Reactions of Hexamethyltungsten(VI) in the Presence of Trimethylphosphine. Synthesis of Methyl, Ethylidyne, Hydrido-, Alkoxo-, and other Tungsten Compounds. *X*-Ray Crystal Structures of *trans*-Ethylidyne(methyl)tetrakis(trimethylphosphine)tungsten(IV) and Trihydrido(phenoxo)tetrakis(trimethylphosphine)tungsten(IV)

By **Kwok W. Chiu, Richard A. Jones,** and **Geoffrey Wilkinson,*** Chemistry Department, Imperial College of Science and Technology, London SW7 2AY
Anita M. R. Galas, Michael B. Hursthouse,* and **K. M. Abdul Malik,** Chemistry Department, Queen Mary College, Mile End Road, London E1 4NS

Hexamethyltungsten(VI) reacts with trimethylphosphine in light petroleum to give $WMe_6(PMe_3)$, which in neat PMe_3 with u.v. irradiation gives the carbyne complex *trans*-$WMe(\equiv CMe)(PMe_3)_4$ in high yield. Under hydrogen $WMe_5(PMe_3)$ gives quantitative yields of $WH_2(PMe_3)_5$ and $WH_4(PMe_3)_4$, with an excess and with three moles of PMe_3 respectively. $WH_2(PMe_3)_5$ yields *cis*-$WI_2(PMe_3)_4$ with MeI, and with methanol in a rare example of oxidative addition as CH_3O and H, to give $WH_3(OMe)(PMe_3)_4$; with phenol, it yields $W(OPh)_4(PMe_3)_3$ which in turn, on reaction with $LiNMe_2$ in tetrahydrofuran, gives $WH_3(OPh)(PMe_3)_4$ and small amounts of $W(NMe_2)_6$. The protonation of $WH_4(PMe_3)_4$ with tetrafluoroboric acid gives $[WH_3(PMe_3)_4][BF_4]$.

The compounds have been studied by ^1H, ^{31}P, and ^{13}C n.m.r. and i.r. spectroscopy and the crystal structures of *trans*-$WMe(CMe)(PMe_3)_4$ (2) and $WH_3(OPh)(PMe_3)_4$ (8) have been determined by *X*-ray crystallography. Crystals of (2) are tetragonal, space group $I\bar{4}2m$, with $a = b = 9.699(1)$, $c = 12.576(1)$ Å, and $Z = 2$. The structure has been refined to $R = 0.014$ for 337 observed diffractometer data. The unsymmetrical molecule is disordered with the Me–C≡W–Me unit adopting two anti-parallel orientations over the same site, thus simulating $\bar{4}$ symmetry. The W≡C and W–C distances are found to be 1.90(3) and 2.45(3) Å, the latter somewhat longer than expected, possibly due to steric crowding. The W–P distance is 2.450(2) Å. Compound (8) is monoclinic, space group $C2/m$, with $a = 14.547(2)$, $b = 13.795(2)$, $c = 13.283(2)$ Å, $\beta = 101.40(2)°$, and $Z = 4$. The structure has been refined to $R = 0.0532$ for 2 836 observed diffractometer data. The molecule has mirror symmetry and although the hydride atoms were not located experimentally, the molecule is presumed to have a dodecahedral geometry with the phosphines in the '*B*' sites. Differences in W–P distances, 2.374(4) to 2.506(6) Å, are attributed to *trans* effects.

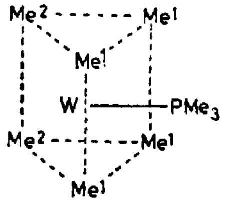
THIS paper describes the synthesis from hexamethyltungsten [1] of some methyl, hydrido- and alkoxo-species.[2]

Spectroscopic data for new compounds are given in Table 1 and analytical data in Table 2.

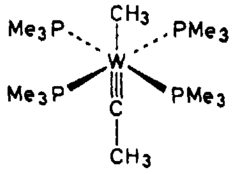
RESULTS AND DISCUSSION

1. *Interaction of Hexamethyltungsten*(VI) *with Trimethylphosphine*.—(*a*) *Hexamethyl*(*trimethylphosphine*)*tungsten*(VI), (1). The interaction of a light petroleum solution of WMe_6 with one mol (or an excess) of trimethylphosphine yields the red crystalline adduct $WMe_6(PMe_3)$, (1). Although the solid decomposes over several hours at ambient temperature it is stable indefinitely under nitrogen or in solution at −20 °C. It can be handled briefly in air and we have not experienced any unpredictable explosions during manipulations as are known for WMe_6.[1] Although microanalytical data could not be obtained, on alkaline hydrolysis, 6.0 mol of methane per mol W are formed, the W–P ratio is 1 : 1 (atomic absorption), and the integration of W–Me and P–Me peak areas in the ^1H n.m.r. spectrum are correct. The molecular weight (cryoscopically in benzene) is normal and no free PMe_3 is observed in ^{31}P n.m.r. spectra, showing that no dissociation occurs in solution.

Unlike the ^1H n.m.r. spectrum of the $PMePh_2$ adduct,[3] which showed broadening of resonances only at −90 °C, the spectra of $WMe_6(PMe_3)$ show greater temperature dependence. At room temperature and above ([$^2H_8$]-toluene) there is a sharp singlet (δ 1.58 p.p.m., area 18, W-*Me*) and a doublet [δ 1.21 p.p.m., ^2J(P–H) 8 Hz, area 9, P-Me_3] but on cooling the former broadens and at −40 °C virtually collapses. On further cooling, two new sets of peaks emerge; at −80 °C there is a singlet (δ 2.52 p.p.m., area 6) and a doublet [δ 1.40 p.p.m., ^3J(P–H) 12 Hz, area 12]. The PMe_3 doublet remains unchanged and all signals broaden slightly on cooling to −100 °C. Coupling of protons of the four equivalent methyl (Me^1) groups with phosphorus could give rise to the doublet (δ 1.40 p.p.m.) while there is no apparent coupling with the Me^2 protons.



(I)



(II)

Carbon-13 n.m.r. spectra also show the presence of two environments for W–Me groups at low temperatures. At −80 °C, the ^1H-coupled spectrum has quartets for both resonances confirming the integrity of W–Me groups (*i.e.* no $W=CH_2$ or $W-CH_2PMe_3$ units). The spectra suggest that at low temperatures the molecule has a structure such as (I).

(*b*) trans-*Ethylidyne*(*methyl*)*tetrakis*(*trimethylphosphine*)-

TABLE 1

Hydrogen-1 and $^{31}P-\{^1H\}$ spectroscopic data

Compound	^1H δ/p.p.m.[a]			Assignment	$^{31}P-\{^1H\}$ δ/p.p.m.[b]
(1) $WMe_6(PMe_3)$	1.58, s	(18)		W–*Me*	−22.6, s,br
	1.21, d	(9)	[^2J(P–H) = 8 Hz]	P*Me*$_3$	
c	2.52, s	(6)		W–*Me*	−18.35, s, sharp
	1.40, d	(12)	[^3J(P–H) = 12 Hz]	W–*Me*	
	1.21, d	(9)	[^2J(P–H) = 8 Hz]	P*Me*$_3$	
(2) *trans*-$WMe(CMe)(PMe_3)_4$	−1.58, quin	(3)	[^3J(P–H) = 9.45 Hz][d]	W–*Me*	−28.32, s [^1J(W–P) = 278 Hz]
	1.50, s	(36)		P*Me*$_3$	
	0.93, s,br	(3)		W≡C–*Me*	
(3) $WH_2(PMe_3)_5$	−5.35, sext (2)	(2)	[^2J(P–H) = 39.6 Hz] [^1J(W–H) = 27.0 Hz]	W–*H*	−34.65, s [^1J(W–P) = 243 Hz]
	1.82, m	(45)		P*Me*$_3$	
(4) $WH_4(PMe_3)_4$	−3.92, m	(4)		W–*H*	−27.34, s [^1J(W–P) = 169.3 Hz][e]
	1.65, m	(36)		P*Me*$_3$	
	−3.92, quin	(4)	[^2J(P–H) = 33.8 Hz] [^1J(W–H) = 27.0 Hz]	W–*H*	
(5) *cis*-$WI_2(PMe_3)_4$	1.77, t	(18)	[^2J(P–H) = 5 Hz]	P*Me*$_3$	−39.6, t [^2J(P–P) = 19.1 Hz][g] [^1J(W–P) = 190.5 Hz]
	1.57, t	(18)	[^2J(P–H) = 5 Hz]	P*Me*$_3$	−57.98, t [^2J(P–P) = 19.0 Hz] [^1J(W–P) = 175.0 Hz]
(6) $WH_3(OMe)(PMe_3)_4$	4.45, s	(3)		O*Me*	−12.64, m
	1.55, m	(36)		P*Me*$_3$	−23.83, m
	−4.23, m, br	(3)		W–*H*	−27.23, m
(7) $W(OPh)_4(PMe_3)_3$	7.17, m,br	(20)		O*Ph*	−43.01, s,br
	1.60, m,br	(27)		P*Me*$_3$	
(8) $WH_3(OPh)(PMe_3)_4$	7.15, m,br	(5)		O*Ph*	−12.0 (A), $^2J(P_A–P_B)$ = 18.6 Hz[h]
	1.30, m	(36)		P*Me*$_3$	−20.6 (B), $^2J(P_B–P_C)$ = 19.5 Hz, $^1J(W–P_B)$ = 202.7 Hz
	−2.40, m	(3)		W–*H*	−25.8 (C), $^2J(P_A–P_C)$ = 47.6 Hz
(9) $[WH_3(PMe_3)_4][BF_4]$	1.66, m	(36)		P*Me*$_3$	5470, s[f]
	−1.60, quin	(3)	[^1J(P–H) = 36 Hz]	W–*H*	

[a] In [$^2H_6$]benzene, at 90 MHz and 35 °C (unless otherwise stated) relative to internal $SiMe_4$ (δ 0.0). Relative areas in parentheses. [b] In [$^2H_6$]benzene–benzene (1 : 9, v/v) at 40.5 MHz and 28 °C. [c] At −80 °C. [d] See text. [e] ^{31}P coupled to W–*H*; quintet, ^2J(P–H) = 23.67 Hz. [f] At 70 °C. [g] In [$^2H_6$]acetone. [h] At 36.2 MHz on a JEOL FX-60.

tungsten(IV), (2). On photolysis of $WMe_6(PMe_3)$ in PMe_3 at −20 °C with u.v. light a solution is obtained from which a pale yellow crystalline complex can be isolated in high yield. This is *trans*-$WMe(CMe)(PMe_3)_4$ whose structure (II) as determined by *X*-ray diffraction is shown in Figure 1. The compound was first formulated[2] as *trans*-$WMe_2(PMe_3)_4$ on the basis of both *X*-ray data and ^{13}C n.m.r spectra and the necessity of reformulation is instructive in that the differences appeared only at a high level of refinement of the *X*-ray data as discussed in the Experimental section, while the ^{13}C resonance of the carbyne carbon was detected only by using a Bruker WM-250 instrument and could not be observed on a Varian XL-100 spectrometer used earlier, even after prolonged data collection. The carbyne carbon resonance occurs at δ 250.95 p.p.m. and remains single in the gated decoupled $^{13}C-\{^1H\}$ spectrum [*cf.* δ values *ca.* 288 p.p.m. in X–W≡CMe(CO)$_4$ [4]]. The WC*Me*, P*Me*$_3$, and W*Me* units give ^{13}C peaks at δ 36.90, 24.8, and −18.07 p.p.m., respectively; all these give quartets in the gated decoupled spectrum confirming their assignments to CH_3 groups.

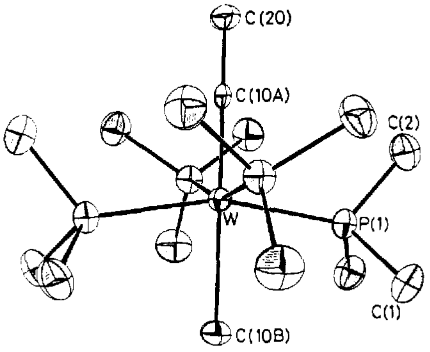


FIGURE 1 The structure of *trans*-ethylidyne(methyl)tetrakis(trimethylphosphine)tungsten(IV), *trans*-$WMe(CMe)(PMe_3)_4$

In the ^1H n.m.r. spectrum, the broad quintet pattern assigned to W*Me* is unchanged at −70 °C. This suggests that the flattened tetrahedron of phosphorus atoms found in the solid (Figure 1) is rapidly inverting in solution so that each ^{31}P nucleus couples equally with the W*Me* protons. We have not observed a peak that can unequivocally be assigned to WC*Me*; in XW≡CMe(CO)$_4$ the methyl resonance[4] occurs at *ca.* δ 2.2 p.p.m., so that in the present compound the peak is probably masked by the PMe_3 resonance. However, the position of the ^{13}C peak for this methyl group agrees with those for the carbonyl compounds at δ *ca.* 38 p.p.m.

The formation of the W≡CMe group and the evolution in the reaction only of methane (mass spectrometry), as in the decomposition of WMe_6[3] and other permethyls, indicates a mechanism involving successive α-hydrogen transfers. Hydrido-carbene intermediates have been proposed in the thermal decomposition of $[WH(CH_2PMe_2Ph)(\eta-C_5H_5)][PF_6]$ and the equilibrium [equation (1)] was suggested as a means of assisting the 1,2-hydrogen shift and carbene formation *via* alkane elimination.[5]

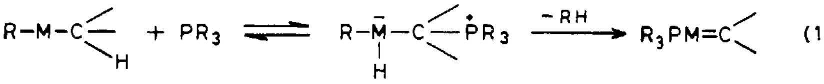
TABLE 2

Analytical data

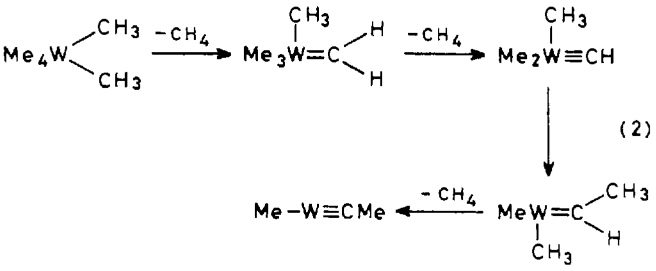
	Found (%)					Calc. (%)				
Compound	C	H	P	O	M [a]	C	H	P	O	M
(1)					355					350
(2)	34.2	8.0	23.5		540	34.0	7.9	23.4		530
(3)	31.7	8.2	26.4		570	31.8	8.3	27.4		566
(4)	30.1	8.3	23.3		480	29.2	7.8	25.1		496
(5)	20.1	5.2	15.6	(34.3) [b]	720	19.3	5.1	16.6	(34.1) [b]	746
(6)	29.7	8.0	22.8	3.2	530	29.9	7.7	23.7	3.1	524
(7)	50.1	6.7	11.2	8.2	630	50.5	6.0	11.9	8.2	787
(8)	37.4	7.7	20.5	2.8	520	37.2	6.9	21.4	2.8	582
(9)	25.3	7.1	19.5		[c]	24.9	6.7	21.4		578

[a] Cryoscopically in benzene. [b] Iodine. [c] Conductivity in CH_3NO_2 at 25 °C and 10^{-3} mol dm^{-3}, $\Lambda = 120\ \Omega^{-1}$ cm^2 mol^{-1}.

Although traces of $Me_3P{=}CH_2$ can be detected by ^1H n.m.r. in the residual PMe_3 used as solvent in the photoreaction, the formation of this ylid by reaction of a $W{=}CH_2$ intermediate with PMe_3 is evidently a very minor side reaction.


(1)

The photochemical reaction could proceed by the pathway (omitting PMe_3 and hydrido-carbene intermediates) shown in equation (2). Methyl transfer to the carbon of a $W{=}CH_2$ intermediate is unlikely since this would produce an ethyl group which would be expected to rapidly eliminate ethylene *via* the well known β-hydride transfer process. The α-H transfer from a W≡CH group to give a carbide W≡C, to which methyl is then transferred, seems doubtful so that the most likely route involves methyl transfer (possibly promoted by PMe_3) to the carbyne to re-form a carbene. Although an intramolecular transfer of this type seems to have no precedent, nucleophilic attacks on carbynes to give carbenes are well established.[6] Since the carbene hydrogen is doubtless more acidic than methyl hydrogens, α-hydrogen transfer from $W{=}CH_2$ to give W≡CH and from W=CHMe to give W≡CMe with loss of methane seems unexceptional and indeed there is a precedent for such conversions in the trimethylphosphine induced conversions of $Ta(CH_2Ph)_3(\eta\text{-}C_5H_5)Cl$ to *trans*-$Ta(CCMe_3)(\eta\text{-}C_5H_5)Cl(PMe_3)_2$ and $Ta(CHCMe_3)(CH_2CMe_3)(\eta\text{-}C_5H_5)Cl$ to *trans*-$Ta(CCMe_3)(\eta\text{-}C_5H_5)Cl(PMe_3)_2$ with elimination of toluene in the first case and neopentane in the second.[7a] There is also a precedent for a W≡CH compound in *trans*-$W(CH)Cl(PMe_3)_4$.[7b]


(2)

A free-radical pathway seems most unlikely and indeed in the photolysis of $TiMe_2(\eta\text{-}C_5H_5)_2$ no methyl radicals were observed.[8]

A diagram of the molecular structure for the carbyne complex is shown in Figure 1, and bond lengths and angles are given in Table 3. Although the distances involving the axial ligands are subject to considerable errors due to least-squares correlation effects, they are worthy of some comment. The W≡C distance of 1.90(3) Å is equal to that found in the molecule $W(CPh)(CO)_4I$.[9] In fact this carbonyl complex is quite similar to (2) (*i.e.* W≡C *trans* to W–X and with four equatorial π-acceptor ligands) and it is interesting to compare the bonding of the ligand *trans* to W≡C. By strict comparison with $W(CPh)(CO)_4I$ and using a value for $r_{cov.}(I)$ of 1.33 Å, we would expect a W–C single-bond length in (2) of *ca.* 2.258 Å. The actual value appears to be at least 0.1 Å greater than this and we presume that this is due partly to the *trans* weakening effect of the W≡CMe group and also perhaps to steric factors, since the W–Me group is strongly compressed by phosphine methyl groups, with C · · · C distances of 2.79 and 2.84 Å. On the other hand, the W–P distance is short and presumably strengthened by π bonding, since the covalent radii sum predicts a value of *ca.* 2.625 Å. Further useful comparison can be made with the molecule $WH_4(PPh_2Et)_4$,[10] also a tungsten(IV) complex with a WP_4 structure very similar [P–W–P angles of 94—99° (*cis*) and 139—142° (*trans*)] to

TABLE 3

Interatomic distances (Å) and interbond angles (°) for *trans*-$WMe(CMe)(PMe_3)_4$ (2), with estimated standard deviations in parentheses

(*a*) Bond lengths

W–P(1)	2.450(2)	W–C(10A)	1.891(25)
P(1)–C(1)	1.862(6)	W–C(10B)	2.448(30)
P(1)–C(2)	1.840(11)	C(10A)–C(20)	1.427(28)

(*b*) Bond angles

P(1)–W–P(1)′	91.4(0)	W–P(1)–C(2)	120.9(4)
P(1)–W–C(10A)	90.9(0)	C(1)–P(1)–C(2)	100.5(4)
W–P(1)–C(1)	116.6(2)		

that in (2), in which the W–P distances are 2.446—2.495(2) Å, average 2.471 Å.

Finally, we compare the bond lengths in (2) with those in the tungsten(VI) complex [$W(CBu^t)(CHBu^t)(CH_2Bu^t)(Me_2PCH_2CH_2PMe_2)$].[11] Here, the W≡C distance [1.81(1) Å] is shorter than in (2), as would be expected, and the W–C distance of 2.26(1) Å again shows that, even allowing for the oxidation state difference, the W–Me bond in (2) does seem to be lengthened.

2. *Tungsten Hydrido-complexes*.—(*a*) *Dihydridopentakis(trimethylphosphine)tungsten*(II), (3). When a dilute solution of $WMe_6(PMe_3)$ in diethyl ether containing excess (>5 mol) of PMe_3 under hydrogen (3 atm) * is slowly warmed from – 78 °C to room temperature, a pale orange solution is formed from which yellow, crystalline $WH_2(PMe_3)_5$ can be isolated quantitatively. The non-rigid phosphite analogue, $WH_2\{P(OMe)_3\}_5$, obtained from $W\{P(OMe)_3\}_6$ has been described [12] while the interaction of WMe_6 in the presence of $PPhPr^i_2$ with hydrogen gives $WH_6(PPhPr^i_2)_3$.[13]

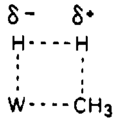
The compound is quite air sensitive and decomposes in air in a few seconds to a brown tar. It is indefinitely stable under nitrogen at room temperature.

The ^1H n.m.r. spectra in [$^2H_8$]toluene show that the seven-co-ordinate molecule is non-rigid † from –80 °C to +80 °C. The W–H units are equally coupled to all five phosphorus nuclei giving a symmetrical 1 : 5 : 10 : 10 : 5 : 1 sextet [δ –5.35 p.p.m., ^2J(P–H) = 39.6 Hz]. The fully and partially proton-decoupled ^{31}P n.m.r. spectra confirm the dihydride formulation since the singlet (δ –34.65 p.p.m.) is split into a triplet when the W–*H* units are allowed to couple. Tungsten-183 satellites are observed in both ^1H and ^{31}P spectra (see Table 1).

(*b*) *Tetrahydridotetrakis(trimethylphosphine)tungsten*(IV), (4). The use of exactly three equivalents of PMe_3 with $WMe_6(PMe_3)$ instead of an excess results in the formation of the tungsten(IV) hydride $WH_4(PMe_3)_4$ (4) in 95% yield. This white crystalline compound is considerably more stable in air than the dihydride and will survive several hours. Other tetrahydrides, $MH_4(PR_3)_4$, are known for both Mo and W with different phosphines.[10,12,14-16] When made directly from WCl_6 the yields are generally low.

The ^1H n.m.r. spectrum of $WH_4(PMe_3)_4$ in the hydride region over the range –20 °C to +50 °C is virtually identical to that [16] for $MoH_4(PEt_3)_4$ over the range –14 °C to +38 °C. Thus, equal coupling of W*H* with all four P nuclei occurs at higher temperatures giving a binomial quintet [δ–3.92 p.p.m., ^2J(P–H) = 33.8 Hz]. At lower temperatures the two outer lines of the quintet remain sharp, while the central region develops into a broad doublet.

Since the hydrogenolysis of WMe_6 where tungsten is in its highest oxidation state cannot involve oxidative addition of hydrogen, the initial attack presumably involves close approach of molecular hydrogen to the co-ordinately unsaturated tungsten atom and the formation of a four-centre transition state (III), similar to those considered in reactions of $H_2(D_2)$ with $ZrH(R)(\eta\text{-}C_5H_5)_2$, R = H or Me, for which a molecular-orbital treatment was given.[17]



(III)

3. *Reactions of Dihydridopentakis(trimethylphosphine)tungsten*(II).—(*a*) *With methyl iodide*. The dihydride reacts exothermically with methyl iodide in tetrahydrofuran (thf) with rapid loss of methane (mass spectrum) and from the solution the red crystalline air-stable iodide *cis*-$WI_2(PMe_3)_4$ (5) can be isolated in high yield. The chloro-analogue has only recently been described and the *trans* structure assigned on the basis of a singlet in the ^1H n.m.r. spectrum.[18] For the iodide however there are two triplets in both the ^1H and ^{31}P-{^1H} n.m.r. spectra, consistent with a *cis* structure.

The compound is a non-conductor in nitromethane. The i.r. spectrum shows a weak band at 1 955 cm^{-1} that is probably an overtone or combination band; it is not a hydride since no high field resonances could be detected nor does the compound give $CHCl_3$ on treatment with CCl_4. Unlike *trans*-$WCl_2(PMe_3)_4$, which gives $W_2Cl_4(PMe_3)_4$ on refluxing in dibutyl ether,[18] *cis*-$WI_2(PMe_3)_4$ was recovered unchanged after refluxing in toluene for 2 d.

(*b*) *With methanol*. Interaction of $WH_2(PMe_3)_5$ with excess of dry methanol in thf gives the light brown moderately air-sensitive hydridomethoxotungsten(IV) complex, $WH_3(OMe)(PMe_3)_4$ (6), in high yield. There are a few clear examples of the oxidative addition of alcohols as RO and H.[19]

The ^1H n.m.r. spectrum shows W–*H* centred at δ –4.23 p.p.m. as a very complex but symmetrical multiplet extending over *ca*. 180 Hz and containing at least 20 lines. The PMe_3 groups give multiplets at δ 1.55 p.p.m. while the W–O*Me* resonance is a singlet δ 4.45 p.p.m. The ^{31}P-{^1H} spectrum is similar to that of $WH_3(OPh)(PMe_3)_4$ (see below) although the resonances are slightly broadened at room temperature; the coupling constants cannot be determined with certainty. The structure is probably similar to that found for the phenoxo-compound.

The methoxo-compound reacts with CO (1 atm), losing hydrogen and methanol and giving *fac*-$W(CO)_3(PMe_3)_3$.[20]

(*c*) *With phenol*. The reaction with excess of phenol leads to loss of hydrogen and formation of the crystalline monomeric green-brown phenoxide $W(OPh)_4(PMe_3)_3$ (7). Little stereochemical information on this seven-co-

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* Throughout this paper: 1 atm = 101 325 Pa; 1 Torr = (101 325/760) Pa.

† For details of $CrH_2\{P(OMe)_3\}_5$ see F. A. van Catledge, S. D. Ittel, C. A. Tolman, and J. P. Jesson, *J. Chem. Soc., Chem. Commun*., 1980, 259.

ordinate species is obtained from ^{31}P-{^{1}H} spectra (broad multiplet δ −43.01 p.p.m.), while the ^{1}H spectrum has only broad multiplets for O*Ph* and P*Me*$_3$ groups at δ 7.17 and 1.60 p.p.m. respectively.

4. *Trihydrido(phenoxo)tetrakis(trimethylphosphine)-tungsten*(IV).—The interaction of $W(OPh)_4(PMe_3)_3$ with excess of lithium dimethylamide, $LiNMe_2$, in thf produces *ca.* 10% of $W(NMe_2)_6$ and *ca.* 75% of $WH_3(OPh)(PMe_3)_4$ (8). The latter yellow crystalline compound is stable for several hours in air and is soluble in hydrocarbons.

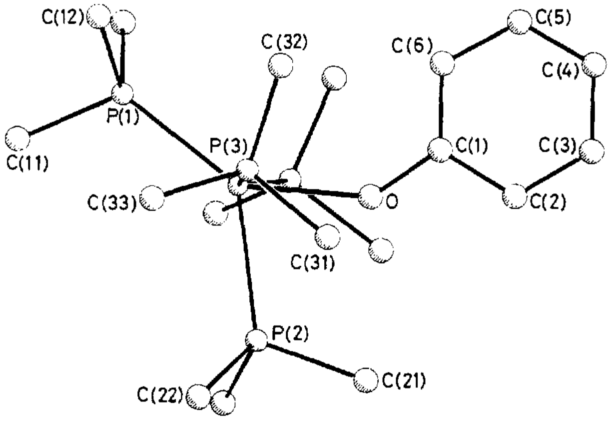


FIGURE 2 The structure of trihydrido(phenoxo)tetrakis(trimethylphosphine)tungsten(IV), $WH_3(OPh)(PMe_3)_4$

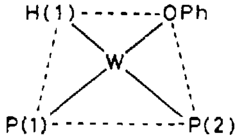
The ^{1}H n.m.r. spectrum has multiplets for both O*Ph* and P*Me*$_3$ resonances (δ 7.15 and 1.30 p.p.m. respectively) and a high-field complex multiplet similar to that for the methoxo-analogue noted above. The ^{31}P-{^{1}H} spectrum shows an AB_2C type pattern indicating the presence of two equivalent and two non-equivalent (and mutually non-equivalent) phosphorus nuclei. Selective decoupling and computer simulation experiments on the ^{1}H, ^{31}P, and ^{13}C spectra are in progress.[21] The non-equivalences of the phosphines is evidently due to the three hydrogen atoms for which there are three suitable ' holes ' in the *X*-ray crystal structure. The i.r. spectrum shows two medium intensity stretches at 1 845 and 1 725 cm^{-1} both in the solid state and in solution [as does $WH_3(OMe)(PMe_3)_4$] which decrease in intensity when the compound is exposed to deuterium (1 atm, 24 h, in light petroleum). A ν(W-D) peak is observed at 1 241 cm^{-1} but more peaks present in this area obscure the other expected peak.

TABLE 4

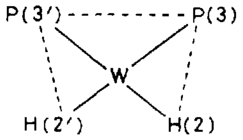
Bond lengths (Å) and angles (°) for $WH_3(OPh)(PMe_3)_4$ (8)

(*a*) Bond lengths			
P(1)–W	2.374(4)	C(21)–P(2)	1.875(15)
P(2)–W	2.506(6)	C(22)–P(2)	1.867(14)
P(3)–W	2.478(4)	C(31)–P(3)	1.865(11)
O–W	2.129(8)	C(32)–P(3)	1.845(14)
C(11)–P(1)	1.851(13)	C(33)–P(3)	1.828(12)
C(12)–P(1)	1.849(11)		
(*b*) Bond angles			
P(2)–W–P(1)	135.7(1)	C(12)–P(1)–C(11)	100.1(5)
P(3)–W–P(1)	96.3(2)	C(21)–P(2)–W	117.0(5)
P(3)–W–P(2)	92.4(2)	C(22)–P(2)–W	117.7(5)
O–W–P(1)	145.8(2)	C(22)–P(2)–C(21)	100.8(5)
O–W–P(2)	78.5(3)	C(31)–P(3)–W	117.1(4)
O–W–P(3)	79.1(3)	C(32)–P(3)–W	117.4(5)
C(11)–P(1)–W	117.3(5)	C(33)–P(3)–W	119.0(5)
C(12)–P(1)–W	118.5(4)	C(32)–P(3)–C(31)	98.3(7)

A molecule of (8) is shown in Figure 2 and some of the more important bond lengths and angles are given in Table 4. Detailed study of these lend much support both to the presence and positioning of three hydride ligands. First of all we note that the positions adopted (purely on the basis of steric factors) for the three hydride atoms lead to an overall dodecahedral co-ordination geometry. The two interlocking trapezoids which can be considered to constitute this geometry are then formed as shown in (IV) and (V). In this way all phosphine groups are placed in the ' *B* ' sites which are most favourable for π bonding, although the difference in W–P distances is considerable and requires further comment (see below). Additional evidence for the presence of hydride atom H(1) is given by the geometry of the phenoxo-ligand. First, the oxygen atom makes a contact of only 2.96 Å with the phosphine methyl group C(21) and must be restricted [*i.e.* by H(1) on the opposite side] from increasing this distance. Second, the coplanarity of the phenyl ring and the P(1), H(1), O, P(2) trapezoid plane places the hydrogen atom on phenyl carbon C(6) in close contact with H(1) and this may explain the larger than expected angles W–O–C(1) [142.3(6)°] and O–C(1)–C(6) [126.2(8)°].



(IV)



(V)

As mentioned earlier, the W–P distances show some differences. The overall WP_4 arrangement is similar to that in compound (2) and also in the tetrahydride $WH_4(PPh_2Et)_4$ [10] (it is interesting to speculate whether this eight-co-ordinated molecule also has dodecahedral geometry); and since all compounds are tungsten(IV) derivatives, the W–P distances might be expected to adopt a fairly uniform value. To some extent this is true with W–P(2) and W–P(3) distances in (8) being close to those in (2) and in the above tetrahydride. The W–P(1) bond in (8), however, is considerably shorter and we can only suggest that this might be attributed to some O(2*p*) ⟶ W(*d*) π bonding leading to enhancement of the W ⟶ P π bonding most nearly *trans* to the W–O bond; *i.e.*, a kind of inverse *trans* influence.

5. *Reaction of Tetrahydridotetrakis(trimethylphosphine)-tungsten*(IV) *with Tetrafluoroboric Acid.*—The interaction of $WH_4(PMe_3)_4$ with aqueous tetrafluoroboric acid in thf leads to the formation of $[WH_3(PMe_3)_4][BF_4]$ (9) as an off-white crystalline solid which is fairly stable in air decomposing only over several hours.

Although selective decoupling ^{31}P n.m.r. experiments were unsuccessful, the complex can be formulated as the trihydride since 1.0 mol hydrogen per tungsten are evolved in reaction (3).

$$WH_4(PMe_3)_4 + H^+BF_4^- \longrightarrow [WH_3(PMe_3)_4][BF_4] + H_2 \quad (3)$$

The ^1H n.m.r. spectrum shows the high-field hydride resonance as a symmetrical quintet [δ −1.6 p.p.m., ^2J(P–H) = 36 Hz], suggesting that the seven-co-ordinate ion is non-rigid as is usual for such species.

EXPERIMENTAL

Microanalyses were by Pascher (Bonn). Spectrometers were as follows: Perkin-Elmer R32 (^1H), Varian XL-100 (^1H, ^{13}C, and ^{31}P), Brucker WM-250 (^{13}C at 62.9 MHz), and Perkin-Elmer 597 (i.r.).

All operations were performed under oxygen-free nitrogen or argon or *in vacuo*, and all solvents except methanol were dried over sodium and distilled from sodium–benzophenone under nitrogen immediately before use. Methanol was dried over magnesium methoxide and distilled under nitrogen. Light petroleum had b.p. 40—60 °C. Melting points were determined in sealed tubes under nitrogen (uncorrected). Analytical data are collected in Table 2.

1. *Hexamethyl(trimethylphosphine)tungsten*(VI), $WMe_6(PMe_3)$, (1).—To a solution [1] of WMe_6 (30 g, 0.11 mol) in isopentane (200 cm³), was added PMe_3 (12 cm³, 0.12 mol) at −20 °C. The solution was cooled to −78 °C, yielding red *crystals* which were collected and dried under vacuum at −30 °C (10 min). The supernatant was evaporated (50 cm³) and a further batch of crystals obtained on cooling to −78 °C. The complex can also be readily crystallised from light petroleum at −20 °C. Yield: quantitative; m.p. and i.r. data were not obtained due to the thermal instability of the compound. N.m.r., ^{13}C-{^1H} in [$^2H_8$]toluene at −80 °C, referenced to $SiMe_4$ (δ 0.0) in p.p.m.: δ 14.10 [d, ^1J(P–C) = 21.1], 38.22 [d, ^1J(P–C) = 17.1 Hz], 79.96 (s). The three signals are all split into quartets in the gated decoupled spectrum, ^1J(C–H) = 122, 124, and 122 Hz respectively.

2. trans-*Ethylidyne(methyl)tetrakis(trimethylphosphine)tungsten*(IV), $WMe(CMe)(PMe_3)_4$, (2).—$WMe_6(PMe_3)$ (1.0 g, 2.9 mmol) in PMe_3 (10 cm³) was photolysed (125-W photochemical reactor, Hanovia Lamps Ltd.) at −20 °C (2 h). The solution was cooled (1 h, −78 °C) and the pale yellow crystalline product collected and dried under vacuum. Although analytically pure it can be recrystallised from petroleum at −20 °C. Yield 1.4 g, 90%, m.p. 170—175 °C (turns brown at *ca.* 150 °C, then black before melting). N.m.r., ^{13}C-{^1H} in [$^2H_6$]benzene at 25 °C: δ −18.07 [quin., ^2J(P–C) = 9.0 Hz], 24.80 (m), 36.90 (s), 250.95 p.p.m. (m). In the gated decoupled spectrum the first three resonances are split into quartets [^1J(C–H) = 104, 129, and 123 Hz respectively]. The $W{\equiv}C{-}Me$ resonance at δ 250.95 p.p.m. is not split. I.r. (Nujol): 1 420s, 1 365m, 1 290s, 1 274s, 1 263s, 1 160w, br, 929s, br, 846s, 711m, 701m, 689s, and 651s cm⁻¹

3. *Dihydridopentakis(trimethylphosphine)tungsten*(II), $WH_2(PMe_3)_5$, (3).—PMe_3 (6.0 cm³, 60 mmol) was added to a solution of $WMe_6(PMe_3)$ (2.0 g, 5.8 mmol) in diethyl ether (35 cm³) at −78 °C in a 500-cm³ pressure bottle. After pressurising with hydrogen (3 atm) the solution was allowed to warm slowly (4 h) to room temperature. The gas above the reaction mixture was replaced with fresh hydrogen at 0.5-h intervals. The solution was evaporated to dryness under vacuum at room temperature yielding yellow ***needles*** of $WH_2(PMe_3)_5$ in quantitative yield. The complex can be recrystallised from light petroleum at −78 °C, m.p. 166—168 °C (decomp.). I.r. (Nujol): 1 934m, 1 775s, br, 1 720s, br, 1 665s, br, 1 655s, br, 1 417s, 1 291s, 1 271s, 1 265s, 1 090w, 937s, br, 848s, 710m, 685s, 661s, 632s, and 550m cm⁻¹.

4. *Tetrahydridotetrakis(trimethylphosphine)tungsten*(IV), $WH_4(PMe_3)_4$, (4).—PMe_3 (1.71 cm³, 17.1 mmol) was added to $WMe_6(PMe_3)$ (2.0 g, 5.8 mmol) in diethyl ether (100 cm³) at 78 °C in a pressure bottle. The solution was allowed to warm slowly to room temperature under hydrogen (3 atm) as described for (3). The yellow-brown homogeneous solution was evaporated to dryness under vacuum and the residue extracted into light petroleum (30 cm³), the solution filtered and evaporated to *ca.* 15 cm³. Cooling (−20 °C) yielded off-white *prisms* which were collected and dried under vacuum. Yield 2.5 g, 90%, m.p. 79—80 °C. I.r. (Nujol): 1 760s, 1 720s, 1 435m, 1 415s, 1 294s, 1 275s, 945s, 850s, 715s, and 655s cm⁻¹.

5. cis-*Di-iodotetrakis(trimethylphosphine)tungsten*(II), $WI_2(PMe_3)_4$, (5).—Methyl iodide (1.20 cm³, 3.65 mmol) was added slowly to $WH_2(PMe_3)_5$ (1.0 g, 1.75 mmol) in thf (50 cm³) at 0 °C. The solution was stirred (10 h) at room temperature, evaporated to dryness under vacuum, and the residue extracted with toluene (20 cm³). The solution was filtered, evaporated to *ca.* 7 cm³, and cooled (−20 °C) to yield red *prisms* which were collected, washed with light petroleum (5 cm³), and dried under vacuum. Yield 1.05 g, 80%, m.p. 210—215 °C (decomp.). I.r. (Nujol): 1 955w, 1 710w, 1 410m, 1 295m, 1 275m, 942s, br, 848m, 800w, 715m, 705m, and 660m cm⁻¹. The compound is slightly soluble in aromatic hydrocarbons and somewhat more soluble in polar organic solvents.

6. *Tris(hydrido)methoxotetrakis(trimethylphosphine)tungsten*(IV), $WH_3(OMe)(PMe_3)_4$, (6).—To $WH_2(PMe_3)_5$ (1.0 g, 1.75 mmol) in thf (40 cm³) at room temperature was added methanol (0.5 cm³, 12.2 mmol) and the solution stirred (10 h) before vacuum removal of solvent. The residue was extracted into toluene (20 cm³), the solution filtered, concentrated to *ca.* 8 cm³, and cooled (−20 °C) to give pale brown *prisms* which were collected, washed with light petroleum (*ca.* 3 cm³ at 0 °C), and dried in vacuum. Yield 0.82 g, *ca.* 90%, m.p. 142—144 °C. The compound can be crystallised from toluene. I.r. (Nujol): 2 132w, 1 970w, 1 940w, 1 810s, 1 405s, 1 270s, 1 090s, 930s, 850s, and 658s cm⁻¹.

On bubbling CO (1 atm) through a solution of *ca.* 0.5 g in 40 cm³ thf for 30 min, *ca.* 0.44 g (92%) of *fac*-$W(CO)_3(PMe_3)_3$ is recovered after concentration to *ca.* 5 cm³ and cooling (−20 °C).

7. *Tetraphenoxotris(trimethylphosphine)tungsten*(IV), $W(OPh)_4(PMe_3)_3$, (7).—To $WH_2(PMe_3)_5$ (1.0 g, 1.75 mmol) in thf (50 cm³) at room temperature was added phenol (0.5 g, 5.25 mmol). After stirring (10 h) and vacuum evaporation, the residual blue oil was extracted into toluene (40 cm³) which was filtered and allowed to stand at room temperature (4 d). The greenish brown crystals were collected, washed with light petroleum (5 cm³), and dried in vacuum. Yield 1.1 g, 80%, m.p. 80—82 °C. The compound is stable for several hours in air as the solid, but solutions are more air sensitive. The compound is soluble in benzene and toluene. I.r. (Nujol): 1 583s, 1 288s, 1 247s, 1 158m, 1 065w, 1 062w, 996w, 944s, 855s, 830w, 758s, 690m, 665w, and 630m cm⁻¹.

8. *Trihydrido(phenoxo)tetrakis(trimethylphosphine)tungsten*(IV), $WH_3(OPh)(PMe_3)_4$, (8).—To $W(OPh)_4(PMe_3)_3$ (0.5 g, 0.64 mmol) in thf (30 cm^3) at room temperature was added $LiNMe_2$ (0.5 g, from $NHMe_2$ and $LiBu^n$) as a slurry in thf (20 cm^3). The mixture was stirred (12 h), evaporated in vacuum, and the residue extracted into toluene (20 cm^3). The filtered solution was concentrated to *ca.* 10 cm^3 and cooled (−20 °C) to give pale yellow crystals which were collected and manually separated from red crystals of $W(NMe_2)_6$ (identified by *X*-ray diffraction study). Yield 0.27 g, 75%, m.p. 187—188 °C. I.r. (Nujol): 3 300w, 2 790w, 2 750w, 1 845m, 1 735m, 1 586s, 1 420w, 1 322m, 1 310m, 1 275m, 1 218w, 1 167w, 1 067m, 1 025m, 990w, 945s, 859m, 850m, 750m, 705, and 662m cm^{-1}.

TABLE 5

Crystal data and details of data collection and structure refinement

(*a*) Crystal data	Compound (2)	Compound (8)
Formula	*trans*-$WMe(CMe)(PMe_3)_4$	$WH_3(OPh)(PMe_3)_4$
Crystal system	Tetragonal	Monoclinic
a/Å	9.699(1)	14.547(2)
b/Å	9.699(1)	13.795(2)
c/Å	12.576(1)	13.283(2)
β/°	(90)	101.40(2)
U/Å^3	1 183.0	2 613.0
Space group	$I\bar{4}2m$	$C2/m$
Z	2	4
D_c/g cm^{-3}	1.49	1.53
F(000)	520	1 224
μ(Mo-K_α)/cm^{-1}	49.1	44.6
(*b*) Data collection		
Crystal size/mm	0.5 × 0.25 × 0.45	0.67 × 0.26 × 0.18
$\theta_{min.}$, $\theta_{max.}$/°	1.5, 25	1.5, 28
Scan width parameters		
(A, B in width = $A + B\tan\theta$)	0.8, 0.35	0.8, 0.35
Horizontal aperture parameters		
(A, B in aperture = $A + B\tan\theta$)	4.0, 0.0	4.0, 0.0
$T_{max.}$/s	60	90
Total data	625	3 515
Total unique data	337	3 288
Observed data	337	2 836
Significance test	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$
(*c*) Refinement		
Number of parameters	51	127
Weighting scheme coefficient g in $w = 1/[\sigma^2(F_o) + g\|F_o\|^2]$	0.004 47	0.000 8
Final $R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.014 4	0.053 2
$R' = [\Sigma\Delta w\|\Delta F\|^2/\Sigma wF_o^2]^{\frac{1}{2}}$	0.019 1	0.053 3

9. *Trihydridotetrakis(trimethylphosphine)tungsten*(IV) *Tetrafluoroborate*, $[WH_3(PMe_3)_4][BF_4]$, (9).—Aqueous fluoroboric acid (0.9 cm^3 of a 40% solution, 4.1 mmol) in thf was added dropwise to $WH_4(PMe_3)_4$ (2.0 g, 4.1 mmol) in thf (30 cm^3) at room temperature. A white precipitate was formed immediately and the colour of the solution became dark brown. It was filtered and the solid washed with thf (2 × 10 cm^3) and recrystallised from methanol at −20 °C. Yield 0.9 g, 40%, m.p. 85—88 °C (decomp.). I.r. (Nujol): 1 835m, 1 828m, 1 460m, 1 322w, 1 292m, 1 070s, br, 950s, 870w, and 736m cm^{-1}.

Crystallographic Studies.—Crystals of both compounds (2) and (8) were sealed under nitrogen in Lindemann capillaries. Unit-cell and crystal orientation data were obtained using the SEARCH and INDEX routines on a Nonius diffractometer and accurate values determined by least-squares refinement using setting angles for 25 automatically centred reflections. Intensity data were recorded in a manner described in detail previously; [22] control reflections showed no significant changes in diffracting power of the crystals during data collection. Crystal data and details of the data collection are given in Table 5. Absorption corrections were applied for both crystals.

The structures were solved by the Patterson technique and developed *via* successive electron-density syntheses. For compound (2), the space group $I\bar{4}2m$ was chosen as a result of the successful analysis and refinement of all atoms in the $W(PMe_3)_4$ grouping, which has $\bar{4}$ symmetry. In our first attempt at structure analysis of this compound, with a morphologically ill defined crystal, the difference map phased on the W position showed one peak on the $\bar{4}$ axis above and below the metal atom, at a distance of *ca.* 2.2 Å. This was refined quite successfully as a carbon atom and in our preliminary publication [2] compound (2) was formulated as *trans*-$WMe_2(PMe_3)_4$.

During later anisotropic refinement, we noticed that the U_{33} parameter for the methyl carbon was very large and ripples occurred each side of it, on the axis. Unable to make reliable absorption corrections, we were reluctant to attach too much significance to this at the time. Subsequently, more crystals of excellent quality became available

TABLE 6

Fractional co-ordinates (× 10^4) of the non-hydrogen atoms for compound (2)

	x	y	z
W	0	0	0
P(1)	1 764(1)	1 764(1)	309(1)
C(1)	1 235(7)	3 286(7)	1 113(6)
C(2)	2 626(8)	2 626(8)	−812(10)
C(10A)	0	0	1 504(20)
C(10B)	0	0	1 947(23)
C(20)	0	0	2 639(23)

and it was decided to recollect the data for this compound. Somewhat surprisingly, the previously mentioned features recurred. A new difference map with the axial atoms omitted showed, on each side of the metal atom, one elongated peak, centred at a distance of 2.0 Å and another weaker one 3.2 Å from the metal atom. After some consideration, it occurred to us that to comply with the known diamagnetism of the compound the best integration of this situation was a disordering of one W–Me and one W≡C–Me group. Subsequent refinement of three half-carbon atoms on the $\bar{4}$ axis at the relevant positions, *ca.* 1.8 (W≡C), 2.2 (W–Me), and 3.2 Å (W≡C–Me), was quite successful. The possibility that the disorder might be removed on adoption of a different space group was considered but not explored exhaustively since the $W(PMe_3)_4$ unit was so well defined (including hydrogen atoms) in space group $I\bar{4}2m$. The final R value suggests to us that both the disorder model and the space group are correct; this structure is probably adopted because the $W(PMe_3)_4$ unit, which is forced to have the characteristic tetrahedrally distorted, $\bar{4}$, MP_4 structure due to steric crowding [*cf.* $Rh(PMe_3)_4$ [22]], dominates the molecular shape and the differences caused by the two axial groups are too small to have any serious effect on the packing.

TABLE 7

Fractional atomic co-ordinates ($\times 10^5$ for W, $\times 10^4$ for other atoms) for compound (**8**)

	x	*y*	*z*
W	22 867(2)	0	23 683(2)
P(1)	3 335(2)	0	1 207(2)
P(2)	541(2)	0	2 209(2)
P(3)	2 401(2)	1 758(2)	2 758(2)
O	2 160(5)	0	3 938(5)
C(1)	2 659(7)	0	4 873(7)
C(2)	2 178(7)	0	5 708(8)
C(3)	2 645(8)	0	6 707(7)
C(4)	3 606(8)	0	6 963(8)
C(5)	4 100(8)	0	6 174(9)
C(6)	3 636(7)	0	5 145(8)
C(11)	2 814(10)	0	−182(8)
C(12)	4 171(6)	1 017(7)	1 261(7)
C(21)	84(9)	0	3 433(11)
C(22)	−130(8)	1 034(11)	1 514(8)
C(31)	1 644(9)	2 241(7)	3 623(9)
C(32)	3 539(9)	2 221(7)	3 459(9)
C(33)	2 143(12)	2 625(7)	1 699(10)

The structure of compound (**8**) was solved and refined routinely for the non-hydrogen atoms. Its structural identification as a trihydride was made on the basis of gaps in the WOP_4 co-ordination sphere and three hydride atoms were placed in idealised positions, to retain the $C_s(m)$ symmetry of the heavy-atom structure.

Details of the refinement for both compounds are given in Table 5. Final atomic co-ordinates are given in Tables 6 and 7. Thermal parameters and lists of $|F_o|$ and F_c have been deposited as Supplementary Publication No. SUP 23009 (25 pp.).*

All computations were carried out on the ICL 2980 at Queen Mary College using programs listed in ref. 23, which also gives the sources of scattering factor data used.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.