The Chemistry of $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$: Synthesis of Hydroxy-hydrido, Fluoro-hydrido, and Silyl-hydrido Derivatives and the Dimerisation of Ethylene and Propene giving η^4-Diene Derivatives. Crystal Structure of $[W(PMe_3)_4H_2(OH_2)F]F$†

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The syntheses of the compounds $[W(PMe_3)_4H_2(OH)_2][BF_4]_2$ (**2**), $[W(PMe_3)_4H_2(OH_2)F]F$ (**3**), $[W(PMe_3)_4H_2F_2]$ (**4**), $[W(PMe_3)_4H_2(OH_2)F][PF_6]$ (**5**), $[W(PMe_3)_4H_2(O_2CCF_3)][CF_3CO_2]$ (**6**) $[W(PMe_3)_5H_2]$ (**7**), $[W(PMe_3)_4H_4]$ (**8**), $[W(PMe_3)_4H_2(SiH_3)_2]$ (**9**), *trans*-$[W(PMe_3)_4(\eta\text{-}C_2H_4)_2]$ (**12**), *cis*-$[W(PMe_3)_2(\eta\text{-}C_4H_6)_2]$ (**13**), and $[W(PMe_3)_3\{\eta\text{-}CH_2C(Me)CHCH(syn\text{-}Me)\}H_2]$ (**14**) are described. They are formed by treatment of $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ with aqueous HBF_4, aqueous HF, aqueous HF then KH, aqueous HPF_6, CF_3COOH, H_2 in liquid PMe_3, H_2 in light petroleum, silane, ethylene, prolonged reaction with ethylene, or propene, respectively. Compounds (**2**)—(**6**), (**9**), and (**14**) are new. The crystal structure of (**3**) has been determined and contains a dodecahedral cation $[W(PMe_3)_4H_2(OH_2)F]^+$ with which the counter anion F^- forms an ion pair *via* hydrogen bonding to the H_2O ligand.

Recently we described the chemistry of the homoleptic trialkylphosphine compound $[Mo(PMe_3)_6]$ [1,2] which showed the metal centre to be extremely electron rich. Related known homoleptic $[M(PMe_3)_n]$ compounds are the 16-electron $[Fe(PMe_3)_4]$,[3,4] the 17-electron $[Co(PMe_3)_4]$,[5] the 18-electron $[M(PMe_3)_4]$ (M = Ni, Pd, or Pt),[3,4,6] $[M(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H]$ (M = Fe,[3,4] Ru,[7–9] or Os[7]), $[\{Ru(PMe_3)_3(\mu\text{-}CH_2PMe_2)_2H\}_2]$,[9] and $[\{Pt(PMe_3)(\mu\text{-}CH_2PMe_2)H\}_2]$.[10]

A common reaction of these compounds is the elimination of a tertiary phosphine ligand accompanied by formation of a $M(\eta^2\text{-}CH_2PR_2)H$ system, *via* a C–H intramolecular oxidative addition reaction, (1). In general, this equilbrium is labile and

$$[M(PMe_3)_n] \rightleftharpoons [M(PMe_3)_{n-2}(\eta^2\text{-}CH_2PMe_2)H] + PMe_3 \quad (1)$$

the reactions of the cyclometallated derivatives correspond closely to those expected for the homoleptic compounds. Here we describe studies concerning the recently reported[11] compound $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ (**1**). Part of this work has been communicated.[12]

Results and Discussion

N.m.r. studies of solutions of (**1**) in the presence of an excess of PMe_3 show no evidence for the presence of an equilibrium concentration of the hexakis compound $[W(PMe_3)_6]$.[11] In a further attempt to synthesise this compound, tungsten atoms were co-condensed into excess PMe_3. The only product isolated, however, was (**1**), formed in *ca.* 20% yield. This suggests that the equilibrium (2) (M = Mo or W) lies essentially to

$$[M(PMe_3)_6] \rightleftharpoons [M(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H] + PMe_3 \quad (2)$$

the right-hand side for tungsten, whereas for molybdenum the $[Mo(PMe_3)_6]$ species dominates.[1] This difference reflects the general tendency of tungsten to adopt a higher oxidation state than molybdenum. A similar trend has been observed for the tertiary phosphine derivatives of Fe,[3] Ru,[7,8] and Os.[7]

Treatment of (**1**) with aqueous HBF_4 gave an orange crystalline complex, $[W(PMe_3)_4H_2(OH)_2][BF_4]_2$ (**2**). Proton and ^{31}P n.m.r. spectra (Table 1) clearly demonstrate the presence of a dodecahedral $W(PMe_3)_4H_2X_2$ unit; for instance the symmetrical 12-line resonance in the ^1H n.m.r. spectrum assignable to WH_2 has the appearance of a doublet of doublets of triplets corresponding to coupling to two pairs of phosphorus nuclei of which one pair are both chemically and magnetically equivalent and the other pair are only chemically equivalent (phosphorus spin system $AA'X_2$). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum consists of two triplet resonances and the $^{31}P\text{-}\{^1H(Me)\}$ n.m.r. spectrum showed a further poorly resolved triplet coupling consistent with the presence of two hydride ligands. The hydroxo hydrogens were not observed in the ^1H n.m.r. spectrum obtained in CD_3OD owing to their exchange with the deuterium of the solvent. However, when the spectrum was recorded in CD_2Cl_2 immediately after preparing the sample (which was necessary owing to decomposition in this solvent), a resonance at δ 4.12 was observed which can be assigned to the two hydroxo protons. The most convincing evidence for the presence of hydroxo (as opposed to aqua) ligands comes from the i.r. spectrum which possesses a very strong band at 3 470 cm^{-1} attributable to an O–H stretching vibration. The sharpness and intensity of this band and the absence of a band in the range *ca.* 1 600—1 700 cm^{-1} associated with a bending vibration of co-ordinated water provide strong evidence for the presence of hydroxo ligands;[13] M–O–H bending vibrations in hydroxide compounds have been observed to occur in the region 600—1 200 cm^{-1}. A ν(W–H) stretch was also observed at 1 960 cm^{-1}. The i.r. spectrum of a sample after treatment with CD_3OD showed that exchange of W–O–H to W–O–D had occurred since the band at 3 470 cm^{-1} was replaced by a new band at 2 565 cm^{-1} (ν_H/ν_D = 1.35). A close examination of the spectra suggests that a band at 1 095 cm^{-1} was replaced by one at 785 cm^{-1} which may be due to a W–O–H bending vibration. However, a precise assignment of this absorbance is not possible since $[BF_4]^-$ also absorbs strongly in this area. Although com-

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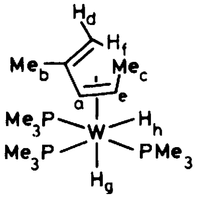
† Aquafluorodihydridotetrakis(trimethylphosphine)tungsten(IV) fluoride.

Supplementary data available (No. SUP 56606, 2 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from editorial office.

Non-S.I. units employed: atm = 101 325 N m^{-2}, Torr = 133 N m^{-2}.

Table 1. Analytical and spectroscopic data; i.r. data (cm $^{-1}$) are for Nujol mulls on CsI plates

Compound, colour, and analytical data (%)[a]	N.m.r.[b] ^{1}H	N.m.r.[b] ^{19}F and ^{31}P
(2) $[W(PMe_3)_4H_2(OH)_2][BF_4]_2$[c] Orange C, 20.4 (20.6); H, 5.5 (5.7)	1.67 [18 H, vcm, J'(P–H) 8.0, 2 PMe_3], 1.43 [18 H, vcm, J'(P–H) 6.4, 2 PMe_3], −1.74 [2 H, ddt, J_d(P–H) 35.7, J_d(P–H) 39.0, J_t(P–H) 56.2, W–H][d] 4.12 (2 H, s, 2 O–H), 1.69 [18 H, vcm, J'(P–H) 8.6, 2 PMe_3], 1.51 [18 H, vcm, J'(P–H) 7.4, 2 PMe_3], −1.47 [2 H, ddt, J_d(P–H) 36.7, J_d(P–H) 40.8, J_t(P–H) 51.4, 2 W–H][e]	^{31}P-{^{1}H}: −12.9 [2 P, t, J(P–P) 7, J(P–W) 223, 2 PMe_3], −16.3 [2 P, t, J(P–P) 7, J(P–W) 223, 2 PMe_3][d]
(3) $[W(PMe_3)_4H_2(OH_2)F]F$[f] Yellow C, 26.2 (26.4); H, 7.4 (7.3)	11.30 (2 H, vbr, OH_2), 1.53 [18 H, vcm, J'(P–H) 8.0, 2 PMe_3], 1.32 [18 H, vcm, J'(P–H) 6.4, 2 PMe_3], −1.56 [2 H, tt, J_t(P–H) 36.7, J_t(P–H) 55.0, 2 W–H][e,g] 1.57 (18 H, br s, 2 PMe_3), 1.37 (18 H, br s, 2 PMe_3), −1.49 [2 H, tt, J_t(P–H) 37.0, J_t(P–H) 55.4, 2 W–H][d]	^{19}F-{^{1}H}: −185.5 (1 F, br), −243.6 (1 F, br)[d] ^{19}F-{^{1}H}: −248.2 [2 F, tt, J_t(P–F) 45, J_t(P–F) 77][e] ^{19}F-{^{1}H}: −231.1 [2 F, tt, J_t(P–F) 51, J_t(P–F) 86][h] ^{31}P-{^{1}H}: −13.0 [2 P, br t, J(P–P) 10, J(P–W) 206, 2 PMe_3], −16.0 [2 P, t, J(P–P) 10, J(P–W) 228, 2 PMe_3][d] ^{31}P-{^{1}H(Me)}: −13.0 (2 P, tt, 2 PMe_3), −16.0 (2 P, tt, 2 PMe_3)[d]
(4) $[W(PMe_3)_4H_2F_2]$[i] Yellow C, 27.1 (27.3); H, 6.8 (7.2)	1.38 [18 H, vcm, J'(P–H) 7.8, 2 PMe_3], 1.27 [18 H, vcm, J'(P–H) 6.8, 2 PMe_3], −1.54 [2 H, ddtt, J_d(P–H) 34.9, J_d(P–H) 37.5, J_t(P–H) 54.8, J_t(F–H) 7.2, 2 W–H][j] ^{1}H-{^{31}P}: 1.38 (18 H, s, 2 PMe_3), 1.27 (18 H, s, 2 PMe_3), −1.54 [2 H, t, J_t(H–F) 7.2, 2 W–H][j]	^{19}F-{^{1}H}: −231.4 [2 F, tt, J_t(P–F) 87, J_t(P–F) 52, 2 W–F][i,j] ^{31}P-{^{1}H}: −12.5 [2 P, tt, J_t(P–P) 11, J_t(P–F) 86, J(P–W) 370, 2 PMe_3], −15.5 [2 P, tt, J_t(P–P) 11, J_t(P–F) 51, J(P–W) 229, 2 PMe_3][j]
(5) $[W(PMe_3)_4H_2(OH_2)F][PF_6]$[k] Yellow C, 22.1 (21.4); H, 6.1 (6.0)	10.33 (2 H, br, OH_2), 1.58 [18 H, vcm, J'(P–H) 8.6, 2 PMe_3], 1.43 [18 H, vcm, J'(P–H) 6.6, 2 PMe_3], −1.79 [2 H, dddt, J_d(F–H) 17, J_d(P–H) 34.7, J_d(P–H) 39.5, J_t(P–H) 58.5, 2 W–H][l]	^{19}F-{^{1}H}: −239.5 [1 F, br qnt, J(P–F) 57, W–F][l,m] ^{31}P-{^{1}H}: −73.8 [2 P, dt, J_d(P–F) 50, J_t(P–P) 14, J(P–W) 182, 2 PMe_3], −81.7 [2 P, dt, J_d(P–F) 64, J_t(P–P) 14, J(P–W) 232, 2 PMe_3][l,m]
(6) $[W(PMe_3)_4H_2(O_2CCF_3)]$-$[CF_3CO_2]$[n] Yellow C, 26.8, (26.8); H, 5.2 (5.3)	1.68 [9 H, d, J(P–H) 8.8, PMe_3], 1.61 [9 H, d, J(P–H) 8.7, PMe_3], 1.53 [18 H, vcm, J'(P–H) 8.0, 2 PMe_3], −1.86 [2 H, dddd, J_d(P–H) 66.2, J_d(P–H) 50.8, J_d(P–H) 40.9, J_d(P–H) 34.1, 2 W–H][l]	^{19}F: −76.8 (3 F, s, CF_3CO_2), −77.0 (3 F, s, CF_3CO_2) ^{31}P-{^{1}H}: −16.1 [2 P, AB portion of ABX_2 system, $\Delta(\delta_A - \delta_B) = 139$, $J(P_A–P_B)$ 49, $J(P_A–P_X) = J(P_B–P_X)$ 12, P_A and P_B], −25.9 [2 P, t, $J(P_A–P_X) = J(P_B–P_X)$ 12, 2 P_X][l]
$[W(PMe_3)_5H(SiH_3)]$[o]	3.70 (3 H, m, SiH_3), 1.58 [9 H, d, J(P–H) 5.6, PMe_3], 1.49 [36 H, d, J(P–H) 4.7, 4 PMe_3], −5.50 [1 H, dqnt, J_d(P–H) 46.4, J_{qnt} (P–H) 35.5, W–H][j]	^{31}P-{^{1}H}: −24.4 [1 P, qnt, J(P–P) 12, J(P–W) 238, PMe_3], −38.6 [4 P, d, J(P–P) 12, J(P–W) 243, 4 PMe_3][j]
(9) $[W(PMe_3)_4H_2(SiH_3)_2]$[p] Yellow C, 25.8 (26.1); H, 7.8 (8.0); Si, 10.5 (10.2)	3.65 [6 H, qnt, J(P–H) 8.0, 2 SiH_3], 1.41 [36 H, d, J(P–H) 8.0, 4 PMe_3], −4.46 [2 H, qnt, J(P–H) 30.4, 2 W–H][q]	^{31}P-{^{1}H}: −37.1 (4 P, s, 4 PMe_3)[p,q]
(14) $[W(PMe_3)_3\{\eta\text{-}CH_2C(Me)\text{-}CHCH(syn\text{-}Me)\}H_2]$[r] Yellow  	4.15 (1 H, m, H_a), 2.47 (3 H, s, 3 H_b), 2.07 [3 H, d, $J(H_c–H_e)$ 6, 3 H_c], 1.50 [9 H, d, J(P–H) 6, PMe_3], 1.30 [9 H, d, J(P–H) 6, PMe_3], 1.23 [9 H, d, J(P–H) 6, PMe_3], 0.68 (1 H, m, H_d), 0.15 (1 H, m, H_e), −0.94 (1 H, m, H_f), −1.23 (1 H, m, W–H_g), −4.30 (1 H, m, W–H_h)[j]	^{31}P-{^{1}H}: −29.6 [1 P, d, J(P–P) 15, J(P–W) 264, PMe_3], −32.5 [1 P, dd, J(P–P) 15, J(P–P) 25, J(P–W) 206, PMe_3], −37.2 [1 P, d, J(P–P) 25, J(P–W) 221, PMe_3][j]

[a] Required values given in parentheses. [b] Given as: chemical shift (δ) [intensity, multiplicity, J in Hz, assignment]. ^{1}H N.m.r. at 300 MHz unless otherwise indicated; ^{31}P-{^{1}H} n.m.r. at 101.26 MHz; ^{19}F-{^{1}H} n.m.r. at 235 MHz; vcm = virtually coupled multiplet. [c] I.r.: 1 960 (w,br) (W–H), 2 820 (s), 3 470 (s,br) (W–OH). Principal changes on deuteriation: hydride (deuteriated analogue) [ratio], 3 470 (2 565) [1.35], 1 185 (855) [1.39], 1 095 (785) [1.39]. [d] In CD_3OD. [e] In CD_2Cl_2. [f] I.r.: 1 740 (m,br) (OH_2), 1 890 (m,br) (W–H), 2 750 (s,br) (OH). [g] Spectrum obtained immediately after sample preparation. [h] In [$^2H_8$]thf. [i] I.r.: 1 835 (s), 1 900 (s) (W–H). [j] In [$^2H_6$]benzene. [k] I.r.: 1 430 (s), 1 700 (s,br), 1 980 (w,br) (W–H), 2 700 (br) (O–H). [l] In CD_3CN. [m] $[PF_6]^-$ not recorded. [n] I.r.: 1 700 (s), 1 720 (s) (C=O), 1 805 (w), 1 955 (m,br) (W–H). Conductivity of a 1.03×10^{-3} mol dm^{-3} solution in MeCN is 90.35×10^{-6} Ω^{-1} cm^2 mol^{-1}, suggesting a 1:1 electrolyte. [o] Not isolated (see text). [p] I.r.: 1 860 (m) (W–H), 2 040 (s) (Si–H). [q] In [$^2H_8$]toluene. [r] m/e 496, P^+ (^{184}W).

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pounds containing bridging hydroxo-groups are common,[14,15] few monomeric hydroxo complexes have been reported previously.[16] Examples are $[Hf(\eta\text{-}C_5Me_5)_2H(OH)]$[17] and $[Os(PMe_3)_4H(OH)]$.[7] Related mononuclear hydroxo derivatives include $[Hf(\eta\text{-}C_5Me_5)_2(OH)_2]$, $[Zr(\eta\text{-}C_5Me_5)_2(OH)_2]$, $[Hf(\eta\text{-}C_5Me_5)_2(OH)Cl]$, and $[Zr(\eta\text{-}C_5Me_5)_2(OH)Cl]$.[17,18]

Reduction of (**2**) with sodium–potassium alloy gives the hydrido derivatives $[W(PMe_3)_4H_4]$ and $[W(PMe_3)_3H_6]$ as a 6:1 mixture.

Protonation of $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ (**1**) with aqueous HF gave a pale yellow, diethyl ether-soluble complex, $[W(PMe_3)_4H_2(OH_2)F]F$ (**3**). The ^{1}H n.m.r. spectrum of (**3**) in CD_3OD shows a hydride resonance at δ −1.49 which appears as a triplet of triplets and may be interpreted as coupling of the W-hydrogens to two inequivalent sets of two PMe_3 ligands. The ^{1}H n.m.r. spectrum of (**3**) in CD_2Cl_2 (obtained immediately after sample preparation) is very similar to that in CD_3OD but includes a very broad resonance, centred at δ 11.30, which could only be observed from the integral, and may be assigned to a co-ordinated aqua ligand (Figure 1). The ^{31}P-{^{1}H} n.m.r. spectrum

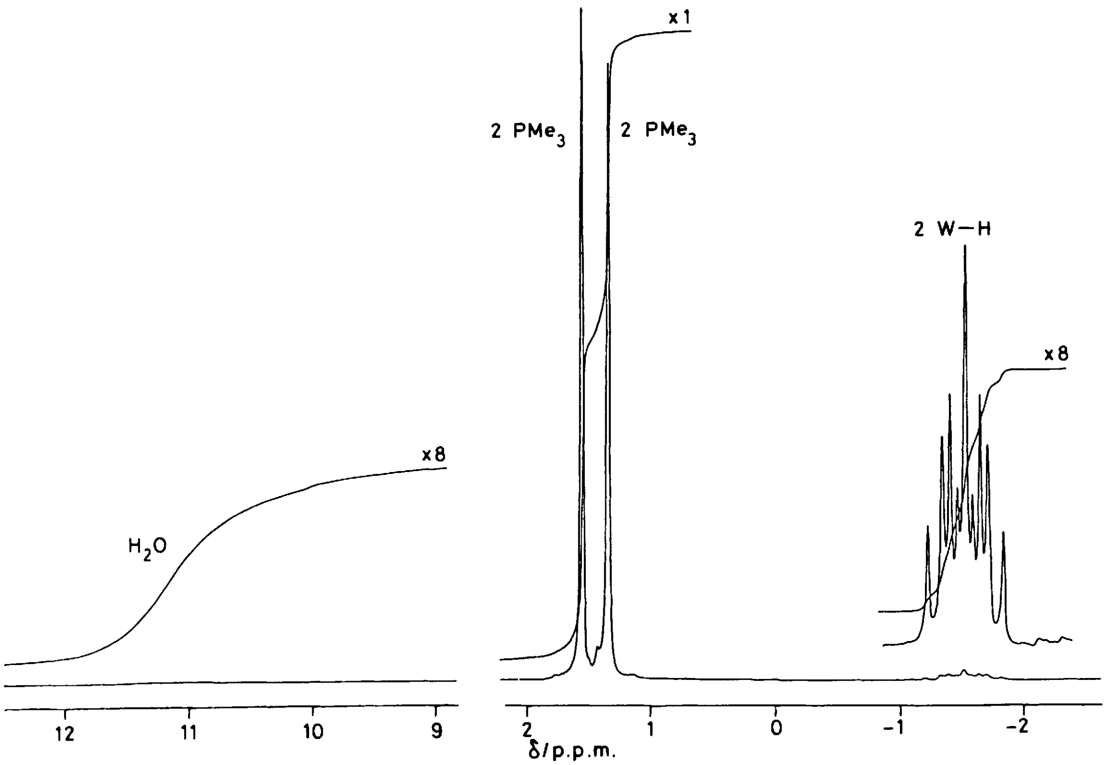


Figure 1. ^1H N.m.r. spectrum of $[W(PMe_3)_4H_2(OH_2)F]F$ (3) in CD_2Cl_2

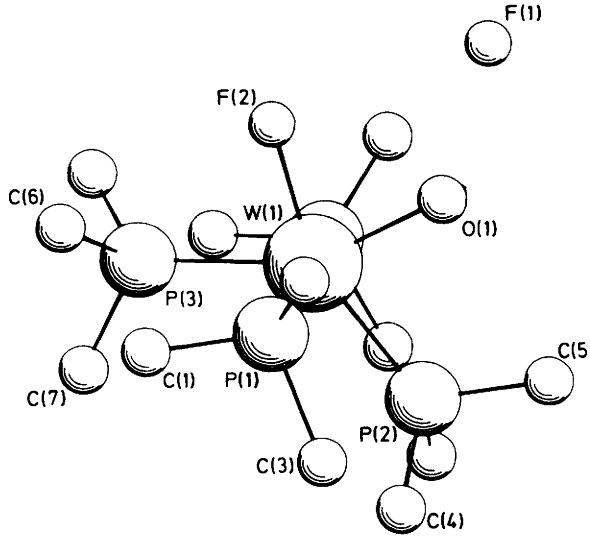


Figure 2. The structure of $[W(PMe_3)_4H_2(OH_2)F]F$ (3)

Table 2. Bond lengths (Å) and angles (°) in (3) with e.s.d.s in parentheses

(*a*) Bond lengths

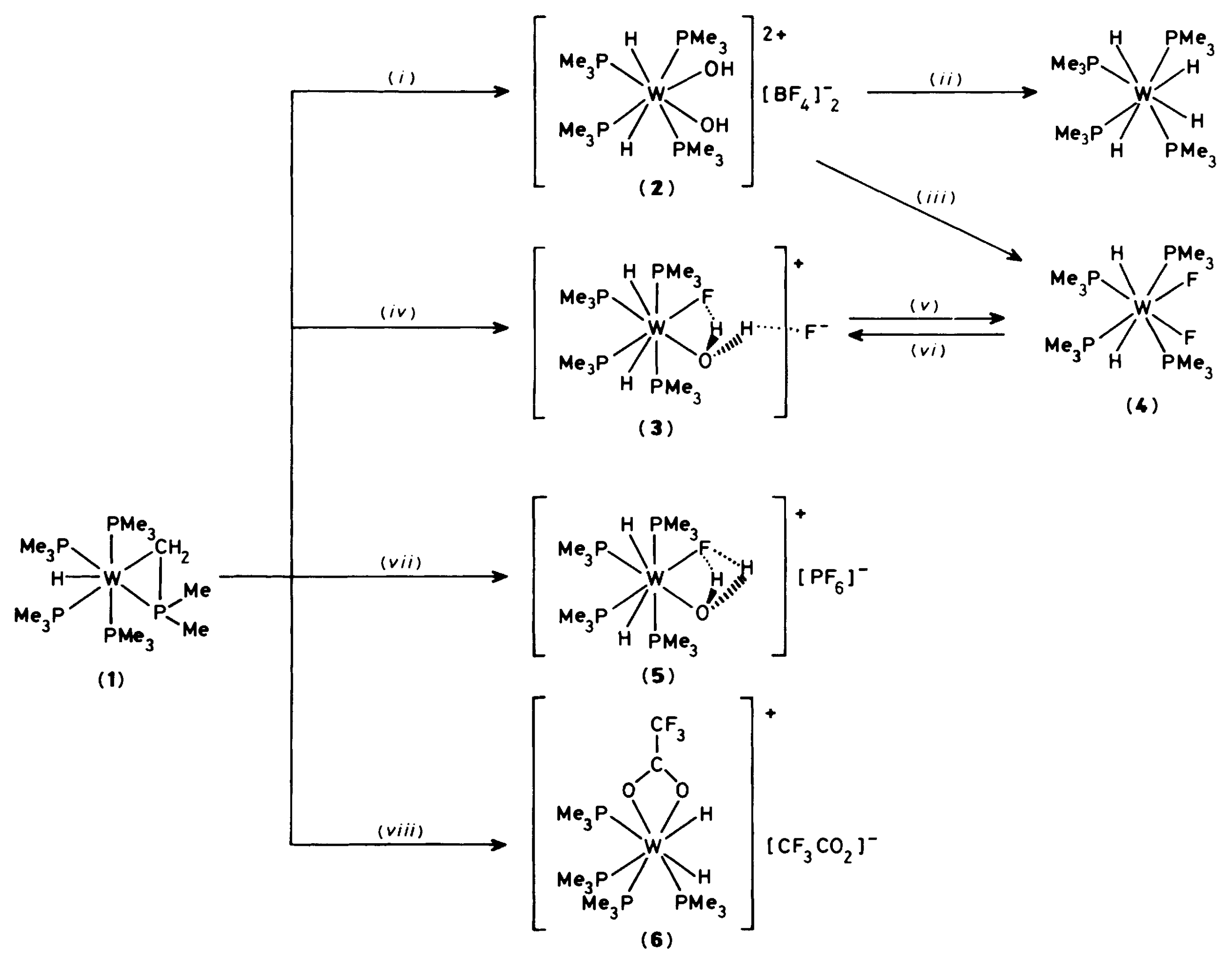
W(1)–P(1)	2.473(3)	P(1)–C(1)	1.77(2)
W(1)–P(2)	2.451(4)	P(1)–C(2)	1.83(2)
W(1)–P(3)	1.453(5)	P(1)–C(3)	1.93(2)
W(1)–O(1)	2.084(9)	P(2)–C(4)	1.83(1)
W(1) • • • F(1)	4.14(2)	P(2)–C(5)	1.80(2)
W(1)–F(2)	2.08(1)	P(3)–C(6)	1.83(2)
O(1) • • • F(1)	2.40(2)	P(3)–C(7)	1.81(3)
O(1) • • • F(2)	2.59(2)	F(1) • • • F(2)	3.32(2)

(*b*) Bond angles

P(1)–W(1)–P(1)	161.2(2)	O(1)–W(1)–P(3)	152.4(3)
P(2)–W(1)–P(1)	86.81(6)	F(2)–W(1)–P(1)	96.37(8)
P(3)–W(1)–P(1)	84.91(7)	F(2)–W(1)–P(2)	157.2(4)
P(3)–W(1)–P(2)	127.2(3)	F(2)–W(1)–P(3)	75.7(4)
O(1)–W(1)–P(1)	98.17(8)	F(2)–W(1)–O(1)	76.7(4)
O(1)–W(1)–P(2)	80.4(3)		

in CD_3OD consists of two triplets and selective decoupling of the methyl protons produces an extra triplet coupling in the ^{31}P-$\{^1H(Me)\}$ n.m.r. spectrum, thus demonstrating the presence of two hydride ligands. No coupling to fluorine was observed in either the ^1H or ^{31}P-$\{^1H\}$ n.m.r. spectrum. This initially suggested that there was no fluorine bound to tungsten in the complex. However, the ^{19}F-$\{^1H\}$ n.m.r. spectrum in CD_3OD possesses two very broad resonances at very different chemical shifts at δ −185.5 and −243.6. All the magnetic nuclei present in the system are of spin $I = \frac{1}{2}$, thus the broad nature of these resonances suggests that some exchange process occurs between co-ordinated and non-co-ordinated fluorine at such a rate that coupling to phosphorus and hydride ligands is not observed.

The ^1H and ^{19}F-$\{^1H\}$ n.m.r. spectra of (3) in $[^2H_8]$thf (thf = tetrahydrofuran) showed marked differences (see Table 1). The hydride resonance, which in CD_3OD was a triplet of triplets corresponding to coupling to only the phosphorus nuclei, displayed in $[^2H_8]$thf additional splitting assignable to ^{19}F coupling. This resonance collapses to a triplet in the ^1H-$\{^{31}P\}$ n.m.r. spectrum and thus demonstrates the presence of two fluorine ligands attached to tungsten. The ^{19}F-$\{^1H\}$ n.m.r. spectrum in $[^2H_8]$thf consists of a sharp triplet of triplets [J(P–F) 51 and 86 Hz] corresponding to coupling to four phosphorus nuclei. In addition, a resonance at δ 2.95 in the ^1H



Scheme 1. Reactions of (**1**) with protonic acids. (*i*) aqueous HBF_4; (*ii*) Na(K) alloy in thf; (*iii*) KH in thf; (*iv*) aqueous HF; (*v*) KH in thf; (*vi*) traces of H_2O; (*vii*) aqueous HPF_6; (*viii*) CF_3COOH

n.m.r. spectrum was assigned to non-co-ordinated water. These results suggested a $W(PMe_3)_4H_2F_2{\cdot}H_2O$ formulation in thf solutions and that there are exchange processes occurring in methanol solutions.

The *X*-ray crystal structure of (**3**) has been determined[12] and shows the compound consists of an ion pair. The structure of the cation $[W(PMe_3)_4H_2(OH_2)F]^+$ is based on a dodecahedral geometry with crystallographic mirror symmetry in the plane W(1),F(2),O(1),P(2),P(3). It has an equatorial plane containing two PMe_3 ligands and mutually cisoid F and H_2O ligands (Figure 2). The O(1)–W(1) distance (2.084 Å, Table 2) is a little shorter than 2.129 Å in $[W(PMe_3)_4H_3(OPh)]$, but much longer than a double bond length (1.70 Å).[19] It seems reasonable to assume a single bond between O(1) and W(1). The F(2)–W(1) distance (2.08 Å) agrees with 1.86—2.07 Å in $[WO(O_2)(ONC_9H_7)_2F_4]{\cdot}3H_2O$ (ONC_9H_7 = 8-hydroxyquinoline).[20] Although hydrogen atoms were not observed directly, the O(1)–F(2) distance of 2.59(2) Å, which is intermediate between an F–H···F interaction (2.3—2.6 Å) and an O–H···O interaction (2.6—2.8 Å), and the angle F(2)–W(1)–O(1) of 76.7(4)° suggest that interligand hydrogen bonding may be present as indicated in Figure 3. The anion F(1) is also at a hydrogen-bonded distance from O(1) (2.40 Å), in agreement with the broad O–H absorption in the i.r. spectrum which is distinct from that of $[W(PMe_3)_4H_2(OH)_2][BF_4]_2$ (**2**) which contains a sharp, strong absorption corresponding to a non-hydrogen-bonded hydroxo moiety. This may be contrasted with the compounds $[Zr(\eta\text{-}C_5Me_5)_2(OH)Cl]$ and $[Zr(\eta\text{-}C_5Me_5)_2(OH)_2]$ which show no significant intramolecular hydrogen bonding;[18] in $[Zr(\eta\text{-}C_5Me_5)_2(OH)Cl]$ the Cl–Zr–O angle is 98.8(1)° and in $[Zr(\eta\text{-}C_5Me_5)_2(OH)_2]$ the O–Zr–O angle is 99.7(3)° and the O···O distance 3.025(12) Å.

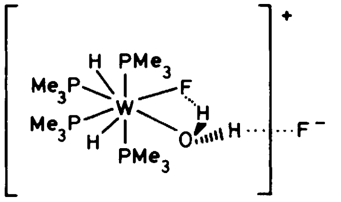


Figure 3. The structure of $[W(PMe_3)_4H_2(OH_2)F]F$ (**3**) showing the suggested positions of the hydrogen atoms

Solutions of (**3**) in thf and Et_2O exhibit the equilibrium (3)

$$[W(PMe_3)_4H_2(OH_2)F]F \rightleftharpoons [W(PMe_3)_4H_2F_2] + H_2O \quad (3)$$

in which the aqua ligand is readily displaced by the counter ion F^- giving the neutral compound $[W(PMe_3)_4H_2F_2]$ (**4**). Compound (**4**) can be isolated from solutions of (**3**) after treatment with KH; (**4**) can be converted into (**3**) by recrystallisation from wet diethyl ether. The neutral compound (**4**) in $[^2H_6]$benzene possesses a ^1H n.m.r. spectrum which is similar to that of (**2**)

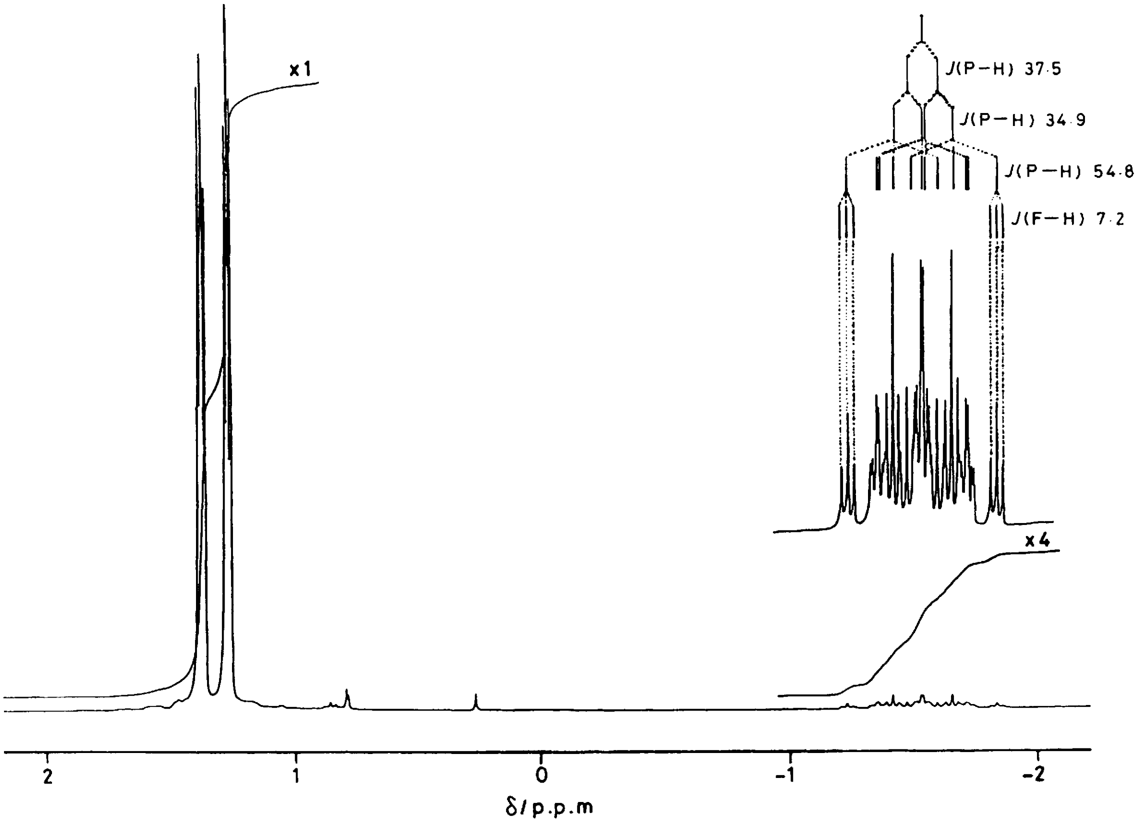


Figure 4. ^1H N.m.r. spectrum of $[W(PMe_3)_4H_2F_2]$ (**4**) in $[^2H_6]$benzene

except for the absence of the resonances attributable to the equilibrium concentration of H_2O (Figure 4). The hydride resonance is a doublet of doublets of triplets of triplets. This pattern collapses to a triplet in the ^1H-$\{^{31}P\}$ n.m.r. spectrum and thus assigns a triplet coupling of the hydrides to fluorine with J(H–F) 7.2 Hz. The remaining doublet of doublet of triplets coupling is also readily assigned to the typical hydride–phosphorus couplings observed in a rigid dodecahedral geometry. The ^{31}P-$\{^1H\}$ n.m.r. spectrum consists of two triplets of triplets with J(P–P) 11, J(P–F) 86, J(P–P) 11, and J(P–F) 51 Hz. The ^{19}F-$\{^1H\}$ n.m.r. spectrum is a triplet of triplets with J(P–F) 87 and 52 Hz. The difference (1 Hz) in the determination of the P–F coupling constants from the ^{19}F and ^{31}P n.m.r. spectra is within experimental error.

These data are, however, inconsistent with a rigid dodecahedral or any other reasonable eight-co-ordinate geometry, considering the magnetic equivalence of the fluorine nuclei with respect to both sets of phosphorus nuclei and protons. The chloro analogues of (**4**), namely $[W(PMe_3)_4H_2Cl_2]$[21,22] and $[W(PMe_2Ph)_4H_2Cl_2]$,[23] have been synthesised recently. The crystal structure of $[W(PMe_2Ph)_4H_2Cl_2]$ is based on a dodecahedral arrangement with *cis* hydrido and *cis* chloro ligands.[24] An analogous structure is, therefore, proposed for (**4**) and it is considered that the n.m.r. data are most readily explained either by there being second-order effects leading to an apparent over-simplification of the spin system, or by an intramolecular exchange of fluorine atoms which would therefore lead to their magnetic equivalence with respect to both sets of PMe_3 ligands and also hydride ligands.

We note that hydrido-fluoro complexes are rare.[24] Compound (**4**) reacts with Na(K) alloy in thf to give the well known $[W(PMe_3)_4H_4]$.[25]

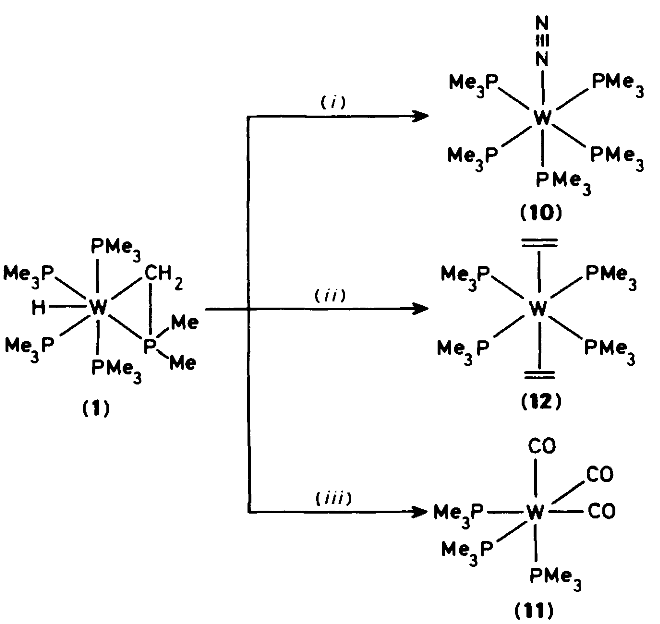
The protonation of $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ with aqueous HPF_6 gives the the hexafluorophosphate analogue of (**3**), namely, $[W(PMe_3)_4H_2(OH_2)F][PF_6]$ (**5**). The analytical and spectroscopic data characterising (**4**) and all other new compounds described in this work are given in Table 1, and are only discussed where further clarification may be required. Protonation of (**1**) with CF_3CO_2H gives the complex $[W(PMe_3)_4H_2(O_2CCF_3)][CF_3CO_2]$ (**6**); the spectral data (Table 1) for (**6**) show the presence of both bidentate and non-co-ordinated trifluoroacetato groups.

Treatment of (**1**) with dihydrogen in PMe_3 solvent gave pale yellow crystals of $[W(PMe_3)_5H_2]$ (**7**) in high yield. However, treatment of (**1**) in light petroleum (b.p. 100—120 °C) at *ca.* 65 °C with H_2 (2.5 atm) gave $[W(PMe_3)_4H_4]$ (**8**)[25] in high yield. There was no evidence for the presence of the assumed intermediate (**7**) under these conditions. The previous synthesis of (**7**) required WMe_6 as the precursor; this compound is explosive and difficult to prepare.[25] The synthesis described here represents a much more convenient, and larger scale route to (**7**).

When (**1**) is treated with silane at *ca.* 45 °C pale yellow crystals of $[W(PMe_3)_4H_2(SiH_3)_2]$ (**9**) can be isolated. The i.r. spectrum shows bands at 2 040 and 1 860 cm^{-1} assignable to ν(Si–H) and ν(W–H) respectively. The ^1H n.m.r. spectrum in $[^2H_8]$toluene at room temperature includes a quintet hydride resonance at δ −4.46, a single PMe_3 resonance at δ 1.41, and a five-line silyl resonance at δ 3.65. The data suggest that the molecule is fluxional, a characteristic which is common for eight-co-ordinate complexes.[26] Variable-temperature ^1H n.m.r. studies showed a gradual variation in appearance upon cooling and at −60 °C a spectrum was obtained which showed two types of PMe_3 ligands and complex hydride and silyl resonances. The reaction of (**1**) with SiH_4 in [$^2H_6$]benzene was monitored by ^1H and ^{31}P n.m.r. spectroscopy. After 12 h at 50 °C the major features of the ^1H n.m.r. spectrum showed resonances at δ 3.70 assignable to a SiH_3 group and a hydride resonance at δ -5.50 (doublet of quintets) assignable to W-hydrogens. The corresponding ^{31}P-{^1H} n.m.r. spectrum showed two resonances which appear as a doublet and quintet at δ -38.6 and -24.4 respectively. The data are therefore consistent with an initial oxidative addition of SiH_4 to give $[W(PMe_3)_5H(SiH_3)]$ as an intermediate which further reacts with silane, giving (**9**).

Treatment of (**1**) at *ca.* 60 °C with N_2 gives the previously described dinitrogen derivative $[W(PMe_3)_5(N_2)]$ (**10**).[27] Compound (**1**) reacts with carbon monoxide forming *fac*-$[W(PMe_3)_3(CO)_3]$ (**11**)[28] (Scheme 2).

$[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ reacts with C_2H_4 to give the known[25] *trans*-$[W(PMe_3)_4(C_2H_4)_2]$ (**12**). However, prolonged reaction between (**1**) and ethylene (2 atm) results in the oxidative dimerisation of C_2H_4 and formation of the bis-η-butadiene compound $[W(PMe_3)_2(\eta\text{-}C_4H_6)_2]$ (**13**), together with the dimerisation of ethylene to but-1-ene. The reaction was monitoried by ^1H n.m.r. spectroscopy on a solution of (**1**) in [$^2H_6$]benzene under C_2H_4 (1 atm). After 12 h at room temperature the mixture largely consisted of unreacted (**1**) together with (**12**) (*ca.* 20%). The mixture was then heated at *ca.* 65 °C and after 12 h (**1**) was still present, but the major species was (**12**). In addition, there were bands assignable to but-1-ene and a species with resonances at δ 3.8, 3.3, -0.3, and -0.54 in the ^1H n.m.r. spectrum and which probably contains a butadiene ligand. Prolonged heating (4 d) resulted in the total consumption of (**1**) and the formation of (**13**).[13] Treatment of pure *trans*-(**12**) with ethylene gave (**13**) showing that (**12**) can act as an intermediate in the formation of (**13**). The compound $[W(PMe_3)_2(\eta\text{-}C_4H_6)_2]$ (**13**) has been previously prepared, either from butadiene and (**1**),[11] or from $[W(\eta\text{-}C_4H_6)_3]$ and trimethylphosphine.[29]



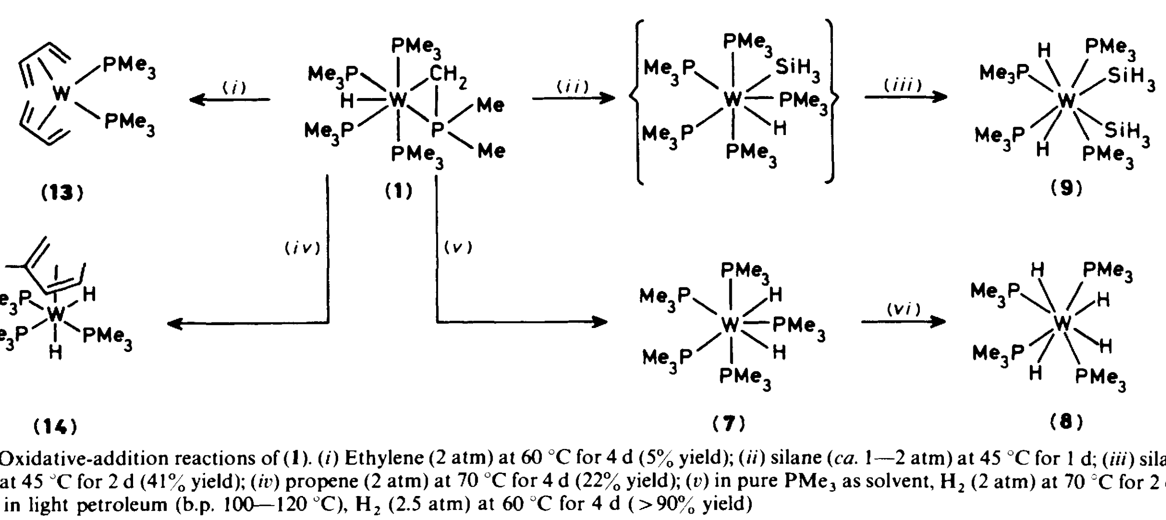
Scheme 2. Substitution reactions of (**1**). (*i*) N_2 (1 atm) at *ca.* 60 °C for 7 d; (*ii*) C_2H_4 (1—2 atm) at r.t. for 1 d; (*iii*) CO (2 atm) at 60 °C for 18 h

The dimerisation of C_2H_4 to but-1-ene is well known[30] but the further conversion to buta-1,3-diene has been previously reported only from the reaction between ethylene and the dimers $[Ti_2(\mu\text{-}\sigma{:}\eta^5\text{-}C_5H_4)(\eta\text{-}C_5H_5)_3]$ and $[Ti_2(\mu\text{-}\eta^5{:}\eta^{5'}\text{-}C_{10}H_8)(\mu\text{-}H)_2(\eta\text{-}C_5H_5)_2]$[31] and the monomer $[Ti(\eta\text{-}C_5Me_5)_2(C_2H_4)]$.[32] However, no η-butadiene–titanium species were detected in these reactions. As yet, we have not discovered the fate of the two hydrogens lost from the ethylene during the formation of butadiene.

The reaction of $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ and propene gave $[W(PMe_3)_3\{\eta\text{-}CH_2C(Me)CHCH(\textit{syn}\text{-}Me)\}H_2]$ (**14**) and it may be inferred that the η-diene ligand and two hydrogen ligands originate from two propene molecules.

The 2-methylpenta-1,3-diene ligand is assigned the η^4-*cis-syn* structure (see Table 1) on the basis of n.m.r. spectra. In particular, the H_a–H_e coupling constant is 7 Hz which is most consistent with a *syn* disposition rather than *anti*. The structure is supported by the observation of a marked increase in intensity of the resonance of H_f when H_c is irradiated which represents a nuclear Overhauser effect and thus demonstrates the proximity of these nuclei. The oxidative dimerisation of propene has been observed previously with $[\{Mo(\eta\text{-}C_6H_6)(\eta\text{-}C_3H_5)Cl\}_2]$–$AlEtCl_2$ mixtures to give $[Mo(\eta\text{-}C_6H_6)(\eta\text{-}C_3H_5)\{\eta^4\text{-}\textit{cis}\text{-}CH_2C(\textit{anti}\text{-}Me)CHCH(\textit{anti}\text{-}Me)\}]^+$[33] and with $[Re(PPh_3)_2H_7]$ to give $[Re(PPh_3)_2\{\eta^4\text{-}CH_2C(Me)CHCH(\textit{anti}\text{-}Me)\}H_3]$.[34]

The structures proposed for the new compounds are shown in the Schemes 1—3. Compound (**1**) is exceptionally reactive, especially with respect to oxidative-addition reactions, as shown by the sequential conversion of (**1**) to the d^2 compounds (**8**) and (**9**). The substitution chemistry of (**1**) and of the related compound $[Mo(PMe_3)_6]$ contradicts the normal order of ligand preference. For example, dinitrogen and ethylene do not



Scheme 3. Oxidative-addition reactions of (**1**). (*i*) Ethylene (2 atm) at 60 °C for 4 d (5% yield); (*ii*) silane (*ca.* 1—2 atm) at 45 °C for 1 d; (*iii*) silane (*ca.* 1—2 atm) at 45 °C for 2 d (41% yield); (*iv*) propene (2 atm) at 70 °C for 4 d (22% yield); (*v*) in pure PMe_3 as solvent, H_2 (2 atm) at 70 °C for 2 d (83% yield); (*vi*) in light petroleum (b.p. 100—120 °C), H_2 (2.5 atm) at 60 °C for 4 d (>90% yield)

normally displace tertiary phosphine ligands. This reversal can be broadly understood as a consequence of the electroneutrality principle. Thus, the metal centres of (**1**) and $[Mo(PMe_3)_6]$ are so electron rich that they prefer to lose the basic, donor, PMe_3 ligands and replace them with weakly donor ligands so that the electron density at the metal centre is reduced. The recent preliminary report[35] on the reaction of (**1**) with methanol further illustrates the desire for the tungsten centre of (**1**) to react so as to reduce the electron density. The methanol undergoes dehydrogenation giving the (η^2-formaldehyde)dihydride, $[W(PMe_3)_4(\eta^2\text{-}CH_2O)H_2]$.[35] In this context, we note that the formation of butadiene from ethylene may be associated with exceptionally electron-rich metal centres.

Experimental

All manipulations of air- and moisture-sensitive materials were carried out in an inert atmosphere achieved by the use of a dual vacuum/N_2 (or Ar) line using standard Schlenk techniques or in a dry-box under an atmosphere of N_2. Reactions involving neat trimethylphosphine or gases (3 atm) were carried out in glass ampoules sealed with a Teflon tap supplied by J. Young (Acton, London W3). N_2 and Ar were purified by passage through a gas drying column containing BASF catalyst and 4A molecular sieves. All solvents were thoroughly deoxygenated before use by repeated pumping followed by admission of N_2 (or Ar). Solvents were dried and purified by refluxing over a suitable drying agent, followed by distillation under a N_2 atmosphere. Toluene and light petroleum (b.p. 100—120 °C) were dried over molten sodium; benzene and tetrahydrofuran were dried over molten potassium; light petroleum (b.p. 30—40 and 40—60 °C) and pentane were dried over sodium–potassium alloy (1:3 w/w). Deuteriated solvents for n.m.r. were stored over activated molecular sieves or a potassium film and transferred by trap-to-trap distillation. Elemental analyses were obtained from the microanalytical department of this laboratory or from Alfred Bernhardt Ltd., Germany. Nuclear magnetic resonance spectra were recorded on the following instruments: JEOL JNM-PMX60, Bruker AM-250, Bruker WH-300, Bruker WH-400, Bruker AM-500. Chemical shifts (δ/p.p.m.) are relative to $SiMe_4$ for ^1H and ^{13}C spectra, relative to $(CF_3)_2CO$ for ^{19}F, and relative to $P(O)(OMe)_3$ for ^{31}P. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (qnt), multiplet (m), and virtually coupled multiplet (vcm).

Infrared spectra were recorded on either a Pye-Unicam SP2000 grating spectrophotometer, a Perkin-Elmer 457 grating spectrophotometer, or a Perkin-Elmer 1710 FT spectrophotometer. Mass spectra were recorded on an AEI MS 902 mass spectrometer updated by a data handling system supplied by Mass Spectroscopy Services Ltd.

(η^2-Dimethylphosphinomethyl)hydridotetrakis(trimethylphosphine)tungsten(II), (**1**).—*Method A.* A modification of the published procedure[11] was used. Na(K) alloy (1:3 w/w, 10 g) was placed in a glass ampoule in a liquid N_2 bath, and PMe_3 (40 cm^3) was condensed into the ampoule. The ampoule was kept in the liquid nitrogen bath and WCl_6 (10 g, 25.2 mmol) was added *via* a large bore poly(vinyl chloride) tube into the ampoule. Throughout this manipulation the N_2 was maintained at only slightly greater than atmospheric pressure in order to prevent condensation of liquid N_2. The ampoule was evacuated and then allowed to warm to room temperature (r.t.). A nitrogen atmosphere was admitted to the ampoule at r.t. which was then stirred at r.t. for 2 weeks. The excess PMe_3 was recovered *via* trap-to-trap distillation and the contents of the ampoule were extracted with light petroleum (b.p. 40—60 °C, 3 × 200 cm^3) and filtered giving a pale yellow solution. The solvent was removed *in vacuo* at *ca.* 30 °C giving pure $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ as a bright yellow powder. Yield, 7.5 g (25%).

Method B. The apparatus for synthesis using tungsten atoms has been described elsewhere.[36] Tungsten atoms (1.9 g, 10.33 mmol) were co-condensed with PMe_3 (70 cm^3) at −196 °C giving an orange matrix. The product was extracted from the apparatus with Et_2O (1 l), passed through a Celite bed and the solvent removed under reduced pressure at *ca.* 30 °C. The residue was extracted into light petroleum (b.p. 40—60 °C, 100 cm^3) and the mixture filtered. The ^1H n.m.r. spectrum of a small portion of this solution showed it to consist of pure $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$. The solvent was removed under reduced pressure at *ca.* 30 °C and the residue sublimed (80 °C, 10^{-4} Torr) onto a liquid N_2 probe giving yellow $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$. Yield, 1.0 g, (17%).

Dihydridodihydroxotetrakis(trimethylphosphine)tungsten(VI) *Bis(tetrafluoroborate)*, (**2**).—Compound (**1**) (900 mg, 1.60 mmol) in light petroleum (b.p. 40—60 °C, 60 cm^3) was treated dropwise with a solution of $HBF_4{\cdot}Et_2O$ in Et_2O (*ca.* 5%) with constant stirring until an orange solid was deposited in an almost colourless solution. The mixture was filtered and the residue was washed with Et_2O (2 × 10 cm^3), and extracted into thf (150 cm^3). The orange extract was filtered and then concentrated to *ca.* 50 cm^3 and cooled to −40 °C giving orange needle crystals. These were separated by filtration, washed with thf (2 × 2 cm^3) and dried *in vacuo.* The small amount of white $[PHMe_3][BF_4]$ which crystallized was separated by hand. Yield, 300 mg (27%).

Aquafluorodihydridotetrakis(trimethylphosphine)tungsten(IV) *Fluoride*, (**3**).—*Method A.* A stirred solution of (**1**) (350 mg, 0.62 mmol) in light petroleum (b.p. 40—60 °C, 20 cm^3) was treated dropwise with a 5% solution of aqueous HF (40%) in Et_2O. Initially an orange solution was obtained containing a yellow deposit. Addition of the HF solution was continued until the solution became pale yellow. The mixture was filtered and the residue washed with light petroleum (b.p. 40—60 °C, 2 × 10 cm^3). The residue was extracted into Et_2O (50 cm^3) and the extract was filtered. The yellow filtrate was concentrated to *ca.* 10 cm^3 and cooled to −40 °C giving yellow crystals which were filtered and washed with Et_2O at −78 °C. Yield, 250 mg (74%).

Method B. The compound $[W(PMe_3)_4H_2F_2]$ (200 mg, 0.38 mmol) in Et_2O (20 cm^3) was treated with H_2O (*ca.* 0.05 cm^3). The solution was concentrated and placed at −40 °C. The yellow crystals which formed were separated by filtration, washed with light petroleum (b.p. 40—60 °C, 2 × 5 cm^3) and dried *in vacuo.* Yield, 100 mg (49%).

Difluorodihydridotetrakis(trimethylphosphine)tungsten(IV), (**4**).—The compound $[W(PMe_3)_4H_2(OH_2)F]F$ (500 mg, 0.92 mmol) in thf (20 cm^3) was treated with excess KH (1.0 g). The initially orange solution became yellow-orange immediately and a gas was evolved. The mixture was stirred at r.t. for 3 h and then solvent was removed under reduced pressure at 40 °C. The residue was extracted into light petroleum (b.p. 40—60 °C, 40 cm^3). The extract was filtered giving a yellow-orange filtrate which was concentrated to *ca.* 5 cm^3 and cooled to −40 °C. The resulting pale yellow crystals were filtered off and washed with light petroleum (2 × 2 cm^3) at −78 °C and dried *in vacuo.* Yield, 400 mg (83%).

Aquafluorodihydridotetrakis(trimethylphosphine)tungsten(IV) *Hexafluorophosphate*, (**5**).—A stirred solution of (**1**) (700 mg, 1.24 mmol) in light petroleum (b.p. 40—60 °C, 20 cm^3) was treated in a dropwise manner with a solution of aqueous HPF_6 (65%) in Et_2O (*ca.* 5%). Initially, an orange solution containing a yellow deposit was obtained and the addition was stopped when the solution possessed a pale yellow colour. The mixture was filtered and the residue extracted into Et_2O (30 cm^3) and filtered giving a yellow-green solution. The Et_2O was removed under reduced pressure at r.t. giving a yellow-green solid. Yield, 75 mg (9%).

Method B. A stirred solution of (**1**) (330 mg, 0.62 mmol) in Et_2O (30 cm^3) was treated with a solution of aqueous HPF_6 (65%) in Et_2O (*ca.* 5%) and a yellow precipitate was formed in a yellow solution. The mixture was filtered and the yellow solid washed with Et_2O (2 × 5 cm^3) and then extracted into thf (60 cm^3). The mixture was filtered giving a lime-green solution which was concentrated and placed at −40 °C for 1 h. White crystals (of $[PHMe_3][BF_4]$) were formed and removed by filtration. The mother-liquor was concentrated further and placed at −40 °C for 12 h. Lime-green crystals formed which were separated by filtration, washed with cold thf (2 × 2 cm^3), and dried *in vacuo*. Yield, 75 mg (19%).

*Dihydrido(trifluoroacetato-*O,O′*)tetrakis(trimethylphosphine)tungsten*(IV) *Trifluoroacetate*, (**6**).—A stirred solution of (**1**) (200 mg, 0.35 mmol) in light petroleum (b.p. 40—60 °C, 25 cm^3) was treated dropwise with a solution of CF_3CO_2H in Et_2O (*ca.* 2 cm^3, 10%). Initial addition resulted in the formation of a yellow solid and a red solution which steadily became pale yellow. The addition was stopped when the onset of formation of a red oil was observed. The mixture was filtered and the yellow solid washed with Et_2O (10 cm^3) and dissolved in thf (20 cm^3). The mixture was filtered and the yellow filtrate was concentrated to *ca.* 5 cm^3 and placed at −40 °C. The resulting yellow crystals were separated, washed with thf (2 × 2 cm^3) at −78 °C and dried *in vacuo*.

Reaction of $[W(PMe_3)_4H_2(OH)_2][BF_4]_2$ *with* Na(K) *Alloy in Tetrahydrofuran.*—A solution of $[W(PMe_3)_4H_2(OH)_2][BF_4]_2$ (50 mg, 0.07 mmol) in thf (10 cm^3) was treated with an excess of Na(K) alloy (1:3 w/w) and stirred at r.t. for 1 h. The mixture was filtered giving a yellow solution and the solvent was removed under reduced pressure at *ca.* 40 °C. The residue was extracted into light petroleum (b.p. 40—60 °C, 10 cm^3) and the mixture filtered. The light petroleum was removed under reduced pressure at *ca.* 30 °C giving a white residue which was identified by ^1H n.m.r. spectroscopy as a mixture of $[W(PMe_3)_4H_4]$ and $[W(PMe_3)_3H_6]$ in the ratio 6:1.

Dihydridopentakis(trimethylphosphine)tungsten(II), (**7**).—Compound (**1**) (1.2 g, 2.12 mmol) in PMe_3 (20 cm^3) was treated with H_2 (2 atm) in a glass ampoule and stirred at 70 °C for 2 d. The PMe_3 was recovered *via* trap-to-trap distillation and the residual yellow solid was extracted into light petroleum (b.p. 40—60 °C, 20 cm^3). The mixture was filtered and the solvent was removed from the filtrate under reduced pressure at *ca.* 30 °C giving a bright yellow powder. Yield, 1.0 g, (83%).

Tetrahydridotetrakis(trimethylphosphine)tungsten(IV), (**8**).—Compound (**1**) (1.4 g, 2.48 mmol) in light petroleum (b.p. 100—120 °C, 25 cm^3) was treated with H_2 (2.5 atm) in a glass ampoule and stirred at 60 °C for 4 d. The solvent was removed under reduced pressure at *ca.* 60 °C and the residue extracted into light petroleum (b.p. 40—60 °C, 30 cm^3) and filtered giving a colourless solution. The solvent was removed under reduced pressure at *ca.* 30 °C giving a white crystalline solid. Yield, 1.1 g (90%).

Dihydridodisilyltetrakis(trimethylphosphine)tungsten(IV), (**9**).—Compound (**1**) (500 mg, 0.89 mmol) in light petroleum (b.p. 40—60 °C, 15 cm^3) in a glass ampoule was cooled to −196 °C in a liquid N_2 bath. Silane (*ca.* 10 mmol) was added and the mixture allowed to warm to r.t.; the solution was heated at 45 °C for 2 d. The mixture was cooled to −196 °C in a liquid N_2 bath, under N_2, and the tap of the glass ampoule replaced by a Suba-seal. A rapid flow of N_2 was then passed through the glass ampoule and the excess of silane, greatly diluted by the dinitrogen flow, was vented into the fume cupboard as the ampoule was allowed to warm to r.t. The residue was extracted into light petroleum (b.p. 40—60 °C, 30 cm^3) and the extract was filtered into a previously flamed-out Schlenk vessel giving a yellow-orange solution. This was concentrated (to *ca.* 2 cm^3) and placed at −40 °C. Yellow crystals formed which were separated by filtration, washed with light petroleum (b.p. 40—60 °C, 2 × 2 cm^3) and dried *in vacuo*. Yield, 200 mg (41%).

A solution of (**1**) (*ca.* 100 mg, 0.18 mmol) in C_6D_6 (*ca.* 1 cm^3), in an n.m.r. tube, was treated with SiH_4 (0.36 mmol) and heated at 50 °C for 1 d. The ^1H and ^{31}P n.m.r. data (Table 1) suggest that the product was mainly $[W(PMe_3)_5H(SiH_3)]$.

Dinitrogenpentakis(trimethylphosphine)tungsten(0), (**10**).—A solution of (**1**) (100 mg, 0.18 mmol) in light petroleum (b.p. 100—120 °C) was treated with N_2 (1 atm) and stirred at 65 °C for 1 week. The solvent was removed under reduced pressure at *ca.* 60 °C and the residue extracted into light petroleum (b.p. 40—60 °C, 30 cm^3), filtered and concentrated to *ca.* 1 cm^3 and cooled at −40 °C. The resulting orange crystals were separated by filtration and dried *in vacuo*. Yield, 50 mg (48%).

fac-*Tricarbonyltris(trimethylphosphine)tungsten*(0), (**11**).—Compound (**1**) (300 mg, 0.53 mmol) in light petroleum (b.p. 100—200 °C, 20 cm^3) was treated with CO (2 atm) and stirred at 60 °C for 18 h. The solvent was removed under reduced pressure at *ca.* 60 °C and the residue was extracted into light petroleum (b.p. 40—60 °C, 50 cm^3) and filtered giving a pale yellow filtrate. The solution was concentrated to *ca.* 15 cm^3 and cooled at −40 °C. The white crystals which formed were separated by filtration and washed with light petroleum (b.p. 40—60 °C, 2 × 2 cm^3) and dried *in vacuo*. Yield, 80 mg (30%).

Compound (**1**) (370 mg, 1.52 mmol) in light petroleum (b.p. 100—120 °C, 20 cm^3) was treated with one equivalent of CO (1.5 mmol), and stirred at 65 °C for 1 d, the products were identified by ^1H n.m.r. spectroscopy to be a mixture of $[W(PMe_3)_5(CO)]$, *fac*-$[W(PMe_3)_3(CO)_3]$, and mainly unreacted (**1**).

*Bis(*η*-ethylene)tetrakis(trimethylphosphine)tungsten*(0), (**12**) *and Bis(*η*-butadiene)bis(trimethylphosphine)tungsten*(0), (**13**).—Compound (**1**) (500 mg, 0.89 mmol) in light petroleum (b.p. 100—120 °C, 25 cm^3) in a Fischer–Porter pressure bottle was treated with C_2H_4 (2 atm) and stirred at 60 °C for 4 d. The mixture was filtered and the solvent removed under reduced pressure at *ca.* 60 °C. The residue was extracted into light petroleum (b.p. 40—60 °C, 20 cm^3) and filtered. One fifth of the solution was transferred, the solvent removed under reduced pressure at *ca.* 30 °C, and the ^1H n.m.r. spectrum of the residue was obtained. This demonstrated the presence of $[W(PMe_3)_2(\eta\text{-}C_4H_6)_2]$ and another unidentified compound containing a butadiene ligand. The solvent was removed from the remaining solution under reduced pressure at *ca.* 30 °C and the residue sublimed (60 °C, 10^{-4} Torr) onto a water-cooled probe giving an orange sublimate, but the greater part of the residue decomposed to an insoluble solid. The sublimate was extracted into MeOH (2 cm^3) and removal of the MeOH under reduced pressure at *ca.* 40 °C gave $[W(PMe_3)_2(\eta\text{-}C_4H_6)_2]$. Yield, *ca.* 20 mg (5%).

The reaction was subsequently followed by ^1H n.m.r. spectroscopy. A solution of (**1**) (50 mg, 0.09 mmol) in $[^2H_6]$benzene (0.5 cm^3) in a 5 mm n.m.r. tube was treated with C_2H_4 (1 atm) and the tube was sealed. The reaction was monitored by recording the ^1H n.m.r. spectrum at intervals. After 12 h at r.t. the mixture

Table 3. Atomic co-ordinates (× 10^4) for (**3**) with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W(1)	0	2 419.1(2)	2 500
P(1)	1 715(2)	2 424(2)	2 173(3)
P(2)	0	4 214(3)	1 852(5)
P(3)	0	840(4)	1 394(6)
C(1)	2 098(13)	1 406(16)	1 324(20)
C(2)	2 592(14)	2 391(17)	3 261(25)
C(3)	2 061(18)	3 642(26)	1 353(18)
C(4)	949(11)	4 659(12)	965(14)
C(5)	0	5 236(13)	2 848(17)
C(6)	976(15)	−63(14)	1 582(20)
C(7)	0	1 008(22)	−64(21)
O(1)	0	3 193(7)	3 982(8)
F(1)	0	2 664(16)	5 847(15)
F(2)	0	1 219(9)	3 626(9)

consisted largely of unreacted (**1**) and [W(PMe$_3$)$_4$(η-C$_2$H$_4$)$_2$]. After heating at 70 °C for a further 12 h an unidentified butadiene complex was formed and bands assignable to but-1-ene were observed. After a further 4 d at 70 °C there was evidence for the formation of [W(PMe$_3$)$_2$(η-C$_4$H$_6$)$_2$].

Reaction of [W(PMe$_3$)$_4$(η-C$_2$H$_4$)$_2$] *with* C$_2$H$_4$ *in* [^{2}H$_6$]-*benzene.*—A solution of [W(PMe$_3$)$_4$(η-C$_2$H$_4$)$_2$] (50 mg, 0.09 mmol) in [^{2}H$_6$]benzene (0.5 cm^3) in a 5 mm n.m.r. tube was saturated with C$_2$H$_4$ and the tube was sealed. The mixture was heated at 70 °C for 12 h and the ^{1}H n.m.r. spectrum showed the presence of the unidentified butadiene complex (**13**) and but-1-ene. After 5 d the major product was [W(PMe$_3$)$_2$(η-C$_4$H$_6$)$_2$].

Thermolysis of [W(PMe$_3$)$_4$(η-C$_2$H$_4$)$_2$] *in* [^{2}H$_6$]*benzene.*—A solution of [W(PMe$_3$)$_4$(η-C$_2$H$_4$)$_2$] (50 mg, 0.09 mmol) in [^{2}H$_6$]benzene (0.5 cm^3) in a 5 mm n.m.r. tube was heated at 70 °C for 14 d. No change was observed in the ^{1}H n.m.r. spectrum.

Dihydrido(cis,syn-2-*methylpenta*-1,3-*diene*)*tris*(*trimethylphosphine*)*tungsten*(II), (**14**).—Compound (**1**) (600 mg, 1.06 mmol) in light petroleum (b.p. 40—60 °C, 50 cm^3) in a Fischer–Porter bottle was saturated with propene (2 atm) and stirred at 70 °C for 4 d. The solvent was removed under reduced pressure at *ca.* 30 °C and the residue was extracted into light petroleum (b.p. 40—60 °C, 20 cm^3) and filtered giving an orange solution. The light petroleum was removed under reduced pressure at *ca.* 30 °C and the residue was sublimed (60—120 °C, 10^{-4} Torr) onto a water-cooled probe giving a yellow sublimate and leaving a substantial residue. The yellow sublimate was washed from the probe with pentane which was removed under reduced pressure giving a yellow solid. Yield, 100 mg (22%).

The reaction was subsequently monitored by ^{1}H n.m.r. spectroscopy. A solution of (**1**) (50 mg, 0.09 mmol) in [^{2}H$_6$]-benzene (0.5 cm^3) was saturated with C$_3$H$_6$ and sealed at −196 °C. The solution was heated at 65 °C and the reaction monitored by recording the ^{1}H n.m.r. spectrum. After 12 h the mixture largely consisted of unreacted (**1**) with only traces of (**14**) but after 2 weeks, conversion to the diene product was essentially complete.

Crystal Data.—C$_{12}$H$_{40}$F$_2$OP$_4$W, M = 546.3, orthorhombic, space group $Cmc2_1$, a = 14.223(4), b = 12.907(3), c = 12.343(4) Å, U = 2 265.746 Å^3, Z = 4, D_c = 1.601 Mg m^{-3}, λ = 0.7106 Å, μ(Mo-K_α) = 56.86 cm^{-1}, $F(000)$ = 1 048. Final R = 0.0440 for 1 937 observed reflections, $I > 3\sigma(I)$.

An orange crystal of dimensions 0.35 × 0.55 × 0.55 mm was sealed in a capillary under an inert atmosphere, and characterized by oscillation and Weissenberg photographs. Unit-cell parameters were refined from setting angles of 25 reflections ($38 < 2\theta < 40°$) measured on an Enraf-Nonius CAD-4 diffractometer. Intensities of 3 058 independent reflections with indices in the ranges h $\bar{1}$—11, k $\bar{1}$—16, l $\bar{1}$—19 were collected and 1 937 of these with $I > 3\sigma(I)$ were considered observed after Lorentz and polarization and absorption[37] corrections (maximum absorption correction 2.49). The merging R factor was 0.049.

Crystallographic calculations were carried out on the in-house VAX 11/750 computer with the CRYSTALS package.[38] The tungsten atom was found from a Patterson synthesis and the structure solution was developed by the difference electron-density method. No hydrogen atoms were found. After convergence of the full-matrix least-squares refinement (first with isotropic and then anisotropic thermal parameters), an empirical Chebyshev weighting scheme[39] with four coefficients [989.14, 1 341.71, 420.14, and 14.76 for $A(0)$, $A(1)$, $A(2)$ and $A(3)$ respectively] was applied. Anomalous scattering and extinction corrections[40] were included giving at convergence final values of R = 0.0440 and R' = 0.0621.* The atomic co-ordinates are listed in Table 3.

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* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

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