Synthesis of (η-Cyclopentadienyl)(trimethylphosphine)tungsten Derivatives and Related Chemistry*

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New or improved syntheses of the compounds $[W(\eta\text{-}C_5H_5)(PMe_3)_2H_3]$, $[W(\eta\text{-}C_5H_6)(PMe_3)_3H_2]$, $[W(\eta\text{-}C_5H_5)(PMe_3)_3H_2][BF_4]$, $[W(\eta\text{-}C_5H_5)(PMe_3)_3H]$, $[W(\eta\text{-}C_5H_5)(PMe_3)H_5]$, $[W(\eta\text{-}C_5H_4Et)(PMe_3)H_5]$, $[W(\eta\text{-}C_5H_5)(\eta^2\text{-}C_5H_8)(PMe_3)_2H]$, $[W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Et)H_2]$, $[W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Et)Cl_2]$, $[W(\eta\text{-}1,3\text{-}C_6H_8)(PMe_3)_3H_2]$, and $[W(\eta^4\text{-}C_5H_5\text{-}exo\text{-}CHPh_2)(PMe_3)_3H_2]$ are described. N.m.r. studies on $[W(PMe_3)_5H(D)]$ show that the HD moiety is not present as an η^2-HD ligand.

Although mono(η-cyclopentadienyl)tungsten complexes are well known,[1–3] the derivatives are normally restricted to compounds containing CO, NO, and halide as co-ligands. Recently we reported the synthesis of some (η-ethylcyclopentadienyl)(trimethylphosphine)tungsten derivatives using $[W(\eta^2\text{-}CH_2PMe_2)(PMe_3)_4H]$ as the key starting material.[4] Here we describe further syntheses and some reactions of electron-rich, half-sandwich (η-cyclopentadienyl)(trimethylphosphine)tungsten derivatives in which the precursor tungsten compounds are the polyhydride compounds $[W(PMe_3)_3H_6]$,[5,6] $[W(PMe_3)_4H_4]$,[5,6] or $[W(PMe_3)_5H_2]$.[4] Some interconversion reactions of these polyhydrides are also discussed. Part of this work has been communicated.[7]

Results and Discussion

Treatment of the readily available dihydride $[W(PMe_3)_5H_2]$ (**1**) with cyclopentadiene gives yellow air-sensitive crystals of $[W(\eta\text{-}C_5H_5)(PMe_3)_2H_3]$ (**2**) in good yield. The compound (**2**) is also formed in the reaction of $[W(PMe_3)_4H_4]$ (**3**) with cyclopentadiene, but in small yields; other products of this reaction were the hexahydride $[W(PMe_3)_3H_6]$ (**4**) and, in trace amounts, the well known[8] $[W(\eta\text{-}C_5H_5)_2H_2]$ (**5**). The structures and reactions described in this study are shown in Schemes 1 and 2.

Treatment of the hexahydride (**4**) with cyclopentadiene gave a high yield of yellow crystalline $[W(\eta\text{-}C_5H_6)(PMe_3)_3H_2]$ (**6**) and the ^1H n.m.r. spectrum of the reaction mixture showed bands assignable to cyclopentene.

The reaction between the tetrahydride (**3**) and cyclopentadiene proceeds only under photochemical activation. The reaction was monitored by ^1H n.m.r. spectroscopy and the initial product was (**6**). Further photolysis in the presence of an excess of cyclopentadiene gave, sequentially, $[W(\eta\text{-}C_5H_5)(PMe_3)_2H_3]$ (**2**), then a further intermediate which the ^1H n.m.r. data suggest to be $[W(\eta\text{-}C_5H_5)(\eta^2\text{-}C_5H_8)(PMe_3)_2H]$, and finally $[W(\eta\text{-}C_5H_5)_2H_2]$ (**5**).

The ^1H n.m.r. spectrum of (**6**) showed the two W hydrogens to be inequivalent, and the $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum of (**6**) showed two broad singlets assignable to these hydrogens. The assignment of the spectrum was assisted by nuclear Overhauser enhancement (n.O.e.) experiments, see the Figure. For example, irradiation of the hydride resonance at δ −4.62 resulted in a significant enhancement (2.2%) of the ring protons at δ 3.98, whereas irradiation of the hydride resonance at δ −1.18 resulted in no observable enhancement of any proton. These observations allow assignment of the resonance at δ −4.62 to the hydride ligand which lies in the plane of the phosphorus atoms. Although substantial changes in intensity are observed for the relevant resonances, the n.O.e. data do not permit distinction between the *exo* and *endo* protons of the CH_2 moiety of the cyclopentadiene ligand since it cannot be predicted, *a priori*, whether the *exo* or *endo* proton will lie closest to the vicinal protons. The empirical 'W-rule'[9] states that the *exo* proton should couple most strongly to the phosphorus nuclei. The resonances assigned to the CH_2 protons occur at δ 3.38, a doublet with J(H–H) 7.2 Hz, and at δ 5.61, which is a more complex multiplet due to phosphorus coupling, and therefore is assigned to H_{exo}. The i.r. spectrum of (**6**) shows a strong band at 2 709 cm^{-1} assignable to $\nu(C\text{–}H_{exo})$.[9]

Treatment of $[W(\eta\text{-}C_5H_6)(PMe_3)_3H_2]$ (**6**) with $HBF_4\cdot Et_2O$ gave white crystalline $[W(\eta\text{-}C_5H_5)(PMe_3)_3H_2][BF_4]$, (**7**). The ^1H n.m.r. spectrum of (**7**) shows two bands assignable to W–hydrogen resonances, a doublet of quartets at δ 0.70 and a triplet of triplets at δ −6.45. The value for J(H–H) = 8.4 Hz confirms that the two hydrogens are not bonded as an η^2-H_2 ligand.[10] A n.O.e. experiment assigns the resonance at δ −6.45 to the hydride which lies in the plane of the phosphorus atoms. The data characterising all the new compounds described in this work are given in the Table and will only be discussed where interpretation is not straightforward.

Treatment of compound (**7**) with potassium hydride causes deprotonation giving the monohydride, $[W(\eta\text{-}C_5H_5)(PMe_3)_3H]$ (**8**). This is characterised, in particular, by the quartet hydride resonance at δ −10.61 in the ^1H n.m.r. spectrum and a doublet phosphorus resonance in the partially decoupled $^{31}P\text{-}\{^1H\text{–}Me\}$ n.m.r. spectrum. The spectra show that (**8**) is fluxional at room temperature. Deprotonation of compound (**6**) can also be achieved using aqueous potassium hydroxide. Treatment of (**8**) with $HBF_4\cdot Et_2O$ re-forms (**7**).

The compound (**8**) did not react with dihydrogen (2 atm at 55 °C for 2 d) but photolysis in the presence of dihydrogen gave the d^0 pentahydride $[W(\eta\text{-}C_5H_5)(PMe_3)H_5]$ (**9**), in almost quantitative yield (n.m.r.). Similarly, photolysis of (**2**) in the presence of dihydrogen (1 atm) gives high yields of (**9**). The pentahydride (**9**) is also formed in a slow reaction of (**2**) with dihydrogen at 50 atm and 65 °C. It was prepared previously by co-condensation of tungsten atoms with a mixture of cyclopentane and trimethylphosphine.[11] The presence of five hydrogen ligands in (**9**) is convincingly demonstrated by the observation of a sextet in the selectively decoupled $^{31}P\text{-}\{^1H\text{–}Me\}$ n.m.r. spectrum. Low-temperature ^1H n.m.r. studies (at 300 MHz) on $[W(\eta\text{-}C_5H_5)(PMe_3)H_5]$, which produced no change in the n.m.r. spectrum down to *ca.* −40 °C, suggest that the structure is based on a pentagonal bipyramid with axial η-C_5H_5 and PMe_3 ligands with the hydrides in the pentagonal

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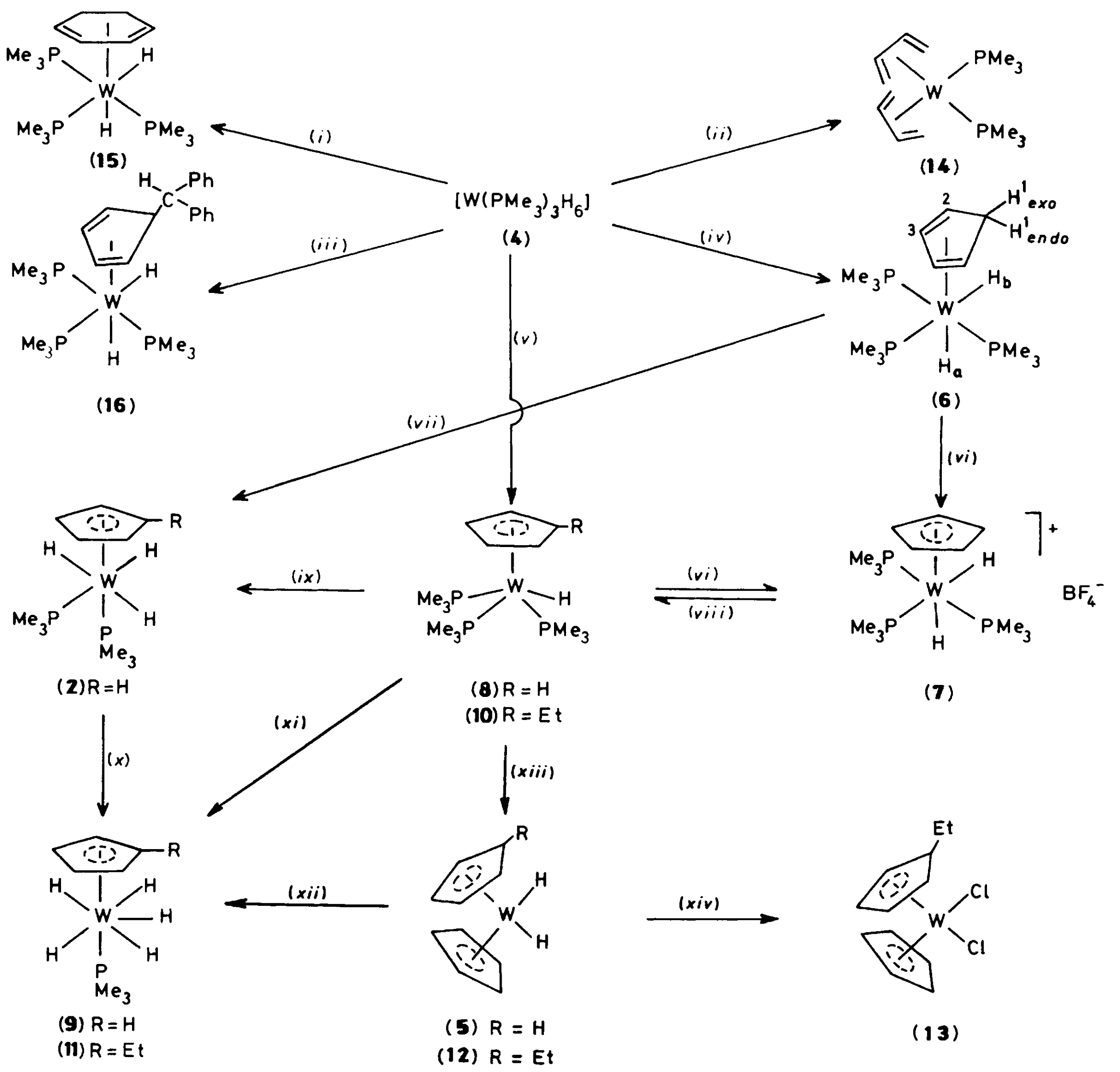
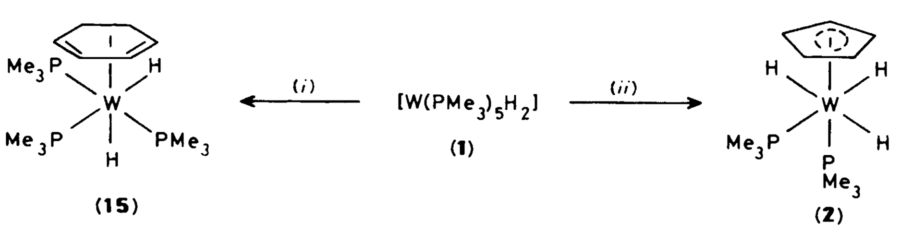
* *Non-S.I. units employed:* atm ≈ 101 325 Pa, Torr ≈ 133 Pa, eV ≈ 1.6×10^{-19} J.



Scheme 1. (*i*) Cyclohexa-1,3-diene in benzene at 65 °C for 5 d; (*ii*) butadiene at *ca.* 100 °C for 3 d; (*iii*) 6,6-diphenylfulvene at 70 °C for 4 d; (*iv*) cyclopentadiene at 80 °C for 3 d; (*v*) spiro[2,4]hepta-4,6-diene at 80 °C for 6 d, 41%, (**10**); (*vi*) $HBF_4 \cdot Et_2O$ at r.t.; (*vii*) H_2 (3 atm), photolysis for 3 d; (*viii*) KH, then water [or KOH(aq)]; (*ix*) H_2 (2.5 atm) and photolysis for 12 h, 87%; (*x*) R = H, H_2 (2.5 atm), photolysis for 18 h; (*xi*) R = H, H_2 (2.5 atm), photolysis for 12 h; R = Et, H_2 (2.5 atm), photolysis for 3 d; (*xii*) R = H, cyclopentadiene, 140 °C, 12 h, *ca.* 65%; (*xiii*) R = Et, cyclopentadiene, photolysis for 3 d; (*xiv*) CCl_4 for *ca.* 2 min



Scheme 2. (*i*) Cyclohexa-1,3-diene at 60 °C for 2 weeks; (*ii*) cyclopentadiene at 65 °C for 3 d, 16%

plane. However, since it is well established that nine-co-ordinate compounds containing hydrogen ligands have low energy barriers to intramolecular exchange of hydrogen ligands,[12–14] the data do not exclude a structure for (**9**) with a lower symmetry than that shown in Scheme 1.

Photolysis of the previously described $[W(\eta\text{-}C_5H_4Et)(PMe_3)_3H]^4$ (**10**) under dihydrogen gave $[W(\eta\text{-}C_5H_4Et)(PMe_3)H_5]$ (**11**) in good yield.

In a search for alkane activation chemistry, $[W(\eta\text{-}C_5H_6)(PMe_3)_3H_2]$ (**6**) was subjected to prolonged photolysis in $[^2H_{12}]$cyclohexane. However, the ^1H n.m.r. spectrum of the reaction mixture provided no evidence for H–D exchange but

Table. Analytical and spectroscopic data

	N.m.r. data[b]	
Compound, colour, and analysis (%)[a]	^{1}H	^{13}C and ^{31}P
(2) $[W(\eta\text{-}C_5H_5)(PMe_3)_2H_3]$ Yellow C, 32.2 (32.7); H, 6.5 (6.4)[d]	4.23 (5 H, 4 lines, C_5H_5), 1.44 [18 H, d, J(P–H) 8.2, 2 PMe_3], −5.27 [3 H, t, J(P–H) 35, 3 W–H][c]	$^{31}P\text{-}\{^1H\}$: −26.8 [s, J(P–W) 234, 2 PMe_3][c] $^{31}P\text{-}\{^1H\text{–}Me\}$: −26.8 (q)[c]
(6) $[W(\eta\text{-}C_5H_6)(PMe_3)_3H_2]$ Yellow[e] C, 34.9 (35.0); H, 7.4 (7.3)	5.61 (1 H, m, $H^1{}_{exo}$), 3.98 (2 H, br s, 2 H^3), 3.38 [1 H, d, J(H–H) 7.2, $H^1{}_{endo}$], 1.53 (2 H, br s, 2 H^2), 1.38 [18 H, d, J(P–H) 6.5, 2 PMe_3], 1.25 [9 H, d, J(P–H) 6.8, PMe_3], −1.18 [1 H, br q, J_q(P–H) 45.0, W–H_b], −4.62 (1 H, br, W–H_a)[c]	^{13}C: 63.5 [d, J(C–H) 176, 2 C^2 or 2 C^3], 48.6 [tq, J_t(C–H) 127, J_q(P–C) 5, C^1], 31.1 [d, J(C–H) 159, 2 C^3 or 2 C^2], 27.1 [dq, J_d(P–C) 29, J_q(C–H) 128, 2 PMe_3], 26.5 [dq, J_d(P–C) 24, J_q(C–H) 128, PMe_3][c] $^{31}P\text{-}\{^1H\}$: −30.27 [2 P, d, J(P–P) 12, J(P–W) 227, 2 PMe_3], −33.64 [1 P, t, J(P–P) 12, J(P–W) 237, PMe_3][c]
(7) $[W(\eta\text{-}C_5H_5)(PMe_3)_3H_2][BF_4]$ White C, 29.8 (29.7); H, 5.8 (6.0)[f]	4.83 [5 H, t, J(P–H) 1.8, C_5H_5], 1.66 [27 H, d, J(P–H) 10.5, 3 PMe_3], 0.70 [1 H, dq, J_d(H–H) 8.4, J_q(P–H) 50.0, W–H_b], −6.45 [1 H, tt, J_d(P–H) 8.4, J_d(H_a–H_b) 8.4, J_t(P–H) 39.8, W–H_a][g]	^{13}C: 83.3 [dt, J_d(C–H) 181, ^3J_t(C–H) 7, C_5H_5], 26.6 [dq, J_d(P–C) 35, J_q(C–H) 128, 2 PMe_3], 25.9 [dq, J_d(P–C) 32. J_q(C–H) 128, PMe_3][g] $^{31}P\text{-}\{^1H\}$: −33.42 [2 P, d, J(P–P) 16, J(P–W) 214, 2 PMe_3], −39.10 [1 P, t, J(P–P) 16, J(P–W) 237, PMe_3][g]
(8) $[W(\eta\text{-}C_5H_5)(PMe_3)_3H]$ Orange-yellow[h] C, 35.0 (35.15); H, 6.75 (6.9)	4.39 (5 H, s, C_5H_5), 1.43 [27 H, vcm, J'(P–H) 5.7, 3 PMe_3], −10.61 [1 H, q, J(P–H) 48.2, J(W–H) 46, W–H][c]	^{13}C: 78.2 [d, J(C–H) 171, C_5H_5], 33.2 [qm, J(C–H) 124, 3 PMe_3][c] $^{31}P\text{-}\{^1H\}$: −31.4 [s, J(P–W) 335, 3 PMe_3][c] $^{31}P\text{-}\{^1H\text{–}Me\}$: −31.4 [d, J(P–H) 48.2, J(P–W) 335, 3 PMe_3][c]
(9) $[W(\eta\text{-}C_5H_5)(PMe_3)H_5]$ White C, 29.1 (29.1); H, 6.0 (5.8)[i]	4.83 [5 H, d, J(P–H) 2.1, C_5H_5], 1.47 [9 H, d, J(P–H) 9.7, PMe_3], −3.95 [5 H, d, J(P–H) 42.4, J(W–H) 42.5, 5 W–H][c]	$^{31}P\text{-}\{^1H\}$: −22.2 [s, J(P–W) 49, PMe_3][c] $^{31}P\text{-}\{^1H\text{–}Me\}$: −22.2 (sxt, PMe_3)[c]
(11) $[W(\eta\text{-}C_5H_4Et)(PMe_3)H_5]$ White C, 33.6 (33.5); H, 6.7 (6.4)[j]	4.93 (2 H, m, 4 lines, 2 H_a or 2 H_b), 4.78 (2 H, m, 4 lines, 2 H_b or 2 H_a), 2.39 [2 H, q, J(H–H) 7.4, $C_5H_4CH_2CH_3$], 1.46 [9 H, d, J(P–H) 9.8, PMe_3], 1.07 [3 H, t, J(H–H) 7.4, $C_5H_4CH_2CH_3$], −3.71 [5 H, d, J(P–H) 42.2, J(W–H) 42.8, 5 W–H][c]	^{13}C: 110.0 (s, C_c), 80.5 (d, 2 C_a or 2 C_b), 78.3 (d, 2 C_b or 2 C_a), 29.4 [dq, J_d(P–C) 36, PMe_3], 23.2 (t, CH_2), 16.1 (q, CH_2CH_3)[c]
(12) $[W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Et)H_2]$ Orange C, 40.2 (41.9); H, 4.8 (4.7)	4.51 (2 H, br s, 2 H_a or 2 H_b), 4.37 (5 H, s, C_5H_5), 4.17 (2 H, br s, 2 H_b or 2 H_a), 2.46 [2 H, q, J(H–H) 7.5, CH_2], 1.17 [3 H, t, J(H–H) 7.5, CH_3], −11.81 [2 H, s, J(W–H) 74.4, 2 W–H][c]	^{13}C: 103.8 (s, C_c), 74.0 [d, J(C–H) 177, 2 C_a or 2 C_b], 72.0 [dt, ^1J_d(C–H) 180, ^3J_t(C–H) 6, C_5H_5], 67.1 [d, J(C–H) 186, 2 C_b or C_a], 23.5 [t, J(C–H) 128, CH_2], 15.9 [q, J(C–H) 126, CH_3][c]
(13) $[W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Et)Cl_2]$ Olive-green C, 34.8 (34.9); H, 3.4 (3.2)	5.7 (5 H, s, C_5H_5), 5.54 (2 H, m, 2 H_a or 2 H_b), 5.12 (2 H, m, 2 H_b or 2 H_a), 2.34 [2 H, q, J(H–H) 7.5, CH_2], 1.09 [3 H, t, J(H–H) 7.5, CH_3][k]	
(15) $[W(\eta\text{-}1,3\text{-}C_6H_8)(PMe_3)_3H_2]$ Light brown C, 36.0 (36.4); H, 7.4 (7.5)[l]	3.85 (2 H, br, 2 H of C_6H_8), 2.54 [2 H, d, J(H–H) 8.7, 2 H of C_6H_8], 2.20 (2 H, br, 2 H of C_6H_8), 1.75 [2 H, d, J(H–H), 8.7, 2 H of C_6H_8], 1.35 [18 H, d, J(P–H) 7.4, 2 PMe_3], 1.28 [9 H, d, J(P–H) 6.6, PMe_3], −1.53 [br q, J(P–H) 40, W–H_b], −5.55 (br, W–H_a)[c]	^{13}C: 68.3 [d, J(C–H) 168, C_a or C_b], 47.6 [d, J(C–H) 142, C_b or C_a], 28.8 [t, J(C–H) 125, C_c], 26.7 [dq, J(P–C) 27, J(C–H) 127, 2 PMe_3], 26.2 [poorly resolved dq, J(P–C) 27, PMe_3][m] $^{31}P\text{-}\{^1H\}$: −30.9 [d, J(P–P) 14, J(P–W) 220, 2 PMe_3], −32.1 [t, J(P–P) 14, J(P–W) 242, PMe_3][m] $^{31}P\text{-}\{^1H\text{–}Me\}$: −30.9 (dt, 2 PMe_3), −32.1 (tt, PMe_3)[m]
(16) $[W(\eta\text{-}C_5H_5CHPh_2)(PMe_3)_3H_2]$ Yellow-orange[n]	7.36—7.18 (10 H, m, 2 Ph), 5.35 (1 H, s, H^5 or H^6), 4.82 (4 H, m, 2 H^7 and 2 H^8), 1.75 (9 H, d, J(P–H) 7.9, PMe_3], 1.55 [18 H, d, J(P–H) 8.9, 2 PMe_3], 1.01 (1 H, m, W–H_b), *ca.* 1.0 [1 H, located by double resonance, H^6 or H^5], −5.84 [1 H, dddt, J_d(H–H) 1.0, ^2J_d(H–H) 9.5, J_d(P–H) 7.0, J_t(P–H) 35.5, W–H_a][o]	^{13}C: 145.1 (s, 2 C^4), 129.7 (d, 4 C^2 or 4 C^3), 129.3 (d, 4 C^3 or 4 C^2), 127.5 (d, 2 C^1), 88.3 (d, 2 C^7 or 2 C^8), 82.7 (d, C^6 or C^5), 75.2 (d, 2 C^8 or 2 C^7), 51.9 (d, C^5 or C^6), 26.4 [dq, J_d(P–C) 35, 2 PMe_3], 25.6 [dq, J_d(P–C) 31, PMe_3][o] $^{31}P\text{-}\{^1H\}$: −33.4 [d, J(P–P) 16, J(P–W) 210, 2 PMe_3], −40.9 [t, J(P–P) 16, J(P–W) 239, PMe_3][o]

[a] Calculated values are given in parentheses. [b] Data given as: chemical shift (δ), relative intensity, multiplicity, J in Hz, assignment; vcm = virtually coupled multiplet, br = broad, s = singlet, d = doublet, t = triplet, q = quartet, qnt = quintet, sxt = sextet. ^{31}P N.m.r. at 101.26, ^{13}C at 62.89, and ^{1}H at 300 MHz, unless otherwise stated. Where multiplicity for ^{13}C n.m.r. data is given without accompanying J(C–H) data then these spectra were obtained under off-resonance decoupling or continuous-wave conditions so that accurate values for J(C–H) could not be determined. [c] In [$^2H_6$]benzene. [d] m/z 400, M^+ (^{184}W) − 4 H. [e] ν(W–H) 1 746s, ν(C–H_{exo}) 2 709m cm^{-1}. [f] ν(W–H) (CsI plates, Nujol mull 1 841w br, 1 910w br cm^{-1}. [g] In [$^2H_4$]methanol. [h] m/z 477, M^+ (^{184}W) − H. [i] m/z 326, M^+ (^{184}W) − 4 H. [j] ν(W–H) 1 847s cm^{-1}. [k] In [$^2H_6$]dimethyl sulphoxide. [l] m/z 494, M^+ (^{184}W). [m] In [$^2H_8$]toluene. [n] m/z 645, M^+ (^{184}W) − H. ν(W–H) 1 833m br and 1 917m br cm^{-1}. [o] In [$^2H_6$]acetone.

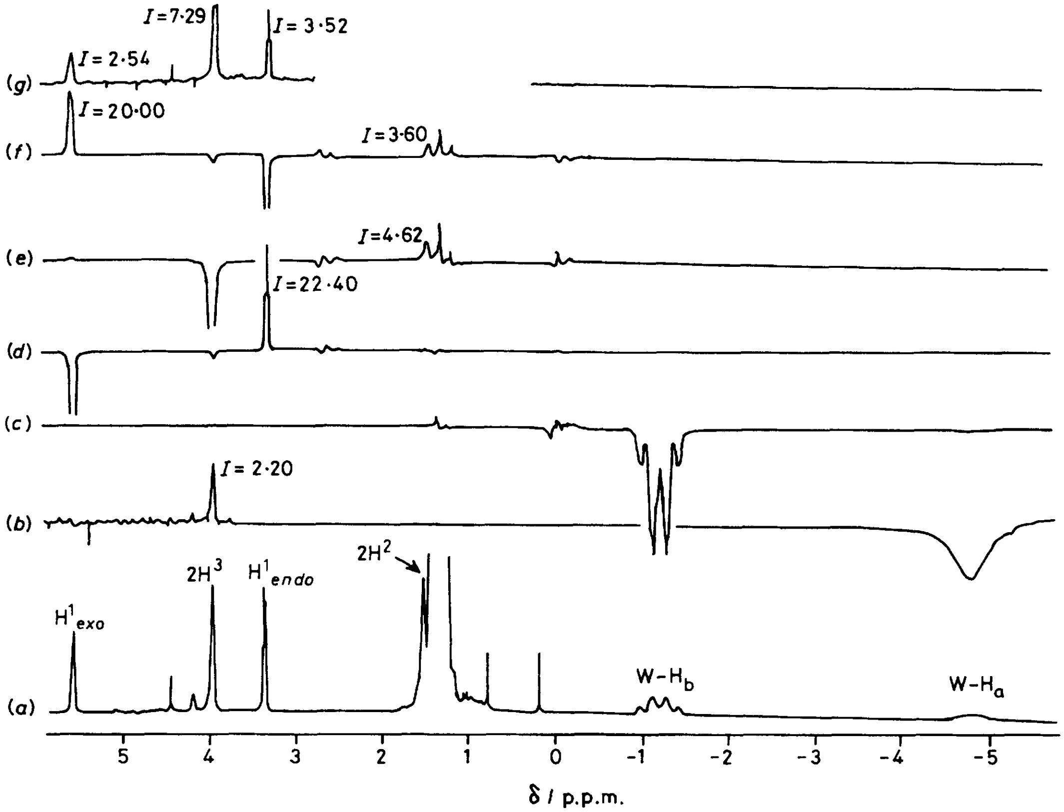


Figure. Nuclear Overhauser difference experiments on compound (**6**). (*a*) The basic ^1H n.m.r. spectrum; (*b*)—(*g*) on irradiation at H_a, H_b, H^1_{exo}, H^3, H^1_{endo}, and H^2 respectively. Enhancement factors (*I*) are given as %

showed that, *inter alia*, [W(η-C_5H_5)(PMe_3)H_5] (**9**) and [W(η-C_5H_5)(PMe_3)$_2$$H_3$] (**2**) were formed. The photolysis of [W(η-C_5H_6)(PMe_3)$_3$$H_2$] (**6**) in the presence of cyclopentadiene gave [W(η-C_5H_5)$_2$$H_2$] (**5**) (n.m.r.). Compound (**5**) is also formed by treatment of [W(η-C_5H_5)(PMe_3)H_5] with cyclopentadiene at 140 °C for 12 h. The photolysis of the ethylcyclopentadienyl derivative, [W(η-C_5H_4Et)(PMe_3)$_3$H] (**10**), with cyclopentadiene gave the mixed-ring metallocene dihydride, [W(η-C_5H_5)(η-C_5H_4Et)H_2] (**12**). This dihydride can be converted into the dichloride [W(η-C_5H_5)(η-C_5H_4Et)Cl_2] (**13**) by addition of CCl_4.

We have explored the reactions of the polyhydrides (**1**), (**3**), and (**4**) with other mono- and di-enes. Generally it is found that [W(PMe_3)$_5$$H_2$] (**1**) and [W($PMe_3$)$_4$$H_4$] (**3**) are photochemically reactive whereas the colourless, d^0 hexahydride [W(PMe_3)$_3$$H_6$] (**4**) is photochemically inert but thermally active.

Treatment of (**1**) with C_2H_4 initially gives *trans*-[W(η-C_2H_4)$_2$(PMe_3)$_4$], while further reaction gives *inter alia* the previously described[4,15] bis(η-butadiene) compound [W(η-C_4H_6)$_2$(PMe_3)$_2$][16] (**14**), in which two ethylene moieties have been oxidatively dimerised. In this respect, (**1**) reacts in a similar manner to [W(η^2-CH_2PMe_2)(PMe_3)$_4$H].[4] Compound (**14**) is also formed by treatment of (**4**) with butadiene. The reaction was monitored by ^1H and ^{13}C n.m.r. spectroscopy which showed there to be an intermediate tungsten hydride species which had bands assignable to a co-ordinated η-butadiene ligand (see Experimental section); we speculate that this intermediate species is [W(η-C_4H_6)(PMe_3)$_3$$H_2$].

Treatment of compound (**1**) with cyclohexa-1,3-diene gives [W(η-1,3-C_6H_8)(PMe_3)$_3$$H_2$] (**15**). The hexahydride (**4**) reacts thermally with cyclohexa-1,3-diene to give (**15**) together with the tetrahydride (**3**). Compound (**3**) was also formed to various extents in the reactions between (**4**) and cyclopentene, pentamethylcyclopentadiene, and cyclohexene. The basic features of the ^1H n.m.r. spectrum of (**15**) are similar to those of the other [W(η^4-diene)(PMe_3)$_3$$H_2$] complexes with hydride resonances occurring as a quartet at δ −1.53, which possesses further smaller coupling, and a broad featureless resonance at δ −5.55. The broadness of the resonance assigned to the hydride which lies in the plane of the phosphorus atoms and the broadness of the resonance due to diene protons of the η-1,3-C_6H_8 ligand suggested, at first, that the structure of (**15**) might contain an η-cyclohexenyl group in which there was an agostic[17] C–H→W bond. However, the ^{13}C n.m.r. spectrum shows there to be only one triplet, *J*(C–H) 125 Hz, and two doublets, *J*(C–H) 142 and 168 Hz, assignable to the η-1,3-C_6H_8 ligand. In addition, low-temperature ^1H n.m.r. spectra, although complicated, showed there to be no significant movement to lower frequency of the hydride resonance at δ −5.55. Therefore, (**15**) is formulated as the η^4-diene–hydride shown in Scheme 2.

Treatment of compound (**4**) with 6,6-diphenylfulvene resulted in transfer of a hydrogen to the exocyclic double bond to give [W(η^4-C_5H_5-*exo*-$CHPh_2$)(PMe_3)$_3$$H_2$] (**16**). The i.r. spectrum shows no bands in the region 2 700—2 900 cm^{-1} which suggests that the diphenylmethyl group is located in the *exo* position, as shown in Scheme 1.

In order to confirm the proposed nature of the bonding of the dihydrogen system in (**1**) the monodeuterio compound [W(PMe_3)$_5$H(D)] {or [W(PMe_3)$_5$(η^2-HD)]} was synthesised from [W(η^2-CH_2PMe_2)(PMe_3)$_4$H] and HD in PMe_3 as the solvent. The hydride resonance occurs at δ −5.44 compared to δ −5.40 for (**1**), presumably an isotope shift. The W–H resonance in the ^1H-{^{31}P} n.m.r. spectrum at 250 MHz appeared as a 1:1:1 triplet with a value of *J*(H–D) 1.5 Hz. In comparison with the value of *J*(H–D) 33.5 Hz for the compound

$[W(PPr^i_3)_2(CO)_3(\eta^2\text{-HD})]$[10] and J(H–D) 43.2 Hz for the HD molecule,[18] this value can be seen to be indicative of a dihydride formulation for (**1**). It seems probable that (**1**) is structurally analogous to $[Mo(PMe_3)_5H_2]$.[19]

The difference between the bonding of the hydrogen ligands of (**1**) and $[W(PPr^i_3)_2(CO)_3(\eta^2\text{-}H_2)]$ may be associated with the greater π-accepting ability of the carbonyl ligands compared to the more electron-donating PMe_3. In consequence, the tungsten centre of (**1**) would be more electron-rich than that of $[W(PPr^i_3)_2(CO)_3(\eta^2\text{-}H_2)]$ and hence will support the oxidative addition of the η^2-H_2 ligand in the hypothetical molecule $[W(PMe_3)_5(\eta^2\text{-}H_2)]$ giving (**1**). We note that compounds (**1**) and (**4**) have very low first ionisation potentials, 5.37 and 5.50 eV respectively.[20]

Photolysis of the tetrahydride (**3**) in the presence of dihydrogen gives quantitative conversion into $[W(PMe_3)_3H_6]$ (**4**), which is photochemically stable. No reaction was observed between $[W(PMe_3)_4H_4]$ and dihydrogen at room temperature in the absence of photolysis. Photolysis of (**3**) in the presence of an excess of both PMe_3 and H_2 did not form (**4**). Treatment of (**4**) with PMe_3 re-forms (**3**). It appears that thermolysis of (**4**) and photolysis of (**3**) gives the same intermediate, *i.e.* $[W(PMe_3)_3H_4]$.

In summary, we have described the syntheses of a variety of mono(η-cyclopentadienyl)(tertiary phosphine)tungsten compounds from readily accessible starting materials. For convenience many of the syntheses were carried out on a small (mg) scale. However, there is no reason to believe that these reactions could not be performed on a larger (gram) scale. There is likely to be an extensive chemistry of these electron-rich half-sandwich compounds, analogous to that of the related and previously described half-sandwich compounds[21] such as $[Nb(\eta\text{-}C_5Me_5)(PMe_3)_2H_4]$,[22] $[Ta(\eta\text{-}C_5Me_5)(PMe_3)_2H_4]$,[21,22] $[Mo(\eta\text{-}C_5H_5)(PMe_3)_3H]$,[23] $[Mo(\eta\text{-}C_5H_5)(dmpe)H_3]$[24] [dmpe = 1,2-bis(dimethylphosphino)ethane], $[Mn(\eta\text{-}C_5H_5)(PMe_3)_2H_2]$,[25] $[Re(\eta\text{-}C_5H_5)(PPh_3)_2H_2]$,[16] and $[M(\eta\text{-}C_5Me_5)(PMe_3)H_2]$ (M = Ir or Rh).[21,26]

Experimental

All manipulations of air- and/or 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 PMe_3 or gases (3 atm) were carried out in glass ampoules sealed with a Teflon tap supplied by J. Young (Acton). Dinitrogen and Ar were purified by passage through a gas-drying column containing commercial BASF catalyst and 4 Å 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 (thf) 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. spectroscopy 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, WH-300, WH-400, and AM-500 instruments. Chemical shifts (δ/p.p.m.) are relative to $SiMe_4$ for ^1H and ^{13}C, and to $P(O)(OMe)_3$ for ^{31}P spectra.

I.r. 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. The apparatus for metal vapour synthesis has been described elsewhere.[27]

The compounds $[W(PMe_3)_5H_2]$,[4] $[W(\eta\text{-}C_5H_4Et)(PMe_3)_3H]$,[4] $[W(PMe_3)_4H_4]$,[5,6] and $[W(PMe_3)_3H_6]$[5,6] were prepared as described previously.

(η-Cyclopentadienyl)trihydridobis(trimethylphosphine)tungsten, (**2**).—The dihydride (**1**) (2.0 g, 3.53 mmol) in light petroleum (b.p. 100—120 °C, 20 cm^3) in a Young's ampoule was treated with freshly distilled cyclopentadiene (1.5 cm^3) and the mixture was heated at 65 °C for 3 d. The solvent was removed under reduced pressure at *ca.* 30 °C and the residue was extracted into pentane (30 cm^3). The mixture was filtered and the pale yellow filtrate concentrated to *ca.* 5 cm^3 and placed at −40 °C. The pale yellow needle-like crystals which formed were separated by filtration, washed with pentane (2 × 2 cm^3), and dried *in vacuo* giving $[W(\eta\text{-}C_5H_5)(PMe_3)_2H_3]$ (**2**), 0.25 g (16%).

(η-Cyclopentadiene)dihydrotris(trimethylphosphine)tungsten, (**6**).—The hexahydride (**4**) (2.0 g, 4.79 mmol) in light petroleum (b.p. 100—120 °C, 40 cm^3) in a Young's ampoule was treated with freshly distilled cyclopentadiene (3 cm^3) and the mixture stirred at 80 °C for 3 d. The mixture was filtered and the volatile components removed from the filtrate under reduced pressure at *ca.* 70 °C giving a yellow-orange oil. The oil was sublimed [room temperature (r.t.), 10^{-4} Torr] onto a liquid-N_2 cooled probe for 6 h and the sublimate was discarded. The residue, still oily, was extracted into pentane (20 cm^3) and filtered. The yellow filtrate was concentrated to *ca.* 5 cm^3 giving a viscous solution which was cooled to −80 °C. Yellow crystals formed over a period of 3 d. The crystals were separated by filtration and washed with pentane (3 × 2 cm^3) at −78 °C. Yield 1.5 g, 65%.

(η-Cyclopentadienyl)dihydrotris(trimethylphosphine)tungsten Tetrafluoroborate, (**7**).—A stirred solution of $[W(\eta\text{-}C_5H_6)(PMe_3)_3H_2]$ (**6**) (150 mg, 0.31 mmol) in light petroleum (b.p. 40—60 °C, 15 cm^3) was treated dropwise with a solution of $HBF_4{\cdot}Et_2O$ in Et_2O (0.3 mol dm^{-3}, *ca.* 1 cm^3). A white deposit formed in a yellow solution and the addition was continued until the solution became colourless. The mixture was filtered and the residue was washed with light petroleum (b.p. 40—60 °C, 2 × 20 cm^3), extracted into thf (100 cm^3) at *ca.* 50 °C, and filtered. The colourless filtrate was concentrated to *ca.* 60 cm^3, filtered, cooled to −40 °C and then −80 °C. Small white crystals formed which were separated by filtration, washed with thf (2 × 5 cm^3) at −78 °C, and dried *in vacuo*. Yield 75 mg, 42%.

(η-Cyclopentadienyl)hydridotris(trimethylphosphine)tungsten, (**8**).—*Method A*. The compound $[W(\eta\text{-}C_5H_6)(PMe_3)_3H_2]$ (**6**) (700 mg, 1.46 mmol) in light petroleum (b.p. 40—60 °C, 30 cm^3) was treated dropwise with a solution of $HBF_4{\cdot}Et_2O$ in Et_2O (0.3 mol dm^{-3}, 5 cm^3) until a white deposit was obtained in a colourless solution. The mixture was filtered and the residue washed with light petroleum (b.p. 40—60 °C, 30 cm^3) and dried *in vacuo*. The solid was stirred in thf (50 cm^3) and KH (*ca.* 100 mg) was added. The mixture was filtered after 2 h at r.t. leaving a white solid residue. It was considered that an insoluble anionic complex arising from further deprotonation may have been formed since it was found necessary to hydrolyse the solid. Tetrahydrofuran (thf) (20 cm^3) was added to the solid followed by the dropwise addition of water. The mixture was filtered and the residue dried *in vacuo*. The residue was extracted into thf

(2 × 100 cm^3), filtered, and the combined filtrates taken to dryness giving a residue which was extracted into pentane (40 cm^3). The mixture was filtered and the pentane removed under reduced pressure giving pure [W(η-C_5H_5)(PMe_3)$_3$H] (**8**) as a yellow-orange powder. Yield 150 mg, 21%.

Method B. The compound [W(η-C_5H_5)(PMe_3)$_3H_2$][BF_4] (**7**) (100 mg, 0.18 mmol) in methanol (10 cm^3) was treated with KOH (100 mg, 1.79 mmol). The methanol was removed *in vacuo* after 24 h and the residue was extracted into light petroleum (b.p. 40—60 °C, 20 cm^3). The mixture was filtered and the solvent removed from the filtrate under reduced pressure to give a yellow-orange solid. Yield *ca.* 50 mg, 60%.

Protonation of [W(η-C_5H_5)(PMe_3)$_3$H] (**8**) *with* HBF_4.—A solution of [W(η-C_5H_5)(PMe_3)$_3$H] (40 mg, 0.08 mmol) in light petroleum (b.p. 40—60 °C, 15 cm^3) was treated dropwise with a solution of HBF_4·Et_2O in Et_2O (0.3 mol dm^{-3}). A white deposit formed in a yellow solution and the addition was stopped when the solution became colourless. The mixture was filtered and the solid was washed with light petroleum (b.p. 40—60 °C, 2 × 15 cm^3) and extracted into thf (60 cm^3) giving a colourless solution. The mixture was filtered, concentrated to *ca.* 20 cm^3, and placed at −80 °C. White crystals separated and were filtered and dried *in vacuo.* They were shown to be pure (**7**) by microanalysis and the ^{1}H n.m.r. spectrum. Yield 30 mg, 63%.

(η-*Cyclopentadienyl*)*pentahydrido*(*trimethylphosphine*)-*tungsten*, (**9**).—*Method A.* The compound [W(η-C_5H_5)(PMe_3)$_3$H] (**8**) (50 mg, 0.10 mmol) in light petroleum (b.p. 40—60 °C, 20 cm^3) in a Young's ampoule was treated with H_2 (2.5 atm) and photolysed using a 500-W medium-pressure mercury lamp for 12 h. The solvent was removed under reduced pressure and the residue extracted into pentane (10 cm^3) and filtered. The solvent was removed under reduced pressure giving [W(η-C_5H_5)(PMe_3)H_5] (**9**). Yield 30 mg, 87%.

Method B. The compound [W(η-C_5H_5)(PMe_3)$_2H_3$] (**2**) (200 mg, 0.50 mmol) in pentane (15 cm^3) in a Young's ampoule was treated with H_2 (2.5 atm) and photolysed for 18 h using a 500-W medium-pressure mercury lamp. A colourless solution was obtained. The solvent was removed under reduced pressure at *ca.* 25 °C. The residue was extracted into pentane (25 cm^3) and the mixture filtered. The filtrate was concentrated to *ca.* 5 cm^3 at *ca.* 30 °C and allowed to cool to r.t., forming white crystals. After cooling to −40 and then −80 °C, the crystals which formed were separated by filtration, washed with pentane (2 × 2 cm^3) at −78 °C, and dried *in vacuo.* Yield 100 mg, 61%.

(η-*Ethylcyclopentadienyl*)*pentahydrido*(*trimethylphosphine*)-*tungsten*, (**11**).—The compound [W(η-C_5H_4Et)(PMe_3)$_3$H] (**10**) (250 mg, 0.49 mmol) in light petroleum (b.p. 40—60 °C, 20 cm^3) in a Young's ampoule was treated with H_2 (2.5 atm) and photolysed with a 500-W medium-pressure mercury lamp for 3 d. The solvent was removed under reduced pressure at r.t. and the residue was extracted into pentane (20 cm^3). The mixture was filtered and the solution was concentrated to *ca.* 2 cm^3 and placed at −80 °C. The white crystals which formed were separated by filtration and washed with pentane (2 × 1 cm^3) at −78 °C. Yield 80 mg, 45%.

Photolysis of [W(η-C_5H_6)(PMe_3)$_3H_2$] *with* C_5H_6.—The compound [W(η-C_5H_6)(PMe_3)$_3H_2$] (**6**) (20 mg, 0.04 mmol) in [$^2H_6$]benzene (0.5 cm^3) in a 5-mm n.m.r. tube was treated with freshly distilled cyclopentadiene (0.05 cm^3) and the mixture photolysed with a 500-W medium-pressure mercury lamp. After 2 d the formation of [W(η-C_5H_5)$_2H_2$] was observed by ^{1}H n.m.r. spectroscopy.

Reaction of [W(η-C_5H_5)(PMe_3)H_5] *with Cyclopentadiene.*—The compound [W(η-C_5H_5)(PMe_3)H_5] (**9**) (*ca.* 10 mg, 0.03 mmol) in [$^2H_6$]benzene (0.5 cm^3) in a 5-mm n.m.r. tube was treated with freshly distilled cyclopentadiene (0.05 cm^3) and the contents sealed *in vacuo* at −196 °C. The reaction was monitored by recording the ^{1}H n.m.r. spectrum. No change was observed on heating for 12 h at 65 and 18 h at 100 °C. However, heating at 140 °C for 12 h resulted in the formation of [W(η-C_5H_5)$_2H_2$].

Photolysis of [W(η-C_5H_6)(PMe_3)$_3H_2$].—A solution of [W(η-C_5H_6)(PMe_3)$_3H_2$] (**6**) (10 mg, 0.02 mmol) in pentane (10 cm^3) was photolysed in a quartz vessel using a 500-W medium-pressure mercury lamp for 3 d. The solvent was removed under reduced pressure and the ^{1}H n.m.r. spectrum of the residue identified it as containing [W(η-C_5H_5)(PMe_3)H_5] (**9**) and [W(η-C_5H_5)(PMe_3)$_2H_3$] (**2**) (*ca.* 1:1).

Photolysis of [W(η-C_5H_6)(PMe_3)$_3H_2$] *under* H_2.—The compound [W(η-C_5H_6)(PMe_3)$_3H_2$] (**6**) (20 mg, 0.04 mmol) in light petroleum (b.p. 40—60 °C, 5 cm^3) in a quartz ampoule was treated with H_2 (3 atm) and photolysed using a 500-W medium-pressure mercury lamp for 3 d. The solvent was removed under reduced pressure and the ^{1}H n.m.r. spectrum of the residue identified it as containing [W(η-C_5H_5)(PMe_3)H_5] (**9**) (*ca.* 60%), [W(η-C_5H_5)(PMe_3)$_2H_3$] (**2**) (*ca.* 30%), and [W(PMe_3)$_3H_6$] (**4**) (*ca.* 10%).

Photolysis of [W(PMe_3)$_4H_4$] (**3**) *with Cyclopentadiene in* [$^2H_6$]*Benzene.*—The compound (**3**) (50 mg, 0.10 mmol) in [$^2H_6$]benzene (0.5 cm^3) in a 5-mm n.m.r. tube was treated with freshly distilled cyclopentadiene (*ca.* 0.05 cm^3) and the tube sealed *in vacuo* at −196 °C. The sample was photolysed by a 500-W medium-pressure mercury lamp and the ^{1}H n.m.r. spectrum monitored over a period of time showing the sequential formation of (**6**), [W(η-C_5H_5)(PMe_3)$_2H_3$] (**2**), [W(η-C_5H_5)(η^2-C_5H_8)(PMe_3)$_2$H], and [W(η-C_5H_5)$_2H_2$] (**5**).

(η-*Cyclopentadienyl*)(η-*ethylcyclopentadienyl*)*dihydrido*-*tungsten*, (**12**).—The compound [W(η-C_5H_4Et)(PMe_3)$_3$H] (150 mg, 0.30 mmol) in light petroleum (b.p. 40—60 °C, 10 cm^3) was treated with freshly distilled cyclopentadiene (0.2 cm^3) and photolysed in a quartz ampoule with a 500-W medium-pressure mercury lamp for 3 d. The mixture was taken to dryness, extracted into pentane (10 cm^3), and filtered. The solution was concentrated to *ca.* 1 cm^3 and placed at −80 °C. The orange crystals which formed were separated by filtration and washed with pentane (2 × 0.5 cm^3) at −78 °C. Yield of [W(η-C_5H_5)(η-C_5H_4Et)H_2] (**12**): 50 mg, 50%.

Dichloro(η-*cyclopentadienyl*)(η-*ethylcyclopentadienyl*)-*tungsten*, (**13**).—The compound [W(η-C_5H_5)(η-C_5H_4Et)H_2] (30 mg, 0.09 mmol) in pentane (15 cm^3) was treated with CCl_4 (1 cm^3). A flocculent olive-green deposit formed after *ca.* 2 min. The mixture was filtered and the residue washed with pentane (3 × 10 cm^3) and dried *in vacuo* giving an olive-green powder. Yield *ca.* 30 mg, 83%.

Reaction of Compound (**1**) *with* C_2H_4.—The compound (**1**) (50 mg, 0.09 mmol) in [$^2H_6$]benzene (0.5 cm^3) in an n.m.r. tube was saturated with C_2H_4 and sealed under reduced pressure at 196 °C. The mixture was heated to 70 °C. After 2 d the ^{1}H n.m.r. spectrum demonstrated that the mixture contained [W(η-C_2H_4)$_2$(PMe_3)$_4$].

Reaction of Compound (**4**) *with Butadiene; Synthesis of* (**14**).—Compound (**4**) (500 mg, 1.2 mmol) in light petroleum (b.p. 100—120 °C, 20 cm^3) in a Young's ampoule was treated with butadiene (2 cm^3) and heated at *ca.* 100 °C for 3 d. The solvent was removed under reduced pressure and the residue was extracted into light petroleum (b.p. 40—60 °C, 20 cm^3), filtered, and the filtrate was concentrated to *ca.* 0.5 cm^3 and placed at -80 °C. The product did not crystallise and the ^{1}H n.m.r. spectrum identified it as an approximately equimolar mixture of [W(η-C_4H_6)$_2$(PMe_3)$_2$] and [W(η-C_4H_6)(PMe_3)$_3$$H_2$]. N.m.r. spectra of the latter, in [$^2H_8$]toluene: ^{1}H, δ 3.55 (2 H, br s, 2 H$_a$), 1.30 (27 H, br s, 3 PMe$_3$), 0.95 (2 H, br s, 2 H$_b$), -0.92 (2 H, br s, 2 H$_c$), -1.56 (1 H, m, H$_e$), and -4.25 (1 H, m, H$_d$); ^{13}C, δ 70.0 (d, C^1), 31.3 [tq, J_q(P–C) 3, C^2], 26.7 (q, PMe$_3$), and 26.3 (q, 2PMe$_3$); ^{31}P-{^{1}H}, δ -28.8 [2 P, br s, J(P–W) 232 Hz, 2PMe$_3$] and -35.1 (1 P, br s, PMe$_3$). Sublimation (60 °C, 10^{-4} Torr) of the mixture onto a water-cooled probe resulted in no change in the composition of the mixture. However, extraction into MeOH resulted in decomposition of the proposed intermediate [W(η-C_4H_6)(PMe_3)$_3$$H_2$] and the isolation of pure [W(η-C_4H_6)$_2$(PMe_3)$_2$].

(η-*Cyclohexa*-1,3-*diene*)*dihydrotris*(*trimethylphosphine*)-*tungsten*, (**15**).—Compound (**1**) (100 mg, 0.18 mmol) in [$^2H_6$]benzene in a 5-mm n.m.r. tube was treated with cyclohexa-1,3-diene (0.05 cm^3) and the tube sealed *in vacuo* at -196 °C. The mixture was heated at 60 °C for 2 weeks and the ^{1}H n.m.r. spectrum demonstrated that *ca.* 90% (**15**) was formed. Compound (**3**) was not formed in this reaction.

Reaction of [W(PMe_3)$_3$$H_6$] (**4**) *with Cyclohexa*-1,3-*diene*.—Compound (**4**) (50 mg, 0.12 mmol) in [$^2H_6$]benzene (0.5 cm^3) in a 5-mm n.m.r. tube was treated with cyclohexa-1,3-diene (0.05 cm^3) and the tube sealed *in vacuo* at -196 °C. The mixture was heated at *ca.* 65 °C for 5 d giving (**15**) in *ca.* 80% yield and also smaller quantities of (**3**).

Reaction of Compound (**4**) *with Cyclopentene*.—Compound (**4**) (300 mg, 0.72 mmol) in toluene (30 cm^3) was treated with cyclopentene (2 cm^3) and the mixture stirred at 65 °C for 3 weeks. The mixture was filtered and the toluene removed from the filtrate under reduced pressure at *ca.* 70 °C. The ^{1}H n.m.r. spectrum of the residue identified the presence of [W(η-C_5H_5)(PMe_3)$_2$$H_3$] (**2**) and [W($\eta$-$C_5H_5$)$_2$$H_2$] (**5**).

[η-exo-5-(*Diphenylmethyl*)*cyclopentadiene*]*dihydridotris*(*trimethylphosphine*)*tungsten*, (**16**).—Compound (**4**) (300 mg, 0.72 mmol) in light petroleum (b.p. 100—120 °C, 30 cm^3) was stirred with 6,6-diphenylfulvene (200 mg, 0.87 mmol) at 70 °C for 4 d. Over this period a yellow deposit separated from an orange solution. The mixture was filtered and the solid extracted into thf (25 cm^3) and filtered. The solution was concentrated and placed at -40 °C giving yellow-orange crystals which were filtered off, washed with cold thf (2 × 2 cm^3), and dried *in vacuo*. Yield *ca.* 50 mg (10%).

Reaction of [W(η^2-CH_2PMe_2)(PMe_3)$_4$H] *with* HD; *Synthesis of* [W(PMe_3)$_5$H(D)].—The compound [W(η^2-CH_2PMe_2)(PMe_3)$_4$H] (100 mg, 0.17 mmol) in PMe$_3$ (3 cm^3) in a Young's ampoule was treated with HD and heated at 65 °C for 12 h. The PMe$_3$ was recovered and a ^{1}H n.m.r. spectrum obtained of the residue. The HD was generated by the addition of D_2O (0.3 cm^3, 1.17 mmol) to NaH under PMe$_3$ at -196 °C, evacuating the system, and allowing to warm to r.t.

Photolysis of [W(PMe_3)$_4$$H_4$] *under* H_2; *Synthesis of* (**4**).—Compound (**3**) (100 mg, 0.20 mmol) in light petroleum (b.p. 40—60 °C, 20 cm^3) in a Young's ampoule (50 cm^3) was treated with H_2 (2 atm) and photolysed with a 500-W medium-pressure mercury lamp for 2 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. The solvent was removed from the colourless filtrate giving white flakes of pure (**4**). Yield 75 mg, 88%. Heating a solution of compound (**3**) (100 mg, 0.20 mmol) in light petroleum (b.p. 100—120 °C, 20 cm^3) in a Young's ampoule with H_2 (2 atm) resulted only in recovery of (**3**).

Reaction of Compound (**4**) *with* PMe$_3$; *Synthesis of* [W(PMe_3)$_4$$H_4$].—Compound (**4**) (50 mg, 0.12 mmol) in [$^2H_6$]benzene (0.5 cm^3) was treated with PMe$_3$ (0.05 cm^3) and heated at 55 °C for 3 d. The conversion into (**3**) was observed to be quantitative by ^{1}H n.m.r. spectroscopy.

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