 2[(cp)Zr(dbzm)_2Cl] \quad (9)$$

$$[(cp)_2ZrCl_2] + [(cp)_2Zr(dbzm)_2] \longrightarrow 2[(cp)Zr(dbzm)_2Cl] \quad (10)$$

$$[(cp)Zr(acac)_2Cl] + CHMe_2OH + Et_3N \longrightarrow [(cp)Zr(acac)_2(OCHMe_2)] + [Et_3NH]Cl \quad (11)$$

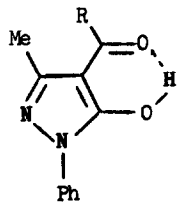
$$[\{(cp)Zr(acac)_2\}_2O] + 2HF \longrightarrow 2[(cp)Zr(acac)_2F] + H_2O \quad (12)$$

in terms of a mixture of four stereoisomers having trigonal bipyramidal geometry, and $^{13}C\{^1H\}$ NMR spectra of $[(cp)_2Zr(dik)Br(H_2O)]$ (dik = dbzm or acac) have been attributed to a mixture of four octahedral stereoisomers [49]; further investigation of these systems is needed.

$[Zr(acac)_2Cl_2]$ reacts with two equivalents of PhMgBr or one equivalent of Ph_2M (M = Mg, Cd or Hg) in thf at low temperatures yielding $PhZr(acac)_2Cl$. Because only one of the two chlorine atoms could be substituted, $[Zr(acac)_2Cl_2]$ and $PhZr(acac)_2Cl$ were formulated as chlorine-bridged dimers, $[X(acac)_2Zr(\mu\text{-}Cl)_2Zr(acac)_2X]$ (X = Cl or Ph) [50]; however, $[Zr(acac)_2Cl_2]$ is known to be a monomer in nitrobenzene solution [51], and no molecular weight data for $PhZr(acac)_2Cl$ were reported [50]. Reaction of $PhZr(acac)_2Cl$ with four equivalents of PhLi results in phenyl-substitution of the chelate ring {equation (13)}. $(PhCH_2)_2Zr(acac)_2$ was obtained when $(PhCH_2)_4Zr$ in Et_2O at -40 °C was treated with two equivalents of Hacac [50].

$$PhZr(acac)_2Cl + 2PhLi \longrightarrow PhZr(3\text{-}Phacac)_2Cl + 2LiH \qquad (13)$$

The heterocyclic tetrakis(β-diketonates) $[Zr(pmbzp)_4]$ and $[Zr(pmtfp)_4]$ {pmbzpH = 1-phenyl-3-methyl-4-benzoylpyrazole-5-one (*7*); pmtfpH = 1-phenyl-3-methyl-4-trifluoroethanoylpyrazole-5-one (*8*)} have been prepared, the former complex by extraction of zirconium(IV) from HNO_3, HCl, or H_2SO_4 solutions



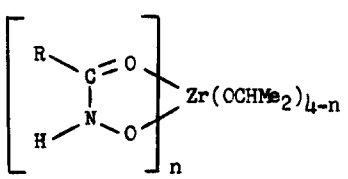
(7; R = Ph)

(8; R = CF_3)

with a trichloromethane solution of the pyrazolone, while the latter complex was synthesised by reaction of stoicheiometric amounts of anhydrous $ZrCl_4$ and the pyrazolone in CCl_4 at reflux. These compounds have been characterised by chemical analysis and IR spectroscopy [52,53]. The rate of extraction and back-extraction of $[Zr(pmbzp)_4]$ in aqueous sulphate-trichloromethane systems has been investigated [54]. Several solvent extraction studies of hafnium(IV) in mixed-ligand systems containing thenoyltrifluoroacetone and some other complexing agent, such as tributylphosphate [55], a dialkyl sulphoxide [56], or furoyltrifluoroacetone [57], have also been reported.

The ultraviolet spectra of $M(acac)_2X_2$ (M = Ti, Zr, Ge, or Sn; X = halide) complexes are due to ligand $\pi \longrightarrow \pi^*$ transitions perturbed by different amounts of metal-ligand π-bonding. There is considerably more metal-diketonate π-bonding in the titanium complexes than in the zirconium, germanium, and tin analogues [58].

Arylhydroxamato- complexes (*9*) have been prepared by reaction of the



(9; R = Ph or CH_2Ph; n = 1, 2, 3 or 4)

appropriate hydroxamic acid with $Zr(OCHMe_2)_4$ in benzene at reflux; the value of *n* depends on the stoicheiometry of the reaction mixture [59].

1:1 and 1:2 complexes of hafnium(IV) with glycolic, tartaric, and citric acids and 1:1, 1:2, and 1:3 complexes with lactic and malic acids have been identified and their stability constants determined in a 1.0–3.0 *M* $HClO_4$ medium. Under these conditions, complex formation occurs with loss of one proton to give five-membered chelate rings in which the hydroxy and carboxylate groups of the hydroxy acid anion coordinate to the hafnium atom [60]. Stability constants have also been reported for 1:1 and 1:2 complexes of oxozirconium(IV) with lapachol {2-hydroxy-3-(3-methyl-2-butenyl)-1,4-naphthoquinone} [61].

Several TGA, DTGA, and DTA studies of the thermal decomposition of divalent metal oxozirconium(IV) oxalates have been reported. The compounds investigated include $MgZrO(C_2O_4)_2.7H_2O$ [62], $CaZrO(C_2O_4)_2.5H_2O$ [63], $CaZrO(C_2O_4)_2.7H_2O$ [64], $SrZrO(C_2O_4)_2.4H_2O$ [64], $BaZrO(C_2O_4)_2.4H_2O$ [62], $BaZrO(C_2O_4)_2.7H_2O$ [65], $CdZrO(C_2O_4)_2.5H_2O$ [66], and $PbZrO(C_2O_4)_2.4H_2O$ [62]. The decomposition of most of these compounds involves three major processes: (i) dehydration of the hydrated compounds; (ii) decomposition of the oxalates to carbonates; (iii) conversion of the carbonates to metal zirconates $MZrO_3$. The thermal decomposition of $[NH_4]_2ZrO(C_2O_4)_2.3H_2O$, $H_2ZrO(C_2O_4)_2.3H_2O$, and $ZrO(C_2O_4).5.5H_2O$ has also been studied [67].

A trifluoroethanoate complex having composition $Zr_2(CF_3COO)_5(OH)_3(H_2O)_3$ has been synthesised by reaction of $ZrOCl_2.8H_2O$ with excess trifluoroethanoic acid and characterised by IR and Raman spectroscopy and by TGA. This compound reacts with 1,10-phenanthroline in aqueous EtOH yielding $Zr(CF_3COO)_2(phen)(OH)_2(H_2O)_2$ [68].

8.1.3 Mixed-metal oxides and oxyanion salts

Intermediate phases of orthorhombic symmetry in the HfO_2–Ta_2O_5 system having compositions ranging from $5HfO_2.Ta_2O_5$ to $7HfO_2.Ta_2O_5$ have been prepared by heating the co-precipitated metal hydroxides at temperatures up to 1400 °C. The unit cell parameters of these phases have been determined by powder X-ray diffraction [69].

The IR and Raman spectra of the compounds $A_2B_2O_7$ (A = La or Nd; B = Zr or Hf) having the pyrochlore structure have been assigned on the basis of normal coordinate analysis [70]. New quaternary oxides $AErBB'O_7$ (A = Pb or Cd; B = Zr or Hf; B' = Nb or Ta) with the pyrochlore structure have been synthesised from ABO_3 and $ErB'O_4$ by solid phase reactions at 1000–1300 °C [71].

An X-ray diffraction study of the double sulphate $Hf(SO_4)_2.2Na_2SO_4.2H_2O$ shows that the crystals contain $[Hf(SO_4)_4(H_2O)_2]^{4-}$ anions, connected by sodium cations. The hafnium atom is dodecahedrally coordinated by eight oxygen atoms from two

bidentate sulphate ligands, two monodentate sulphate ligands, and two water molecules {r(Hf–O) = 2.09–2.33 Å} [72]. A rather different structure has been found for $Hf(SO_4)_2.Na_2SO_4.3H_2O$. In this compound the hafnium atom is again surrounded by eight oxygen atoms from four sulphate ligands and two water molecules; however, two of the sulphate ligands are bidentate bridging, giving infinite spiral chains in which the repeating unit is $[Hf(SO_4)_3(H_2O)_2]^{2-}$ {r(Hf–O = 2.08–2.26 Å}. The chains are held together by sodium cations and by water molecules [73].

Seven different potassium zirconium sulphates have been isolated in the $KCl–ZrO_2–H_2SO_4–H_2O$ system at 20 °C [74]. The thermal decomposition of the compounds isolated in the $Rb_2SO_4–HfO_2–H_2SO_4–H_2O$ system, *viz.* $Rb_2Hf_2O_2(SO_4)_3.6H_2O$, $Rb_2Hf_2O(SO_4)_4.4H_2O$, $Rb_2Hf(SO_4)_3.2H_2O$, and $Rb_4Hf(SO_4)_4.H_2O$, has been studied by DTA, IR, and X-ray diffraction measurements [75].

A powder X-ray diffraction study has established that $Zr(SeO_3)_2$ and $Hf(SeO_3)_2$ are isostructural. Lattice parameters of the orthorhombic unit cells have been reported [76].

Zirconium phosphates continue to be of interest as inorganic ion exchangers. This area will not be reviewed here; however, several leading references to the adsorption [77], intercalation [78], and ion exchange [79–84] properties of these materials are noted. XPES investigations of α-$Zr(HPO_4)_2.H_2O$ and γ-$Zr(HPO_4)_2.2H_2O$ have been reported [85], and the stereochemistry of transition metal ions in partially exchanged forms of zirconium phosphates has been studied [86]. Considerable progress has also been made in the synthesis and characterisation of new organic derivatives of zirconium phosphates [87–92].

The conditions for isolation of crystals of $Cs_2M(MoO_4)_3$ and $Cs_8M(MoO_4)_6$ (M = Zr or Hf) from caesium polymolybdate melts have been investigated, and the X-ray crystal structure of $Cs_8Zr(MoO_4)_6$ has been determined. It consists of $[ZrMo_6O_{24}]^{8-}$ units that are linked together by the caesium cations to give a three-dimensional framework. The zirconium atoms are octahedrally coordinated by six oxygen atoms {r(Zr–O) = 2.10 Å (4x) and 2.12 Å (2x) which are corner-shared with six distorted $\{MoO_4\}$ tetrahedra [93].

8.1.4 Complexes with S- and Se-donor ligands

Five-coordinate fluorenyl *N,N*-disubstituted dithiocarbamato- complexes of the type $[(\eta^5\text{-}C_{13}H_9)_2Zr(S_2CNR_2)Cl]$ and $[(\eta^5\text{-}C_{13}H_9)_2Zr(S_2CNRR')Cl]$ (R = Me, Et, or $CHMe_2$; R' = Ph or C_6H_{11}) have been prepared by reaction in dimethoxyethane of equimolar amounts of $[(\eta^5\text{-}C_{13}H_9)_2ZrCl_2]$ and the appropriate anhydrous sodium *N,N*-disubstituted dithiocarbamate. These compounds are monomeric in boiling benzene, and nonelectrolytes in nitrobenzene. Their IR spectra indicate a bidentate

attachment of the dithiocarbamate ligands [94,95].

Diphenoxybis(dithiocarbamato)zirconium(IV) complexes, $[Zr(S_2CNR_2)_2(OPh)_2]$ and $[Zr(S_2CNRR')_2(OPh)_2]$ (R = Me, Et, or $CHMe_2$; R' = C_6H_{11}), have been synthesised from $Zr(OPh)_2Cl_2$ and anhydrous $Na[S_2CNR_2]$ or $Na[S_2CNRR']$ in thf at reflux. Molecular weight, conductance, and IR data indicate that these complexes are six-coordinate; however, it is not known whether they have octahedral *cis* or *trans* stereochemistry [96].

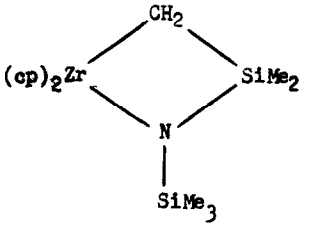
Reaction of stoicheiometric amounts of $[(cp)_2MCl_2]$ (M = Zr or Hf) or $[(\eta^5\text{-}C_5H_4Me)_2ZrCl_2]$ with $Na[S_2CN(CHMe_2)_2]$ or $Na(S_2CN(Me)(Ph))$ in CH_2Cl_2 or thf at reflux yields seven-coordinate complexes of the type $[(cp)M\{S_2CN(CHMe_2)_2\}_3]$, $[(cp)M\{S_2CN(Me)(Ph)\}_3]$, $[(\eta^5\text{-}C_5H_4Me)Zr\{S_2CN(CHMe_2)_2\}_3]$, and $[(\eta^5\text{-}C_5H_4Me)Zr\{S_2CN(Me)(Ph)\}_3]$. These compounds are of interest as examples of seven-coordinate chelates that are stereochemically rigid on the NMR time scale. 60 MHz ^1H NMR spectra at 30 °C have been interpreted in terms of capped trigonal prismatic and capped octahedral structures [97-99]. However, the spectra are not well enough resolved to draw any stereochemical conclusions, and capped trigonal prismatic and capped octahedral structures seem unlikely in view of the established pentagonal bipyramidal structures of the analogous $[(cp)Ti(S_2CNMe_2)_3]$ and $[(cp)Zr(S_2CNMe_2)_3]$ complexes [100,101]. Moreover, in interpreting the NMR spectra of the *N*-methyl-*N*-phenyl derivatives [99], the investigators have not taken into account the possibility of geometric isomerism arising from the asymmetry of the dithiocarbamate ligands.

Aromatic and aliphatic thioketones undergo hydrozirconation with $[(cp)_2Zr(H)(Cl)]$ to give sulphur-zirconium compounds $[(cp)_2Zr(SCHR_2)(Cl)]$ that can be cleaved by appropriate reagents in convenient, one-pot syntheses of a variety of organic sulphur compounds [102]. New selenium-containing complexes $[(\eta^5\text{-}C_5H_4R)_2M(SeR')_2]$ (M = Zr or Hf; R = H or CMe_3; R' = Me or Ph) have been synthesised, and have been characterised by their ^1H NMR, IR, and mass spectra. The methyl derivatives $[(\eta^5\text{-}C_5H_4R)_2M(SeMe)_2]$ were prepared by insertion of seleinum into the M-Me bonds of $[(\eta^5\text{-}C_5H_4R)_2MMe_2]$, while the phenyl analogues $[(\eta^5\text{-}C_5H_4R)_2M(SePh)_2]$ were obtained by reaction of $[(\eta^5\text{-}C_5H_4R)_2MCl_2]$ with PhSeLi [103].

$EuZrS_3$ and $EuHfS_3$ have been synthesised by heating a stoicheiometric mixture of EuS, sulphur, and zirconium or hafnium [104]. Polycrystalline, homogeneous solid solutions $Hf(Se_xTe_{1-x})_2$ have been prepared from the elements at 800 °C. The hexagonal *a* parameter of these layered phases varies linearly with composition, but the *c* parameter varies parabolically. The non-linear variation of the *c* parameter is attributed to packing mismatches in the layers [105].

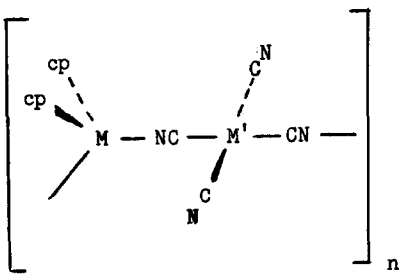
8.1.5 Complexes with N-donor ligands

$[(cp)_2Zr\{N(SiMe_3)_2\}_2]$ has been prepared by reaction of $[(cp)_2ZrCl_2]$ with two equivalents of $Li[N(SiMe_3)_2]$ in Et_2O. Owing to steric crowding around the zirconium atom, this compound exhibits pairwise inequivalence of the four $SiMe_3$ groups in ^1H and $^{13}C\{^1H\}$ NMR spectra. The barrier, $\Delta G^{\ddagger}$, to rotation about the Zr-N bond, determined from the ^1H NMR spectra, is 75 kJ mol^{-1} at the coalescence temperature of 85 °C. Reaction of equimolar amounts $[(cp)_2Zr(H)(Cl)]$ and $Li[N(SiMe_3)_2]$ occurs with facile γ-hydrogen elimination, yielding the zirconium metallacycle (*10*) [106].



(10)

Polymeric amorphous solids having composition $\{(cp)_2MM'(CN)_4\}_n$ (M = Zr or Hf; M' = Pd or Pt) have been obtained by reaction of $[(cp)_2MI_2]$ and $[Bu_4N]_2[M'(CN)_4]$ in ethanenitrile. IR and Raman spectra of these materials point to a cyanide-bridged structure (*11*) that has *trans* square-planar geometry about the palladium or platinum atom [107].



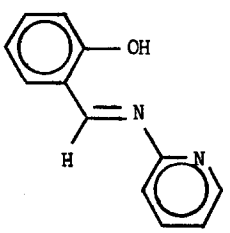
(11)

Treatment of a hot methanolic solution of appropriate zirconyl salts with 1,10-phenanthroline mono-*N*-oxide (phenNO), in the presence of the dehydrating agent 2,2-dimethoxypropane, yields the oxozirconium(IV) complexes $ZrO(phenNO)X_2$ (X = Cl, Br, NCS, or NO_3), $ZrO(phenNO)_2I_2$, or $ZrO(phenNO)_3[ClO_4]_2$. In dmso or dmf, the $ZrO(phenNO)X_2$ complexes are nonelectrolytes while $ZrO(phenNO)_2I_2$ and $ZrO(phenNO)_3[ClO_4]_2$ behave as 1:2 electrolytes. The structures of these complexes

are unknown. However, several conclusions have been drawn on the basis of IR studies: (i) phenNO behaves as a bidentate ligand, coordinating through the *N* and *O* atoms; (ii) the NCS ligands bond to zirconium through the *N* atom; (iii) the nitrate ligands are bidentate; and (iv) the perchlorate compounds contain uncoordinated $[ClO_4]^-$ ions. A weak IR band at 950–980 cm^{-1} has been assigned to ν(Zr=O) [108], but this assignment is open to question in view of the lack of evidence for the existence of the Zr=O group in oxozirconium(IV) compounds.

The (η^5-cyclopentadienyl)(η^5-indenyl)(8-quinolinolato)- complexes $[(cp)(\eta^5\text{-}C_9H_7)Zr(8\text{-}O\text{-}quin)]X$ (X = Cl, Br, I, $ZnCl_3(H_2O)$, or $HgCl_3$) and $[(cp)(\eta^5\text{-}C_9H_7)Zr(8\text{-}O\text{-}quin)]_2[CdCl_4]$ have been synthesised in aqueous media; IR and ^{1}H NMR spectra and electrical conductance measurements support formulation of these compounds as ionic salts that contain four-coordinate $[(cp)(\eta^5\text{-}C_9H_7)Zr(8\text{-}O\text{-}quin)]^+$ cations [109,110].

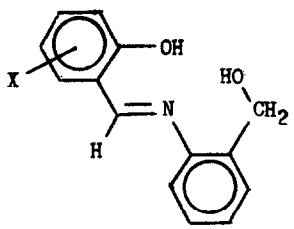
N-(2-pyridyl)salicylaldimine (*12*; pysalH) reacts with $Zr(OCHMe_2)_4.CHMe_2OH$ in



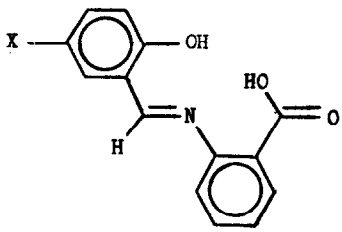
(12; pysalH)

benzene at reflux to give $[Zr(pysal)_n(OCHMe_2)_{4-n}]$ complexes, where the value of n = 1, 2, or 3 depends on the stoicheiometry of the reaction mixture. Molecular weight measurements in benzene point to monomeric complexes in which the coordination number of zirconium is 5, 6 or 7 for n = 1, 2 or 3, respectively. Prolonged heating under reflux of a 4:1 molar mixture of pysalH and $Zr(OCHMe_2)_4.CHMe_2OH$ did not yield the fully substituted complex $[Zr(pysal)_4]$ [111]. Related *N*-arylsalicylaldiminato- complexes ZrO(Arsal)Cl and $ZrO(Arsal)_2$ have been prepared by reaction of 1:1 and 2:1 mole ratios of the Schiff base and $ZrOCl_2.8H_2O$ in MeOH-Et_2O. The ZrO(Arsal)Cl complexes can also be obtained from a 1:1:1 molar mixture of $ZrOCl_2.8H_2O$, salicyladehyde and aromatic amine [112].

Reaction in methanol of $ZrOCl_2.8H_2O$, sodium ethanoate, and the tridentate Schiff bases (*13*; H_2L) yields new Schiff base complexes of the type $ZrO(HL)_2$. IR spectra indicate that the Schiff bases behave as monobasic *ONO*-tridentate ligands, bonding to zirconium through the phenolate oxygen, azomethine nitrogen, and hydroxylic oxygen atoms. The complexes are monomeric in biphenyl, and they exhibit a medium intensity IR band at 880–925 cm^{-1}, which has been attributed to ν(Zr=O). If these compounds do contain a Zr=O group, the zirconium atom would be seven coordinate [113]. The dibasic tridentate Schiff bases (*14*; H_2L) react with



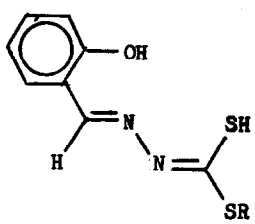
(13; H_2L; X = H, 5-Cl, 5-Br, 5-NO_2, 4-MeO_2, 5-MeO, 3-EtO, 3,5-Cl_2 or 5,6-benzo)



(14; H_2L; X = H, Cl or Br)

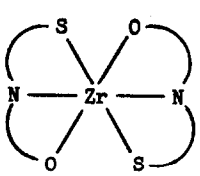
aqueous zirconium nitrate to give complexes having composition $Zr(OH)_2(L)(H_2O)$. IR spectra of these compounds support an *ONO*-tridentate attachment of the $(L)^{2-}$ anion [114].

Complexes of the type $[\{Zr(OCHMe_2)_2(L)\}_2]$ and $[Zr(L)_2]$ containing *ONS*-donor tridentate Schiff base ligands derived from *S*-alkyldithiocarbazates (*15*; H_2L) have been prepared by reaction of stoicheiometric amounts of $Zr(OCHMe_2)_4.CHMe_2OH$

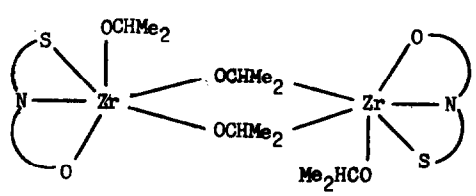


(15; H_2L; R = Me or CH_2Ph)

and H_2L in benzene at reflux. Molecular weight measurements in boiling trichloromethane indicate that the $[Zr(L)_2]$ complexes are monomeric, while the $[\{Zr(OCHMe_2)_2(L)\}_2]$ analogues are dimeric. Six-coordinate structures (*16*) and (*17*) have been proposed. The $[\{Zr(OCHMe_2)_2(L)\}_2]$ complexes undergo an alkoxide exchange reaction with 2-methylpentane-2,4-diol ($C_6H_{14}O_2$) yielding the $[Zr(C_6H_{12}O_2)(L)]$ complexes, which appear to be monomeric and therefore five-coordinate [115].

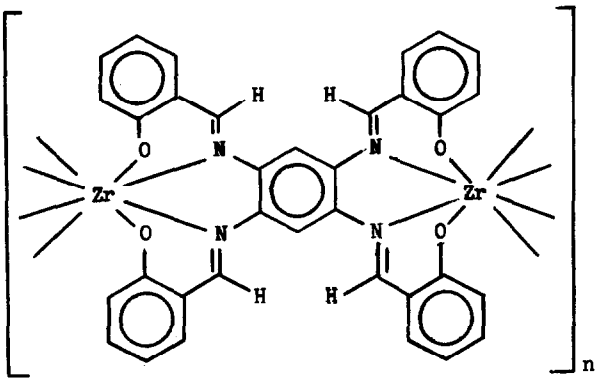


(16)



(17)

A glossy red polymer (*18*), having molecular weight of approximately



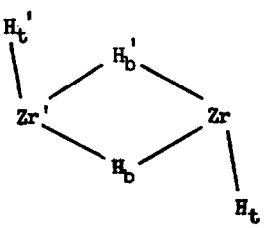
(*18*)

20,000–40,000, has been synthesised by condensation of tetrakis(salicylaldehydato)-zirconium(IV) and 1,2,4,5-tetraaminobenzene in dry dmso [116].

The new *meso*-tetraphenylporphyrin complex $[Zr(TPP)Cl_2]$ has been prepared by reaction of $TPPH_2$ with $ZrCl_4$ in boiling benzonitrile. The electronic spectrum of $[Zr(TPP)Cl_2]$ and the kinetics of TPP dissociation in acidic media suggest that the zirconium atom lies considerably out of the plane of the TPP ligand with both chlorine atoms being located on the same side of the TPP plane [177].

8.1.6 Hydride complexes

The binuclear zirconocene hydride complex $[\{(\eta^5\text{-}C_5H_4Me)_2ZrH(\mu\text{-}H)\}_2]$ has been prepared by reaction in thf of $[(\eta^5\text{-}C_5H_4Me)_2ZrCl_2]$ with two equivalents of $Li[AlH(OCMe_3)_3]$ and has been characterised by chemical analysis, IR and ^1H NMR spectra, and single-crystal X-ray diffraction. This complex has a centrosymmetric structure in which two $\{(\eta^5\text{-}C_5H_4Me)_2ZrH\}$ units are linked by two three-centre, two-electron Zr–H–Zr bonds. Important distances and angles in the region of the planar $\{Zr_2H_4\}$ core (*19*) are: $r(Zr\text{-}H_t) = 1.78(2)$ Å,; $r(Zr\text{-}H_b) = 2.05(3)$ Å;



(*19*)

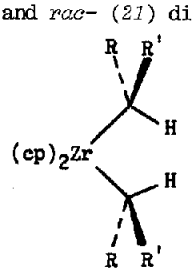
$r(Zr\text{-}H_b') = 1.94(2)$ Å; $H_t\text{-}\hat{Zr}\text{-}H_b = 70(1)^\circ$; $H_b\text{-}\hat{Zr}\text{-}H_b' = 60(1)^\circ$; $H_t\text{-}\hat{Zr}\text{-}H_b' = 130(1)^\circ$ $Zr\text{-}\hat{H}_b\text{-}Zr' = 120(1)^\circ$ [118].

8.1.7 Organometallic compounds

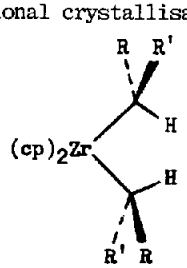
This section reviews selected studies of organozirconium(IV) and organohafnium(IV) compounds that have not been discussed in previous sections.

Substituted metallocene–dialkyl- complexes of the type $[(\eta^5\text{-}C_5H_4R)_2M(CH_2SiMe_3)_2]$ (M = Zr and R = Me or CMe_3; M = Hf and R = Me, Et, or $CHMe_2$) have been synthesised by reaction of $[(\eta^5\text{-}C_5H_4R)_2MCl_2]$ with two equivalents of $Li[CH_2SiMe_3]$ in Et_2O. Reaction of $[(cp)_2MCl_2]$ (M = Zr or Hf) with one equivalent of Me_3SiCH_2MgCl yields the alkyl-chloro- complexes $[(cp)_2M(CH_2SiMe_3)Cl]$ [34]. Dialkyl- complexes of the type $[(cp)_2MRR']$ (M = Zr or Hf) have been prepared, where R and/or R' is a neopentyl-type ligand, *viz.* CH_2CMe_3, CH_2SiMe_3, CH_2SnMe_3, or $CH(SiMe_3)_2$. Carbon monoxide inserts into the Zr–C bond of $[(cp)_2ZrR_2]$ (R = CH_2CMe_3 or CH_2SiMe_3) to give the η^2-acyl compounds $[(cp)_2Zr(COR)(R)]$. In the case of the mixed-alkyl complex $[(cp)_2Zr\{CH(SiMe_3)_2\}Me]$, CO inserts into the more hindered (and weaker) Zr–C bond yielding $[(cp)_2Zr\{COCH(SiMe_3)_2\}Me]$. Single-crystal X-ray studies of $[(cp)_2Zr(CH_2CMe_3)_2]$ and $[(cp)_2Zr(CH_2SiMe_3)_2]$ indicate that the $Zr\text{-}C_\sigma$ and Zr–(centroid cp) distances are slightly longer in the case of the complex that contains the sterically more demanding neopentyl group; however, the differences in the distances do not appear to be significant [36].

$[(cp)_2Zr(R^*)_2]$ complexes containing the new, chiral alkyl ligand R* {R* = $CH(SiMe_3)(C_6H_4\text{-}2\text{-}Me)$} have been prepared by reaction in Et_2O of $[(cp)_2ZrCl_2]$ with two equivalents of LiR*(tmen). The reaction product has been separated into *meso-* (*20*) and *rac-* (*21*) diastereomers by fractional crystallisation. The



(20; R = $SiMe_3$, R' = C_6H_4-2-Me)

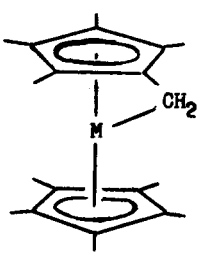


(21; R = $SiMe_3$, R' = C_6H_4-2-Me)

configurations of the diastereomers have been assigned on the basis of their ^1H NMR spectra. Photolysis or controlled thermolysis converts the *meso*-diastereomer to the *rac*-diastereomer, the greater thermodynamic stability of which has been attributed to less repulsion between the sterically bulky $SiMe_3$ groups [119].

The first authentic example of a difference in the structural chemistry of organozirconium and organohafnium compounds has been found in the structures of the tetrakis(cyclopentadienyl)- complexes. The structure of $[(cp)_2Hf(\eta^1\text{-}C_5H_5)_2]$ displays two σ- and two π-bonded cyclopentadienyl ligands, while the structure of $[(cp)_3Zr(\eta^1\text{-}C_5H_5)]$ shows one σ- and three π-bonded cyclopentadienyl groups. The metal carbon(σ) bond length is considerably shorter in $[(cp)_2Hf(\eta^1\text{-}C_5H_5)_2]$ {2.38(2) Å} than in $[(cp)_3Zr(\eta^1\text{-}C_5H_5)]$ {2.447(6) Å} [120].

The photochemical decomposition of $[(\eta^5\text{-}C_5Me_5)_2MPh_2]$ (M = Ti or Zr) has been investigated. Whereas decomposition of $[(\eta^5\text{-}C_5Me_5)_2TiPh_2]$ involves predominantly reductive elimination of biphenyl, at least 75% of the decomposition of $[(\eta^5\text{-}C_5Me_5)_2ZrPh_2]$ occurs by stepwise homolysis of the Zr-C(σ) bonds. Photolysis in the presence of carbon monoxide gives moderately large amounts of $[(\eta^5\text{-}C_5Me_5)_2M(CO)_2]$, suggesting that the metallocenes $[(\eta^5\text{-}C_5Me_5)_2M]$ are intermediates. A further intermediate (*22*) is suggested by the presence of

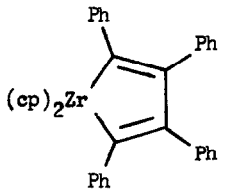


(22)

2,3,4,5-tetramethylfulvene and pentamethylcyclopentadiene among the reaction products [121].

Reaction of $[(\eta^5\text{-}C_5Me_5)MCl_3]$ (M = Zr or Hf) with $MeCH{=}CHCH_2MgBr$ at low temperature gives the 1-methallyl- complexes $[(\eta^5\text{-}C_5Me_5)M(C_4H_7)_3]$, which are readily converted upon heating to the more stable 1-methallyl-butadiene complexes $[(\eta^5\text{-}C_5Me_5)M(\eta^3\text{-}C_4H_7)(\eta^4\text{-}C_4H_6)]$ plus *trans*-but-2-ene. Only $[(\eta^5\text{-}C_5Me_5)Hf(C_4H_7)_3]$ could be isolated; it is fluxional and its IR and NMR spectra suggest that it consists of a complex mixture of isomers containing η^1- and η^3-1-methallyl groups. The $[(\eta^5\text{-}C_5Me_5)M(\eta^3\text{-}C_4H_7)(\eta^4\text{-}C_4H_6)]$ complexes also show fluxional behavior, but this is limited to the η^3-1-methallyl group [122, 123].

The X-ray crystal structure of the 2,3,4,5-tetraphenylzirconole $[(cp)_2Zr(C_4Ph_4)]$ (*23*) has been determined. The metallacyclic ring is planar to within 0.05 Å, and the π-electron density within the ring is largely localised {$r(C_2\text{-}C_3)$ = 1.363(7) Å; $r(C_3\text{-}C_4)$ = 1.500(7) Å; $r(C_4\text{-}C_5)$ = 1.358(8) Å}. The Zr-C_σ bond distances (2.265(6) and 2.250(5) Å) are *ca.* 0.06 Å longer than the Hf-C distances in $[(cp)_2Hf(C_4Ph_4)]$. A comparison of Zr-C and Hf-C bond distances in the literature indicates that the Hf-C bond lengths are shorter for all common carbon-atom hybridisations {C(sp), C(sp^2), C(sp^3), and C(η^5)} [124].



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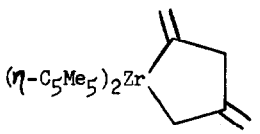
New *exo*-unsaturated zirconacyclopentanes (*24*) and (*25*) have been prepared



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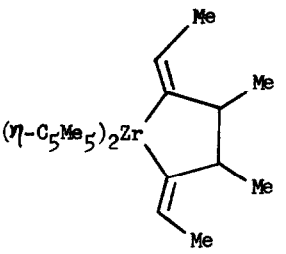
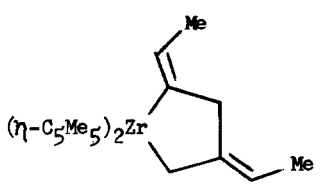


(25)

by reaction of allene or 1,3-dimethylallene, respectively, with $[\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2(N_2)]$. Asymmetric substitution of the *exo*-methylene groups in the 2- and 4-positions of the metallacyclic ring has been established for compound (*24*) by single-crystal X-ray crystallography and by ^1H and ^{13}C NMR spectra of its solutions. NMR spectra indicate that the ethylidene groups in (*25*) are located in the symmetrically disposed 2- and 5-positions [125]. The reaction of methylallene with $[\{(\eta\text{-}C_5Me_5)_2Zr(N_2)\}_2(N_2)]$ in toluene at -45 °C produces a 70:30 mixture of two isomers which have been identified as (*26*) and (*27*), respectively, on the basis of ^1H and ^{13}C NMR spectra. The configuration



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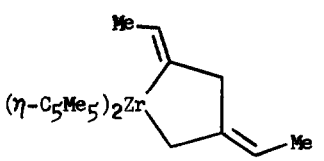
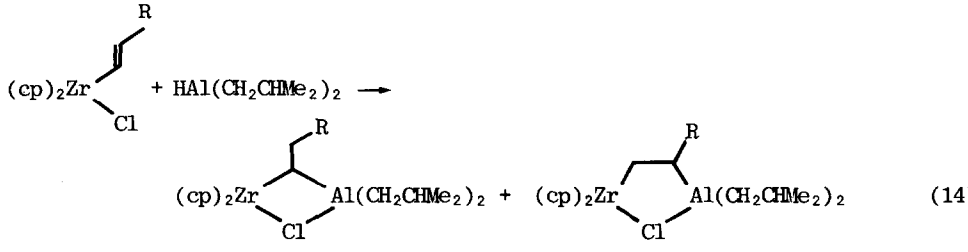


(27)

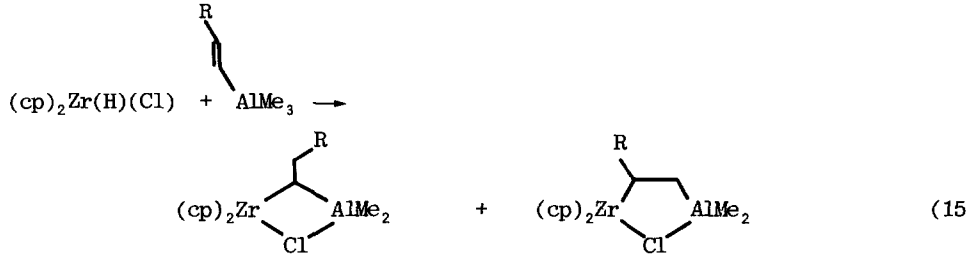
of the 4-ethylidene methyl group has not been established, but it is the same in both isomers. The mechanistic implications of these results have been discussed [126].

"Long-chain" alkylidene-bridged heterobimetallic complexes (*28*) and (*30*) have been prepared by either (i) addition of an organoaluminium hydride to an

alkenylzirconium complex {reaction (14)} or (ii) addition of $[(cp)_2Zr(H)(Cl)]$ to the double bond of an organoaluminium alkenyl {reaction (15)}. Addition to the double bond in the reverse direction produces compounds (*29*) and (*31*), usually in small amounts. The direction of addition depends on the steric bulk of the

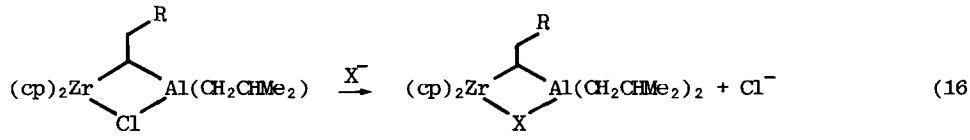


(*28*; R = Me, Bu or CMe_3) (*29*; R = Me, Bu or CMe_3) (14)



(*30*; R = Me, Bu or CMe_3) (*31*; R = Me, Bu or CMe_3) (15)

substituent R. Compound (*28*; R = CMe_3) reacts with one equivalent of either Na[OMe], Na[SMe], $Li[NEt_2]$, $Li[PPh_2]$, or $Li[CH_2CMe_3]$ in benzene to give the ligand metathesis products (*32*) {reaction (16)} [127].

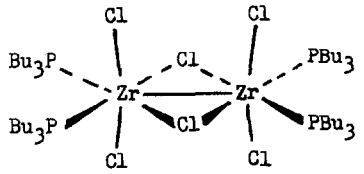


(*28*; R = CMe_3) (*32*; R = CMe_3; X = OMe, SMe, NEt_2, PPh_2 or CH_2CMe_3) (16)

3.2 ZIRCONIUM(III) COMPOUNDS

$Cs_3Zr_2I_9$ has been prepared by reaction of CsI, ZrI_4, and zirconium metal in sealed tantalum tubes at 750–850 °C. This compound has the $Cs_3Cr_2Cl_9$ structure (space group $P6_3/mmc$). Close-packed CsI_3 layers are stacked in the hexagonal c direction with stacking sequence ABACBC, and two-thirds of the octahedral interstices are filled with Zr^{3+} ions in pairs so as to give $[Zr_2I_9]^{3-}$ confacial bioctahedra. $Cs_3Y_2I_9$ has the same structure. On going from the d^0 yttrium(III) compound to the d^1 zirconium(III) compound, the metal-metal distance in the bioctahedra decreases from 4.052(9) to 3.129(4) Å owing to formation of a metal-metal bond in the zirconium compound. Accompanying this very substantial axial compression of the bioctahedra are correspondingly large changes in the bond angles in the $M(\mu\text{-}I)_3M$ bridging region {$\hat{I}\text{-}\hat{Y}\text{-}I = 82.5°$ and $Y\text{-}\hat{I}\text{-}Y = 80.8°$ in $Cs_3Y_2I_9$; $\hat{I}\text{-}\hat{Zr}\text{-}I = 93.9°$ and $Zr\text{-}\hat{I}\text{-}Zr = 65.0°$ in $Cs_3Zr_2I_9$} [128].

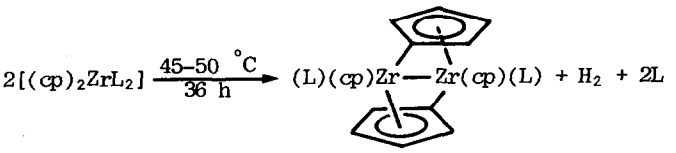
Zirconium(III) complexes of the type $[\{ZrCl_3(PR_3)_2\}_2]$ (R = Et, Pr, or Bu) have been prepared in high yield by reduction of $[ZrCl_4(PR_3)_2]$ with one equivalent of sodium amalgam [129]. The less soluble methyl derivative $[\{ZrCl_3(PMe_3)_2\}_2]$ was obtained earlier by photolysis of $[Zr(CH_2CMe_3)_2Cl_2(PMe_3)_2]$ [38]. The butyl derivative has a chlorine-bridged dimeric structure (*33*) with a Zr–Zr bond length of 3.182(1) Å. Distortions from regular octahedral geometry



(33)

include a bending back of the four terminal Zr–Cl bonds away from the central $Zr(\mu\text{-}Cl)_2Zr$ unit {(terminal Cl)-$\hat{Zr}$-(terminal Cl) = 165.1°}. The $[\{ZrCl_3(PR_3)_2\}_2]$ complexes react with ethene and propene to give the zirconium(IV) compounds $[(PR_3)_2Cl_3ZrCH_2CHR'ZrCl_3(PR_3)_2]$ (R' = H or Me). Upon reaction with butadiene, $[\{ZrCl_3(PEt_3)_2\}_2]$ disproportionates to $[ZrCl_4(PEt_3)_2]$ and the bis-allyl-complex $[ZrCl_2(\eta^6\text{-}C_8H_{12})(PEt_3)]$ [129].

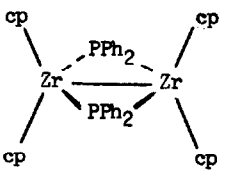
Thermolysis of $[(cp)_2ZrL_2]$ (L = PMe_2Ph or $PMePh_2$) in toluene at 45–50 °C {equation (17)} produces approximately equimolar amounts of dihydrogen and diamagnetic, dimeric zirconium(III) complexes that have been formulated as $\eta^1,\eta^5\text{-}C_5H_4$-bridged species (*34*) on the basis of their ^1H and $^{13}C\{^1H\}$ NMR spectra. The proposed route for formation of the $[\{(cp)(\mu\text{-}[\eta^1,\eta^5\text{-}C_5H_4])ZrL\}_2]$ complexes



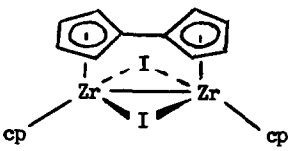
(17)

(*34*; L = PMe_2Ph or $PMePh_2$)

involves phosphine dissociation to give the 16-electron species $[(cp)_2ZrL]$, followed by two successive oxidative additions of Zr(II) into the C–H bonds of cp ligands and subsequent reductive elimination of H_2. Dihydrogen and compound (*34*; L = PMe_2Ph) are also produced when toluene or thf solutions of "zirconocene" are treated with excess PMe_2Ph. This result suggests that "zirconocene" is a polymeric zirconium(IV) compound that contains hydride and η^1,η^5-C_5H_4 bridges. Compound (*34*; L = $PMePh_2$) reacts with two equivalents of $PHPh_2$ yielding the substitution product $[\{(cp)(\mu\text{-}[\eta^1,\eta^5\text{-}C_5H_4])Zr(PHPh_2)\}_2]$ and the PPh_2-bridged zirconium(III) compound (*35*). Reaction of (*34*; L = $PMePh_2$) with one equivalent of I_2 affords the $C_{10}H_8$-bridged zirconium(III) complex (*36*) [130].



(*35*)



(*36*)

Reduction of the metallocene -dialkyl complexes $[(\eta^5\text{-}C_5H_4R)_2ZrR'_2]$ with sodium naphalenide in thf gives paramagnetic species that were once thought to be $[(\eta^5\text{-}C_5H_4R)_2ZrR'_2]^-$ *anions on the basis of their EPR spectra* [131]. *The EPR spectra* have now been reinterpreted in the light of cyclic voltametry data, which indicate that the $[(\eta^5\text{-}C_5H_4R)_2ZrR'_2]$ complexes undergo irreversible one-electron reduction yielding $[C_5H_4R]^-$ and $[(\eta^5\text{-}C_5H_4R)ZrR'_2]$ [34]. In contrast, the complex $[(cp)_2Zr(R^*)(Cl)]$ {R* = $CH(SiMe_3)(C_6H_4\text{-}2\text{-}Me)$} *is* reduced reversibly to $[(cp)_2Zr(R^*)(Cl)]^-$ [119].

A single-crystal X-ray study has shown that the compound $[(C_6Me_6)_3Zr_3Cl_6][Al_2Cl_7]_2$ *contains trinuclear cations in which the zirconium atoms are located at the vertices* of an equilateral triangle. Each edge of the triangle is bridged by two chlorine atoms. The fifth coordination site on each zirconium atom is occupied by an η^6-C_6Me_6 group. Important distances are $\bar{r}$(Zr–Zr) = 3.35 Å, $\bar{r}$(Zr–Cl) = 2.56 Å, and $\bar{r}$[Zr–(centroid C_6Me_6)] = 2.17 Å. The formal oxidation state of zirconium in this compound is $+2^2/_3$ [132].

8.3 ZIRCONIUM(II) AND HAFNIUM(II) COMPOUNDS

Zirconium(II) cluster compounds Zr_6X_{12} (X = Cl or Br), isostructural with Zr_6I_{12}, have been prepared by reaction of zirconium(I) halides with dihydrogen at 630–780 °C {equation (18)}. If alkali chlorides are present during the ZrCl–H_2

$$12ZrX(s) + 6H_2(g) \longrightarrow Zr_6X_{12}(s) + 6ZrH_2(s) \qquad (18)$$

reaction, new isostructural compounds $M_2Zr_7Cl_{18}$ (M = Na, K, or Cs) are obtained {equation (19)}. An X-ray study of the potassium compound shows that crystalline

$$16ZrCl(s) + 2MCl(s) + 9H_2(g) \longrightarrow M_2Zr_7Cl_{18}(s) + 9ZrH_2(s) \qquad (19)$$

$K_2Zr_7Cl_{18}$ contains octahedral $[ZrCl_6]^{2-}$ anions {r(Zr–Cl) = 2.474(2) Å} and $[Zr_6Cl_{12}]$ clusters. The clusters consist of an octahedron of zirconium atoms slightly compressed along the $\bar{3}$ axis and edge-bridged by twelve chlorine atoms {r(Zr–Zr) = 3.224(1) and 3.178(1) Å; $\bar{r}$(Zr–Cl) = 2.558 Å. Each zirconium atom of the cluster is attached, in addition, through a radially directed Zr–Cl bond (2.770 Å) to a Cl atom of a neighbouring $[ZrCl_6]^{2-}$ anion. Thus each $[Zr_6Cl_{12}]$ cluster is linked to six different $[ZrCl_6]^{2-}$ ions, and each $[ZrCl_6]^{2-}$ ion is in turn attached to six different $[Zr_6Cl_{12}]$ clusters. The formula of this compound may be written as $Zr_6Cl_{12}\cdot K_2[ZrCl_6]$. The potassium ions occupy fairly large cavities with twelve nearest neighbour chlorine atoms at distances of 3.47–3.66 Å [133].

A second polymorph of zirconium(II) iodide, α-ZrI_2, has been synthesised by reaction of ZrI_4 with zirconium metal in a tantalum tube having a temperature gradient extending from 850 to 750 °C. Black, lath-like crystals of α-ZrI_2 were found in the 775 °C region of the tube. This phase has a distorted CdI_2-type structure in which the zirconium atoms are displaced by 0.440 Å from the octahedral centres, giving infinite zig-zag metal chains parallel to the b axis of the monoclinic crystal {r(Zr–Zr) = 3.182(3) Å} [134].

The kinetics of the reaction of gaseous ZrI_4 with zirconium metal to give reduced zirconium iodides on the surface of the metal has been studied in the temperature range 300–500 °C [135]. The pressures of gaseous ZrI_4 over solid zirconium iodides in the composition range ZrI to Zr have been measured by the torsion-effusion method [136]. Enthalpies of formation of ZrI_3, ZrI_2, and ZrI have been estimated from data in the literature [137].

A new method for preparation of $[(\eta^5\text{-}C_5Me_5)_2M(CO)_2]$ (M = Ti or Zr) has been reported; $[(\eta^5\text{-}C_5Me_5)_2MCl_2]$ in thf under an atmosphere of carbon monoxide is reduced with magnesium powder activated by mercury(II) chloride. The previously unknown hafnium analog $[(\eta^5\text{-}C_5Me_5)_2Hf(CO)_2]$ has been synthesised using "super-

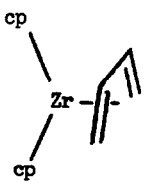
activated" Rieke magnesium (prepared from anhydrous $MgCl_2$ and potassium metal in thf). The structures of all three $[(\eta^5\text{-}C_5Me_5)_2M(CO)_2]$ complexes have been determined by X-ray diffraction. The metal–carbon bonds to the carbonyl ligands {r(Ti–CO) = 2.01(1) Å; r(Zr–CO) = 2.145(9) Å; r(Hf–CO) = 2.14(2) Å} are shorter than those in the analogous $[(cp)_2M(CO)_2]$ complexes, owing to enhanced π backbonding in the pentamethylcyclopentadienyl derivatives [138].

Following an earlier communication [139], a full paper has been published describing the preparation and reactivity of bis(η^5-cyclopentadienyl)bis(phosphine)-zirconium(II) complexes $[(cp)_2ZrL_2]$ (L = $PMePh_2$ or PMe_2Ph; L = dmpe or dppe). These compounds are produced by ligand-induced reductive elimination of methylcyclohexane from $[(cp)_2Zr(CH_2C_6H_{11})(H)]$ {equation (20)}. Reactions of the

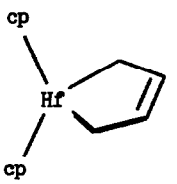
$$[(cp)_2Zr(CH_2C_6H_{11})(H)] + 2L \longrightarrow [(cp)_2ZrL_2] + C_6H_{11}Me \qquad (20)$$

$[(cp)_2ZrL_2]$ complexes with H_2, CO, other phosphines, alkynes, alkenes, arenes, and organic halides have been investigated. These reactions appear to proceed *via* an intermediate 16-electron $[(cp)_2ZrL]$ complex [140].

$[(cp)_2M(diene)]$ (M = Zr or Hf) complexes have been prepared by reaction of $[(cp)_2MCl_2]$ with magnesium dienes in thf. The variable temperature ^1H NMR spectra of the zirconium and hafnium butadiene complexes in toluene-d_8 are surprisingly different. $[(cp)_2Zr(C_4H_6)]$ exhibits temperature dependent spectra consistent with an η^4-*s-cis* geometry (*37*), with rapid exchange of *syn* an *anti*-protons at temperatures above *ca.* 10 °C. However, the ^1H NMR spectrum of $[(cp)_2Hf(C_4H_6)]$ is essentially temperature independent over the range +80 to -90 °C. This result has been interpreted in terms of a metallacyclopentene structure (*38*) [141]. Earlier, Erker *et al.* suggested that a zirconacyclopentene is an intermediate in



(*37*)



(*38*)

the exchange of *syn*- and *anti*-protons in $[(cp)_2Zr(\eta^4\text{-}s\text{-}cis\text{-}C_4H_6)]$ [142].

8.4 ZIRCONIUM(0) AND HAFNIUM(0) COMPOUNDS

$[Hf(\eta^5\text{-}C_4H_6)_2(dmpe)]$ has been prepared by reaction of magnesium butadiene, $Mg(C_4H_6)\cdot 2thf$, with $HfCl_4$ and dmpe in thf. An analogous synthesis using $ZrCl_4\cdot 2thf$ in place of $HfCl_4$ gives a mixture of $[Zr(\eta^4\text{-}C_4H_6)_2(dmpe)]$ (65%) and

[{Zr(η^4-C_4H_6)$_2$(dmpe)}$_2$dmpe] (35%). [Hf(η^4-C_4H_6)$_2$(dmpe)] has a structure based on a distorted C_2 octahedral geometry. The butadiene ligand is attached to hafnium in an η^4-fashion; however, the Zr-C and C-C bond lengths indicate some distortion toward a metallacyclopentene structure [143].

Co-condensation of zirconium or hafnium vapours, derived from a positive hearth electron-gun furnace, with a mixture of toluene (or benzene) and trimethylphosphine yields the bent bis(η^6-arene) complexes [(η^6-C_6H_5Me)$_2$M(PMe_3)] (M = Zr or Hf) and [(η^6-C_6H_6)$_2$Hf(PMe_3)]. These compounds have been isolated from light petroleum ether as green-black crystals. They are extremely sensitive to oxygen and traces of water but appear to be stable indefinitely at room temperature. A preliminary communication of this work was published earlier [144]; a detailed description of the metal-vapour syntheses is now available [145].

8.5 BINARY COMPOUNDS

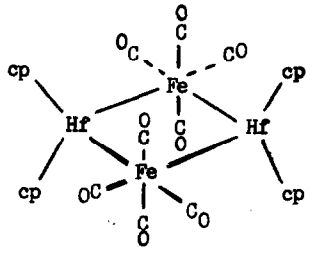
This section gives a brief mention of the X-ray structures of two compounds that are not easily classified in terms of formal oxidation states. Hf_3Sb has the Fe_3P-type structure (space group *I*4) [146], and $Zr_{14}P_9$ has a structure based on a complex arrangement of nine inequivalent {PZr_6} trigonal prisms with one to three additional zirconium atoms located outside the quadrilateral faces [147].

8.6 COMPLEXES WITH METAL-METAL BONDS

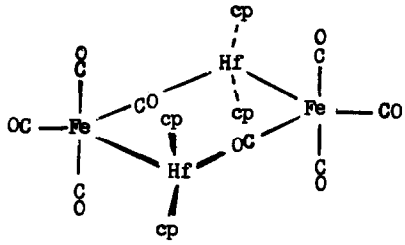
The d^2 18-electron bis-arene complexes [(η^6-C_6H_5Me)$_2$M($SnMe_3$)$_2$] (M = Zr or Hf) have been prepared by reaction of [(η^6-C_6H_5Me)$_2$M(PMe_3)] with hexamethylditin. An X-ray study of the hafnium complex has established a distorted tetrahedral structure, analogous to that of 18-electron [(cp)$_2$$MX_2$] (M = Mo or W) complexes, with a Sn-Hf-Sn angle less than 90° (81.14°). Bond distances to the hafnium atom are *r*(Hf-Sn) = 2.953(1) Å and *r*(Hf-C) = 2.43-2.52 Å [148].

The first compound having a hafnium-transition metal bond, (cp)$_2$HfFe(CO)$_4$, has been synthesised from [(cp)$_2$$HfCl_2$] and Na_2[Fe(CO)$_4$]. This compound exhibits two ν(Hf-Fe) Raman bands (at 184 and 138 cm^{-1}) and four ν(CO) IR bands (in the 2040-1940 cm^{-1} region), consistent with a dimeric structure (*39*) having four terminal CO groups and local C_{2v} symmetry at the iron atoms. A minor product of this synthesis, also obtained following dissolution of (cp)$_2$HfFe(CO)$_4$ in thf, shows a ν(CO) IR band at 1683 cm^{-1}, suggesting that it may be the isocarbonyl complex (*40*) [149].

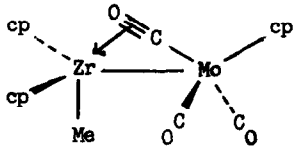
The structure of the heterometallic dinuclear alkyl [(cp)$_2$Zr(Me)Mo(CO)$_3$(cp)] has been elucidated by IR and variable temperature ^{13}C NMR spectroscopy. The spectral data, particularly a ν(CO) band at 1545 cm^{-1} and two ^{13}C carbonyl



(39)

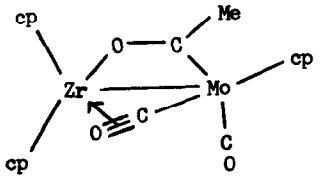


(40)



(41)

resonances (relative intensity 1:2) at -80 °C, point to a structure (*41*) having a four-electron μ-η^1,η^2-carbonyl bridge. The carbonyl groups are mobile, with a barrier $\Delta G^{\ddagger}$ of 40 kJ mol^{-1} for migration of the bridging carbonyl group to one of the two equivalent terminal carbonyl sites. Compound (*41*) reacts rapidly with CO at room temperature yielding the η^2-ethanoyl complex $[(cp)_2Zr(\eta^2\text{-}COMe)Mo(CO)_3(cp)]$. ^{13}C labelling experiments have established that the carbon in the ethanoyl carbonyl group comes from the added CO, not from the bridging carbonyl group. On standing in toluene solution, $[(cp)_2Zr(\eta^2\text{-}COMe)Mo(CO)_3(cp)]$ slowly loses one equivalent of CO yielding the ethanoyl-bridged complex (*42*) whose structure has been established



(42)

by X-ray diffraction. Compound (*42*) has r(Zr-Mo) = 3.297(1) Å and C-O distances reflecting three different bond orders {terminal r(C-O) = 1.147(4) Å; bridging r(C-O) = 1.241(4) Å; ethanoyl r(C-O) = 1.285(3) Å} [150].

8.7 ZIRCONIUM-91 NMR STUDIES

This last section notes the first chemical studies utilizing ^{91}Zr NMR spectroscopy. The ^{91}Zr nucleus (I = 5/2; Q = -0.21 x 10^{-28} m^2) has a relative abundance of 11.23%. ^{91}Zr NMR signals have been observed for $[(cp)_2ZrX_2]$ (X = Cl, Br, or I) and $[(cp)_2ZrClBr]$ in thf, $[NH_4]_2[ZrF_6]$ in D_2O, H_2ZrCl_6 in conc. HCl, and $[Zr(BH_4)_4]$ in toluene-d^8. The spectra were obtained at 8.37 MHz on a Bruker WH90 spectrometer operating at 25 °C. The signals of the $[(cp)_2ZrX_2]$ (X = Cl, Br, or I) complexes and the $[ZrX_6]^{2-}$ (X = F or Cl) ions exhibit an inverse halogen dependence, *i.e.* the resonances shift to *higher* field with increasing electronegativity of the halogen. Line widths at half-maximum amplitude for the $[(cp)_2ZrX_2]$ and $[ZrX_6]^{2-}$ complexes are in the range 19-276 Hz. The narrowest line observed so far (line width 5 Hz) has been found in the ^{1}H- and ^{11}B-decoupled ^{91}Zr NMR spectrum of $[Zr(BH_4)_4]$. ^{1}H-decoupled and ^{11}B-decoupled ^{91}Zr spectra along with ^{1}H and ^{11}B spectra of $[Zr(BH_4)_4]$ have yielded coupling constants $^{J}(^{91}Zr-^{1}H\ obsd)$ = 28 Hz and $^{J}(^{91}Zr-^{11}B)$ = 18 Hz. The spectra have been interpreted in terms of rapid rotation of the tridentate borohydride groups, which exchanges bridging and terminal hydrogen atoms [151,152].

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LIST OF ABBREVIATIONS

$acac_2enH_2$	*N,N'*-ethylenebis(acetylacetimine)
acacH	pentane-2,4-dione
$adipH_2$	adipic acid
alaH	alanine
Am	amyl
5^1-AMP	5^1-adenosine monophosphate
amq	8-aminoquinoline
[14]aneS_4	1,4,8,11-tetrathiacyclotetradecane
{9}anN_3	1,4,7-triazacyclononane
APW	augmented plane wave
argH	arginine
asp	aspartate
benzacH	benzoylacetone
biimH	2,2'-biimidazole
bipy	2,2'-bipyridine
4,4'-bipy	4,4'-bipyridine
bipyam	di(2-pyridyl)amine
bipym	2,2'-bipyrimidine
biquin	2,2'-biquinoline
bot	benzoxazole-2-thione
b.p.	boiling point
bpdo	2,2'-bipyridine *N,N'*-dioxide
bpz	2,2'-bipyrazine
BPz_4	tetrakis(pyrazol-1-yl)borate
bq	1,2-benzoquinone
bqd	benzoquinone dioximate
bta	2,2'-bi-2-thiazoline
Bu	butyl
^tBu	*t*-butyl (CMe_3)
Bz	benzyl
bzd	benzidine
bzo[15]eneS_4	3,6,10,13-tetrathiabicyclo[13.4.0]nonadec-1,16,18-triene
$catH_2$	catechol (1,2-dihydroxybenzene)
CD	circular dichroism
CF	crystal field

1,3-chxn	*cis*-1,3-cyclohexanediamine
$citH_3$	citric acid
3-CNacacH	3-cyanopentane-2,4-dione
cod	cycloocta-1,5-diene
cot	cyclooctatetraene
cotr	cyclooctatriene
cp	η^5-cyclopentadienyl
cpta	*trans*-1,2-diaminocyclopentane
CT	charge transfer
CV	cyclic voltammetry
cych	cyclohexyl
cyclam	1,4,8,11-tetraazacyclotetradecane
cyclen	1,4,7,10-tetraazacyclododecane
cyclops	difluoro{3,3'-(trimethylenedinitrilo)bis(2-butanoneoximato)}-borate
cysH	cysteine
dap	2,6-diacetylpyridine
dbzmH	dibenzoylmethane
dea	diethylacetamide
dehpH	di-(2-ethylhexyl)phosphonic acid
$dhaqH_2$	1,4-dihydroxyanthraquinone
diars	1,2-phenylenebis(dimethylarsine)
dien	diethylenetriamine {bis(2-aminoethyl)amine}
dik	β-diketonate
dim	2,3-Me_2-[14]-1,3-diene-1,4,8,11-N_4 {Me_2[14]dieneN_4}
(+)-diop	(+)-2,3-*O*-diisopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
dma	dimethylacetamide
dmbpdo	3,3'-dimethyl-2,2'-bipyridine *N,N'*-dioxide
dme	1,2-dimethoxyethane
dmen	*N,N'*-dimethyl-1,2-diaminoethane
dmf	dimethylformamide
dmg	dimethylglyoximato
$dmgH_2$	dimethylglyoxime
dmhH	5,5-dimethylhexane-2,4-dione
dmhpH	2,4-dimethyl-6-hydroxypyrimidine
dmpe	1,2-bis(dimethylphosphino)ethane
dmppl	3,4-dimethyl-1-phenylphosphole
dmpzlH	3,5-dimethylpyrazole

dmso	dimethylsulphoxide
dmu	*N,N'*-dimethylurea
dpae	1,2-bis(diphenylarsino)ethane
dpam	bis(diphenylarsino)methane
dpaq	8-(diphenylarsino)quinoline
dpen	*N,N'*-diphenyl-1,2-diaminoethane
dpg	diphenylglyoximato
dppa	2-(diphenylphosphino)anisole
dppba	2-(diphenylphosphino)benzaldehyde
dppe	1,2-bis(diphenylphosphino)ethane
dppee	*cis*-1,2-bis(diphenylphosphino)ethene
dpphe	1,6-bis(diphenylphosphino)hex-3-ene
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
dppq	8-(diphenylphosphino)quinoline
dpt	bis(3-aminopropyl)amine
DSC	differential scanning calorimetry
DTA	differential thermal analysis
1,2-dta	1,2-dithiane
dtbiH	2,4-dithiobiuret
dtbH	dithiobenzoic acid
dtc	dithiocarbamate
DTGA	differential thermogravimetric analysis
2,5-dth	2,5-dithiohexane
$dtoxH_2$	1,2-dithiooxalic acid
dttf	dibenzotetrathiafulvalene
DV	discrete variational
DVM	discrete variational method
ECL	electrochemiluminescence
$eddaH_2$	*N,N'*-ethylenediaminediacetic acid
$edptaH_4$	ethylenediphosphinetetraacetic acid
$edtaH_4$	ethylenediaminetetraacetic acid
edtp	*N,N,N',N'*-tetrakis(2'-benzimidazolylmethyl)-1,2-diaminoethane
EHMO	extended Hückel molecular orbital
EHT	extended Hückel theory
en	1,2-diaminoethane
ENDOR	electron-nuclear double resonance
EPR	electron paramagnetic resonance
epyden	2,6-bis{5-(1,4-diazahexyl)}pyridine
Et	ethyl

etdp	2-ethyltetraphenoxodiphosphazine
EXAFS	extended X-ray absorption fine structure
fbts	1-(α)-furyl-4-benzylamidothiosemicarbazone
glyH	glycine
Hb	haemoglobin
$HBPz_3$	hydrotris(pyrazol-1-yl)borate
$hedpH_4$	1-hydroxyethane-1,2-diphosphonic acid
hfacacH	1,1,1,5,5,5-hexafluoropentane-2,4-dione
hisH	histidine
hmpa	hexamethylphosphoramide
hmta	hexamethylenetetraamine
HOMO	highest occupied molecular orbital
HO-8-quin	8-hydroxyquinoline
HPLC	high pressure liquid chromatography
imdaH	iminodiethanoic acid
imdien	1,9-bis(4-imidazoyl)-2,5,8-triazanonane
imdpt	1,11-bis(4-imidazoyl)-2,6,10-triazaundecane
imidH	imidazole
IR	infrared
isonic	isonicotinamide
IT	intervalence transition
LMCT	ligand-to-metal charge transfer
LUMO	lowest unoccupied molecular orbital
lysH	lysine
$malH_2$	malonic acid
MbH_2	myoglobin
mbtH	mercaptobenzothiazole
Me	methyl
3-Me-acacH	3-methylpentane-2,4-dione
Mecp	methylcyclopentadienyl
1-Mecyt	1-methylcytosine
Meen	*N*-methyl-1,2-diaminoethane
Me_2en	*N*,*N*-dimethyl-1,2-diaminoethane
1-Meimid	1-methylimidazole
$2,9\text{-}Me_2phen$	2,9-dimethyl-1,10-phenanthroline

mhpH	6-methyl-2-hydroxypyridine
MLCT	metal-to-ligand charge transfer
mnt	maleonitrile dithiolate
MO	molecular orbital
m.p.	melting point
$MPIXH_2$	*meso*-porphyrin-IX
$MPIXDMEH_2$	*meso*-porphyrin-IX-dimethyl ester
mppl	3-methyl-1-phenylphosphole
$[MV]^{2+}$	1,1'-dimethyl-4,4'-bipyridinium dication (methyl viologen or Paraquat)
$[N(2amet)pipzH_3]^{3+}$	*N*-(2-ammoniumethyl)piperazinium trication
nbd	[2.2.1]-bicyclohepta-1,3-diene
nic	nicotinamide
nmp	*N*-methyl-2-pyrrolidine
NMR	nuclear magnetic resonance
$N,N\text{-}Et_2en$	*N*,*N*-diethyl-1,2-diaminoethane
$5\text{-}NO_2\text{-}phen$	5-nitro-1,10-phenanthroline
np	2-naphthyl
NQR	nuclear quadrupole resonance
$ntaH_3$	nitriloethanoic acid
ntbt	tris(2-benzothiazolylmethyl)amine
OAc	ethanoate
$O\text{-}en\text{-}N\text{-}tnH_4$	3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane
$OEPH_2$	octaethylporphyrin
ompha	octamethylpyrophosphoramide
8-O-quin	8-hydroxyquinoline anion
ORD	optical rotary dispersion
ornH	ornithine
OTTLE	optically transparent thin layer electrode
ox	oxalate
PcH_2	phthalocyanine
penH	penicillamine
PES	photoelectron spectroscopy
Ph	phenyl
L-phe	L-phenylalanine
phen	1,10-phenanthroline
$4,7\text{-}Ph_2\text{-}phen$	4,7-diphenyl-1,10-phenanthroline

pip	piperidine
pmbzpH	1-phenyl-3-methyl-4-benzoylpyrazole-5-one
pmdt	1,1,4,7,7-pentamethyldiethylenetriamine
pmtfpH	1-phenyl-3-methyl-4-etrifluoroethanoylpyrazole-5-one
1,2-pn	1,2-diaminopropane
1,3-pn	1,3-diaminopropane
PPIXDBE	protoporphyrin-IX-dibutyl ester
PPIXDME	protoporphyrin-IX-dimethyl ester
ppl	1-phenylphosphole
PPP	Pariser-Parr-Pople
$P(py)_3$	tris(2-pyridyl)phosphine
pq	2-(2-pyridyl)quinoline
Pr	propyl
^{i}Pr	*iso*-propyl (CMe_2H)
proH	proline
$ptaH_3$	phosphinetriacetic acid
purH	purine
PVP	poly(4-vinylpyridine)
py	pyridine
py-2,6-$(CO_2H)_2$	pyridine-2,6-dicarboxylic acid
pydien	1,9-bis(2-pyridyl)-2,5,8-triazanonane
pydpt	1,11-bis(2-pyridyl)-2,6,10-triazaundecane
pyNO	pyridine *N*-oxide
py-2-OH	2-hydroxypyridine
pysalH	*N*-(2-pyridyl)salicylaldimine
py-3-SO_3H	pyridine-3-sulphonic acid
pz	pyrazine
pzlH	pyrazole
ϕ	quantum yield
quin	quinoline
quin-8-OH	8-hydroxyquinoline
r	bond length
RDS	Raman difference spectroscopy
$salH_2$	salicylic acid
sal_2enH_2	*N*,*N'*-ethylenebis(salicylideneimine)
sal_2phenH_2	*N*,*N'*-*o*-phenylenebis(salicylideneimine)
sal_2propH_2	*N*,*N'*-trimethylenebis(salicylideneimine)

sbts	1-salicyl-4-benzylamidothiosemicarbazone
SCE	saturated calomel electrode
SCF	self-consistent field
SCMP	self-consistent Madelung potential
SDS	sodium dodecyl sulphate
serH	serine
SERS	surface enhanced Raman spectroscopy
SHE	standard hydrogen electrode
sq	1,2-benzosemiquinone
$squH_2$	squaric acid
SW	scattered wave
T_C	Curie temperature
T_N	Néel temperature
$taaH_2$	1,8-dihydrodibenzo[*b*,*i*][1,4,8,11]tetraazaannulene
tach	*cis*,*cis*-1,3,5-triaminocyclohexane
tame	1,1,1-tris(aminomethyl)ethane
$tartH_2$	tartaric acid
tbcyclen	1,4,7,10-Bz_4-[12]ane-1,4,7,10-N_4
$TBPH_2$	tetrabenzoporphyrin
tcne	tetracyanoethene
TCNQ	7,7,8,8-tetracyanoquinodimethane (2,5-cyclohexadiene-$\Delta 1\alpha,4\alpha'$ dimalonitrile)
$tedtaH_4$	thiobis(ethylenenitrilo)tetraacetic acid
teen	*N*,*N*,*N'*,*N'*-tetraethyl-1,2-diaminoethane
teoa	triethanolamine
terpy	2,2':6',2"-terpyridine
2,3,2-tet	1,4,8,11-tetraazaundecane
3,2,3-tet	1,5,8,12-tetraazadodecane
3,3,3-tet	1,5,9,13-tetraazatridecane
tetren	1,11-diamino-3,6,9-triazaundecane
tfa	trifluoroethanoate
tfacacH	1,1,1-trifluoropentane-2,4-dione
TGA	thermogravimetric analysis
thf	tetrahydrofuran
thrH	threonine
tht	tetrahydrothiophene
thtfacH	2-thenoyltrifluoropropanone
tim	2,3,9,10-Me_4-[14]-1,3,8,10-tetraene-1,4,8,11-N_4 (Me_4[14]tetraeneN_4)

tipp	tri(isopropyl)phosphate
$TIPPPH_2$	*meso*-tetra(isopropyl-4-phenyl)porphyrin
TLC	thin layer chromatography
tmc	tetramethylcyclam
tmen	*N,N,N',N'*-tetramethyl-1,2-diaminoethane
tmH_3	thiomalic acid
tmp	trimethylphosphate
tmso	tetramethylenesulphoxide
tmtu	tetramethylthiourea
tmu	tetramethylurea
$TPPH_2$	*meso*-tetraphenylporphyrin
tpt	2,4,6-tri(2-pyridyl)-1,3,5-triazine
tren	2,2',2"-triaminotriethylamine
trien	1,8-diamino-3,6-diazaoctane (triethylenetetraamine)
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane
ttp	tri-4-tolylphosphate
$TTPH_2$	*meso*-tetra(4-tolyl)porphyrin
tu	thiourea
UV	ultraviolet
UVPES	ultraviolet photoelectron spectroscopy
UV-VIS	ultraviolet-visible
UV-VIS-NIR	ultraviolet-visible-near infrared
$\Delta V^{\ddagger}$	activation volume
VT	variable temperature
xan	xanthate, $[S_2C(OR)]^-$
XPES	X-ray photoelectron spectroscopy
ZFS	zero field splitting