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SYNTHESIS, CRYSTAL STRUCTURES AND SOME REACTIONS OF ZEROVALENT TRIS[BIS-1,2-(DIMETHYLPHOSPHINO)ETHANE] DERIVATIVES OF CHROMIUM, MOLYBDENUM, TUNGSTEN, VANADIUM, NIOBIUM AND TANTALUM

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Summary

Co-condensation of the vapours of the metals M = Cr, Mo, W, V, Nb, Ta with an excess of bis-1,2-(dimethylphosphino)ethane (dmpe) gives the neutral, zerovalent compounds $M(dmpe)_3$. X-ray structure analysis shows that the crystals are isomorphous (cubic, space group *Im*3*m*, *a* 10.922(3), 11.058(5), 11.040(5), 11.041(3), 11.194(4) and 11.164(3) Å respectively) and contain isolated molecules which have an essentially octahedral distribution of the six phosphorus atoms about the metal centre. The compound $Cr(dmpe)_3$ reacts with methyl iodide giving *trans*-$CrI_2(dmpe)_2$. $Mo(dmpe)_3$ reacts with hydrochloric acid forming the dihydrido derivative isolated as the hexafluorophosphate salt $[Mo(dmpe)_3H_2][PF_6]_2$. $Mo(dmpe)_3$ also reacts with iodine or methyl iodide forming the paramagnetic cation $[Mo(dmpe)_3]^+$ which was isolated as the hexafluorophosphate salt.

Introduction

The tertiary diphosphine ligand $Me_2PCH_2CH_2PMe_2$ (dmpe) is well known to act as a chelate ligand to transition metal centres in a variety of normal oxidation states but, in particular, it can stabilize zero- and low-valent states of the transition metals.

The pioneering use of this ligand by Chatt and co-workers is exemplified by the synthesis of the compounds $M(dmpe)_3$ (M = Cr, Mo and W) [1].

The dmpe ligand is more electron-releasing (basic) than most tertiary phosphine ligands so that the d^n electrons in its low-valent metal compounds have relatively

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high energies, i.e. dmpe complexes tend to have electron-rich metal centres. We have used the dmpe ligand to assist in the stabilisation of transition metal-dinitrogen systems [2,3] and in the provision of transition metal centres which will activate saturated carbon–hydrogen bonds [4]. Similarly, Chatt and Tolman have shown that the metal centres in the systems $M(dmpe)_2$ ($M = Fe$ or Ru) will insert into carbon–hydrogen bonds [5,6].

Here we describe a study of the reaction between dmpe and metal atoms which has been carried out in order to synthesise new electron-rich, low-valent transition metal compounds of the earlier transition metals and to explore their properties. A preliminary account of part of this work has appeared [6].

Results and discussion

Co-condensation of the vapours of the metals $M = Cr$, Mo, W, V, Nb or Ta, generated from an electron-gun furnace operating at a positive potential [7], with an excess of dmpe gives excellent yields of the neutral compounds $[M(dmpe)_3]$ ($M = Cr$ (**1**), Mo (**2**), W (**3**), V (**4**), Nb (**5**) and Ta (**6**)). All these metal atom reactions gave yields of ca. 50%, based on metal arriving at the co-condensation surface, which are higher than those in the formation of bis-benzene-metal compounds $[M(\eta\text{-}C_6H_6)_2]$ from co-condensation of the metal with excess of benzene (typically ca. 30%) [7]. The new compounds $M(dmpe)_3$ ($M = Nb$ and Ta) form highly air-sensitive dark red crystals.

The ESR spectra of the compounds **4** and **5** show the compounds are para-

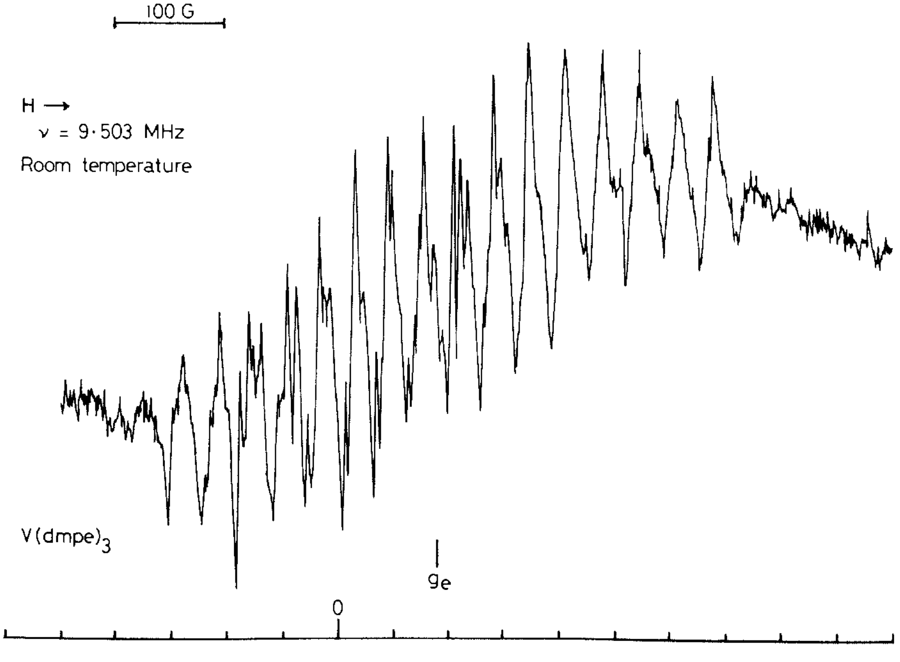


Fig. 1. ESR (9.504 GHz, modulation amplitude 8 G) spectrum of $V(dmpe)_3$ at room temperature in toluene (maximum gain).

magnetic. V(dmpe)$_3$ in toluene solution at room temperature exhibits a very weak ESR spectrum (Fig. 1) containing at least eighteen lines ($\langle a \rangle_{\rm iso}$ = 30–24 G) centred at $\langle g \rangle$ = ca. 2.0. This spectrum is superimposed on a broad impurity feature which could be reduced in intensity but not eliminated by recrystallisation. The intensity of the spectrum increased about a hundred fold at 77 K (Fig. 2) as would be expected for a rapidly relaxing d^5, ^2E_g (D_{3d} symmetry) ground state. No uniquely satisfying interpretation can be offered but the spectrum can be understood in terms of an almost isotropic coupling to ^{51}V ($I = 7/2$. $A_{\parallel}^{\rm V} = 25$, $A_{\perp}^{\rm V} = 29$ G) and anisotropic coupling to n ^{31}P nuclei ($A_{\parallel}^{\rm P} = 280/n$, $A_{\perp}^{\rm P} = 110$ G, $g_{\parallel} = 2.04$, $g_{\perp} = 2.03$) where $n = 1$ or 3. The ESR spectrum of Nb(dmpe)$_3$ was less well resolved than that of **4**. For comparison, V(CO)$_6$ gives no ESR spectrum at room temperature because of rapid relaxation of the $^2T_{2g}$ ground state [8].

The crystal structures of the compounds **1**–**6** have been determined (vide infra).

Treatment of **1** with methyl iodide gives good yields of the pale green compound *trans*-Cr(dmpe)$_2$I$_2$ (**9**). The *trans* structure is proposed on the basis of the observation of only a single band in the infrared spectrum assignable to a Mo–I stretching frequency (at 350 cm^{-1}). Only very broad bands were observed in the ^{1}H NMR spectrum suggesting that the compound is paramagnetic, as has been shown for the compound *trans*-WCl$_2$(PMe$_3$)$_4$ [9].

The compound Mo(dmpe)$_3$ (**2**) readily undergoes a one-electron oxidation on treatment with iodine forming the paramagnetic cation [Mo(dmpe)$_3$]$^+$ which was isolated as the hexafluorophosphate salt (**7**). The ^{1}H NMR spectrum of **7** shows only broad bands at δ 15, −4.2 and −15 consistent with a paramagnetic cation.

Treatment of **2** with methyl iodide also causes oxidation giving the compound [Mo(dmpe)$_3$]I which on heating to 250 °C gives a yellow-green material whose mass spectrum showed a parent ion peak at $m/e = 650$ which is consistent with the formulation [Mo(dmpe)$_2$I$_2$].

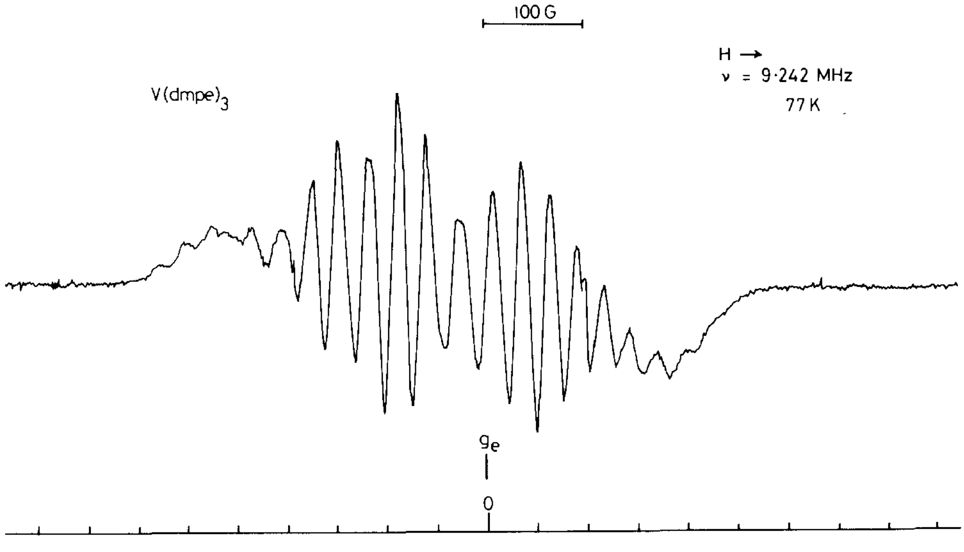


Fig. 2. ESR (9.242 GHz, modulation amplitude 4 G) spectrum of V(dmpe)$_3$ at 77 K in frozen toluene.

TABLE 1

ANALYTICAL AND SPECTROSCOPIC DATA

Compound	Colour	Analytical data (%)[a]		Selected IR data[b]
		C	H	
(**5**) Nb(dmpe)$_3$	Dark-red	39.7	8.8[c]	615vs, 910vs
		(39.8)	(8.9)	
(**6**) Ta(dmpe)$_3$	Dark-red	34.0	7.5	
		(34.2)	(7.7)	
(**8**) [Mo(dmpe)$_3$H$_2$][PF$_6$]$_2$	Yellow	26.0	6.1	1730, 1695[d e]
		(25.8)	(6.0)	
(**7**) [Mo(dmpe)$_3$]I	Light-green	30.6	7.0	
		(31.3)	(7.0)	
(**9**) Cr(dmpe)$_2$I$_2$	Green	24.7	5.3[f]	350vs[g]
		(24.7)	(5.3)	

[a] Calculated values given in parenthesis. [b] Mulls, in cm^{-1}. [c] %P: 34.0 (34.2) [d] ν(Mo–H). [e] ^{1}H NMR data (in $(CD_3)_2CO$), given as: chemical shift (τ), [relative intensity, multiplicity (J in Hz), assignment] 7.32 [12H, d, CH_2CH_2], 7.64 [36H, s, 12Me], -17.06 [2H, septet, (J(P–H) 36), MoH$_2$]. ^{31}P NMR: 79.26 ppm [singlet]. [f] %I: 41.0 (41.9). [g] ν(Cr–I).

Treatment of **2** with aqueous acid followed by addition of hexafluorophosphate gives the dihydrido compound [Mo(dmpe)$_3$H$_2$][PF$_6$]$_2$ (**8**). The compound has been characterised by the data in Table 1. In particular, the ^{1}H NMR spectrum shows a binomial septet at δ -7.06 and the infrared spectrum has a broad band between 1695–1730 cm^{-1} assignable to the Mo-hydrogens.

The ^{1}H NMR spectrum also shows the presence of very broad minor bands at δ 29, 4, -11 and -21. It was not found possible to separate this component by recrystallisation. The appearance and position of the bands suggests the presence of a paramagnetic species, possibly [Mo(dmpe)$_3$H]PF$_6$. The same bands were observed in the ^{1}H NMR spectrum of the product formed by addition of aqueous acid and hexafluorophosphate to **7** and the ^{1}H NMR spectrum also showed that some **8** had been formed.

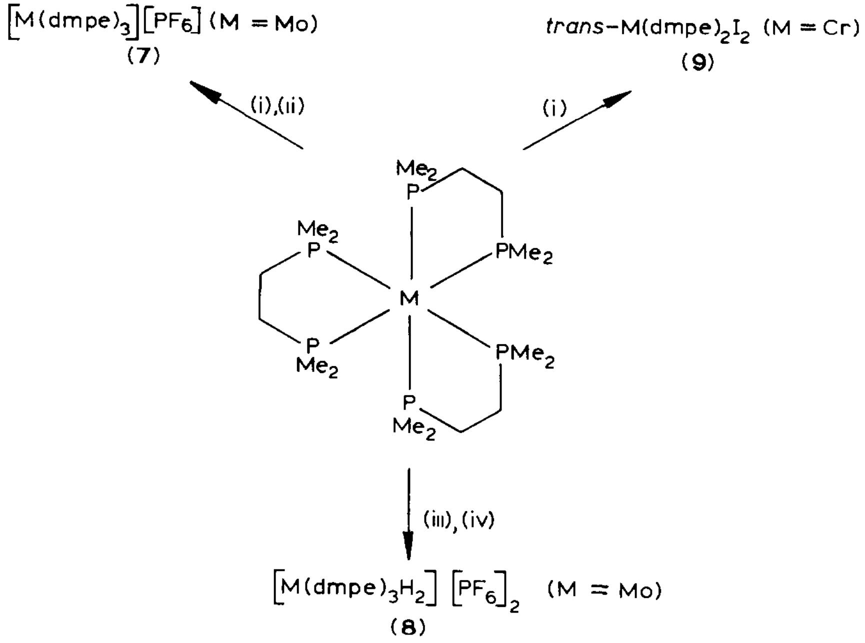
It appears that addition of acid to **2** causes mainly the addition of two protons together with oxidation giving a small quantity of **7**.

Discussion

The reactions and structures proposed for the new compounds **5**–**9** are shown in Scheme 1.

The molecular structure and atom-numbering scheme for M(dmpe)$_3$ are shown in Fig. 4. The atom labelled P(1) is in the equivalent position x, y, z; P(2) is in $y, x, \bar{z}$; P(3) in $\bar{y}, \bar{z}, x$; P(4) in $\bar{x}, z, y$; P(5) in $z, \bar{x}, \bar{y}$; P(6) in $\bar{z}, \bar{y}, \bar{x}$. The environment of the metal atom can be described as an octahedron compressed along one of its three-fold axes.

Although the 32 symmetry of the M–P bonds seems certain, it is very likely that there are various other equally good refinement models with different conformations of the dmpe ligand. The conformational possibilities for the diphosphine ligands are numerous, as shown in Fig. 3 and the high disorder observed in all the compounds **1**–**6** prevents us from ruling out these different conformations. For example it is



SCHEME 1. (i) M = Cr, Mo, W, V, Nb, Ta, yields ca. 55%. (ii) Methyl iodide in toluene at room temperature, 88%. (iii) HCl gas, 5 min then NH_4PF_6aq., > 90%. (iv) Methyl iodide in toluene, 85%.

impossible to distinguish the disordered model **c** from the disordered model **d** in an electron density map because the average electron distribution is more or less the same in both models. However, as observed in other molecules containing disordered dmpe ligands [11–13], the position of the phosphorus atoms remains the same in all conformations [10–12].

The variations in M–P bond lengths are in agreement with the expected trends. The general decrease (of ca. 0.12 Å) for the metals of all three periods from the Group Va to the Group VIa is related to the *d*-orbital penetration of core electrons and the small change from period 5 to period 6 is attributed to the lanthanide contraction. The comparison of bond lengths in $M(dmpe)_3$ with literature values (see

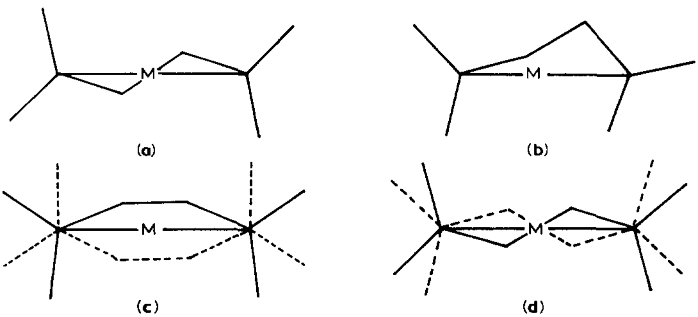


Fig. 3. Some of the possible conformations for the diphosphine ligand viewed along the P–M–P bisectrix. The dotted lines in **c** and **d** show another possible conformation in the disordered model.

TABLE 2

SELECTED BOND LENGTHS (A) AND BOND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES (The atom numbering refers to Fig. 4)

	Cr	Mo	W	V	Nb	Ta
M–P	2.313(2)	2.421(3)	2.414(6)	2.412(4)	2.526(3)	2.500(6)
P(1)–C(1)	1.88(3)	1.89(4)	1.86(5)	1.92(4)	1.96(5)	1.93(5)
P(1)–C(2)	2.00(3)	1.99(5)	2.04(7)	1.88(5)	1.90(4)	1.97(5)
P(1)–C(3)	1.93(4)	1.98(4)	1.96(6)	1.96(4)	2.06(4)	2.03(5)
C(1)–C(11)	1.46(3)	1.51(3)	1.49(3)	1.48(3)	1.49(3)	1.49(3)
M–P(1)–C(1)	115.5(7)	115(9)	116(2)	114(1)	110(2)	114(2)
M–P(1)–C(2)	120.6(7)	121(2)	122(3)	125(2)	123(2)	125(2)
M–P(1)–C(3)	123(2)	119(2)	119(2)	116(2)	110(2)	114(2)
C(1)–P(1)–C(2)	97.2(8)	98(2)	101(3)	95(2)	93(2)	96(2)
C(1)–P(1)–C(3)	99(5)	104(2)	105(2)	108(2)	116(2)	113(2)
C(2)–P(1)–C(3)	97(4)	95(3)	89(4)	94(2)	105(2)	93(3)
P(1)–C(1)–C(11)	105(1)	107(2)	108(2)	104(2)	100(3)	102(2)
P(1)–M–P(2) P(3)–M–P(4) P(5)–M–P(6)	76.0(3)	75.7(2)	75.3(5)	75.3(3)	74.6(2)	73.0(4)
P(1)–M–P(3) P(1)–M–P(5) P(2)–M–P(4) P(2)–M–P(6) P(3)–M–P(5) P(4)–M–P(6)	96.9(2)	97.10(9)	97.3(2)	97.3(2)	97.61(9)	98.4(2)
P(1)–M–P(4) P(2)–M–P(5) P(3)–M–P(6)	170.1(2)	169.9(2)	169.6(2)	169.6(10)	169.2(2)	168.0(2)
P(1)–M–P(6) P(2)–M–P(3) P(5)–M–P(4)	90.85(3)	90.89(2)	90.94(5)	90.94(4)	91.02(2)	91.25(5)

Fig. 4 and Table 2,3) shows that the metal–phosphorus distance is significantly shorter when the metal is formally zerovalent than when it is in a higher oxidation state. The observed values are ca. 0.30 Å smaller than the M–P bond lengths predicted by the sum of single-bond radii. This suggests very significant π-character in the metal–phosphorus bond arising from $d_\pi \rightarrow d_\pi$M–P back-donation.

It must be emphasized that the surprisingly low *R*-values and the small e.s.d's do not reflect a very good determination of bond angles and bond distances but show that our assumptions about the geometry of the molecules are compatible with the experimental data.

Experimental

All the reactions and manipulations were carried out under dinitrogen or in vacuo. All solvents were thoroughly dried and distilled before use. Celite 545 was supplied by Koch-Light Ltd. Microanalyses were by A. Bernhardt or by the microanalytical laboratory of this department. Infrared spectra were recorded as mulls on a Perkin–Elmer 457 instrument and were calibrated with polystyrene film. ^1H NMR spectra were determined using Bruker WH-90, JNM-PMX 0 or Bruker FT 300 spectrometers. Mass spectra were recorded on an A.E.I. M.S.9 spectrometer. Gas-liquid chromatography (GLC) was carried out on a Pye 104 chromatograph using a 10% KCl-alumina column. ESR spectra were run on a Varian E109 spectrometer calibrated with MnO in MgO. Solutions were prepared by condensing dried, deoxygenated toluene (B.D.H. Aristar) onto the recrystallised **4** or **5**, the extract being filtered directly into the ESR tube.

Each metal sample was pre-melted in the furnace hearth before use in a co-condensation experiment. This was done to remove any dissolved gases.

Bis-1,2-(dimethylphosphino)ethane

The method of Chatt et al. [26] via the reaction between $Cl_2PCH_2CH_2PCl_2$ and methylmagnesium halide was used with minor modifications. First, the compound $Cl_2PCH_2CH_2PCl_2$ was prepared in the manner reported, [27], with the following procedure which gave reliable and satisfactory yields. A 1 l stainless steel autoclave was charged with white phosphorus (29 g) and phosphorus trichloride (325 cm^3). The addition of 100 g of iron rod in the form of nails (1″) was found to improve yields. The sealed high-pressure vessel was then pressurised with 35 atm of ethylene. The temperature of the vessel was then raised slowly over a period of 6 h until the temperature was 215 °C. The reaction mixture was stirred continuously. The pressure increased with heating and when the temperature was ca. 215 °C the pressure was a maximum of ca. 110 atm. The pressure then began to decrease as the reaction proceeded. After heating at ca. 215 °C for 18 h the pressure had dropped to ca. 10 atm. The vessel was then allowed to cool to room temperature and the products were extracted with diethyl ether (4 × 400 cm^3). The extract was filtered and the more volatile components were removed from the filtrate under reduced pressure. The less

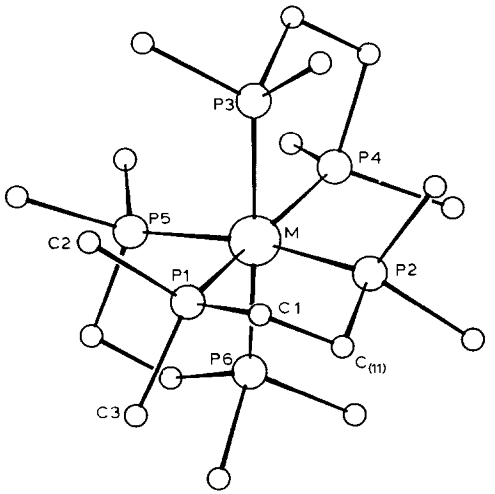


Fig. 4. The molecular structure of $M(Me_2PCH_2CH_2PMe_2)_3$. The atoms labelled P(2), P(3), P(4), P(5) and P(6) are related to P(1) by the operations $y, x, 0$; $\bar{y}, 0, x$; $x, 0, y$; $0, \bar{x}, \bar{y}$ and $0, \bar{y}, \bar{x}$ respectively and the atom labelled C(11) to that labelled C(1) by the operation $y, x, \bar{z}$.

volatile fraction (ca. 150 cm^3) was placed in a greaseless distillation apparatus and the fraction which distilled at ca. 23–24 °C (1 mmHg, ca. 20 g) was discarded. The second major fraction distilling at 68–70 °C and 1.0 mmHg was collected. Yield 139 cm^3, 29.8% based on phosphorus.

Synthesis of M(dmpe)$_3$ (M = Cr, Mo, W, V, Nb, and Ta, (1–6) using the metal atoms

The co-condensation reactions with the metal atoms were carried out using the apparatus described [7].

The pre-melted metal ingot and the furnace lid were weighed before and after each experiment in order to ascertain the quantity of metal leaving the furnace. It is assumed that all the metal leaving the furnace is available for reaction with the cocondensate. In a typical experiment, 2–3 g of metal were co-condensed into 30–40 cm^3 of dmpe. After the co-condensation reaction had been terminated (normally after about a 3–4 h run), the walls of the reaction vessel were allowed to warm to room temperature and the product was extracted by washing the vessel out with tetrahydrofuran. The tetrahydrofuran extract was filtered through a Celite bed to remove any unreacted metal and the volatile components of the filtrate were distilled under reduced pressure. The excess of dmpe was thus separated from the involatile reaction products and was recovered from the tetrahydrofuran by a distillation. The involatile residues, which were dark-brown oils, were then placed in a Soxhlet thimble and were extracted with hot toluene (1 l) for 2 d. The extract was then concentrated under reduced pressure giving crystals of the product. These were collected, washed with cold toluene and then petroleum ether (30–40 °C) and dried in vacuo. The compounds **1**–**6** were only slightly soluble in toluene but could be recrystallised from hot, dilute solutions.

Tris[bis-1,2-(dimethylphosphino)ethane]molybdenum hexafluorophosphate (7)

Method A. The compound Mo(dmpe)$_3$ (0.10 g, 0.18 mmol) in toluene (250 cm^3) was treated with iodine (0.2 g, 0.8 mmol) in toluene in a dropwise manner. The purple colour of the iodine solution was immediately discharged and a flocculant yellow precipitate formed. Addition of iodine was continued until the colour of the reaction mixture showed the presence of a trace of excess iodine. The yellow solid was separated, washed with toluene and dried in vacuo. It was then extracted with water (30 cm^3) and the extract was filtered giving a clear yellow filtrate. Aqueous ammonium hexafluorophosphate was added giving a yellow precipitate which was collected, washed with water (3 × 15 cm^3) and the solid was recrystallised from acetone/water mixture as light-green crystals, yield 95%.

Method B. The compound Mo(dmpe)$_3$ (0.10 g, 0.18 mmol) in toluene (250 cm^3) was treated with excess methyl iodide (2.0 cm^3). The mixture was stirred at 50 °C for 4 h and a yellow precipitate gradually appeared. This was converted to the hexafluorophosphate salt as described in method A.

Tris[bis-1,2-(dimethylphosphino)ethane]dihydridomolybdenum bishexafluorophosphate (8)

The compound Mo(dmpe)$_3$ (0.1 g, 0.18 mmol) in toluene (250 cm^3) was treated with gaseous hydrogen chloride. An immediate reaction occurred giving a yellow precipitate. This was collected, washed with toluene and then extracted into water (30 cm^3). The aqueous extract was filtered and aqueous ammonium

TABLE 3

COMPARATIVE STRUCTURAL DATA FOR PHOSPHINE–METAL COMPLEXES

Compound	Bite angle (°) (in dmpe–M complexes)	M–P distance (Å)
V(dmpe)$_3$	75.3(3)	2.412(4)
(η^3-C_3H_5)V(CO)$_4$P(Ph)$_3$ [13]		2.486(2)
		2.485(2)
Sum of the covalent radii of Cr^0 [14] and P [15]	–	2.58
Cr(dmpe)$_3$	76.0(3)	2.313(2)
$Cr_2(CH_2SiMe_3)_4(PMe_3)_2$[16]	–	2.466(1)
		2.453(1)
Nb(dmpe)$_3$	74.6(2)	2.526(3)
(η^5-C_5H_5)NbH$_2$(CO)(PPh$_3$) [17]	–	2.547(14)
		2.583(15)
Sum of the covalent radii of Mo^0 [14], and P [15]	–	2.72
Mo(dmpe)$_3$	75.7(2)	2.421(3)
[Mo^0(η-$C_6H_3(CH_3)_3$)(dmpe)]$_2$N$_2$ [18]	79.4(1)	2.402^a
Ta(dmpe)$_3$	73.0(4)	2.500(6)
(η-C_5H_5)$_2$Ta(dmpe)Cl·CH$_3$CN [19]	77.21(4)	2.535^a
TaCl(η^4-$C_{10}H_8$)(dmpe)$_2$ [20]	78.21(4)	2.585(1)
		2.630(1)
	75.90(4)	2.614(1)
		2.567(1)
TaH(PPh$_2$)$_2$(dmpe)$_2$ [21]	74.1(2)	2.568(7)
		2.623(7)
	76.0(2)	2.555(7)
		2.599(7)
TaH(CO)$_2$(dmpe)$_2$ [10]	75.8(3)	2.514(6)^a
	75.90(4)	2.614(1)
		2.567(1)
Sum of the covalent radii of W^0 and P [14]	–	2.69
W(dmpe)$_3$	75.3(5)	2.414(6)
WI$_2$(CO)$_3$(dmpe) [22]	74.8(4)–76.0(4)^b	2.494(5)–2.579(6)^b
WI(CO)$_2$(dmpe)$_2$ [23]	74.5(2)	2.527(7)
		2.559(7)
	75.1(2)	2.563(7)
		2.537(6)
W(CCMe$_3$)(CHCMe$_3$)(CH$_2$CMe$_3$dmpe [24]	75.47(9)	2.577(3)
		2.450(3)
WCl$_4$(dmpe)$_2$·C$_7$H$_8$ [25]	–	2.451(2)
W(η^6-$C_6H_5CH_3$)(η^3-CH_2CHCH_2)-(dmpe)PF$_6$ [26]	75.1(3)	2.495(8)
		2.485(8)
	76.2(4)	2.425(8)
		2.463(7)

^{a} Average values. ^{b} Range over five crystallographically independent molecules.

hexafluorophosphate was added to the filtrate. The resulting yellow precipitate was collected, washed with water, dried in vacuo and finally recrystallised from acetone/water as yellow prism crystals, yield 92%.

trans-Bis[bis-1,2-(dimethylphosphino)ethane]diiodochromium

The compound Cr(dmpe)$_3$ (0.1 g, 0.17 mmol) in toluene (200 cm^3) was treated with an excess of methyl iodide (2.0 cm^3). The mixture was stirred at room temperature for 12 h giving a light green precipitate. This was collected, dried in vacuo, and then extracted with dichloromethane. The extract was filtered and the filtrate was concentrated under reduced pressure giving green needle crystals, yield 88%.

X-ray analysis

For X-ray work the crystals were mounted under dry argon in glass capillaries. After survey by precession photography, the crystals were set up on a Nonius CAD-4F diffractometer and cell dimensions and orientation matrix obtained from the setting angles of 25 reflections. The crystal data and experimental details are summarized in Table 4. For all compounds: cubic, space group $Im3m$ (from Laue symmetry, systematic absences and structure analysis). Mo-K_α radiation (graphite monochromator), λ 0.71069 Å. The intensities of reflections with sin θ/λ,

TABLE 4

CRYSTAL DATA AND EXPERIMENTAL DETAILS

M =	Cr	Mo	W	V	Nb	Ta
Chemical formula	$C_{18}H_{48}P_6Cr$	$C_{18}H_{48}P_6Mo$	$C_{18}H_{48}F_6W$	$C_{18}H_{48}P_6V$	$C_{18}H_{48}P_6Nb$	$C_{18}H_{48}P_6Ta$
Molecular weight	502.4	542.3	634.3	501.4	543.3	631.4
a (Å)	10.922(3)	11.058(5)	11.040(5)	11.041(3)	11.194(4)	11.164(3)
U (Å^3)	1303	1352	1346	1346	1403	1391
D_c (Mg m^{-3}) for $Z = 2$	1.28	1.34	1.56	1.24	1.38	1.51
Linear absorption coefficient (mm^{-1})	0.82	0.83	4.90	0.75	0.76	4.51
F(000)	540	576	640	538	574	638
Sin θ/λ max.	0.595	0.66	0.594	0.66	0.70	0.594
Scan angle θ_s	1.20	1.10	1.20	1.10	1.10	1.30
Number of reflexions used in the final refinement	164	176	141	117	217	147
Chebyshev coefficients	23.5	15.7	113.3	Unit weight	59.5	36.3
	27.3	15.4	110.7		72.7	2.8
	17.5	6.1	28.3		30.15	22.4
		4.1				
Final R-values:						
R	0.045	0.047	0.037	0.052	0.066	0.036
R_w	0.046	0.062	0.052	0.064	0.079	0.039

TABLE 5

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS WITH E.S.D.'S IN PARENTHESES

	Atom	x/a	y/b	z/c	U_{iso}
Cr(dmpe)$_3$	Cr(1)	0.0000	0.0000	0.0000	0.021(1)
	P(1)	0.2102(2)	0.0257(4)	0.0000	0.025(1)
	C(1)	0.265(2)	0.185(2)	0.035(2)	0.039(6)
	C(2)	0.315(2)	−0.062(2)	0.122(3)	0.040(9)
	C(3)	0.310(2)	−0.01(2)	−0.141(2)	0.06(1)
Mo(dmpe)$_3$	Mo(1)	0.0000	0.0000	0.0000	0.0250(6)
	P(1)	0.2173(3)	0.0273(4)	0.0000	0.022(1)
	C(1)	0.270(3)	0.186(3)	0.033(3)	0.05(1)
	C(2)	0.323(4)	−0.060(4)	0.117(4)	0.06(1)
	C(3)	0.311(4)	−0.020(5)	−0.145(4)	0.05(1)
W(dmpe)$_3$	W(1)	0.0000	0.0000	0.0000	0.0209(6)
	P(1)	0.2169(6)	0.0280(8)	0.0000	0.034(3)
	C(1)	0.271(4)	0.184(6)	0.029(5)	0.05(2)
	C(2)	0.329(7)	−0.070(8)	0.109(7)	0.08(3)
	C(3)	0.311(5)	−0.027(6)	−0.141(5)	0.05(2)
V(dmpe)$_3$	V(1)	0.0000	0.0000	0.0000	0.021(1)
	P(1)	0.2166(3)	0.0279(5)	0.0000	0.031(2)
	C(1)	0.267(3)	0.189(3)	0.038(3)	0.05(1)
	C(2)	0.325(4)	−0.047(4)	0.107(4)	0.06(1)
	C(3)	0.303(3)	−0.024(4)	−0.146(4)	0.05(1)
Nb(dmpe)$_3$	Nb(1)	0.0000	0.0000	0.0000	0.0275(6)
	P(1)	0.2236(3)	0.0301(3)	0.0000	0.042(1)
	C(1)	0.262(5)	0.195(4)	0.047(4)	0.10(2)
	C(2)	0.327(4)	−0.036(3)	0.118(3)	0.071(9)
	C(3)	0.293(3)	−0.026(3)	−0.161(3)	0.063(9)
Ta(dmpe)$_3$	Ta(1)	0.0000	0.0000	0.0000	0.0347(6)
	P(1)	0.2215(5)	0.0330(7)	0.0000	0.048(3)
	C(1)	0.268(4)	0.194(4)	0.042(3)	0.07(2)
	C(2)	0.335(4)	−0.048(4)	0.108(4)	0.07(2)
	C(3)	0.305(4)	−0.027(5)	−0.150(4)	0.06(2)

sin θ/λ(max) were measured by an $\omega/2\theta$ scan with a variable scan rate and an scan angle of $(\theta_s + 0.35 \tan\theta)°$. Reflections with $I < 3\sigma(I)$, where $\sigma(I)$ is the standard deviation based on simple counting statistics were not included in subsequent calculations. Lorentz and polarization, and for the tantalum and tungsten complexes, empirical absorption corrections [28] were applied to the final merged data set of independent structure amplitudes. The diffractometer measurements confirmed the cubic symmetry and the systematic absences (hkl: $h + k + l = 2n + 1$) found by prcession technique. As a typical example, for the compound Cr(dmpe)$_3$, 4295 reflections were collected over one octant of the reciprocal space, 2027 reflections confirmed the systematic absence and the merge of 1781 reflections $I > 3\sigma(I)$ provided 164 independent reflections with a merging R-value of 0.0269. At this stage, some of the strongest reflections were excluded from the analysis because they were recorded at a count rate for which the dead time was very significant (0 1 1 and 0 0 2 for all the structures but $Ta(dmpe)_3$, for $Nb(dmpe)_3$ 1 1 2 and for $Mo(dmpe)_3$ 1 1 2 and 2 2 2).

With two molecules per unit cell, the only possible crystallographic site for the metal atom (Wyckoff a) has the symmetry *m*3*m*. We introduced the hypothesis (consistent with the IR spectra) that the 3 dmpe ligands are equivalent, that is to say that the environment of the metal atom has point symmetry 32. Each molecule will occupy one of the 8 possible sites with symmetry 32 so that the average of the electron distribution has the symmetry *m*3*m*.

Although a Patterson function suggested that the phosphorus atoms were on the four-fold axis (Wyckoff e), electron difference syntheses showed that these atoms were located in general position very near the mirror planes. To avoid ill-conditioned matrices, the phosphorus atoms were placed in the mirror planes (Wyckoff j) with iosotropic thermal parameters. The low final values for these parameters indicate that the phosphorus atoms are sufficiently close to the mirror planes to allow this artifice.

The carbon atoms were then placed and refinement of the 17 parameters (scale, U_{iso} for each atom, x and y for the phosphorus atom and x, y and z for each of the three carbon atoms) was carried out using this disordered model with various Waser constraints [29,30]. These slack constraints were gradually loosened and then withdrawn in the last cycles of refinement. In the final stages, for all the structures, with the exception of $V(dmpe)_3$ refined with unit weights, each reflection was assigned a weight according to $w = 1/\sum_{r=1}^{n} A_r T_r(x)$ where n is the number of coefficients A_r, for a Chebyshev series, T_r is the polynomial function and x is $|F_0|/|F_0(\max)|$ [31] (Table 4). All calculations were performed on the Oxford University ICL 2980 computer with CRYSTALS package [32]. Neutral atomic scattering factors and dispersion corrections were taken from ref. 34 p. 234. Observed structure amplitudes and structure factors calculated from the final atomic coordinates are given in Table 5. Lists of observed and calculated structure factors are available from the authors.

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