Trimethylphosphine–Tungsten Chemistry: Hydrido, Silyl, Fluoro, Hydroxy, and Aquo Derivatives: Crystal Structure of $[W(PMe_3)_4H_2(OH_2)F]F$

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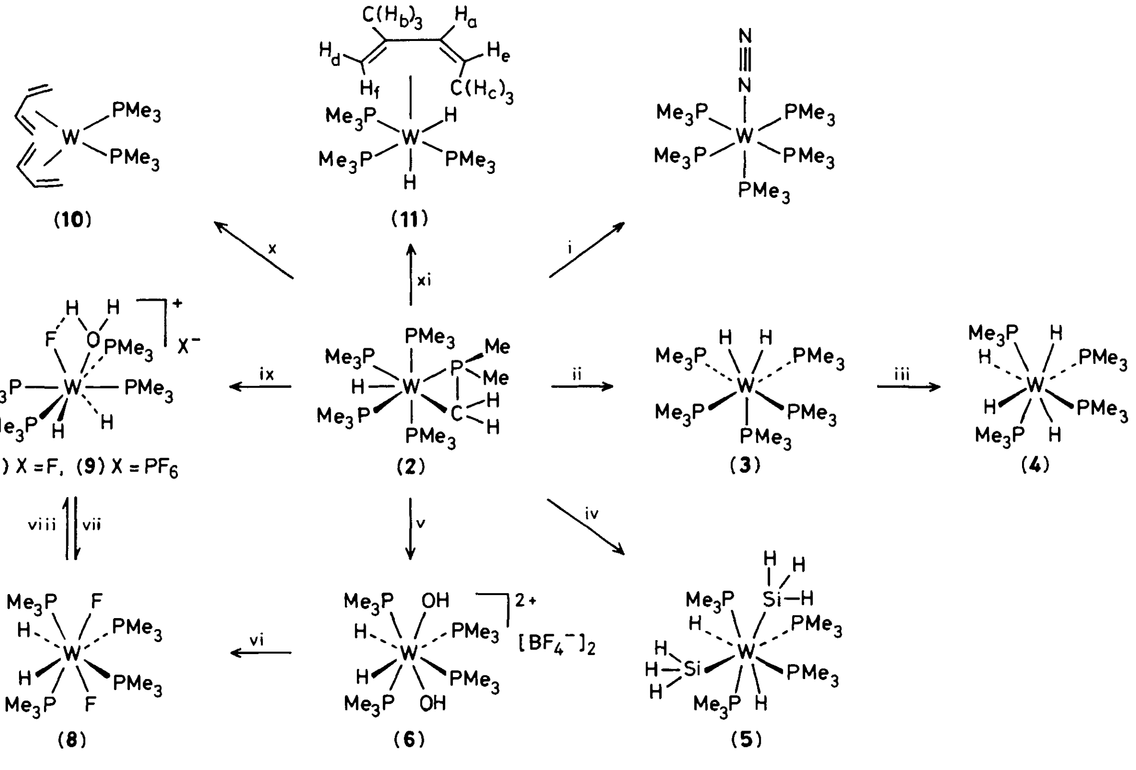
The compounds $W(PMe_3)_4H_2X_2$ (X = H, F, SiH_3), $[W(PMe_3)_4H_2(OH)_2]^{2+}[BF_4^-]_2$, and $[W(PMe_3)_4H_2(OH_2)F]F$, whose crystal structure has been determined, are described; $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ reacts with ethylene giving *inter alia* $W(\eta\text{-}C_4H_6)_2(PMe_3)_2$.

Hexakis(trimethylphosphine)molybdenum (**1**) undergoes substitution of PMe_3 ligands by molecules such as dinitrogen and ethylene, giving $Mo(PMe_3)_5N_2$ and $Mo(PMe_3)_4(\eta\text{-}C_2H_4)_2$ respectively. Dinitrogen and ethylene are not normally able to replace tertiary phosphine ligands and we attribute the driving force for these reactions of $Mo(PMe_3)_6$ to the resulting reduction of electron density on the molybdenum centre in the products. In other words, the molybdenum centre in (**1**) is excessively electron rich and substitution by ligands such as dinitrogen, which are poorer electron donors than PMe_3, reduces the 'electronic pressure'. In benzene solution (**1**) undergoes spontaneous dissociation of a PMe_3 ligand forming the compound $Mo(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, *viz.* equation (1).[1]

$$\underset{(1)}{M(PMe_3)_6} \rightleftharpoons M(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H + PMe_3 \quad (1)$$

Attempts to prepare the tungsten analogue of (**1**) by co-condensation of tungsten atoms and an excess of PMe_3 gave only the compound $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (**2**), in 20% yield. (**2**) is more conveniently prepared by reduction of WCl_6 by sodium–potassium alloy in pure PMe_3.[2] There is no evidence for the presence of $W(PMe_3)_6$ in benzene solutions of (**2**) containing an excess of free PMe_3. The tungsten atom is slightly larger than molybdenum so that the shift of the equilibrium in equation (1) to the right-hand side for tungsten reflects the greater stability of the higher oxidation state for tungsten compared to molybdenum. Here we describe some reactions of (**2**) (in Scheme 1) which demonstrate that there is a very strong drive to release electron density at the metal centre in this compound.

Treatment of (**2**) with dihydrogen formed initially $W(PMe_3)_5H_2$ (**3**),[3] and then $W(PMe_3)_4H_4$ (**4**).[3] Since (**2**) is readily available on a 10-gram scale this reaction provides a convenient route to (**3**) and (**4**). Addition of an excess of silane to (**2**) gave the bis-silyl derivative $W(PMe_3)_4(SiH_3)_2H_2$ (**5**). (**2**) also reacts readily with CO and N_2 giving *fac*-$W(PMe_3)_3(CO)_3$[4] and $W(PMe_3)_5N_2$[5] respectively. Attempts to protonate (**2**) with tetrafluoroboric acid gave the dihydroxy-



Scheme 1. i, N_2(2 atm) at 50 °C, *ca.* 50%; ii, H_2 (2 atm) in PMe_3 as solvent at 65 °C, *ca.* 95%; iii, H_2(2 atm), light petroleum (100—120 °C) at 60 °C, *ca.* 90%; iv, SiH_4, light petroleum (b.p. 40—60 °C) at 45 °C, *ca.* 45%; v, *ca.* 5% HBF_4 aq. in Et_2O at room temperature (r.t.), >70%; vi, KH in tetrahydrofuran (THF) at r.t., 20%; vii, KH in THF at r.t., >70%; viii, crystallise from wet Et_2O, >80%; ix, HX aq. (*ca.* 5%) in Et_2O, (X = F, PF_6), r.t., *ca.* 75%; x, C_2H_4 (2 atm), in light petroleum (b.p. 100—120 °C) at 60 °C, 7 days, *ca.* 30% (by n.m.r. spectroscopy); xi, C_3H_6 (2 atm), in light petroleum (b.p. 100—120 °C) at 70 °C, *ca.* 30%.

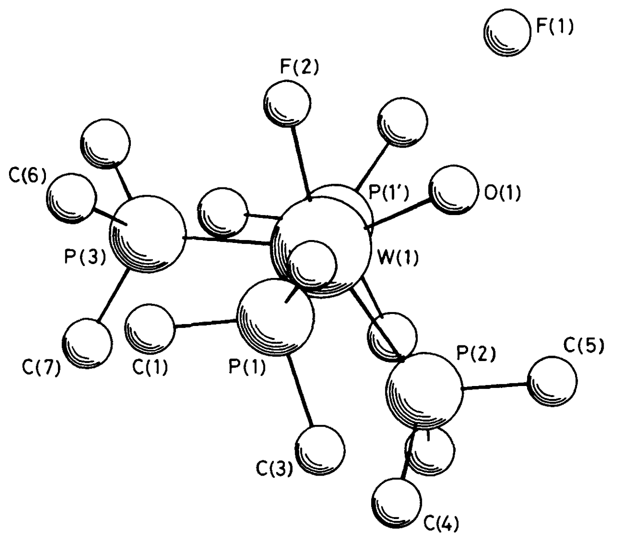


Figure 1. The structure of $[W(PMe_3)_4H_2(OH_2)F]^+F^-$ [F(2), O(1), P(2), and P(3) lie on the mirror plane and hydrogen atoms are omitted]. Selected bond distances (Å) and angles (°): W(1)–F(2) 2.08(1), W(1)–O(1) 2.084(9), W(1)–P(1) 2.473(3), W(1)–P(2) 2.451(4), W(1)–P(3) 2.453(5); O(1)–W(1)–F(2) 76.7(4), P(1)–W(1)–F(2) 96.37(8), P(2)–W(1)–F(2) 157.2(4), P(3)–W(1)–F(2) 75.7(4), P(1)–W(1)–O(1) 98.17(8), P(2)–W(1)–O(1) 80.4(3), P(3)–W(1)–O(1) 152.4(3), P(1)–W(1)–P(2) 86.81(6), P(1)–W(1)–P(3) 84.91(7), P(2)–W(1)–P(3) 127.2(3), P(1)–W(1)–P(1') 161.2(2).

dihydrido dicationic compound $[W(Pme_3)_4H_2(OH)_2]^{2+}[BF_4^-]_2$ (**6**). Treatment of (**2**) with hydrofluoric acid formed the aquo-fluoride $[W(PMe_3)_4H_2(OH_2)F]F$ (**7**), whose crystal structure has been determined.

Crystal data: $C_{12}H_{40}OF_2W$, M = 546.3, orthorhombic, space group $Cmc2_1$, a = 14.223(4), b = 12.907(3), c = 12.343(4) Å, U = 2265.75 Å^3, Z = 4, D_c = 1.601 g cm^{-3}, $F(000)$ = 1048, graphite-monochromated Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 56.86 cm^{-1}. 3058 Independent reflections were collected on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by Patterson and electron density methods and refined by full-matrix least-squares to R = 0.0432 (R_w = 0.0595) for 1937 observed reflections with $I > 3\sigma(I)$.†

The structure of (**7**) is shown in Figure 1. The compound consists of an ion-pair. The cation has mirror symmetry in the plane F(2)O(1)P(2)P(3), an equatorial belt of four PMe_3 ligands, and mutually *cisoid* F and OH_2 ligands. Although hydrogen atoms were not observed directly, the distance O(1)–F(2) 2.59(2) Å, which is intermediate between an F–H ··· F interaction (2.3—2.5 Å) and an O–H ··· O interaction (2.6—2.8 Å), and the angle F(2)–W(1)–O(1) 76.7(4)° suggests that interligand hydrogen bonding may be present. The anion F(1) is also at a hydrogen bonded distance from O(1) [O(1)–F(1) 2.40(2) Å]. This is in agreement with the broad O–H absorption at 2750 cm^{-1} in the i.r. spectrum. The presence of two hydride ligands was shown by n.m.r. and i.r. spectroscopy [ν(W–H) 1875 cm^{-1}] and their relative positions in the cation may be inferred from the dodecahedral geometry of the related compound $W(PMe_3)_4H_3(OPh)$.[3] In solution the aquo ligand of (**7**) is readily displaced by the counterion, F^-, giving the neutral compound $W(PMe_3)_4H_2F_2$ (**8**), which can be isolated by treatment of solutions of (**7**) with KH. (**7**) is reformed by crystallisation of (**8**) from wet diethyl ether Protonation of (**2**) with HPF_6 produced $[W(PMe_3)_4H_2(OH_2)F]PF_6$ (**9**), in which the aquo ligand is not readily displaced by the non-co-ordinating PF_6^- counterion.

Treatment of (**2**) with ethylene at a pressure of two atmospheres formed *inter alia* the bis-butadiene compound $W(\eta\text{-}C_4H_6)_2(PMe_3)_2$ (**10**). The catalytic conversion of ethylene into ethane and buta-1,3-diene by the titanium dimers $[\mu\text{-}(\eta^1:\eta^5C_5H_4)](\eta\text{-}C_5H_5)_3Ti_2$ and $[\mu\text{-}(\eta^5:\eta^5\text{-}C_{10}H_8)](\mu\text{-}H)_2(\eta\text{-}C_5H_5)_2Ti_2$ has been reported[6] but no intermediate organometallic species were isolated.

The compound (**10**) is also formed by treatment of (**2**) with butadiene,[7] or by reaction of $W(\eta\text{-}C_4H_6)_3$ with PMe_3.[8] Similarly, the molybdenum analogue $Mo(\eta\text{-}C_4H_6)_2(PMe_3)_2$ is formed in the reaction between butadiene and (**1**). Treatment of (**2**) in light petroleum (b.p. 100—120 °C) with propene gave the compound $W(PMe_3)_3[\eta\text{-}CH_2{=}C(Me)CH{=}C(\textit{cis}\text{-}Me)H]H_2$ (**11**).

The reactions and structures proposed for the new compounds (**2**)—(**11**) are shown in Scheme 1. All the new compounds have been characterised by microanalysis and n.m.r. spectroscopy.‡

In conclusion, compound (**2**) is oxidised by dihydrogen and by silane to the formally 4+ oxidation state. In the presence of proton acids (**2**) gives dihydride compounds, including unusual examples of fluoro-hydride derivatives, and (**2**) reacts with ethylene giving two butadiene ligands. We associate this

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Satisfactory microanalyses were obtained for all new compounds except for (**11**) for which the stoicheiometry is indicated by observation of the parent ion in the mass spectrum. The labelling of atoms for the n.m.r. data is shown in Scheme 1: vct = virtually coupled triplets. Spectroscopic data [J in Hz, ^{31}P n.m.r. rel. to ext. $(MeO)_3P$ in D_2O]. (**5**), ^1H n.m.r. in $[^2H_8]$toluene at r.t.: δ 3.65 [6H, quintet, J(P–H) 8.0, $2SiH_3$], 1.41 [36H, d, J(P–H) 8.0, $4PMe_3$], −4.46 [2H, quintet, J(P–H) 30.4, 2W–H]; $^{31}P\{^1H\}$ n.m.r. in $[^2H_8]$toluene: δ −37.1 p.p.m.; i.r. (mull): ν(W–H) 1860, ν(Si–H) 2020 cm^{-1}. (**6**), ^1H n.m.r. in CD_2Cl_2 (obtained immediately): δ 4.12 [2H, s, 2 O-H], 1.69 [18H, vct, J'(P–H) 4.3, $2PMe_3$], 1.51 [18H, vct, J'(P–H) 3.7, $2PMe_3$], −1.47 [2H, ddt, J_t(P–H) 51.4, J_d(P–H) 40.8, J_d(P–H) 36.7, 2W–H]; $^{31}P\{^1H\}$ n.m.r. in CD_3OD: δ −12.86 [2P, t, J(P-P) 7.0, J(P–W) 233, $2PMe_3$], −16.27 p.p.m. [2P, t, J(P–P) 7.0, J(P–W) 233, $2PMe_3$]; i.r. (mull): ν(O–H) 3470, ν(W–H) 1960 cm^{-1}. (**7**), ^1H n.m.r. in $[^2H_8]$THF, as for $W(PMe_3)_4H_2F_2$ (**8**) but also with unco-ordinated H_2O at δ 2.95. (**8**), ^1H n.m.r. in C_6D_6: δ 1.38 [18H, vct, J'(P–H) 3.9, $2PMe_3$], 1.27 [18H, vct, J'(P–H) 3.4 $2PMe_3$], −1.54 [2H, 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, 2W–H]; $^1H\{^{31}P\}$: δ 1.38 (18H, s, $2PMe_3$), 1.27 (18H, s, $2PMe_3$), −1.54 [2H, t, J(F–H) 7.2, 2W–H], $^{31}P\{^1H\}$ n.m.r. in C_6D_6: δ −12.50 [2P, tt, J_t(P–P) 10.5, J_t(P–F) 85.6, J(P–W) 370, $2PMe_3$], −15.46 p.p.m. [2P, tt, J_t(P–P) 10.5, J_t(P–F) 51.3, J(P–W) 229, $2PMe_3$]. The ^{31}P n.m.r. selectively methyl decoupled spectrum is complicated but demonstrates the presence of 2W–H. $^{19}F\{^1H\}$ n.m.r. in C_6D_6 (relative to $CFCl_3$): δ −231.1 p.p.m. [tt, J_t(P–F) 86.8, J_t(P–F) 52.0, 2W–F]. (**9**), ^1H n.m.r. in CD_3CN: δ 10.33 (2H, br., OH_2), 1.58 (18H, vct J'(P–H 4.3, $2PMe_3$], 1.43 [18H, vct, J'(P–H) 3.3, $2PMe_3$], −1.79 [2H, dddt, J_d(F–H) 17, J_d(P–H) 34.7, J_d(P–H) 39.5, J_t(P–H) 58.5, 2W-H]; $^{31}P\{^1H\}$ n.m.r. in CD_3CN: δ −73.77 [2P, dt, J_d(P–F) 49.5, J_t(P–P) 13.5, J(P–W) 182, $2PMe_3$], −81.69 p.p.m. [2P, dt, J_d(P–F) 63.8, J_t(P–P) 13.5, J(P–W) 232, $2PMe_3$]. $^{19}F\{^1H\}$ n.m.r. in CD_3CN (relative to $CFCl_3$): −239.5 p.p.m. (5 lines). (**11**), ^1H n.m.r. in C_6D_6: δ 4.15 (1H, m, H_a), 2.47 (3H, s, $3H_b$), 2.07 [3H, d, $J(H_c\text{–}H_e)$ 6, $3C\text{–}H_c$], 1.50 [9H, d, J(P–H) 6, PMe_3], 1.30 [9H, d, J(P–H) 6, PMe_3], 1.23 [9H, d, J(P–H) 6, PMe_3], 0.68 (1H, m, H_d), 0.15 (1H, m, H_e), −0.94 (1H, m, H_f), −1.23 (1H, m, W–H), −4.30 (1H, m, W–H); assignments made in conjunction with $^1H\{^{31}P\}$ double resonance experiments; $^{31}P\{^1H\}$ n.m.r. in C_6D_6: δ −29.55 [1P, d, $J(P_a\text{–}P_b)$ 15.2, J(P–W) 264, P_a], −32.50 [1P, dd, $J(P_a\text{–}P_b)$ 15.2, $J(P_b\text{–}P_c)$ 24.6, J(P–W) 206, P_b], −37.15 p.p.m. [1P, d, $J(P_b\text{–}P_c)$ 24.6, J(P–W) 221, P_c]. Relative geometry of P_a, P_b, and P_c is undetermined.

unusual chemistry with the exceptionally electron-rich nature of the tungsten centre of (**2**).

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References

1 F. G. N. Cloke, K. P. Cox, M. L. H. Green, J. Bashkin, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1982, 30; K. P. Cox, J. Bashkin, M. Brookhart, F. G. N. Cloke, A. E. Derome, P. D. Grebenik, J. C. Green, M. L. H. Green, and P. M. Hare, *J. Chem. Soc., Dalton Trans.*, 1984, in the press.
2 V. C. Gibson, P. D. Grebenik, and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1983, 1101.
3 K. W. Chiu, R. A. Jones, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse, and K. M. Abdul Malik, *J. Chem. Soc., Dalton Trans.*, 1981, 1204.
4 R. Mathieu, M. Lenzi, and R. Poilblanc, *Inorg. Chem.*, 1970, **9**, 2030.
5 E. Carmona, J. M. Marin, M. L. Poveda, R. D. Rogers, and J. L. Atwood, *J. Organomet. Chem.*, 1982, **238**, C63.
6 G. P. Pez, *J. Chem. Soc., Chem. Commun.*, 1977, 560.
7 V. C. Gibson, P. M. Hare, and M. L. H. Green, unpublished results.
8 J. R. Bleeke, personal communication.