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ZIRCONIUM AND HAFNIUM ORGANOMETALLIC COMPOUNDS: ANALYSIS AND CLASSIFICATION OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA

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CONTENTS

ABBREVIATIONS

acac	acetylacetone
Ar	9-anthryl (in $OC(SiMe_3):CHAr$)
bzcp	benzylcyclopentadienyl
CH_2CMe_3	neopentyl
CH_2PhF	4-fluorobenzyl
C_3H_5	allyl
C_4H_6	1,3-butadiene
C_4Ph_4	tetraphenylbutadienediyl
C_6H_6	benzene
C_6H_{10}	cis-2,3-dimethylbutadiene
C_9H_7	indenyl

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$C_{10}H_7$	napthyl
CNT	centroid of a ring
COD	cyclooctadienyl
COMe	acetyl
COT	cyclooctatetraenyl
cp	cyclopentadienyl
cp*	pentamethylcyclopentadienyl
cpBu	t-butylcyclopentadienyl
cpMe	methylcyclopentadienyl
$cpSiMe_3$	trimethylsilylcyclopentadienyl
dmb	s-cis-η^4-2,3-dimethylbutadiene
dme	1,2-dimethoxyethane
dmpe	1,2-bis(dimethylphosphino)ethane
dphb	s-cis-η^4-2,3-diphenylbutadiene
fℓ	fluorenyl
hfac	hexafluoroacetylacetonate
hx	hexagonal
LX	ligand with donor atom X.
m	monoclinic
Me	methyl
NC_4H_4	pyrrolyl
OBu	t-butoxy
$OCCPh_2$	diphenylketene
Ocpt	1-oxacyclopentane
$o-(CH_2)_2C_6H_4$	o-xylidene
or	orthorhombic
OR'	2,6-di-tert-butylphenolate
OR'-OMe	4-methoxy-2,6-di-t-butylphenolate
PEt_2	diethylphosphide
Ph	phenyl
py	pyridine
SPh	phenylmercaptide
S_2CNEt_2	N,N'-diethyldithiocarbamato
S_2CNMe_2	N,N'-dimethyldithiocarbamato
tg	tetragonal
thf	tetrahydrofuran
$(thind)_2en$	ethylenebis(4,5,6,7-tetrahydro-1-indenyl)
tm	1,1'-trimethylenedicyclopentadienyl
tp	tropolonate
tr	triclinic
trg	trigonal

1. INTRODUCTION

The large increase in the number of transition metal compounds with metal to carbon bonds has represented a major part of the rapid growth of organometallic chemistry since the 1950's. In general, the cyclopentadienyl radical has been one of the most widely found π-electron donors, and most of the zirconium and hafnium organometallics have at least one of these ligands. The organometallic chemistry of the group IVB elements has been an active field of study for some time, covering aspects of both bonding and catalytic activity. The exploration of the chemistry of hafnium has always been less extensive than that of zirconium, and this is reflected in the data in this review. The number of determined crystal structures has increased rapidly, and many have been summarized in annual reports (refs.1,2), but there has not yet been a comprehensive overview and classification of the data. The available structural information for titanium organometallics has also been surveyed (ref.3), and this review completes the data for Group IVB, up to the end of June 1985, or volume 102 of Chemical Abstracts.

The number of structural examples increases from hafnium to titanium, with over one hundred and fifty organotitanium examples (ref.3). Comparisons are made between these three elements, and with the corresponding data for vanadium, niobium, and tantalum (ref.4-6). The structures have been divided into mononuclear, homo-binuclear, and hetero-oligonuclear systems, and presented in order of increasing complexity of the coordination sphere.

2. MONONUCLEAR COMPOUNDS

(i) Zirconium and Hafnium Derivatives with Unidentate, or One Multidentate, Carbon Ligand

The crystal and structural data for these types of zirconium and hafnium organometallics are collected in Table 1, where it can be seen that the zirconium coordination numbers range from four to eight. There are only three examples for hafnium, with tetrahedral (ref.8) and pseudo-octahedral coordination (ref.11) about the Hf(IV) atom. The zirconium(IV) atom in $Zr(CH_2Ph)_4$ (ref.8) and in $Zr(f\ell)_2C\ell_2$ (ref.15), has approximately tetrahedral coordination. The environment about both the zirconium and the hafnium in $M(CH_2Ph)_4$ consists of four unidentate benzyl ligands with Zr-C bond distances ranging from 223(1) to 229(1) pm, and Hf-C bonds from 223(1) to 227(1) pm. The C-M-C angles vary from 94° to 120° (M=Zr), and from 99° to 118° (M=Hf), which demonstrates considerable deviation from an ideal tetrahedral environment. This deviation is somewhat larger for the zirconium compound.

In $Zr(COT)(thf)C\ell_2$ (ref.14) and $Zr(COD)(dmpe)H$ (ref.19), the zirconium(IV) atoms are in pseudo octahedral environments. The zirconium(IV) atom in $Zr(cp)(acac)_2C\ell$ has been regarded as eight coordinate in one study (ref.16), and six coordinate in another (ref.17). The former is consistent with the view that the cp moiety forms three bonding molecular orbitals with the metal, while the latter argues that since the cp moiety replaces a monodentate $C\ell$ ligand, it too should be considered monodentate.

There are few examples (refs.20-22) where the molecular compound exhibits a pentagonal bipyramidal geometry. The crystal structure of $Zr(cp)(tp)_3$ (ref.21) is shown in Figure 1 as an example. The zirconium(IV) atom is in a seven coordinate environment with a slightly distorted pentagonal bipyramidal geometry. Five of the six ligating atoms lie in the equatorial plane about the zirconium, at a mean Zr–O distance of 221(1,5) pm, while the sixth oxygen (Zr–O = 216(1) pm) and the cyclopentadienyl ring occupy the two axial positions.

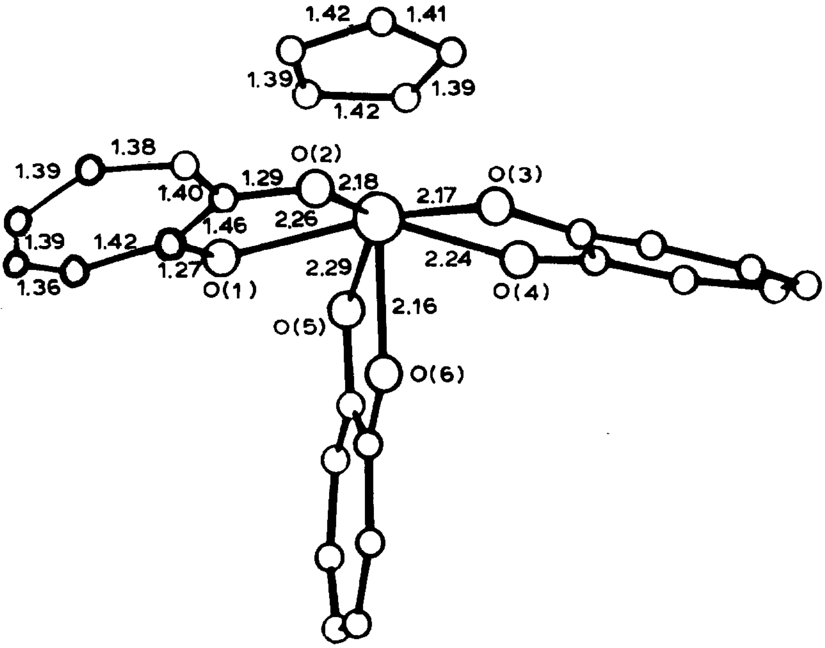

Figure 1. The Structure of $Zr^{IV}(\eta^5\text{-}cp)(tp)_3$
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TABLE 1. STRUCTURAL DATA FOR MONONUCLEAR ZIRCONIUM AND HAFNIUM ORGANOMETALLICS WITH UNIDENTATE (MULTIDENTATE) CARBON LIGANDS (LIGAND)[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	L-M-L [°]	Ref.
$Zr^{IV}(CH_2Ph)_4$[c]	or	Pbca	8	1994.5(6)		C[b] 227(1,3)	109(1,15)	7,8
				1371.6(7)				
				1630.7(5)				
$Hf^{IV}(CH_2Ph)_4$[c]	or	Pbca	8	2014.6(13)		C 225(1,2)	109(1,10)	8
				1365.6(7)				
				1038.6(14)				
$Zr^{IV}(CH_2Ph)_3(OR')$		C2/c	8	1749.9(10)		O 194.2(9)	110.4(5,18.1)[d]	9
				1056.6(6)	95.79(2)	C 227.7(16,19)		
				3276.9(12)		C 259.1(17)		
$Zr^{IV}(CH_2PhF)_3(OR')$		$P2_1/c$	4	948.0(3)		O 193.4(3)	107.6(2,3.0)[e]	9
				3360.5(19)	114.20(2)	C 226.1(5,9)		
				1060.8(2)		C 264.0(5)		
$Zr^{IV}(CH_2Ph)_2(OR')(OR'-OMe)$		$P2_1/n$	4	1768.3(9)		O 192.0(4,17)	109.7(3,5.1)[f]	9
				1134.2(5)	101.01(2)	C 225.8(9,15)		
				1947.0(11)				
$Zr^{IV}(CH_2Ph_4)_4(dmpe)$	tr	$P\bar{1}$	2	1130.7(1)	91.71(8)	P 287.4(4,12)	69.9(1)	10
				1377.3(1)	96.750(9)	C 232.6(6,61)		
				1145.2(1)	114.47(8)			
						P 268.4(1,9	72.16(3)	
						C 238.4(4,35)		

TABLE 1. Continued page 2

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	L-M-L [°]	Ref.
Zr^{IV}(Me)$_4$(dmpe)$_2$	or	P2$_1$2$_1$2	2	1249.0(3) 1124.5(1) 888.2(3)		P 281.4(6,2) C 244.0(8,10)	69.4(2),133.2(1,2.5)	10
Hf^{IV}(η^4-C$_4$H$_6$)$_2$(dmpe)^g	tr	P$\bar{1}$	4	1327.4(2) 1495.2(2) 931.9(1)	9714(1) 101.82(1) 109.76(1)	P 269.2(1,7) C 238.4(4,35)	72.00(3)	11
Zr(η^8-COT)(η^3-C$_3$H$_5$)(OBu)^g	m	P2$_1$/n	8	1569.6(6) 1611.7(3) 1253.1(6)	 111.05(1)	O 192.1(2) (η^3)C 248.4(5,33) (η^8)C 247.8(6,45) O 190.0(2) (η^3)C 247.9(4,22) (η^8)C 248.1(4,57)		12
Zr(η^8-COT)(η^3,η^3-deca-2,7-diene-4,9-diyl)		P2$_1$/n	4	1264.6(4) 1418.5(4) 837.3(2)	 95.89(2)	(η^3)C 258.0(1,246) (η^8)C 249.9(1,49)		13
Zr^{IV}(η^8-COT)(thf)Cℓ_2	or	Cmca	8	1232.8(2) 1197.3(2) 1758.1(3)		O 227.4(2) Cℓ 249.6(1) C 246.1(3,21)	84.8(1,2.4)	14
Zr^{IV}(η^5-fℓ)(η^3-fℓ)Cℓ_2	m	P2$_1$/n	4	1234.7 1377.1 1192.2	 98.2	Cℓ 242.0(2,5) (η^3)C 251.5(10,46) (η^5)C 255.9(10,162)	93.6(1)	15

TABLE 1. Continued page 3

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M–L [pm]	L–M–L [°]	Ref.
Zr^{IV}(η^5–cp)(acac)$_2$Cℓ	m	P2$_1$/c	4	842(1)		O 215(1,5)	79.1(5,1.3)	16
				1566(1)	123.25(4)	Cℓ 250(1)		
				1517(2)		(cp)C 255(5)		
Zr^{IV}(η^5–cp)(acac)$_2$Cℓ	m	P2$_1$/c	4	840		O 216		17
				1560	123.4	Cℓ 250		
				1505		(cp)C 253		
Hf^{IV}(η^5–cp)(acac)$_2$Cℓ		P2$_1$/c	4	867				18
				1533	124.0			
				1485				
Zr^{II}(η^5–COD)(dmpe)H	or	Pbcn	8	1493.6(5)		H 167	68.5(–,12.5)^h	19
				2034.2(6)		P 277.0(4,40)		
				1727.8(6)		(cp)C 245(1,2)		
Zr^{IV}(η^5–cp)(hfac)$_3$	m	P2$_1$/n	4	1348(2)		O 222.2(6,56)	75.3(2,7.6)	20
				2303(2)	94.52(8)	(η^5)C 253(1,2)		
				895(1)				
Zr^{IV}(η^5–cp)(tp)$_3$·	tr	P$\bar{1}$	2	983	103.7	O 220(1,6)		21
·CH$_2$Cℓ$_2$				1244	94.2	(cp)C 252–259		
				1388	128.4			

TABLE 1. Continued page 4

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	L-M-L [°]	Ref.
$Zr^{IV}(\eta^5\text{-cp})(S_2CNMe_2)_3PhCl$	m	$P2_1/c$	4	1158.2(2)		S 269.0(1,35)	73.72(4,11.95)	22
				1675.6(3)	90.58(1)	(cp)C 251.5(6,4)		
				1401.6(2)				
$Zr^{IV}(\eta^5\text{-cp})(S_2CNMe_2)_3\cdot$	tr		2	997.5(2)	97.53(2)			22
$\cdot CH_2Cl_2$				1425.8(3)	110.16(1)			
				962.7(2)	92.70(2)			

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in brackets is the e.s.d., and the second is the maximum deviation from the mean value.

b. The chemical identity of the coordinating atom or ligand.

c. At 233 K

d. The value of O-Zr-C angle; the C-Zr-C angles are 34.7(5), 89.7(6) and 120.9(6)°.

e. The value of O-Zr-C angle; the C-Zr-C angles are 105.5(2,1.0) and 123.0(2)°.

f. The value of O-Zr-C angle; the C-Zr-C angle is 110.0(3)°, and the O-Zr-O angle is 116.2(2)°.

g. There are two crystallographically independent molecules.

h. The value of H-Zr-P angle; the P-Zr-P angles are, 82.1(1,12.3) and 136.2(1,5.0)°.

Examination of the data in Table 1 reveals zirconium and hafnium in an oxidation state of +4, with one example of +2. In $Hf(C_4H_6)_2(dmpe)$ (ref.11) and $Zr(COT)(C_3H_5)(OBu)$ (ref.12), two crystallographically independent molecules are present which differ only by degree of distortion. Two such species coexisting in the same crystal represents the typical class of distortion isomerism (ref.23). The Zr-C bond distances are lengthened in the order: $(\eta^4\text{-}C_4H_6) < (\eta^5\text{-COD}) < (\eta^8\text{-COT}) < (\eta^3\text{-allyl}) < (\eta^3\text{-f}\ell) < (\eta^5\text{-cp}) < (\eta^8\text{-f}\ell) < (\eta^6\text{-deca-2,7-diene-4,9-diyl})$. In general the mean Zr-L bond distance increases with the van der Waals radius of the ligating atom: 167 (H,120 pm) < 208.9 pm (O, 152 pm) < 232.7 pm (η^1-C, 170 pm) < 247.2 pm (Cℓ, 175 pm) < 269.0 pm (S, 180 pm) < 278.7 pm (P, 180 pm).

(ii) Bis(cyclopentadienyl)-Zirconium and-Hafnium Organometallics

Crystal and structural data for mononuclear zirconium and hafnium organometallic compounds with two and three multidentate carbon donors are gathered in Table 2. From one hundred and twenty-one structures,

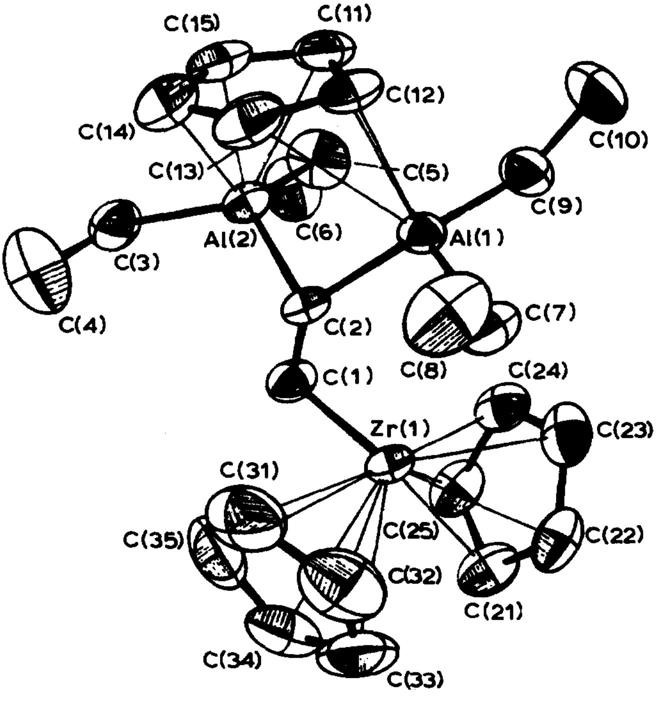

Figure 2. The Structure of $Zr^{IV}(\eta^5\text{-cp})_2\{(Et_2A\ell)_2Et\}(cp)$
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sixty-seven of them belong to this class. From a structural point of view, these compounds can be divided into five groups.

The first is represented by the red crystals of $Zr(\eta^5\text{-cp})_2[(Et_2A\ell)_2Et]\cdot(cp)$ (ref.24), where the zirconium(IV) atom is η^5-bonded to two cyclopentadienyl ligands, and to the $(Et_2A\ell)_2Et$ anion via carbon, as shown in Figure 2.

The overwhelming majority of the derivatives belong to the second group which has the general formula $(\eta^5\text{-cp})_2ML_2$, where L represents either two unidentate or one bidentate ligand. Examples of the former include: two identical L, such as H_2O (ref.25), LO (ref.26), LN (refs.27,28), F_2 (ref.29), Cℓ (refs.30-41), CO (refs.42-44), Me (refs.45-47), I (ref.29), LC (refs.48-50), Et_2P (ref.56); two different L, HO and Cℓ (refs.57-59), LC and LO (ref.60), LO and Cℓ (ref.61), LSi and Cℓ (ref.62). Examples of bidentate ligands are the LC systems (refs.51-55). The crystal structure of yellow, mildly air sensitive $Zr(\eta^5\text{-cp})_2(\eta^1\text{-NC}_4H_4)_2$ (ref.27) is shown in Figure 3 as a representative example of this wide group. The zirconium atom has a distorted tetrahedral environment consisting of two cyclopentadienyl and two pyrrolyl ligands.

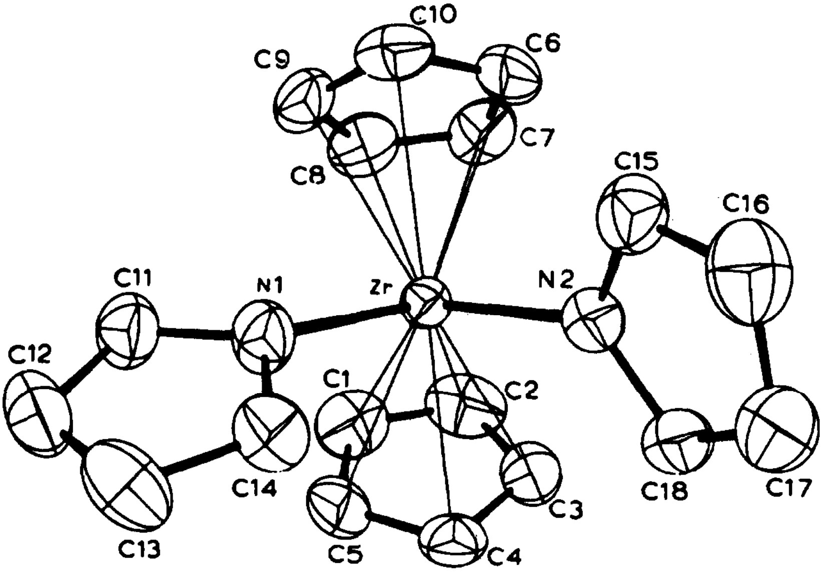

Figure 3. The Structure of $Zr(\eta^5\text{-cp})_2(\eta^1\text{-NC}_4H_4)_2$
Reproduced with permission from Inorg. Chem., (ref.27)

The third group has the general formula $M(\eta^5\text{-cp})_2L_3$, where all the L can be unidentate, H_2O (ref.63); or one L unidentate and the other bidentate, Cℓ and LS_2 (ref.64), Me and LCO (refs. 26, 65, 66, 68), and Cℓ with LCO (ref.67). The fourth group consists of $Hf(\eta^5\text{-cp})_2(BH_4)_2$ (ref.69), and $Zr(\eta^5\text{-cp})_2$ $(\eta^4\text{-LC})$ (refs.70–72) where in addition to the cyclopentadienyl ligands, the two BH_4 groups are coordinated to the metal atom through two H atoms in the hafnium case, and a tetradentate carbon ligand is found in the coordination sphere of the metal atom in the zirconium case.

The remaining group consists of $Zr(\eta^5\text{-cp})_3(\eta^1\text{-cp})$ (ref.74–77), and $Hf(\eta^5\text{-cp})_2(\eta^1\text{-cp})_2$ (refs.78,79), for which the structures are shown in Figure 4.

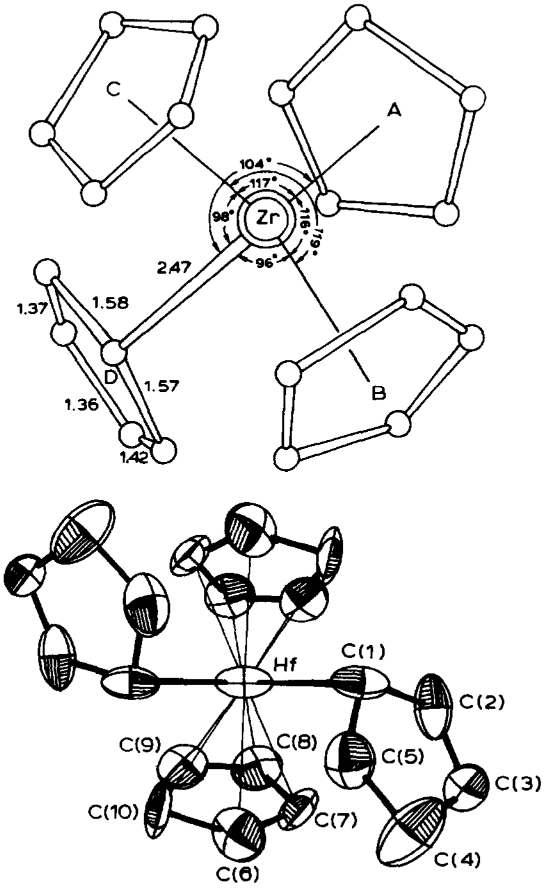

Figure 4. The Structure of $Zr(\eta^5\text{-cp})_3(\eta^1\text{-cp})$ (top)
Reproduced with permission from J. Chem. Soc., Chem. Commun. (ref.74)
and $Hf(\eta^5\text{-cp})_2(\eta^1\text{-cp})_2$ (bottom)
Reproduced with permission from J. Am. Chem. Soc., (ref.79)

As can be seen from the Figure, a distorted tetrahedral environment about the zirconium atom is built up of three η^5-cp rings and one η^1-cp ring, while for the hafnium it consists of two η^5- and two η^1-cp rings. The mean Zr–C bond distances are longer than the mean Hf–C distances. The zirconium compound exists in two isomeric forms, orthorhombic (ref.74) and monoclinic (ref.77), differing by degree of distortion and representing another example of distortion isomerism (ref.23). There are another three examples (refs.26,34,70) in Table 2 in which two crystallographically independent molecules are present and differ only by degree of distortion. This type of distortion isomerism exists for many other central atoms.

The data in Table 2 show that both zirconium and hafnium can occur in the oxidation state of +2 as well as the more common +4. Only about 20% of the examples have hafnium as the central metal atom.

The mean Zr–C bond distances for the multidentate C ligands increase in the order: 244.9 pm (η^4-dmb) < 245.7 pm (η^4-COT < 248.0 pm (η^3-allyl) < 250.2 pm (η^4-dphb) < 252.5 pm (η^5-cp). The mean Hf–C(cp) bond distance of 249.0 pm is about 3.5 pm shorter than the corresponding distance for zirconium. In the series of unidentate C ligands, the mean Zr–C and Hf–C distances increase, respectively, in the following order: 216.6 and 215.0 pm (CO) < 230.0 and 228.9 pm (Me) < 230.7 and 228 pm (Ph) < 230.0 and 236.0 pm ($CHPh_2$). The Hf–C bond distances are noticeably shorter than those of Zr–C in spite of the fact that the ionic radius of Zr(IV) is only about 1 pm larger than that of Hf(IV) in either 4-coordinate (73 versus 72 pm) or six coordinate (86 versus 85 pm) environments.

In general the mean value of the M–L bond distances increases with the van der Waals radius of the ligating atom: 193.5 pm (Zr–F, 147 pm) < 210.1 pm (Zr–O, 152 pm) < 214.0 pm (Zr–N, 155 pm) < 247.9 pm (Zr–Cℓ, 175 pm) < 258.5 pm (Hf–P, 180 pm) < 283.2 pm (Zr–I, 196 pm).

A list of individual values of (centroid)cp–M–cp(centroid) angles given in Table 3 for compounds of the general formula cp_2ML_2 (unidentate L) shows a range from 116.4° to 148.2°, and the L–M–L angles correspondingly range from 101.4° to 87°. In these clino-sandwich compounds the two angles vary inversely. For example, the smallest L–Hf–L angle of 87° is found in $Hf(\eta^5\text{-cp*})_2(CO)_2$ (ref.44) which also has the largest (centroid)cp–Hf–cp(centroid) angle of 148.2°. It can also be seen that the latter angle closes as the M–cp(centroid) distances increase.

There is a small but noticeable difference of 1.1 pm between the mean M–C(cp) bond distances of the derivatives in Table 1 (253.6 pm) and Table 2 (252.5 pm). The monocyclopentadienyl M–cp bond distances are slightly longer on the average.

TABLE 2. STRUCTURAL DATA FOR MONONUCLEAR BIS(CYCLOPENTADIENYL) ZIRCONIUM AND HAFNIUM ORGANOMETALLICS[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT [°]	L-M-L L-M-CNT [°]	Ref
$Zr^{IV}(\eta^5\text{-}cp)_2\{(Et_2Al)_2Et\}(cp)$		$P2_12_12_1$	4	1141.6(3)		(Et)C 287(6)	c	c	24
				2043.7(3)		(cp)C 212(-,2)			
				1082.1(3)		(cp)C 312(-,2)			
$Zr^{IV}(\eta^5\text{-}cp^*)_2(OH)_2$	m	$P2_1/n$		859.0(1)		O[b] 197.9(8,4)	c	99.7(3)	25
				2156.3(3)	102.88(1)	(cp*)C 255.0	137.9		
				1096.0(2)					
$Zr^{IV}(\eta^5\text{-}cp^*)_2(OH)Cl$	m	$P2_1/c$	4	1382.6(1)		O 195.0(2)	c	98.8(1)	25
				851.1(1)	109.54(1)	Cl 247.76(8)	137.6		
				1798.8(2)		(cp*)C 256.0			
$[Zr^{IV}(\eta^5\text{-}cp)_2(Me)\cdot$	or	$Pca2_1$	4	2581.4(6)	90	O 197.5(3)	221.2(7,6)	95.8(2)	26
$\cdot(O\text{-}C(Me)\text{=}CPh_2)$				864.6(2)	90	(CH_3)C 228.9(8)	129.2(2)	106.5(2,3.1)	
				985.1(2)	90	(cp)C c			
$[Zr^{IV}(\eta^5\text{-}cp)_2(O\text{-}C(Me)$	tr	$P\bar{1}$	4	1581.7(2)		O 200.2(6,3)	222.3(8,4)	101.3(2)	26
$\text{=}CPh_2)_2]^d$				1870.5(2)	98.16(2)	(cp)C c	128.5(2)	106.0(3,1.4)	
				1296.5(2)	113.98(2)				
						O 199.1(7,2)	223.0(7,8)	101.4(3)	
						(cp)C c	128.5(2)	106.0(3,1.2)	

TABLE 2. Continued 2

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT [°]	L-M-L L-M-CNT [°]	Ref.
$Zr^{IV}(\eta^5\text{-cp})_2(\eta^1\text{-NC}_4H_4)_2$	m	$P2_1$	4	959.7(5)		N 216.9(2,2)	c	95.68(8)	27
				819.8(5)	91.20(4)	(cp)C 252.0(3,21)	128.5	106.9(–,1.9)	
				1954.6(8)					
$Zr^{IV}(\eta^5\text{-cp})_2(NCO)_2$	or	Pbca	8	973.4(3)		N 211.0(3,9)	219.4(–,1)	96.4(1)	28
				1346.3(4)		(cp)C 249.4(4,23)	130.9	c	
				1796.4(5)					
$Zr^{IV}(\eta^5\text{-cp})_2F_2$	or	F2mm	4	607.6(5)		F 197.5(5)(2x)	221	96.2(3)	29
				1047.5(10)		(cp)C 250(1,2)	127.8(7)	c	
				1484.8(16)					
$Zr^{IV}(\eta^5\text{-cp})_2Cl_2{}^e$	m		2	620		Cℓ 230.9(5)	c	104(2)	30-32
				658	89.9	(cp)C 252.2(5)	134(5)		
				1333					
$Zr^{IV}(\eta^5\text{-cp})_2Cl_2{}^e$						Cℓ 245.9(15)	c	97.8(1.5)	33
						(cp)C 249.2(9)	133.3(2.5)		
$Zr^{IV}(\eta^5\text{-cp})_2Cl_2{}^d$	tr	$P\bar{1}$	4	1406(1)	113.7(1)	Cℓ 244.1(5,5)	220	97.1(2)	34
				809(1)	117.9(1)	(cp)C 249(3,4)	126.6	c	
				1315(1)	99.5(1)				
						Cℓ 244.1(5,2)	219	97.2(2)	
						(cp)C 251(4,7)	127.2	c	

TABLE 2. Continued 3

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT [°]	L-M-L L-M-CNT [°]	Ref
$[Zr^{IV}\{tm(\eta^5\text{-}cp)_2\}C\ell_2]$	or	Pbca	8	827.7(2)		Cℓ 244.1(2,10)	219.2(-,1)	96.92(7)	35
				1392.2(4)		(cp)C 249.4(7,22)	129.5	106.4(-,4)	
				2256.8(5)					
$[Hf^{IV}\{tm(\eta^5\text{-}cp)_2\}C\ell_2]$	or	Pbca	8	817.7(3)		Cℓ 242.3(3,6)	217.6(-,6)	95.87(8)	36
				1391.6(4)		(cp)C 248.2(9,23)	129.5	106.6(-,7)	
				2242.5(9)					
$Zr^{IV}(\eta^5\text{-}bzcp)_2C\ell_2$	or	Aba2	4	1205(1)		Cℓ 246.1(6)	216	94.4(1)	37
				2412(2)		(cp)C 249(3,7)	116.4(7)	c	
				699(1)					
$Zr^{IV}\{(\eta^5\text{-}C_5Me_4)_2C_2H_4\}C\ell_2$	m	C2/c	4	1708(2)		Cℓ 244.1(2)	221.1	98.4(1)	38
				806.7(4)	124.42(5)	C 251.7(3,47)	127.7		
				1641(1)					
$Zr^{IV}\{(\eta^5\text{-}thind)_2en\}C\ell_2{}^f$	m	Cc	4	1636(1)		Cℓ 244(1.1)	222(-,1)	98.6(3)	39
				1007.7(6)	123.1	C 253(2,11)	125.0		
				1430(1)					
$Zr^{IV}(\eta^5\text{-}f\ell)(\eta^3\text{-}f\ell)C\ell_2$	m	$P2_1/n$	4	1234.7		Cℓ c	c	93.6	40
				1377.1	98.2	$(\eta^3 f\ell)$C 250(-,10)	125.5	c	
				1192.2		$(\eta^5 f\ell)$C 240-265			

TABLE 2. Continued 4

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT [°]	L-M-L L-M-CNT [°]	Ref
$Zr^{IV}\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}Cl_2$	m	C2/c	4	1339.1(3)		Cl 243.5(1)	219.5(6)	97.98(4)	41
				996.5(2)	113.37(2)	C 250.0(4,45)	125.4(3)	c	
				1092.2(3)					
$Zr^{IV}(\eta^5\text{-}Mecp)_2Cl_2$						Cl 244.3(1)			41
						C c	128.9(2)		
$Zr^{IV}(\eta^5\text{-}cp)_2I_2$	m	C2/c	4	1420		I 283.2(2)	219	96.2(1)	29
				725	117.1	C 248(2,5)	126.3	c	
				1353					
$Zr^{IV}(\eta^5\text{-}cp)_2(CO)_2$	m	$P2_1/m$	2	652.8(4)		(CO)C 218.7(4)(2x)	218.4	89.2(2)	42
				1144.4(6)	113.58(4)	(cp)C 247.5(6,37)	142.2	103.4(73)	
				813.0(4)					
$Hf^{II}(\eta^5\text{-}cp)_2(CO)_2$	m	$P2_1/m$	2	649.7(4)		(CO)C 216(2)(2x)	216	89.3(9)	43
				1141.1(6)	113.85(5)	(cp)C 245(2,10)	141	103.5(-,5)	
				807.2(4)					
$Zr^{II}(\eta^5\text{-}cp^*)_2(CO)_2$		Pnma	4	1513.7(4)		(CO)C 214.5(9)	220	86.3(5)	44
				1686.0(4)		(cp*)C 249.8(9)	147.4	c	
				828.0(3)					

TABLE 2. Continued 5

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT [°]	L-M-L L-M-CNT [°]	Ref
$Hf^{II}(\eta^5\text{-}cp^*)_2(CO)_2$		Pnma	4	1513.5(4)		(CO)C 214(2)	217	87(1)	44
				1680.7(4)		(cp*)C c	148.2	c	
				826.8(3)					
$Hf^{IV}(\eta^5\text{-}cp)_2(CH_3)_2$	m	$P2_1/c$	4	696.5(2)		(CH_3)C 235.0(8,32)	221.1(-,4)	94.8(3)	45
				1185.7(4)	118.38(2)	(cp)C 250.5(9,34)	132.1	106.0(-,1)	
				1565.5(6)					
$Hf^{IV}(\eta^5\text{-}cp)_2(CH_3)_2$		$P2_1/n$	4	696.5(4)		(CH_3)C 223.7(12,4)	221(-,1)	95.8(5)	46
				1185.4(5)	92.02(3)	(cp)C 250.5(13)	133.0	105.5(-,9)	
				1378.6(6)					
$Zr^{IV}(\eta^5\text{-}cp)_2(CH_3)_2$		$P2_1/n$	4	695.3(3)		(CH_3)C 227.7(5,4)	223(-,0)	95.6(12)	46
				1190.2(5)	91.95(3)	(cp)C 252.5(5)	132.5	105.7(-,6)	
				1383.9(5)					
$Zr^{IV}(\eta^5\text{-}C_9H_7)_2(CH_3)_2$		$P2_12_12$	2	1424.8(4)		(CH_3)C 225.1(6)(2x)	223	96.9(3)	47
				824.4(3)		(C_9H_7)C 254.8(6,74)	120.8(5)	109.2(5,1.3)	
				692.9(3)					
$Hf^{IV}(\eta^5\text{-}C_9H_7)_2(CH_3)_2$		$P2_12_12$	2	1424.3(6)		(CH_3)C 233.2(12)(2x)	2.22	96.0(6)	47
				821.5(4)		(C_9H_7)C 252.7(13,82)	121.0(9)	109.3(8,2.5)	
				691.8(4)					

TABLE 2. Continued 6

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT [°]	L-M-L L-M-CNT [°]	Ref
$Zr^{IV}(\eta^5\text{-}cp)_2(CHPh_2)_2$		$P2_1/n$	4	1265.8(7) 1720.2(7) 1280.7(7)	92.45(5)	C 238.8(6,9) (cp)C 251.3(8,26)	c 128.2	95.5(4) 106.9(–,9)	48
$Hf^{IV}(\eta^5\text{-}cp)_2(CHPh_2)_2$		$P2_1/n$	4	1266.0(9) 1713.0(9) 1291.0(9)	92.39(5)	C 236(3,3) (cp)C 246(4,8)	c 128.2	95.4(9) 107.1(–,1.8)	48
$[Zr^{IV}(\eta^5\text{-}cp)_2(Ph)\cdot$ $\cdot\{CH(SiMe_3)_2\}]$	m	$P2_1/c$	4	1020.8(5) 1199.2(6) 1896.6(8)	99.09(4)	(Ph)C 232.4(7) C 232.9(6) (cp)C 254.2	c 126.9	100.4(2) 106.6(–,4.4)	49
$[Zr^{IV}(\eta^5\text{-}cp)_2(CH_2CMe_3)_2]$	tg	$I\bar{4}$	4	914.2(4) 914.2(4) 2332.6(9)	90	C 229.4(8)(2x) (cp)C 251(3,4)	225 128.3	89.9(4) 108.0(–,1.0)	50
$[Zr^{IV}(\eta^5\text{-}cp)_2(CH_2SiMe_3)_2]$	m	$P2_1/n$	4	1374.5(6) 704.8(3) 2205.7(9)	95.65(4)	C 228.0(4,2) (cp)C 252.3(5,33)	224(–,1) 129.9	97.8(1) 106.1(–,5)	50
$Zr^{IV}(\eta^5\text{-}cp)_2\{(CHSiMe_3)C_6H_4\}$	hx	$P6_3/m$	6	1784.9(8) – 1692.3(8)		C 230.5(4) (cp)C 251.0(5,25)	c 125.0	80.2(2)	51

TABLE 2. Continued 7

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT [°]	L-M-L L-M-CNT [°]	Ref
$Zr^{IV}(\eta^5\text{-cp})_2\{o\text{-}(CH_2)_2C_6H_4\}$	or	$P2_12_12_1$	4	827.6(4)	78.51(3)	C 230.0(6,2)	c	77.3(2)	52
				1107.5(5)	89.47(3)	(cp)C 252.0(6,24)			
				1572.1(7)	73.67(3)				
$Hf^{IV}(\eta^5\text{-cp})_2\{o\text{-}(CH_2)_2C_6H_4\}$	or	$P2_12_12_1$	4	825.1(5)	78.51(3)	C 228(1,0)	c	77.2(4)	52
				1107.0(7)	89.47(3)	(cp)C 251(1,2)			
				1574.8(8)	73.67(3)				
$[Zr^{IV}(\eta^5\text{-cp})_2(C_4Ph_4)]$	m	$P2_1/n$	4	1379.0(5)		C 225.8(6,8)	c	77.5(2)	53
				1113.6(5)	92.82(4)	(cp)C 252.1(7,39)	134.3	107.7(-,4.4)	
				1869.2(7)					
$[Hf^{IV}(\eta^5\text{-cp})_2(C_4Ph_4)]$	m	$P2_1/n$	4	1382.2(8)		C 220(2,2)	221(-,2)	78.7(8)	54
				1114.9(8)	93.18(5)	(cp)C 249(3,6)	134(1)	107.5(1.0,5.5)	
				1869.4(9)					
$[Zr^{IV}(\eta^5\text{-cpSiMe}_3)_2\cdot$	or	$P2_12_12_1$	4	827.6(6)		C 230.0(2)	c	77.4(2)	55
$\cdot\{(o\text{-}CH_2)_2C_6H_4\}]$				1107.5(7)		(cp)C 252.1(7)	c	c	
				1572.1(7)					
$Hf^{IV}(\eta^5\text{-cp})_2(PEt_2)_2^{g}$	tr	$P\bar{1}$	2	949.4(2)	101.15(2)	P 258.5(1,97)	c	98.64(3)	56
				1408.6(3)	108.12(2)	(cp)C c			
				795.3(2)	77.44(2)				

TABLE 2. Continued 8

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT [°]	L-M-L L-M-CNT [°]	Ref
$\mathrm{Zr^{IV}(\eta^5\text{-}cp)_2\{(Et_2A\ell)_2Et\}(C\ell)}$		$P2_12_12_1$	4	1497.6(2)		(Et)C 225.2(9)	c	c	57
				1860.7(5)		$C\ell$ 268.6(9)			
				827.8(1)		(cp)C 255.8(9,79)			
$\mathrm{Zr^{IV}(\eta^5\text{-}cp)_2(Me)(C\ell)}$		$P2_1/n$	4	681.0(8)		(Me)C 247.6(9)	223(-,2)	c	46
				1182.1(9)	92.30(4)	$C\ell$ 247.6(9)	c		
				1381.8(9)		(cp)C 251.0(9,21)			
$\mathrm{[Zr^{IV}(\eta^5\text{-}cp)_2(C\ell)\{CH(SiMe_3)_2\}]^h}$	or	$Pna2_1$	4	792(1)		C c			58
		(Pnam)		1193(5)		$C\ell$ c			
				2059(6)		(cp)C c			
$\mathrm{[Zr^{IV}(\eta^5\text{-}cpBu)_2\cdot}$	m	$P2_1/n$	4	1049.6(6)		C 232.4(8)	227(-,1)	98.2(2)	59
$\mathrm{\cdot\{CH(SiMe_3)_2\}(C\ell)]}$				1525.0(8)	100.48(5)	$C\ell$ 245.2(2)	128.1	106.5(-,1.2)	
				1827.2(9)		(cp)C 256.0(8,116)			
$\mathrm{[Zr^{IV}(\eta^5\text{-}cpSiMe_3)_2\cdot}$	m	$P2_1/n$	4	1052.5(5)		C 232.7(3)	225(-,1)	99.9(1)	59
$\mathrm{\{CH(SiMe_3)_2\}(C\ell)]}$				1532.0(7)	98.73(4)	$C\ell$ 244.7(1)	129.1	106.3(-,1.5)	
				1906.4(8)		(cp)C 254.3(4,66)			
$\mathrm{Zr(\eta^5\text{-}cp)_2\{OC(Ph)_2(CH_2)_4\}}$						C 231.1(7)			60
						O 194.6(4)			
						(cp)C c			

TABLE 2. Continued 9

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT [°]	L-M-L L-M-CNT [°]	Ref
$[Zr^{IV}(\eta^5\text{-cp})_2\{OC(SiMe_3)$	m	$P2_1/c$	4	931.5(5)		O 195.0(4)	220.5(-,3)	98.8(1)	61
$=CHAr\}(C\ell)]$				1647(1)	93.76(1)	Cℓ 246.9(2)	128.3	c	
				1749(1)		(cp)C 247.2–251.8(8)			
$[Zr^{IV}(\eta^5\text{-cp})_2(SiPh_3)(C\ell)]$	m	$P2_1/c$	4	1007.1(4)		Cℓ 243.0(3)	c	93.9(1)	62
				1733.1(7)	121.57(3)	Si 281.3(2)	c	c	
				1632.9(7)		(cp)C 249.0(10,38)			
$[Zr^{IV}(\eta^5\text{-cp})_2(H_2O)_3](CF_3SO_3)_2\cdot$	hx	$P6_3$	6	2194.5(5)		$(H_2O)O$ 223.2(7,37)	220.2(-,9)	72.6(3,8)145.2(2)	63
$\cdot(thf)^g$				–		(cp)C 250.9(9,42)	129.0	c	
				871.1(3)					
$[Zr^{IV}(\eta^5\text{-cp})_2(S_2CNEt_2)(C\ell)]$	m	$P2_1/c$	4	1761.9(4)		Cℓ 255.6(2)	221.9(7,3)	64.6(0)^i	64
				1389.2(3)	93.33(2)	S 267.9(2,44)	129.4(3)	c	
				710.2(1)		(cp)C 251.2(6,181)			
$[Zr^{IV}(\eta^5\text{-cp})_2(Me)_2$	m	$P2_1/a$	4	1158.2(2)	90	$(CH_3)C$ 232.2(6)	223.8(7,5)	66.5(2,10.0)	26
$\{\eta^2\text{-O-C(Me)-NPh}\}]$				1203.9(3)	97.57(2)	N 229.7(4)	129.5(2)	104.8(2,12.3)	
				1224.3(2)	90	O 229.8(4)			
						(cp)C c			
$[Zr^{IV}(\eta^5\text{-cp}^*)_2(py)\cdot$		$P2_1/n$	4	1740.69(13)		C 218.1(2)	227.8(-,2)	36.16(6)^j	65
$\cdot(C,O\text{-}\eta^2\text{-}H_2O\text{-}CO)]$				1618.41(14)	91.946(9)	O 212.6(1)	138.8	c	
				860.76(7)		(py)N 240.3(1)			
						(cp*)C c			

TABLE 2. Continued 10

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT [°]	L-M-L L-M-CNT [°]	Ref
$[Zr^{IV}(\eta^5\text{-cp})_2(Me)(\eta^2\text{-COMe})]$	or	Pnma	4	1239.7(1)		C 219.7(6)	221.7	31.2(2)[k]	66
				708.6(1)		O 229.0(4)	129.8(4)	c	
				1405.1(1)		(CH_3)C 233.6(7)			
						(cp)C 251.1(6,17)			
$[Zr^{IV}(\eta^5\text{-cp})_2(\eta^2\text{-COSiMe}_3)C\ell]$	m	$P2_1/n$	4	976.08(12)		C 218.3(2)	c	ℓ	67
				1286.94(16)	91.974(10)	O 224.8(1)	c	c	
				1268.37(15)		$C\ell$ 253.6(1)			
						(cp)C c			
$[Zr^{IV}(\eta^5\text{-cp})_2(\eta^2\text{-OCCH}_2)\cdot$	tr	$P\bar{1}$	2	1074.5(5)	119.40(3)	C 219.6(8)	c	35.6(2)[m]	68
$\cdot(Me)]Na(thf)_2$				1444.9(9)	91.26(4)	O 218.1(5)	c	c	
				1206.0(4)	114.83(4)	(CH_3)C 234.9(3)			
						(cp)C c			
$Hf^{IV}(\eta^5\text{-cpMe})_2(BH_4)_2$	m	C2/c	4	1456.6(3)		H 209.5(8,26)	218.8(4)	56.2(5,8)	69
				683.9(1)	102.31(2)	C 249.1(4,59)	128.5(3)		
				1395.9(3)					
$Zr(\eta^5\text{-cp})_2(\eta^4\text{-PhCH=CH-CH=CHPh})^d$	or	$P2_12_12_1$	8	848.1(1)		(η^4)C 245.1(17,60)	c	c	70
				2180.3(3)		(cp)C c	125.0		
				2166.7(5)					
						C 243.2(17,73)	c	c	
						(cp)C c	129.4		

TABLE 2. Continued 11

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT [°]	L-M-L L-M-CNT [°]	Ref
$Zr^{IV}(\eta^5\text{-cp})_2(\eta^4\text{-dmb})$		Pnma	4	800.8(1)	90	(η^4)C 230.0(3)	c	c	71
				1172.5(1)	90	(η^4)C 259.7(3)	124		
				1445.2(1)	90	(cp)C 255.8(4,22)			
$Zr^{IV}(\eta^5\text{-cp})_2(\eta^4\text{-dphb})$		$P2_1/c$	4	1015.7(1)	90	(η^4)C 228.9(2,4)	c	c	71
				1463.1(1)	95.46(1)	(η^4)C 271.4(1,5)	125.4		
				1370.6(1)	90	(cp)C 254.8(2,46)			
$Zr(\eta^5\text{-cp})_2(\eta^4\text{-s-cis-}C_6H_{10})$	or	Pnma	4	800.77(9)		(η^4)C 244.9(-,149)	c	c	72
				1172.5(1)		(cp)C 255.8(-,22)	124		
				1445.15(8)					
$Zr(\eta^5\text{-cp})_2(\eta^4\text{-s-trans-}C_4H_6)$	m	$P2_1/n$	4	768.7(1)		(η^5)C 233-248	c	c	72
				1150.3(1)	92.553(7)	(η^5)C c	126		
				1345.53(8)					
$Zr^{II}(\eta^5\text{-cp*})(\eta^4\text{-COT})(\eta^3\text{-}C_3H_5)$	m	C2/c	8	1353.7(5)		(η^3)C 248.0(5,13)	c	c	73
				983.1(4)	113.78(3)	(η^4)C 245.7(6,83)	c		
				2895.4(12)		(η^5)C 251.0(5)			
$Zr^{IV}(\eta^5\text{-cp})_3(\eta^1\text{-cp})$	or	$P2_12_12_1$	4	2083(3)		(η^1)C 247(2)	c	-	74-76
				853(1)		(η^5)C 264(2,10)	117(1,2)	99(1,5)^{n}	
				877(1)					

TABLE 2. Continued 12

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT [°]	L-M-L L-M-CNT [°]	Ref
$Zr^{IV}(\eta^5\text{-cp})_3(\eta^1\text{-cp})$	m	C2/c	8	1333.2(5)		(η^1)C 244.7(6)	c	100(1,1)	77
				906.5(4)	103.40(3)	(η^5)C 258.0(8,63)	117(1,2)		
				2568.4(6)					
$Hf^{IV}(\eta^5\text{-cp})_2(\eta^1\text{-cp})_2$	tg	$P\bar{4}2_1m$	2	958(2)		(η^1)C 234(7)	c	90	78
				958(2)		(η^5)C 250(7,1)	130	108(-,3)	
				812(2)					
$Hf^{IV}(\eta^5\text{-cp})_2(\eta^1\text{-cp})_2$	tg	$P\bar{4}2_1c$	4	979.0(5)		(η^1)C 238(2)	c	87(1,1)	79
				979.0(5)		(η^5)C 240(3,7)	130	108	
				1621.1(8)					

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in brackets is the e.s.d., and the second is the maximum deviation from the mean value.

b. The chemical identity of the coordinating atom or ligand.

c. Not given. d. There are two crystallographic independent molecules.

e. Gaseous by electron difraction. f. at 228 K. g. at 173 K. h. at 133 K.

i. The value of S-Zr-S angle; the Cℓ-Zr-S angle, 72.9(1) and 137.5(1)°.

j. The value of O-Zr-O angle, the N-Zr-O angle is 76.77(5)°.

k. The value of O-Zr-C angle, the O-Zr-C(Me) angle is 79.6(2)°.

ℓ. The Cℓ-Zr-O angle is 80.86(4)°; the Cℓ-Zr-C, 113.42(6).

m. The value of O-Zr-C-angle; the O-Zr-C(Me) angle is 78.4(4)°.

n. The value of $(\eta^1\text{-cp})$O-Zr-C$(\eta^5\text{-cp})$ angle.

3. HOMOBI-AND TRINUCLEAR COMPOUNDS

Bi- and trinuclear compounds for homonuclear zirconium and hafnium organometallics have been characterised, and the relevant data are listed in Table 3. There are several types of bridge between zirconium in the homo-binuclear derivatives, but for hafnium only two structures have been determined.

In [(Hf-cp$_2$Me)$_2$(μ-O)] (ref.45), [(Zr-cp$_2$Me)$_2$(μ-O)] (ref.46), [(Zr-cp$_2$Cℓ)$_2$ (μ-O)] (ref.80), and [(Zr-cp$_2$(SPh)$_2$(μ-O)] (ref.81), two (η^5-cp)$_2$ML moieties are singly bridged via an oxygen atom. In two of the examples, the O atom is symmetrically coordinated (refs.45 and 46), while in the remaining two examples (refs.80 and 81) the bridging is asymmetric. The Hf-L bond distances in the first example (ref.45) are somewhat shorter than those in the zirconium analogue (ref.46), with the exception of the M-C(Me) distance (Table 3). However, the latter may be accounted for by the large estimated standard deviation for this parameter. The M-O-M angle ranges from 165.8(2)° to 174.1(3)°. This angle and the O-M-L angle are related such that the M-O-M angle decreases from the ideal 180° in concert with an increase in the O-M-L angle, which itself is due to steric hindrance associated with L, and a corresponding increase in the value of M-L. For example, both the Zr-S distance and the O-Zr-S angle (101.0° mean value) of the thiophenyl derivative (ref.81) represent the highest such values found in this type of compound. By contrast, the Zr-O-Zr angle at 165.8(2)° is the smallest observed. The methyl derivative (ref.46) illustrates the other extreme with a Zr-C(Me) distance of 227.6(9) pm, an O-Zr-C(Me) angle of 96.3(2)° and the largest M-O-M angle of 174.1(3)°.

The crystal structure of the light yellow [{Zr(η^5-cp)$_2$Cℓ}$_2$(μ-OCH$_2$)] (ref.82) is shown in Figure 5. The oxymethylene bridge between the two (η^5-cp)$_2$ZrCℓ moieties is η^2-C=O bonded to Zr(1) with a Zr-O-Zr bridge angle of 166.9(4)°.

There are two examples in Table 3 where two [Zr(η^5-cp*)$_2$L] moieties are linked by a two-atom bridge. In one of these (ref.83), L is the same (N) in both halves and the bridge is Zr-N=N-Zr. In the other (ref.84), L is PMe$_3$ in one half and I in the other, and the bridge is Zr-O-C(H)-Zr.

Homobinuclear zirconium compounds with two bridging ligands are the most common. The bridging atoms can be either identical: such as H (refs.85,86), Ocpt (ref.87), OH (ref.88), CPMe$_3$ (ref.89), CHSiMe$_2$NSiMe$_3$ (ref.90); or they can be different such as: C$_{10}$H$_7$ (C and H) (ref.91), O and Cℓ (ref.92). The Zr-L-Zr bridge angle ranges from 93.7 to 120, but Table 3 illustrates that there are many absences in the data for this series of compounds, and therefore it may be premature to generalize.

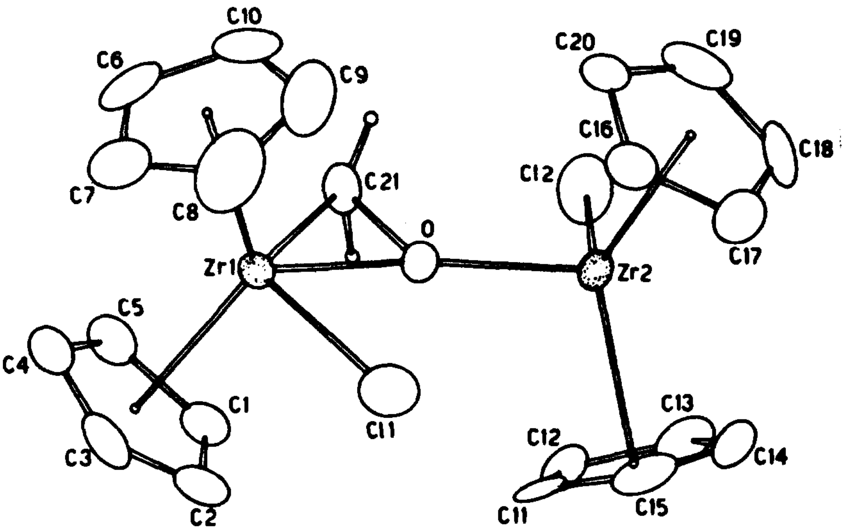

Figure 5. The Structure of $[\{Zr(\eta^5\text{-cp})_2C\ell\}_2(\mu\text{-}OCH_2)]$
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An interesting structure is observed for the triclinic binuclear compound $[Zr(\eta^5\text{-cp})_2(\eta^2\text{-}OCCPh_2)]$ (ref.93) in which the two zirconium atoms are linked by the two =C=O entities with identical Zr-O (216.5(3) pm) and Zr-C (220.4(3) pm) distances.

The molecular structure of another triclinic binuclear compound is shown in Figure 6, where two $(\eta^5\text{-cp})_4ZrC\ell$ units are held together by the ketene ligand. A similar structure has been found for the white crystals of $Zr_2(\eta^2\text{-cp})_4C\ell_2[P(Ph)_2CH{=}CO]$ (ref.96). While the mean Zr-Cℓ bond distances are identical in both compounds, the other Zr-L bond distances are somewhat longer in the latter (Table 3) because of the higher steric hindrance of $P(Ph)_2CH{=}CO$ versus $P(Me)_2CH{=}CO$.

The most unusual type of bridging is that involving a $(OC{=}CHCH_2CMe_3)_2\cdot A\ell Me_2$ ligand (through C-O-Aℓ-O-C), and a methyl group with the carbon atom in a distorted trigonal bipyramidal configuration (ref.96). The structure of this compound is illustrated in Figure 7.

TABLE 3. STRUCTURAL DATA FOR BI-, AND TRINUCLEAR ZIRCONIUM AND HAFNIUM ORGANOMETALLICS[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT[°] CNT-M-L[°]	M-L-M L^c-M-L L-M-L [°]	Ref
$[\{Zr^{IV}(\eta^5\text{-cp})_2(Me)\}_2(\mu\text{-O})]$		$P3_121$	3	801.7(3)		(Me)C[b] 227.6(9)	224(-,0)	174.1(3)	46
						O^c 194.8(1)	128.5	96.3(2)	
				2837.6(6)		(cp)C 252.7(8,32)	106.7(-,3.5)	-	
$[\{Zr^{IV}(\eta^5\text{-cp})_2Cl\}_2(\mu\text{-O})]$	m	C2	4	1388(1)		Cl 245.2(8,8)	221(-,2)	168.9(8)	80
				782(1)	98.88(10)	O^c 195(1,1)	128.4(-,3.7)	98.1(5,1.3)	
				1905(2)		(cp)C 251(4,6)	106.5(-,3.6)	-	
$[\{Zr^{IV}(\eta^5\text{-cp})_2(SPh)\}_2(\mu\text{-O})]$	or	Pbca	8	1645.8(4)		S 254.8(2)	c	165.8(2)	81
				2028.1(5)		O^c 196.8(3,2)	c	101.0(1,2.3)	
				1701.6(4)		(cp)C 254.2(7,48)	c	-	
$[\{Hf^{IV}(\eta^5\text{-cp})_2(Me)\}_2(\mu\text{-O})]$	trg	$P3_221$	3	801.1(2)		CH_3)C 229.5(14)	222.6(-,4)	173.9(3)	45
						O^c 194.1(3)	128.5	96.9(5)	
				2830.0(8)		(cp)C 251.3(15,26)	106.6(-,3.9)	-	
$[\{Zr(\eta^5\text{-cp})_2Cl\}_2(\mu\text{-OCH}_2)]$	m	$P2_1/n$	4	1077.5(2)		Cl 243.3(5,89)	222(1,2)	166.9(4)	82
				1516.6(4)	115.85(2)	C 219(1)	127.9(5,1.3)	c	
				1368.7(3)		O^c 212(1,2)			
						(cp)C c			

TABLE 3. Continued 2

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT[°] CNT-M-L[°]	M-L-M L^c-M-L L-M-L [°]	Ref
$[\{Zr^{II}(\eta^5\text{-}cp^*)_2N_2\}_2(\mu\text{-}N_2)]$	m	$P2_1/n$	4	1483.1(1)		N 218.8(4,0)	223.3(5,4)	d	83
				1699.2(1)	90.00	N^c 208.1(3,6)	141.3(2,2)	87.1(2,6)	
				1626.0(3)		(cp)C 253.5(5,60)	103.7(2,3.4)	-	
$[Zr(\eta^5\text{-}cp)_2(PMe_3)(\mu^2\text{-}C(H)O)$.		C2/c	8	2731.8(4)		P 269.3(2)	221.5(-,15)	-	84
$Zr(\eta^5\text{-}cp^*)_2I].C_6H_6$				1989.5(3)	132.188(10)	I 290.0(1)	135.4	95.4(2,4)	
				1993.2(5)		C^c 211.7(7)	228.2(-,2)^e	-	
						O^c 194.0(5)	134.0^e		
						(cp)C 251.3(9,41)			
						(cp*)C 257.7(8,59)			
$[Zr^{IV}(\eta^5\text{-}cpMe)_2H(\mu\text{-}H)]_2$	tr	$P\bar{1}$	1	639.0(2)	85.39(3)	H 178(2)	c	120(1)	85
				829.1(3)	74.36(3)	H^c 200(3,6)	c	70(1),130(1)	
				1130.8(4)	68.87(2)	(cp)C 251.7(2,48)	c	f	
$[Hf^{IV}(\eta^5\text{-}cpBu)_2H(\mu\text{-}H)]_2$	tr			722(3)	80.4(4)				86
				1031(4)	74.6(4)				
				1247(6)	72.1(3)				
$[Zr(\eta^5\text{-}cp)_2\{\eta^2\text{-}Ocpt\}]_2$	m	$P2_1/n$	2	1709.0(4)		C 238.2(11)	227.0(-,5)	c	87
				834.5(3)	102.90(2)	O^c 221.2(5,22)	125.8	72.2(4)	
				884.1(3)		(cp)C c	c	g	

TABLE 3. Continued 3

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT[°] CNT-M-L[°]	M-L-M L^c-M-L L-M-L [°]	Ref
$[Zr^{IV}(\eta^5\text{-cp})(NO_3)_2(\mu\text{-OH})]_2\cdot$	m	$P2_1/c$	2	882.5(2)		$(NO_3)O$ 229.7(4,23)	222.0	110.3(2)	88
$\cdot(thf)$				1213.7(3)	97.61(2)	$(OH)O^c$ 212.9(4,39)		810(1,7)	
				1301.8(2)		(cp)C 253.2(7)		55.8(2,2)	
$[Zr\{(CH_2)_2PMe_2\}_2(\mu\text{-CPMe}_3)]_2$		$P\bar{1}$	1	1028.8(6)	106.50(6)	C 245.4(5,3)		96.0(2)	89
				1013.2(2)	118.64(5)	C 261.4(5,3)		102.2(2,9.9);159.9(2,4)	
				1033.0(7)	74.19(5)	C^c 215.7(4,2)		65.7(2,1);85.9(2,3.1)	
								144.6(2)	
$[Zr\{N(SiMe_3)_2(\mu\text{-CHSiMe}_2$	or	Pbca	8	1830.7(7)		N 207(1,3)		93.9(6)	90
$\cdot NSiMe_3)]_2$				2603.6(6)		C^c 219(2,3)		83.8(5,2.2);118.6(5,12.6)	
				1942.5(6)				123.0(4,1.3)	
$[Zr(\eta^5\text{-cp})_2(\mu\text{-H})\cdot$	or	Pbca	8	1924.3(8)		C 245.9(8)	255(3,5)	c	91
$Zr\mu\text{-}(2\text{-}\eta^1\text{:}1\text{-}2\text{-}\eta^2\text{-}C_{10}H_7))]$				2050.7(6)		C^c 248(1,19)	124.5(-,1.5)	c	
				1193.1(8)		H^c 200(8,27)		h	
						(cp)C c			
$[\{Zr(\eta^5\text{-cp*})(\eta^1\text{-NC}_4H_4)(C\ell)\}_2\cdot$	m	C2/c	4	1220.3(3)		N 221(1)	c	132.5(8)^i	92
$(\mu\text{-}C\ell)(\mu\text{-}O)][Li(dme)_3]\cdot dme$				3085.3(9)	106.82(4)	Cℓ 247.2(4)	c	j	
				1519.4(4)		$C\ell^c$ 266.5(4)	111.0(-,3.2)	88.3(5,2.0)	
						O^c 191.0(6)			
						(cp*)C 249-257(2)			

TABLE 3. Continued 4

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT[°] CNT-M-L[°]	M-L-M L^c-M-L L-M-L [°]	Ref
$[Zr(\eta^5\text{-}cp)_2I(OC(H)=CO)\cdot$		$P2_1/c$	4	1586.6(4)		I 287.2(1)	222.1(-,3)	-	84
$\cdot Zr(\eta^5\text{-}cp^*)_2]$				1067.3(3)	105.5(2)	C^c 226.8(10)	128.9	k	
				2056.1(4)		O^c 203.6(7,37)	$225.4(-,0)^e$		
						(cp)C 251(2,9)	136.9		
						(cp*)C 255(1,3)			
$[Zr(\eta^5\text{-}cp)_2(\eta^2\text{-}O=O=CPh_2)]_2$	tr	$P\bar{1}$	1	818.7(2)	110.02(2)	C 220.4(3)			93
				1064.2(4)	98.47(2)	O^c 216.5(2,1)			
				1176.1(2)	101.69(3)	(cp)C c			
$Zr_2^{IV}(\eta^5\text{-}cp)_4C\ell_2(PMe_2CH=CO)$	tr	$P\bar{1}$	2	1310.5(10)	88.22(4)	$C\ell$ 256.5(5,5)	223	161.7(5)	94
				1156.8(6)	89.86(5)	C 223(2)	131.4(-,3.3)	ℓ	
				851.3(4)	70.59(5)	O^c 230(1,4)			
						P 272.4(5)			
						(cp)C 249-256(2)			
$Zr_2^{IV}(\eta^5\text{-}cp)_4C\ell_2(PPh_2CH=CO)$		C2/m	4	1700.2(3)		$C\ell$ 256.4(2,7)	222.2(-,5)	162.0(2)	95
				1647.4(2)	112.72(2)	C 226.5(6)	c	c	
				1170.7(2)		O^c 233.6(5,25)			
						P 276.1(2)			
						(cp)C c			

TABLE 3. Continued 5

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-CNT[pm] CNT-M-CNT[°] CNT-M-L[°]	M-L-M L^c-M-L L-M-L [°]	Ref
$[\{Zr_2(\eta^5\text{-}cp)_4(OC{=}CHCH_2CMe_3)_2\cdot$		$P2_1/c$	4	1020.89(7)		C 218.4(6,3)	222.4(1,15)	147.8(3)	96
$\cdot AlMe_2\}(\mu\text{-}CH_3)]$				2021.4(3)	94.375(8)	O 218.1(4,2)	c	75.9(2)	
				1842.1(2)		C^c 250.8(7,52)		37.5(2,3)	
						(cp)C c			
$[Zr^{IV}(\eta^3\text{-}cp)_2(\mu\text{-}O)]_3\cdot C_7H_8$	m	$P2_1/c$	4	1023.0(1)		O^c 195.8(6,8)	228(1,2)	142.5(3,5)	97
				1861.2(2)	92.27(1)	(cp)C 255(1,7)	123.8(5,2)	m	
				1740.6(2)			108.1(4,1.6)		
$[Zr(\eta^5\text{-}cp)_2(\eta^2\text{-}OCH_2)]_3$		$P2_1/c$	4	856.2(1)		C 227.4(10,4)	226.5(-,8)	160.7(3,1)	99
				1558.1(3)	95.679(9)	O^c 215.7(5,28)	c	37.6(3,7)	
				2434.8(3)		(cp)C c		o	
$[Hf^{IV}(\eta^5\text{-}cp)_2(\mu\text{-}O)]_3\text{-}C_6H_5Me$	or	Cmcm	4	1232.2(3)		O^c 195(2,3)	225.5(-,5)	144.5(1.0,1.5)	98
				1747.3(4)		(cp)C 254(3,6)	122.9(-,0)	n	
				1783.6(4)			108.6(-,1)		

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in brackets is the e.s.d., and the second is the maximum deviation from the mean value. b. The chemical identity of the coordinating atom or ligand.
c. The bridge atom (ligand). d. The $Zr\text{-}N^c\text{-}N^c$ angle is 177.1(3,4)°; and Zr-N-N = 177.9(5,1)°. e. The value of Zr-Cr*(CNT) distance and (CNT) cp*-Zr-cp*(CNT) angle. f. The $H^c\text{-}Zr\text{-}H^c$ angle is 60(1)°; the Zr...Zr distance = 345.9(2)pm. g. The $O^c\text{-}Zr\text{-}O^c$ angle is 64.5(4)°.
h. There is Zr...Zr distance of 330.7(2)pm. i. The value of Zr-O-Zr angle; the Zr-Cl-Zr is 82.0(2)°; the $Cl^c\text{-}Zr\text{-}O^c$ angle is 72.2(4)°.
j. The $Cl^c\text{-}Zr\text{-}Cl$ angle is 81.3(1)°; $Cl^c\text{-}Zr\text{-}N$ = 141.3(3)° and $O^c\text{-}Zr\text{-}Cl$ = 133.0(2)°. k. The O-Zr-O angle is 76.9(3)°; the I-Zr-C angle is 100.1(3)°. ℓ. The O-Zr-Cl angle is 84.0(3) and 143.0(3)°; O-Zr-C = 35.1(4)°; O-Zr-P = 69.4(3)°; Cl-Zr-P = 73.6(2)°, and Cl-Zr-C = 119.1(4)°.
m. The value of O-Zr-O angle is 97.5(2,2)°. n. The value of O-Hf-O angle is 97(1,0)°. o. The value of O-Zr-O angle is 79.1(2,3)°.

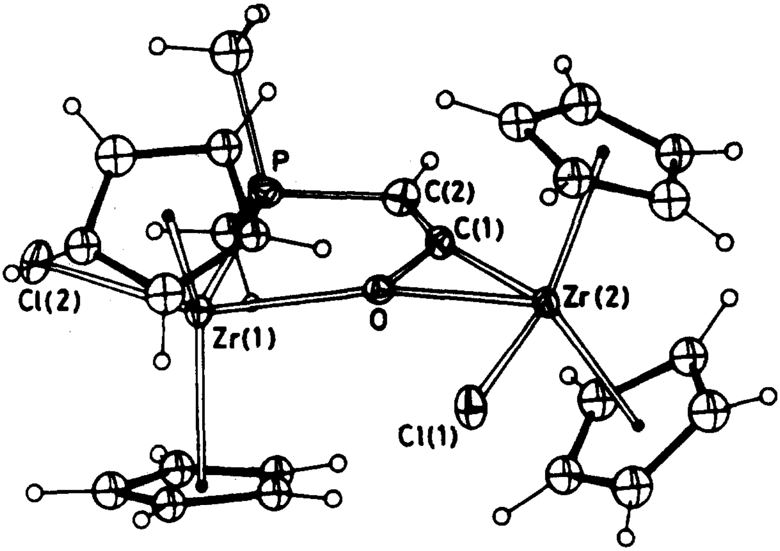

Figure 6. The Molecular Structure of $Zr_2(\eta^5\text{-cp})_4Cl_2(PMe_2CH{=}CO)$
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There are three examples of homo-trinuclear compounds (refs.97-99) and the structure of $[Hf(\eta^5\text{-cp})_2(\mu\text{-O})]_3$ (ref.98) is shown in Figure 8 as a representative example. The three $(\eta^5\text{-cp})_2Hf$ units are bridged by oxygen atoms at the average Hf-O distance of 195(2,3) pm, and a Hf-O-Hf bridge angle of 144.5(1.0,1.5)°.

An overall view of the data in Table 3 reveals that, in general, the mean M-L bond distances in the trinuclear organometallics are somewhat longer than those in the binuclear ones. For example, the mean M-C(cp), M-C(CH_2O), and M-O(μ-OCH_2) distances in the former are: 252.7 pm, 223.7 pm, and 194.5 pm. There are uni-, bi-, and tridentate ligands. In the series with unidentate ligands the mean M-L(terminal) bond distances increase in the order: 192 pm (L=H) $<$ 215.6 (N) $<$ 228.6 pm (C) $<$ 249.7 pm (Cl) $<$ 254.8 pm (S) $<$ 272.6 pm (P) $<$ 288.6 pm (I), corresponding to increasing van der Waals radius of the coordinating atom. The mean M-L (bridge) distances are somewhat longer than the M-L (terminal) ones and

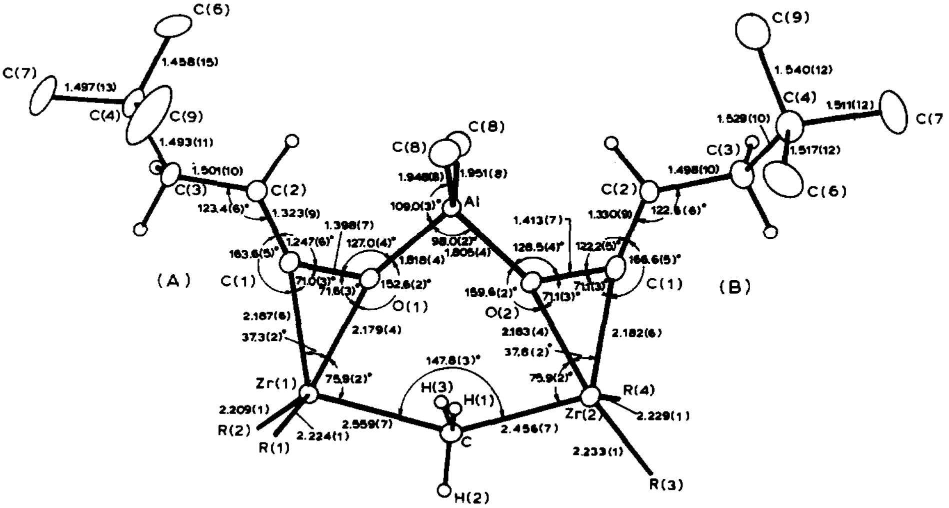

Figure 7. The Structure of $\{Zr_2(\eta^5\text{-cp})_4(OC{=}CHCH_2CMe_3)_2AlMe_2\}(\mu\text{-}CH_3)$
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increase in the order: 194.5 pm (O) < 200 pm (H) < 208.7 pm (N) < 223.6 pm (C) < 266.5 (Cl).

In the series of bidentate ligands with a C atom (terminal) and O atom (bridging), the mean M-L distances increase in the order: CHO < CH_2O < OCHCO < Me_2CCHCO < Ocpt. This reflects both steric and electronic factors. Two examples with tridentate ligands, Ph_2CCO and $P(Ph)_2CHCO$, binding via C and P (terminal), respectively, and O (bridging) follow the same trend.

It may be noted that there is no example with a direct metal-metal bond between the two zirconium or hafnium atoms. The shortest M-M distance of 330.7(2) pm is found in $[Zr(cp)_2(\mu\text{-}H)Zr(\mu\text{-}(2\text{-}\eta^1{:}1\text{-}2\text{-}\eta^2\text{-}C_{10}H_7))]$ (ref. 91) is too large to indicate any metal-metal bond.

4. HETEROBI- AND TRINUCLEAR COMPOUNDS

From the thirteen examples summarized in Table 4, eleven are heterobinuclear and only two are heterotrinuclear. There is only one example of a hafnium derivative. Several types of bridged systems exist in

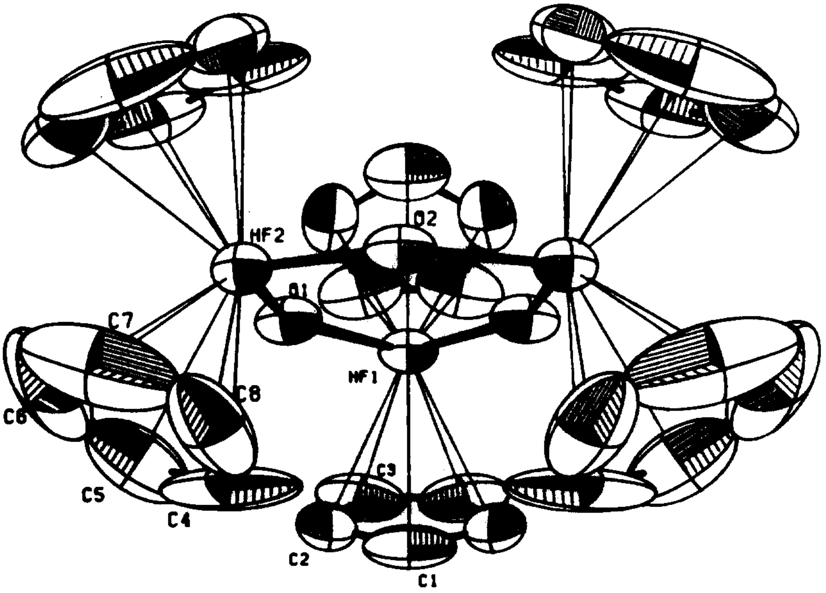

Figure 8. The Molecular Structure of $[Hf(\eta^5\text{-cp})_2(\mu\text{-O})]_3$
Reproduced with permission from J. Cryst. Spectr. Res., (ref.98)

this group. In $cp_2Zr(OCMe_3)Ru(cp)(CO)_2$ (ref. 100) a direct Zr-Ru bond of 291.0(1) pm exists and was the first example of an unbridged bond between zirconium and a later transition metal. A tetrahedral environment about zirconium is built up by two cyclopentadienyl rings, one $OCMe_3$ ligand (Zr-O = 191.0(4) pm), and the remaining position occupied by the ruthenium atom. A similar bond has been found in a heterotrinuclear system $cp_2Zr[Ru(CO)_2cp]_2$ (ref. 101), with a somewhat longer Zr-Ru distance. The molecular structure of this orange complex is shown in Figure 9. In this example the zirconium coordination sphere consists of two cyclopentadienyl rings, and two ruthenium atoms at a distance of 294.3(1,5) pm, which is within metal-metal bonding distance for zirconium to ruthenium.

There are three examples (refs. 102, 103, 104) in which two cp_2ZrL units are linked to another transition metal organometallic moiety (Mo or W) by a carbonyl group in the manner Zr-O-C-M. In the yellow $cp_2Zr(OCMe)(CO)_2Mocp$ (ref. 103), which was formed from the tricarbonyl derivative by slow loss of carbon monoxide, the stereochemistry changes to allow bridging

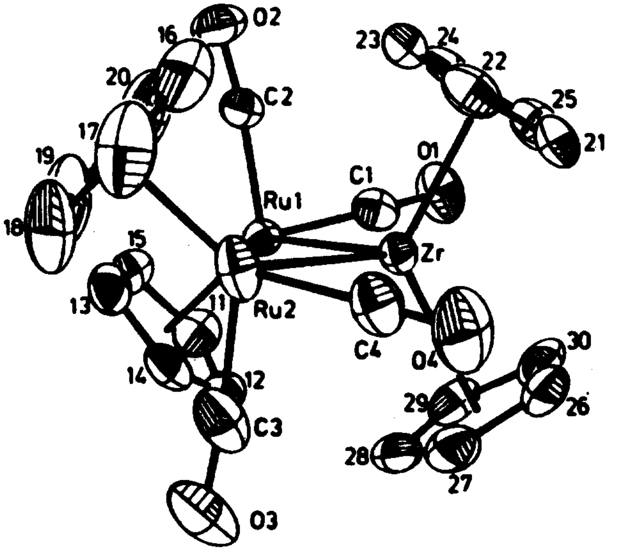

Figure 9. The Molecular Structure of $(\eta^5\text{-cp})_2Zr[Ru(CO)_2(\eta^5\text{-cp})]_2$
Reproduced with permission from Organometallics (ref.101)

by oxycarbene-acetyl (μ-OCMe) and a four electron donor carbonyl (μ-η^2, η^1-CO) (Table 4) in the manner [Zr-O-C(Me)-Mo-C-O].

Doubly bridged systems with two hetero transition metal atoms have been reported (refs. 106-108) in which two metals are bridged by two P-donor ligands. The crystal structure of cp_2 $Zr(\mu\text{-}PPh_2)_2Mo(CO)_4$ (ref. 106) is shown in Figure 10 as a representative example. Two moieties, cp_2Zr and $Mo(CO)_4$, are held together by two PPh_2 ligands through their P atoms. The Zr-P bond distance of 263.0(1,1) pm is about 8.5 pm longer than that of Mo-P at 254.5(1,2) pm, corresponding to the relative covalent radii of these two metal atoms. The steric effects of the cyclopentadienyl rings undoubtedly plays a role in modifying these distances somewhat. The Zr-Mo distance of 329.9(1) pm indicates the absence of a metal-metal bond. Similarly, no metal-metal bond is found in other related compounds such as $cp2Hf(\mu\text{-}PEt2)2Mo(CO)_4$ (ref. 107) and $cp2Zr(\mu\text{-}PPh2)2W(CO)_4$ (ref. 108). The metal-metal distance decreases from 340.0(1) pm in the former to 328.9(1) pm in the latter, and simultaneously the M-P-Zr bridge angle decreases also

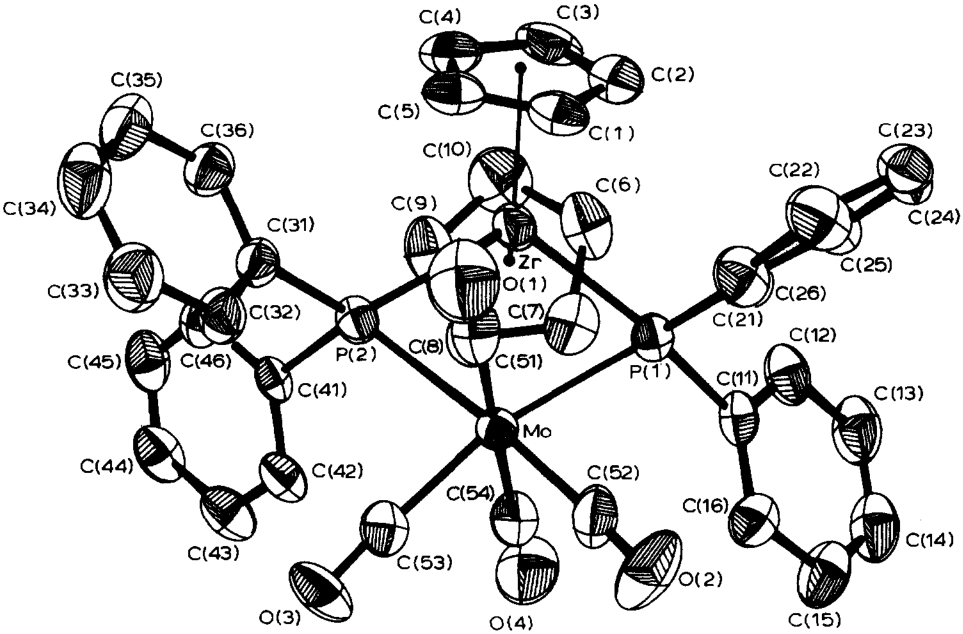

Figure 10. The Structure of $cp_2Zr(\mu\text{-}PPh_2)_2Mo(CO)_4$
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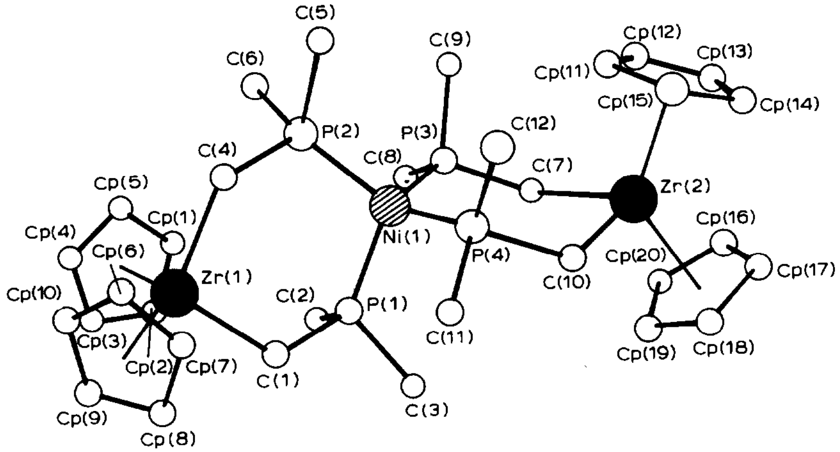
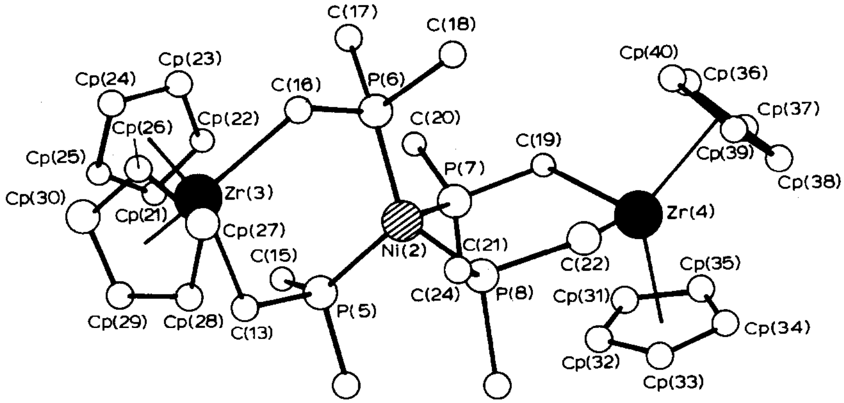
from 83.01(3,0)° to 79.20(8,5)°. Since the sum of the covalent radii for Zr + Hf (293 pm), Hf + Mo (294 pm), and Zr + W (294 pm) are very similar, the shorter M-M distance for the Zr-W system must result primarily from the change of the bridge ligand from PEt_2 to PPh_2. However, the latter ligand is sterically larger, and one might have expected the opposite trend.

Another mixed metal monoclinic dimer $(\eta^5\text{-}cp)_2Co(\mu\text{-}CO)(\mu\text{-}\eta^1, \eta^2\text{-}CO)Zr(\eta^5\text{-}cp^*)$ (ref.109) contains a Co-Zr single bond of 292.6(1) pm. The two carbonyls exhibit different modes of bonding. One of them bridges the metal centres in the usual manner (Co-C(O)-Zr), while the other bridges via a σ-bond to the CO plus a σ-π interaction between zirconium and the CO-π system in a $\mu_2\text{-}\eta^1$, η^2 fashion (Co-C-O-Zr) (Table 4).

Black crystals of $[(cp_2Zr(CH_2PMe_2)_2)_2Ni]$ (ref. 111) represent the only example in Table 4 which contains three transition metals. There are two crystallographically independent molecules, and their crystal structures are shown in Figure 11. The molecules differ by degree of distortion, and



Molecule A



Molecule B

Figure 11. The Structure of $\{(cp)_2Zr(CH_2PMe_2)_2\}_2Ni$ Molecule A, Molecule B. Reproduced with permission from J. Organomet. Chem., (ref.111)

it is a unique example of distortion isomerism in a trinuclear species. There are another two examples (refs. 103, 104) of heterobinuclear compounds in which two crystallographically independent molecules are present, differing by degree of distortion, and these represent further examples of distortion isomers within the same crystal.

Examination of the data in Table 4 shows that the mean Zr-C(cp) distance of 250.3 pm (range 244.8 to 254.2 pm) is about 4.1 pm shorter than the Zr-C(cp) distance of 254.4 pm (range 247.2 to 258.9 pm). There are four different types of CO coordinated to zirconium, with mean distances; Zr-O = 223.0 pm, Zr-C = 234.3 pm, Zr-O(bridge) = 271 pm, and Zr-C(bridge) = 225.3 pm.

TABLE 4. STRUCTURAL DATA FOR HETERO, -BI- AND -TRINUCLEAR ZIRCONIUM AND HAFNIUM ORGANOMETALLICS[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Zr-L [pm]	Zr-CNT[pm] CNT-Zr-CNT CNT-Zr-L	L-Zr-L	Ref
$(\eta^5\text{-cp})_2Zr(OCMe_3)Ru(\eta^5\text{-cp})$.		Pnam	4	1495.3(3)		O[b] 191.0(4)	227.4(4)	98.6(2)	100
$\cdot(CO)_2$				1074.4(2)		Ru 291.0(1)	125.8(4)		
				1292.2(3)		(cp)C c	115.7(3,7.9)		
$[Zr(\eta^5\text{-cp})_2\{Ru(CO)_2(\eta^5\text{-cp})\}_2]$		Pbca	8	1500.0(4)		Ru 294.3(1,5)	227.2(-,1)	100.5(1)	101
				1742.5(3)		(cp)C c	124.7		
				1695.7(4)					
$(\eta^5\text{-cp*})_2(H)ZrO(H)O{=}W(\eta^5\text{-cp})_2$	m	$P2_1/n$	4	1017.8(3)		H 193(4)	224.6(-,1)	98(1)	102
				3561.1(14)	109.93(2)	O 197.0(4)	138.5		
				829.3(2)		(cp*)C 254.7(7,45)			
$(\eta^5\text{-cp})_2Zr^{IV}(OCMe)(CO)_3Mo$.		$P\bar{1}$	4	1454.8(3)	85.24(1)	(CO)O 223.5(3,15)	c	78.7(1)[f]	103
$\cdot(\eta^5\text{-cp})$[d,e]				1280.0(3)	90.06(1)	C 218.6(4)	c	32.5(1),111.2(1)	
				1043.2(2)	73.87(1)	(cp)C 250.2(4,36)	c		
						(CO)O 224.0(3,12)	c	79.7(1)	
						C 218.1(4)	c	32.8(1),112.3(1)	
						(cp)C 250.5(4,37)	c		
$(\eta^5\text{-cp})_2Zr(OCMe)(OC)Mo(CO)$.		$P2_1/n$	4	1523.7(3)	90	(CO)O 227.1(2)	c	127.1(1)[h]	103
$\cdot(\eta^5\text{-cp})$[g]				1335.3(2)	106.98(1)	(CO)C 234.3(3)	c	31.2(1)	
				878.7(1)	90	(OCMe)O 215.6(2)	c	96.2(1)	
						Mo 329.7(1)			
						(cp)C 252.2(3)			

TABLE 4. Continued 2

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Zr-L [pm]	Zr-CNT[pm] CNT-Zr-CNT CNT-Zr-L	L-Zr-L	Ref
$(\eta^5\text{-cp})_2Zr(Me)(\mu\text{-OC})Mo(CO)_2\cdot$		$P2_1/n$	8	1845.1(4)		$(CH)_3C$ 225.1(8)	c	96.3(3)	104
$\cdot(\eta^5\text{-cp})$[i]				1071.3(2)	105.23(1)	(CO)O 210.3(4)	c		
				1967.5(3)		(cp)C 248.8(7,32)	c		
						$(CH_3)C$ 224.3(7)		93.8(3)	
						(CO)O 211.1(4)			
						(cp)C 247.3(10,38)			
$(\eta^5\text{-cp})_2(Cl)Zr(\mu\text{-H})_3Os\cdot$		$P\bar{1}$	4	1511.1(4)		Cl 252.1(3)		98.7(1,2)	105
$\cdot(PMe_2Ph)_3$[j]				2654.1(7)		Os 280.5(1)	121.4		
				1093.1(2)		μ-H c			
						(cp)C c			
$(\eta^5\text{-cp})_2Zr^{IV}(\mu\text{-PPh}_2)_2Mo(CO)_4$	or	$P2_12_12_1$	4	1841.8(2)		μ-P 263.1(1,1)		98.5(1)	106
				1843.5(3)		Mo 329.9(1)	127.0		
				1008.2(1)		(cp)C 250.9(5,37)			
$(\eta^5\text{-cp})_2Hf^{IV}(\mu\text{-PEt}_2)_2Mo(CO)_4$		$P2_1n$	4	1331.5(3)		μ-P 259.4(1,2)		95.30(3)	107
				1829.4(6)	91.21(2)	Mo 340.0(1)			
				1010.3(2)		(cp)C 247.2-251.3			
$(\eta^5\text{-cp})_2Zr^{IV}(\mu\text{-PPh}_2)_2W(CO)_4$	m	$P2_1/c$	4	1464.4(4)		μ-P 253.3(3,4)		98.30(9)	108
				1693.2(4)	100.13(2)	W 328.9(1)			
				1700.3(3)		(cp)C 251.5(11)			

TABLE 4. Continued 3

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Zr-L [pm]	Zr-CNT[pm] CNT-Zr-CNT CNT-Zr-L	L-Zr-L	Ref
$(\eta^5\text{-cp*})_2Zr(\mu\text{-CO})_2Co(\eta^5\text{-cp})$	m	$P2_1/c$	4	1562.4(6)		Co 292.6(1)	223.9(6,1)	39.6(2,4.4)[k]	109
				1388.5(13)	94.01(3)	O 243.1(5)	139.2(5)		
				1122.1(4)		μ-C 225.3(8,20)	109.9(5,4)		
						(Cp*)C 254.1(6,48)			
$(\eta^5\text{-cp})_2Zr(OCallyl)Cr(CO)_5$	or	Pnam	4	2239.8(5)		O 218.8(3)			110
				728.3(2)		C c	129.2(4)		
				1230.2(2)		(cp)C 248.6(5)			
$[\{(\eta^5\text{-cp})_2Zr(CH_2PMe_2)_2\}_2Ni]^i$	tr	$P\bar{1}$	4	1343.3(5)	64.35(2)	C 227.5(8,6)		98.4(3,1.6)	111
				1806.2(3)	76.82(1)	(cp)C 249-256(1)	129.3(-,3)		
				1950.5(2)	71.28(2)				
						C 230.5(9,18)		108.1(3,5.6)	
						(cp)C 250-258(1)	128.4(-,4)		

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in brackets is the e.s.d., and the second is the maximum deviation from the mean value. b. The chemical identity of the coordinating atom or ligand.
c. Not given. d. At 105 K. e. There are two conformers. f. The values for O-Zr-O and O-Zr-Cℓ (2x) bond angles.
g. At 101 K. h. The values for O-Zr-O, (CO)O-Zr-C(CO) and (OCMe) O-Zr-C(CO) angle. i. There are two crystallographically independent molecules. j. At 111 K. ℓ. The value of Co-Zr-C(CO) angle; the CO-Zr-O(CO) angle is 64.5(1)°.

In general, the mean Zr-L bond distances increase in the order: 193 pm (H) < 205.6 pm (LO, excluding CO) < 222.7 pm (LC, excluding CO) < 252.1 pm (Cl). This corresponds to increasing van der Waals radii of the ligand atoms in the order given. The Zr-M' distances are: 280.5 pm (Zr-Os), 292.6 pm (Zr-Co), 293.2 pm (Zr-Ru, mean), 328.9 pm (Zr-W), 329.9 pm (Zr-Mo), and 340.0 pm (Hf-Mo).

5. CONCLUSIONS

From 1969, when the first organozirconium structure was characterised by x-ray analysis, to the end of June 1985, over one hundred organozirconium and almost twenty organohafnium crystal structures have been determined. The majority of these can be seen to be mono- and binuclear, with only four trinuclear examples.

The overwhelming majority of the compounds have the zirconium or hafnium atom in the +4 oxidation state, with a few examples of +2.

Two crystallographically independent molecules, differing by degree of distortion, are present in ten examples (refs. 11, 12, 26, 32, 34, 70, 92, 103, 104, and 111). This coexistence of two species with identical coordination number but diferent degree of distortion has also been noted for titanium organometallics (ref. 3), and is representative of the general class of distortion isomerism (ref. 3).

Four-coordination with a tetrahedral geometry is representative of the overwhelming majority of the zirconium and hafnium organometallic derivatives.

An overall summary of the structural data for the organometallics of titanium (data from ref. 3), zirconium and hafnium is given in Table 5. Some points of interest arising from the data are listed below.

(a) In general, the M-L distance increases in the order: Ti-L < Hf-L < Zr-L.

(b) The mean Zr-C(cp) bond distance in the mononuclear compounds with one cyclopentadienyl ligand is longer than for those with two such ligands. For the titanium analogues the corresponding mean bond lengths are almost equal.

(c) The mean M-L distance in mononuclear compounds with one cyclopentadienyl ligand are longer than for those with two such ligands when L is O or P, but the opposite is true when L is Cl.

(d) The mean M-L distances in homobinuclear compounds are longer than those in mononuclear compounds with two cyclopentadienyl ligands, except Zr-L(C, N, and S).

TABLE 5. Summary of Group IVB Metal-atom (ligand) bond distances (pm)[a]

Coord. atom (ligand)	Metal atom	Mononuclear		Homobinuclear
		mono-cp	Bis-cp	
H	Ti		171-191(181)	(160-229(186))[b]
	Zr	167		173-226(192)
				(194-205(200))[b]
C(cp)	Ti	226.0-243.8(237.8)	230.0-251.0(237.9)	225.0-253.8(238.4)
	Zr	251.1-259.0(253.6)	243.0-270.0(252.5)	248.0-257.4(252.7)
	Hf		240.0-260.9(249.0)	248.7-253.1(251.3)
C(CO)	Ti		200.9-205.0(202.5)	
	Zr		214.5-218.7(216.6)	
	Hf		214.0-216.0(215.0)	
(L)C[c]	Ti	219.7-221.1(220.4)	207.0-224.7(217.0)	217.5-226.0(222.1)
				(208.3-254.0(225.9))[b]
	Zr	223.0-244.9(232.9)	225.0-239.6(231.3)	211.7-238.2(223.7)
				(215.5-266.2(223.6))[b]
	Hf		218.0-238.2(228.2)	229.5
(L)O	Ti	195.4-227.5(208.3)	186.0-215.5(200.3)	192.0-226.0(213.7)
				(203.7-225.0(213.4)[b]
	Zr	190.0-227.4(223.2)	195.0-226.1(210.1)	(194.0-234.0(214.2))[b]
O	Ti			(175.9-188.0(183.9))[b]
	Zr			(191.0-196.8(194.5))[b]
	Hf			(194.1)[b]
(L)N	Ti	187.7-227.0(209.6)	192.2-210.0(200.7)	212.6-222.2(216.2)
				(217.4-226.1(220.2)[b]
	Zr		210.1-240.3(220.9)	204.0-221.0(215.6)
N_2	Ti			(185.7-218.1(200.0))[b]
	Zr		(218.8)	(208.7)[b]
Cl	Ti	220.1-237.2(230.6)	231.0-240.5(235.9)	240.9-251.4(247.7)
				(252.6-261.1(255.7))[b]
	Zr	241.6-250.0(247.2)	243.0-268.6(247.9)	234.4-257.0(249.7)
				(266.5)[b]
	Hf		241.7-244.1(243.5)	
(L)S	Ti	256.5-266.6(261.1)	239.5-245.5(242.9)	(241.6-259.8(248.8))[b]
	Zr	265.5-271.7(269.0)	263.5-272.3(267.9)	254.2-255.4(254.8)
(L)P	Ti	263.6-267.3(265.5)	234.0-258.5(249.7)	
	Zr	273.0-288.5(281.9)		269.3-276.1(272.6)
	Hf	267.5-269.8(268.8)	248.8-268.2(258.5)	

a. The mean value is in parenthesis.

b. The values of a bridge atom (ligand). c. Excluding all multidentate ligands and CO.

(e) The mean M-L(bridge) distances are longer than M-L(terminal), except for Ti-L(O donor) and Zr-L(C donor) where the opposite is true.

(f) As the M-L-M angle opens, the M-M distance increases.

(g) There is no example with a direct bond between Zr-Zr or Hf-Hf atoms, but there are examples of Ti-Ti bonding.

There has been limited interest in the biological properties of the Group IVB metal derivatives. The biscyclopentadienyldichloro derivatives of zirconium and hafnium have been tested for antitumour activity (ref. 112) with little success. The inactivity is believed to be associated with the unfavourably large bite angle of the Cl-M-Cl moiety in these derivatives (ref. 113).

Systematic studies in the field of stereoselectivity of organometallic compounds over the last two decades have fostered wide interest. The factors governing the choice of geometry in these compounds include electronic configuration of the central metal atom, crystal packing forces, and the nature of the ligands. For example, chelating ligands are often found to play a substantial role in the nature of the overall structure, stereochemistry and fluxional behaviour of the organometallic derivatives of the Group IVB metals. A description of the uses of organozirconium compounds as new reagents and intermediates has recently appeared in a publication of the Aldrich Chemical Company (ref.114).

This review, together with that for titanium (ref. 3), represents an overview of the over two hundred and seventy organometallic structures which have been determined for this group of transition metals, and illustrates the rich chemistry of the group, and the many systematic trends which may be observed. A related series for the coordination complexes of these metals is in progress by the same authors.

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