1,2-Bis(dimethylphosphino)ethane (dmpe) Alkyl Compounds of Zirconium(IV) and Hafnium(IV). Crystal Structures of $ZrMe_4(dmpe)_2$ and $Zr(CH_2Ph)_4(dmpe)$ †

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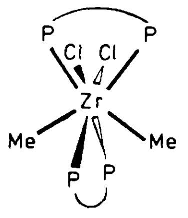
The reaction of $ZrCl_4(dmpe)_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane] with excess $MgMe_2$ gives the dialkyldichloro-complex $ZrMe_2Cl_2(dmpe)_2$, whereas interaction with excess LiMe gives the tetra-alkyl $ZrMe_4(dmpe)_2$. N.m.r. data indicate a rigid structure for the latter molecule at −60 °C, while the *X*-ray crystal structure shows the molecule, which has crystallographic C_2 symmetry, to have dodecahedral geometry with the methyl groups at the (B) sites and the phosphines at the (A) sites: Zr–C 2.440(6), Zr–P 2.814(1) Å. Alkylation of $ZrCl_4(dmpe)_2$ with excess $LiCH_2SiMe_3$ leads to the six-co-ordinate complex $Zr(CH_2SiMe_3)_4(dmpe)$; the analogous compound $Zr(CH_2Ph)_4(dmpe)$ can be prepared from $Zr(CH_2Ph)_4$ and dmpe. The *X*-ray crystal structure of $Zr(CH_2Ph)_4(dmpe)$ shows a severely distorted octahedral geometry consisting of three σ-benzyl groups and one partially π-bonded benzyl group: Zr–C(σ) 2.264(7)—2.368(5), Zr–C_α(π) 2.359(6), Zr ··· C_β(π) 2.788(8), Zr–P 2.862(4), 2.885(4) Å. The preparations and characterizations of some hafnium analogues are also described.

The first authentic binary transition-metal alkyl to be described was tetramethyltitanium, $TiMe_4$, prepared by alkylation of $TiCl_4$ with methyl-lithium at −70 °C.[1] Unfortunately, this complex decomposes above −70 °C,[2] and thus little is known concerning its properties. The zirconium analogue $ZrMe_4$ is even less stable and it is doubtful whether this complex exists even at −78 °C.[3] Subsequently, the use of 'β-stabilized' alkyl groups[4] allowed the isolation of thermally stable species such as $Ti(CH_2Ph)_4$[5] and $Ti(CH_2SiMe_3)_4$.[6] The corresponding zirconium and hafnium complexes were also prepared and such species have been shown to be catalysts for the polymerization of olefins.[7] A study of Lewis-base adducts of $TiMe_4$ showed that $TiMe_4(dmpe)$ [dmpe = 1,2-bis(dimethylphosphino)ethane] was much more thermally stable than the parent alkyl.[8] More recently, compounds of the form $TiRCl_3(dmpe)$ have been shown to possess unusually distorted alkyl groups (R) and M ··· H–C interactions.[9] We now describe some dmpe adducts of tetravalent zirconium and hafnium alkyls.

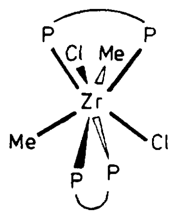
Results and Discussion

Analytical and physical data for new complexes derived by alkylation of the eight-co-ordinate tetrahalogeno-complexes, $ZrCl_4(dmpe)_2$ and $HfCl_4(dmpe)_2$,[10] are given in Table 1; ^1H n.m.r. data are collected in Table 2.

(*a*) *Methyl Compounds*.—The reaction of $ZrCl_4(dmpe)_2$ with excess $MgMe_2$ in diethyl ether gives the colourless petroleum-soluble compound $ZrMe_2Cl_2(dmpe)_2$ in high yield. This complex, like others described here, is sensitive to oxygen, and is particularly sensitive to moisture. The ^1H n.m.r. spectrum of the dimethyldichloro-complex shows two different dmpe methyl (PMe_2) environments and two different dmpe methylene (PCH_2) environments, while the Zr–Me resonance appears as a complex pattern at δ −0.42 p.p.m. If we assume a D_{2d} dodecahedral geometry (see below), two different isomers are possible, one with C_{2v} symmetry (1a) and one with C_2 symmetry (1b). The appearance of only two dmpe methyl environments is most consistent with the adoption of the higher-symmetry structure (1a).



(1a)



(1b)

Excess $MgMe_2$ does not result in alkylation beyond the dimethyl stage, presumably a consequence of the mild nature of dialkylmagnesium reagents. By contrast, alkylation with four equivalents of methyl-lithium rapidly generates $ZrMe_4(dmpe)_2$. This colourless diamagnetic compound is somewhat thermally sensitive and its hydrocarbon solutions decompose over several hours at room temperature. However, the solid may be stored indefinitely at −20 °C under argon.

The i.r. spectrum of $ZrMe_4(dmpe)_2$ contains bands at 2 785m, 1 103s, 512s, and 388m cm^{-1} that do not appear for $ZrCl_4(dmpe)_2$. The first of these bands is assignable to a C–H stretching mode, although it is slightly low in frequency for a methyl group bound to a transition metal. This is possibly due to a perturbation of the electron density in the C–H bonds as a result of the electropositive nature of zirconium. The other three bands may be assigned to various δ_{CH} and ν_{ZrC} modes.

The ^1H n.m.r. spectrum at room temperature indicates that reversible phosphine dissociation is occurring since the Zr–Me resonance is a narrow singlet and the dmpe resonances resemble those of the free phosphine. At −60 °C, the Zr–Me

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† Bis[1,2-bis(dimethylphosphino)ethane-*PP'*]tetramethylzirconium(IV) and tetrabenzyl[1,2-bis(dimethylphosphino)ethane-*PP'*]zirconium(IV).

Supplementary data available (No. SUP 56052, 7 pp.): thermal parameters, H-atom co-ordinates, full bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Analytical data for the new complexes

		Analysis [a] (%)		
Complex	M.p. (θ_c/°C)	C	H	P
$ZrMe_2Cl_2(dmpe)_2$	150 (decomp.)	33.9	7.7	24.7 [b]
		(34.1)	(7.8)	(25.2)
$ZrMe_4(dmpe)_2$	110 (decomp.)	42.4	9.8	26.9
		(42.5)	(9.8)	(27.4)
$HfMe_4(dmpe)_2$	110 (decomp.)	35.5	8.1	22.8
		(35.7)	(8.2)	(23.0)
$Zr(CH_2SiMe_3)_4(dmpe)$	50—52	44.5	10.3	10.6 [c]
		(44.8)	(10.3)	(10.5)
$Zr(CH_2Ph)_4(dmpe)$	155 (decomp.)	67.0	7.3	10.0
		(67.4)	(7.3)	(10.2)

[a] Required values are in parentheses. [b] Cl, 14.4 (14.4%). [c] Si, 20.8 (19.0%).

Table 2. Proton n.m.r. data for the new complexes [a]

Complex	δ/p.p.m.	Assignment
$ZrMe_2Cl_2(dmpe)_2$	1.50 ('t', 20.8)	PCH_2
	1.24 (m)	PCH_2
	1.37 (d, 7.7)	PMe
	1.12 (s)	PMe
	−0.42 (m)	ZrMe
$ZrMe_4(dmpe)_2$ [b]	1.35 ('t', 11.7)	PCH_2
	0.96 (s)	PMe
	−0.80 [c]	ZrMe
$HfMe_4(dmpe)_2$ [b]	1.38 ('t', 10.4)	PCH_2
	1.02 (s)	PMe
	−0.79 [c]	HfMe
$Zr(CH_2SiMe_3)_4(dmpe)$	1.26 ('t', 8.3)	PCH_2
	0.81 ('t', 1.8)	PMe
	0.23 (s)	$SiMe_3$
	1.00 (s)	$ZrCH_2$
$Zr(CH_2Ph)_4(dmpe)$	1.17 ('t', 11.3)	PCH_2
	0.75 (s)	PMe
	6.73 (d, 7.3)	*o*-CH
	7.13 (t, 7.3)	*m*-CH
	6.93 (t, 7.3)	*p*-CH
	1.85 (s)	$ZrCH_2$

[a] In C_6D_6 at 25 °C unless otherwise specified. Multiplicities enclosed in inverted commas indicate non-binomial intensities and the number following is the separation between outer lines (Hz). [b] In $C_6D_5CD_3$, −60 °C. [c] See text.

resonance appears as a symmetrical five-line pattern that approximates to a binomial quintet except that the spacings between the lines are not equal. The spacing between components 1 and 2 (or between components 4 and 5) is 8.21 Hz, while that between components 2 and 3 (or 3 and 4) is 6.47 Hz. This is evidently a second-order pattern corresponding to the X part of an $X_3X'_3X''_3X'''_3AA'A''A'''$ spin system: while an analysis was not attempted, it is apparent that the molecule is not fluxional at −60 °C.

The ^{13}C-{^1H} n.m.r. spectrum at −60 °C contains resonances due to dmpe and a singlet at δ 14.5 due to the Zr–Me groups. The methyl groups should appear as the X part of an A_2BCX spin system and the lack of phosphorus coupling may mean that all the J_{PC} coupling constants are zero. More likely, however, is the possibility that some of the coupling constants have negative signs so that only their sum is zero. The ^{31}P-{^1H} n.m.r. spectrum of $ZrMe_4(dmpe)_2$ at −60 °C shows a singlet at δ −11.3, as expected. The co-ordination chemical shift relative to free dmpe (δ −49.4) is accordingly +38.1 p.p.m.

The reaction of $HfCl_4(dmpe)_2$ with four equivalents of LiMe gives $HfMe_4(dmpe)_2$, whose spectroscopic properties resemble those of $ZrMe_4(dmpe)_2$. Thus, the i.r. spectrum contains bands at 2 892m, 1 122s, 530s, and 386s cm^{-1} assignable to the Hf–Me groups, and the n.m.r. parameters are essentially unchanged. Both $ZrMe_4(dmpe)_2$ and $HfMe_4(dmpe)_2$ also resemble the thorium analogue.[11]

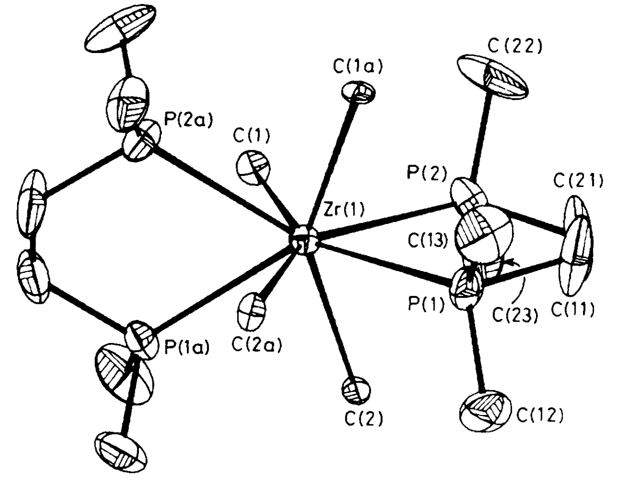

Figure 1. Structure of $ZrMe_4(dmpe)_2$

Table 3. Bond lengths (Å) and angles (°) for $ZrMe_4(dmpe)_2$*

P(1)–Zr(1)	2.815(5)	P(2)–Zr(1)	2.812(6)
C(1)–Zr(1)	2.430(8)	C(2)–Zr(1)	2.449(8)
C(11)–P(1)	1.803(16)	C(12)–P(1)	1.808(15)
C(13)–P(1)	1.832(16)	C(21)–C(11)	1.346(24)
C(21)–P(2)	1.818(18)	C(22)–P(2)	1.857(18)
C(23)–P(2)	1.809(16)		
P(2)–Zr(1)–P(1)	69.4(2)	P(1)–Zr(1)–P(1a)	133.3(1)
P(1a)–Zr(1)–P(2)	130.7(1)	P(2)–Zr(1)–P(2a)	135.7(1)
C(1)–Zr(1)–P(1)	142.9(2)	C(1)–Zr(1)–P(2)	73.6(3)
C(1)–Zr(1)–P(1a)	75.0(3)	C(1)–Zr(1)–P(2a)	76.6(3)
C(2)–Zr(1)–P(1)	75.4(3)	C(2)–Zr(1)–P(2)	73.8(3)
C(2)–Zr(1)–P(1a)	73.2(3)	C(2)–Zr(1)–P(2a)	142.5(2)
C(2)–Zr(1)–C(1)	96.8(4)	C(1)–Zr(1)–C(1a)	94.4(4)
C(1)–Zr(1)–C(2a)	143.9(3)	C(2)–Zr(1)–C(2a)	94.2(3)
C(11)–P(1)–Zr(1)	113.0(6)	C(12)–P(1)–Zr(1)	118.4(6)
C(12)–P(1)–C(11)	103.3(10)	C(13)–P(1)–Zr(1)	118.5(6)
C(13)–P(1)–C(11)	102.7(11)	C(13)–P(1)–C(12)	98.5(9)
C(21)–C(11)–P(1)	120.7(14)	C(21)–P(2)–Zr(1)	113.7(7)
C(22)–P(2)–Zr(1)	117.2(7)	C(22)–P(2)–C(21)	106.2(10)
C(23)–P(2)–Zr(1)	117.9(5)	C(23)–P(2)–C(21)	100.7(9)
C(23)–P(2)–C(22)	98.7(9)	P(2)–C(21)–C(11)	117.2(11)

* The 'a' atoms are related to the parent atom by the molecular two-fold axis.

The geometry of $ZrMe_4(dmpe)_2$ was determined by an *X*-ray crystal structure determination. A view of the molecule is given in Figure 1, while important bond distances and angles are included in Table 3.

Although the cell dimensions differ quite considerably, the complex is isostructural with the analogous tantalum complex, $TaCl_4(dmpe)_2$, which has been shown to have a slightly distorted square-antiprismatic geometry.[12] In spite of the isostructurality there are differences between the bonding geometry of the methyl and chloro-ligands in the two complexes and we find it preferable to define the geometry of our complex as dodecahedral. With reference to the standard descrip-

Table 4. Least-squares plane data for $ZrMe_4(dmpe)_2$ and $TaCl_4(dmpe)_2$.† Atoms used to define the planes are marked (*); deviations are in Å

	$ZrMe_4(dmpe)_2$			$TaCl_4(dmpe)_2$	
Zr(1)	−0.007 *	0.007 *	Ta(1)	−0.001 *	−0.001 *
P(1)	−0.052 *	1.624	P(1)	0.307 *	1.623
P(1a)	1.624	−0.052 *	P(1a)	1.623	0.307 *
P(2)	0.054 *	−1.575	P(2)	−0.303 *	−1.529
P(2a)	−1.575	0.054 *	P(2a)	−1 529	−0.303 *
C(1)	−0.034 *	−2.324	Cl(1)	0.199 *	−2.383
C(1a)	−2.324	−0.034 *	Cl(1a)	−2.383	0.199 *
C(2)	−2.313	−0.040 *	Cl(2)	2.357	−0.202 *
C(2a)	−0.040 *	−2.313	Cl(2a)	−0.202 *	2.357

Interplanar angle 89.56° Interplanar angle 87.9°

† Data from ref. 12.

tion of this geometry,[13] the methyl groups occupy the (B) sites and the chelating phosphines the (A) sites of the trapezia [which are defined by the planes P(1),P(2),C(1),C(2a) and P(1a),P(2a),C(1a),C(2)]. The planarity of the two five-atom groups (*i.e.* the two sets of four previously mentioned, with the addition of the metal atom in each case) is seen in Table 4. The angle between the two planes is 89.56°. The differences between this and the Ta structure [12] are revealed when the data for the latter are analysed similarly. Thus, deviations from the trapezial planes are greater (up to 0.3 Å) and the interplanar dihedral angle (87.9°) is further from the ideal 90°. The differences between the two structures may be yet further evidence that Ta–P π back-bonding,[12] although involving only one *d* electron, may be important enough to cause distortion from the dodecahedral structure towards the square-antiprismatic structure. It is worth noting that when π-bonding ligands are present in a dodecahedral structure, the B sites would be preferred.[14]

The average Zr–C distance in $ZrMe_4(dmpe)_2$, 2.440(6) Å, is slightly greater than the values of 2.25—2.37 Å observed for other Zr–C(sp^3) bonds,[15] and this lengthening must be ascribed to the high co-ordination number of this complex.[16] The Zr–P distances are also rather long at 2.814(1) Å and reflect the mismatch between the hard acid Zr^{IV} and the soft base dmpe. This distance may be compared with those of 2.77—2.86 Å in other zirconium phosphine complexes.[17,18]

(*b*) *Trimethylsilylmethyl Compounds.*—The reaction of $ZrCl_4(dmpe)_2$ with excess $LiCH_2SiMe_3$ gives the colourless petroleum-soluble $Zr(CH_2SiMe_3)_4(dmpe)$. The reduction from eight- to six-co-ordination is due to the large size of CH_2SiMe_3 *vs.* CH_3 so that only one dmpe ligand can be accommodated in the co-ordination sphere.[19] Even this remaining phosphine is not bound securely, since the ^1H n.m.r. spectrum at room temperature indicates reversible phosphine dissociation; reducing the temperature to −50 °C did not result in freezing out of this process. The i.r. spectrum of $Zr(CH_2SiMe_3)_4(dmpe)$ contains weak features at 1 920 and 1 850 cm^{-1} that could possibly be due to distorted alkyl groups, and interactions between the zirconium atom and α-protons on the alkyl groups might be expected based on the structure of isoelectronic $TiMeCl_3(dmpe)$.[9] However, very weak bands in these regions do also occur in i.r. spectra of liquid $M(CH_2SiMe_3)_4$ (M = Sn or Pb).[4] Unfortunately, we have not obtained crystals of the zirconium complex suitable for crystallographic studies.

(*c*) *Benzyl Compounds.*—Tetrabenzylzirconium is known to form adducts with various amines and ethers,[20] and similarly interaction of $Zr(CH_2Ph)_4$ with dmpe in toluene [21] leads to the yellow adduct $Zr(CH_2Ph)_4(dmpe)$. The ^1H n.m.r. spectrum at room temperature again indicates that reversible phosphine dissociation is occurring on the n.m.r. time-scale. Low-temperature studies were precluded because the complex is too insoluble in toluene for spectra to be obtained. However, the i.r. spectrum again shows weak absorbances between 1 800 and 2 000 cm^{-1}, but in this case various combination and overtone modes involving the phenyl groups are expected to appear in this region. In order to unambiguously define the geometry of this complex, we have carried out an *X*-ray crystallographic determination.

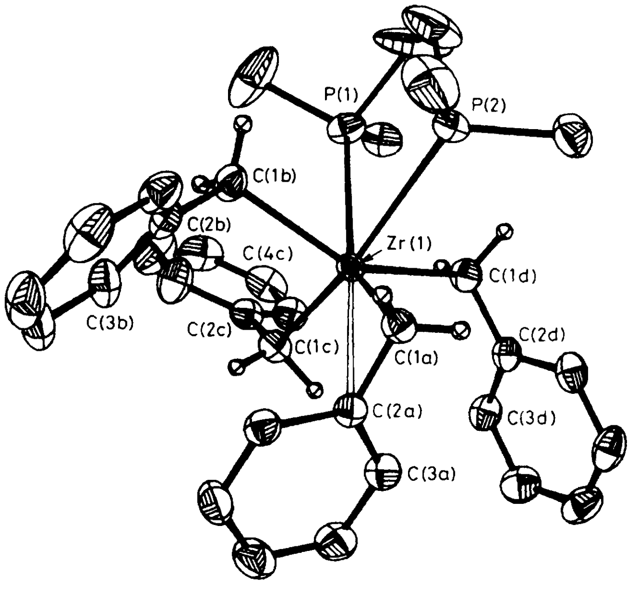

Figure 2. Structure of $Zr(CH_2Ph)_4(dmpe)$

A view of $Zr(CH_2Ph)_4(dmpe)$ is given in Figure 2, while important bond lengths and angles appear in Table 5. The geometry is based on a strongly distorted *cis*-octahedron, with two axial and two equatorial benzyl groups.

The two Zr–P bonds show a small but significant difference in length but surprisingly both are longer than those in the $ZrMe_4(dmpe)_2$, despite the lower co-ordination number. However, the Zr–C bonds in the benzyl derivative are shorter, but quite variable, reflecting perhaps significant differences in inter-ligand steric interactions. It is particularly interesting to compare this structure with those of the tetrabenzyls, MR_4 (M = Ti,[5c,d] Zr,[15a] Hf,[5d] or Sn [5d]). In the transition-metal complexes, the severe metal electron deficiency results in intramolecular interactions of varying amounts between the metal and the π systems of the four benzyl Ph rings. No such interactions occur in the tin compound. Even with the formation of the present diphosphine adduct, the electron count on the metal is formally only 12, and in spite of the greater steric crowding in the co-ordination sphere there is strong evidence for one similar interaction involving the benzyl ligand (a). Thus the Zr–C(1a)–C(2a) angle is 94.2(4)° and the Zr ··· C(2a) distance is 2.788(8) Å whereas the Zr–C(1)–C(2) angles for the other three ligands are 116.6(4), 122.1(4), and 111.1(4)°. It is possible that this difference between the one π-interacting benzyl and the remainder is the cause of the small difference between the Zr–P bond lengths, the longer of which is *trans* to the π interaction (see Figure 2). One final point of note is that although with only one π interaction to supplement the 12-electron count, there is no evidence to suggest that any of the

Table 5. Selected bond lengths (Å) and angles (°) for $Zr(CH_2Ph)_4$-(dmpe)

P(1)–Zr(1)	2.885(4)	P(2)–Zr(1)	2.862(4)
C(1a)–Zr(1)	2.264(7)	C(2a)–Zr(1)	2.788(8)
C(1b)–Zr(1)	2.359(6)	C(1c)–Zr(1)	2.312(6)
C(1d)–Zr(1)	2.368(5)	C(11)–P(1)	1.812(7)
C(12)–P(1)	1.810(10)	C(13)–P(1)	1.844(12)
C(23)–C(13)	1.361(17)	C(21)–P(2)	1.808(7)
C(22)–P(2)	1.835(9)	C(23)–P(2)	1.791(16)
C(2a)–C(1a)	1.468(7)	C(2b)–C(1b)	1.485(7)
C(2c)–C(1c)	1.474(8)	C(2d)–C(1d)	1.485(7)

P(2)–Zr(1)–P(1)	69.9(1)	C(1a)–Zr(1)–P(1)	145.6(1)
C(1a)–Zr(1)–P(2)	75.8(2)	C(2a)–Zr(1)–P(1)	175.3(1)
C(2a)–Zr(1)–P(2)	107.4(2)	C(1b)–Zr(1)–P(1)	73.4(2)
C(1b)–Zr(1)–P(2)	82.6(2)	C(1b)–Zr(1)–C(1a)	100.7(3)
C(1b)–Zr(1)–C(2a)	102.7(2)	C(1c)–Zr(1)–P(1)	95.7(3)
C(1c)–Zr(1)–P(2)	165.5(2)	C(1c)–Zr(1)–C(1a)	118.8(3)
C(1c)–Zr(1)–C(2a)	87.2(3)	C(1c)–Zr(1)–C(1b)	94.5(3)
C(1d)–Zr(1)–P(1)	74.0(2)	C(1d)–Zr(1)–P(2)	82.0(2)
C(1d)–Zr(1)–C(1a)	103.4(3)	C(1d)–Zr(1)–C(2a)	109.6(2)
C(1d)–Zr(1)–C(1b)	147.1(2)	C(1d)–Zr(1)–C(1c)	93.2(3)
C(11)–P(1)–Zr(1)	121.1(3)	C(12)–P(1)–Zr(1)	119.9(4)
C(12)–P(1)–C(11)	100.0(5)	C(13)–P(1)–Zr(1)	109.0(6)
C(13)–P(1)–C(11)	100.6(5)	C(13)–P(1)–C(12)	103.4(7)
C(23)–C(13)–P(1)	121.8(10)	C(21)–P(2)–Zr(1)	119.5(3)
C(22)–P(2)–Zr(1)	117.3(3)	C(22)–P(2)–C(21)	99.4(4)
C(23)–P(2)–Zr(1)	113.2(3)	C(23)–P(2)–C(21)	103.4(4)
C(23)–P(2)–C(22)	101.4(5)	P(2)–C(23)–C(13)	115.7(10)
C(2a)–C(1a)–Zr(1)	94.2(4)	C(3a)–C(2a)–Zr(1)	100.7(4)
C(7a)–C(2a)–Zr(1)	111.4(4)	C(2b)–C(1b)–Zr(1)	116.6(4)
C(2c)–C(1c)–Zr(1)	122.1(4)	C(2d)–C(1d)–Zr(1)	111.1(4)

C–H bonds on the methylene carbons are interacting, since all Zr–C–H angles are near 100°.

The majority of alkyl derivatives of the Group 4 elements are cyclopentadienyl complexes of stoicheiometry $MR_2(\eta\text{-}C_5H_5)_2$. Such 16-electron species are in essence co-ordinatively saturated, and as a result do not contain $M \cdots H\text{–}C$ interactions. By contrast, crystallographic investigations of low-electron-count Group 4 alkyls were, until recently, limited to certain benzyl derivatives in which the unsaturation of the metal centre was satisfied by the π electrons in the phenyl rings.[5b,c,15a,22] It is accordingly something of a historical accident that $M \cdots H\text{–}C$ interactions involving distorted alkyl groups[9] were not discovered long ago, since such distortions * may be anticipated in low-electron-count alkyls of the early transition elements and their adducts with various donor ligands.

Experimental

Microanalyses were by Pascher (Bonn). N.m.r. spectra were recorded on a Bruker WM 250 spectrometer in deuteriotoluene at −60 °C unless otherwise noted; positive chemical shifts (δ/p.p.m.) downfield of $SiMe_4$ (^1H, ^{13}C) or external 85% H_3PO_4 (^{31}P). I.r. spectra were recorded on a Perkin-Elmer 683 spectrometer (Nujol mulls). Melting points are uncorrected, and were determined in closed capillaries under argon. All operations were carried out *in vacuo* or under purified argon. Solvents were distilled from sodium (toluene) or sodium–benzophenone (petroleum, diethyl ether) under nitrogen immediately before use. The petroleum used had a b.p. of 40—60 °C.

Literature routes were used for 1,2-bis(dimethylphosphino)ethane,[23] dimethylmagnesium,[24] methyl-lithium,[25] trimethylsilylmethyl-lithium,[26] $ZrCl_4(dmpe)_2$,[10] $HfCl_4(dmpe)_2$,[10] and $Zr(CH_2Ph)_4$.[5b]

(1) *Bis*[1,2-*Bis*(*dimethylphosphino*)*ethane*]*dichlorodimethylzirconium*(IV).—To $ZrCl_4(dmpe)_2$ (0.12 g, 0.22 mmol) in diethyl ether (50 cm^3) at −78 °C was added $MgMe_2$ (0.4 cm^3 of a 0.62 mol dm^{-3} solution in Et_2O, 0.25 mmol). The solution was allowed to warm to room temperature, and was stirred for 12 h. The solvent was removed, and the residue extracted with petroleum (50 cm^3). The filtered extract was concentrated to *ca.* 10 cm^3 and cooled to −20 °C to give colourless prisms of the complex. Yield: 0.07 g, 63%.

(2) *Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*tetramethylzirconium*(IV).—To $ZrCl_4(dmpe)_2$ (0.51 g, 0.97 mmol) in Et_2O (50 cm^3) was added LiMe (4.0 cm^3 of a 1.1 mol dm^{-3} solution in Et_2O, 4.40 mmol). The solution was stirred for 4 h and the solvent removed; the residue was extracted with petroleum (2 × 40 cm^3) and the combined extracts filtered, concentrated to *ca.* 20 cm^3, and cooled to −20 °C. Colourless prisms of the complex were isolated, and a second crop of crystals was obtained by concentration and cooling of the supernatant. Yield: 0.32 g, 72%. N.m.r.: $^{13}C\text{-}\{^1H\}$, 27.1 ('t', outer line separation 25 Hz, PCH_2), 11.5 (s, PMe), 14.5 (s, Zr–Me); $^{31}P\text{-}\{^1H\}$, −11.3 (s).

(3) *Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*tetramethylhafnium*(IV).—To $HfCl_4(dmpe)_2$ (0.49 g, 0.84 mmol) in Et_2O (50 cm^3) was added LiMe (3.5 cm^3 of a 1.0 mol dm^{-3} solution in Et_2O, 3.50 mmol), and the solution stirred for 4 h. The product was treated as above to give colourless prisms of the complex. Yield: 0.31 g, 68%. N.m.r.: $^{13}C\text{-}\{^1H\}$, 26.3 ('t', outer line separation 28.3 Hz, PCH_2), 10.5 (s, PMe), 18.7 (s, Hf–Me); $^{31}P\text{-}\{^1H\}$, −10.2 (s).

(4) [1,2-*Bis*(*dimethylphosphino*)*ethane*]*tetrakis*(*trimethylsilylmethyl*)*zirconium*(IV).—To $ZrCl_4(dmpe)_2$ (0.67 g, 1.26 mmol) in Et_2O (50 cm^3) was added $LiCH_2SiMe_3$ (5.3 cm^3 of a 0.95 mol dm^{-3} solution in petroleum, 5.04 mmol). The solution was stirred for 12 h, and the solvent removed. The residue was extracted with petroleum (50 cm^3), and the filtered extract concentrated to *ca.* 5 cm^3, and cooled to −20 °C to give colourless prisms of the complex. Yield: 0.42 g, 56%.

(5) *Tetrabenzyl*[1,2-*bis*(*dimethylphosphino*)*ethane*]*zirconium*(IV).—To $Zr(CH_2Ph)_4$ (0.36 g, 0.79 mmol) in toluene (50 cm^3) was added dmpe (0.3 cm^3, 2.00 mmol). The yellow solution was stirred for 30 s and then allowed to stand. Crystallization began after a few minutes, and was completed by cooling to −20 °C to give yellow-orange prisms of the complex. Yield: 0.42 g, 88%. The hafnium analogue was prepared similarly, but was not investigated further.

Crystallographic Studies.—Crystals of both compounds were sealed under argon in Lindemann capillaries. All crystallographic measurements were made using a CAD4 diffractometer, operating in the ω—2θ scan mode with graphite-

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* A distorted *bridged* alkyl was observed in $Cr_2(CH_2SiMe_3)_4(PMe_3)_2$ (R. A. Andersen, R. A. Jones, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1978, 1977) although provisionally ascribed to packing effects in the crystal; other similar distortions in bridged manganese alkyls have been ascribed to $M \cdots H\text{–}C$ interactions (G. C. Howard, G. Wilkinson, M. Thornton-Pett, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1983, 2025). The first metal interaction with C–H bonds of a ligand recognised was that in $Pd(PPh_3)_2[C_4(CO_2Me)_4H]Br$ (D. M. Roe, P. M. Bailey, K. Mosely, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1972, 1273) and many others have been established [see R. G. Teller and R. Bau, *Struct. Bonding (Berlin)*, 1981, **44**, 1; M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, **250**, 395].

Table 6. Fractional atomic co-ordinates ($\times 10^4$) for $ZrMe_4(dmpe)_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zr(1)	5 000	5 000	7 334(1)	C(21)	8 126(12)	6 366(12)	7 067(28)
P(1)	6 067(2)	6 832(2)	8 591(3)	C(22)	7 402(17)	5 578(15)	4 087(19)
C(11)	7 500(14)	7 130(18)	7 782(26)	C(23)	8 335(10)	4 213(12)	6 261(20)
C(12)	6 354(15)	6 849(12)	10 593(15)	C(1)	5 295(7)	3 598(6)	5 475(8)
C(13)	5 284(17)	8 114(9)	8 440(20)	C(2)	6 392(6)	4 299(6)	9 211(9)
P(2)	7 290(3)	5 310(2)	6 139(4)				

Table 7. Fractional atomic co-ordinates ($\times 10^4$) for $Zr(CH_2Ph)_4(dmpe)$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zr(1)	3 878(0.5)	1 831(0.5)	1 805(0.5)	C(4b)	8 590(5)	4 307(4)	3 719(6)
P(1)	2 180(1)	2 925(1)	1 617(1)	C(5b)	9 403(5)	4 596(4)	2 869(6)
C(11)	568(5)	2 336(5)	2 077(5)	C(6b)	8 873(5)	4 570(4)	1 733(7)
C(12)	2 767(7)	4 278(5)	2 292(11)	C(7b)	7 537(4)	4 274(3)	1 420(5)
C(13)	1 737(10)	3 054(11)	46(9)	C(1c)	3 949(5)	1 713(4)	3 820(4)
P(2)	3 334(1)	2 207(1)	−601(1)	C(2c)	3 263(4)	2 164(3)	4 532(3)
C(21)	2 339(6)	1 087(5)	−1 669(4)	C(3c)	1 969(5)	1 592(4)	4 684(4)
C(22)	4 742(7)	2 865(7)	−1 392(6)	C(4c)	1 299(6)	2 037(6)	5 311(5)
C(23)	2 534(11)	3 088(8)	−770(5)	C(5c)	1 919(7)	3 064(5)	5 801(5)
C(1a)	5 053(4)	1 177(3)	823(3)	C(6c)	3 198(8)	3 639(5)	5 682(6)
C(2a)	5 660(3)	907(3)	1 894(3)	C(7c)	3 867(6)	3 206(4)	5 063(5)
C(3a)	4 988(4)	−24(3)	2 439(4)	C(1d)	1 710(4)	475(3)	1 386(4)
C(4a)	5 522(5)	−220(4)	3 497(4)	C(2d)	1 690(3)	−604(3)	1 488(3)
C(5a)	6 728(6)	484(4)	4 047(4)	C(3d)	1 492(4)	−1 100(3)	2 533(4)
C(6a)	7 418(5)	1 396(4)	3 527(4)	C(4d)	1 503(5)	−2 089(4)	2 646(5)
C(7a)	6 896(4)	1 610(3)	2 482(4)	C(5d)	1 713(5)	−2 620(4)	1 710(6)
C(1b)	5 257(4)	3 680(3)	1 972(5)	C(6d)	1 893(4)	−2 156(4)	676(5)
C(2b)	6 687(4)	3 992(3)	2 275(4)	C(7d)	1 888(4)	−1 170(3)	552(4)
C(3b)	7 257(4)	4 022(4)	3 422(5)				

monochromated Mo-K_{α} radiation ($\lambda = 0.710\,69$ Å) in a manner previously described in detail.[27] The structures were solved, developed and refined *via* routine heavy-atom and least-squares methods using standard programs. For the refinement of the tetramethyl compound, hydrogen atoms could not be located experimentally and none was included. For the benzyl complex all hydrogens were located experimentally and refined with individual isotopic thermal parameters. The weighting scheme $w = 1/[\sigma^2(F_o) + g(F_o)^2]$ was used in each case, with the value of g determined in the refinement process, so as to give acceptable agreement analyses.

Crystal data for $ZrMe_4(dmpe)_2$. $C_{16}H_{44}P_4Zr$, $M = 451.2$, orthorhombic, $a = 12.490(3)$, $b = 11.245(1)$, $c = 8.882(3)$ Å, $U = 1\,247.5$ Å^3, space group $P2_12_12$, $Z = 2$ (molecular symmetry C_2), $D_c = 1.20$ g cm^{-3}, μ(Mo-K_{α}) = 5.25 cm^{-1}, $F(000) = 420$, $T = 295$ K.

Data collection. Scan width = $(0.8 + 0.35\tan\theta)^{\circ}$, $1.5 \leqslant \theta \leqslant 30^{\circ}$, scan speed 1.35—6.77° min^{-1}. 2 087 Unique data, 1 524 observed $[I > 3\sigma(I)]$.

Structure refinement. 102 Parameters, weighting factor $g = 0.005$, $R = 0.0598$, $R' = 0.0621$.

Crystal data for $Zr(CH_2Ph)_4(dmpe)$. $C_{34}H_{40}P_2Zr$, $M = 605.22$, triclinic, $a = 11.307(1)$, $b = 13.773(1)$, $c = 11.452(1)$ Å, $\alpha = 91.713(8)$, $\beta = 96.750(9)$, $\gamma = 114.47(8)^{\circ}$, $U = 1\,605.8$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.25$ g cm^{-3}, μ(Mo-K_{α}) = 4.22 cm^{-1}, $F(000) = 636$, $T = 293$ K.

Data collection. Scan width = $(0.8 + 0.35\tan\theta)^{\circ}$, $1.5 \leqslant \theta \leqslant 25.0^{\circ}$, scan speed 1.35—6.77° min^{-1}. 5 639 Unique data, 4 694 observed $[I > 3\sigma(I)]$.

Structure refinement. 502 Parameters, weighting factor $g = 0.0005$, $R = 0.0363$, $R' = 0.0391$.

Final atomic co-ordinates are given in Tables 6 and 7.

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