# Some Chemistry of Half-sandwich η-Arene Tungsten Compounds†

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The compounds $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3]$ and $[W(\eta\text{-}C_6H_5Me)\{SiMe(CH_2PMe_2)_3\}]$ have been prepared from $[W(\eta\text{-}C_6H_5Me)_2]$ and tertiary phosphines. They are protonated by $NH_4BF_4$ to give $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3H]BF_4$ and $[W(\eta\text{-}C_6H_5Me)\{SiMe(CH_2PMe_2)_3\}H]BF_4$, respectively. Reaction of $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3]$ with HCl gas gives the diprotonated cation $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3H_2]^{2+}$. Treatment of $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(dmpe)]PF_6$ [dmpe = 1,2-bis(dimethylphosphino)ethane] with $LiAlH_4$ gives the η-methylcyclohexadienyl complex $[W(\eta^5\text{-}C_6H_6Me)(\eta\text{-}C_3H_5)(dmpe)]$, as a mixture of inseparable isomers. These have been characterised by multinuclear two-dimensional NMR spectroscopy. The fluorohydride $[W(\eta\text{-}C_6H_5Me)(dmpe)H(F)]$ has also been prepared. The X-ray crystal structures of $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3H_2][PF_6]_2$ and $[W(\eta\text{-}C_6H_5Me)(dmpe)H(F)]$ have been determined.

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Bis(η-arene)tungsten compounds have been known since 1960,[1] but only became available in gram quantities by the method of metal vapour synthesis.[2] Previously we have described some chemistry of (η-arene)tungsten compounds derived from $[W(\eta\text{-}C_6H_5R)_2]$ (R = H or Me).[3] More recently we reported the compound $[W(\eta\text{-}C_6H_6)(PMe_3)_2H_2]$ which was prepared by co-condensation of tungsten with cyclohexane and $PMe_3$,[4] by treatment of $[W(PMe_3)_3H_6]$, $[W(PMe_3)_5H_2]$, or $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ with cyclohexa-1,3- or 1,4-diene, or by the reduction of $[W(PMe_3)_4Cl_2]$ in the presence of cyclohexa-1,3-diene.[5] The η-arene compound $[W(\eta^6\text{-}C_6H_5PPr^n_2)(PPhPr^n_2)_2(N_2)]$ has been prepared by the reduction of $WCl_6$ with Mg in the presence of $PPhPr^n_2$.[6] Here we describe some further studies of the chemistry of $[W(\eta\text{-}C_6H_5Me)_2]$ leading to the synthesis of new half-sandwich η-arene derivatives of tungsten.

## Results and Discussion

Treatment of the bis(η-arene) compound $[W(\eta\text{-}C_6H_5Me)_2]$ **1** with neat trimethylphosphine at 200 °C gave air-sensitive, orange crystals of $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3]$ **2**. The formation of **2** by displacement of an η-toluene ring has a parallel with the reactions of $[M(\eta\text{-}C_6H_5Me)_2]$ (M = Mo[7] or Nb[8]) with $PMe_3$. The analytical and spectroscopic data characterising **2** and the other new compounds described below are given in Table 1, and will not be further discussed except where interpretation is not straightforward.

Compound **2** shows a first He I photoionisation band at 4.99 eV (*ca.* 8 × $10^{-19}$ J), which may be assigned to the ionisation of an electron from the predominantly non-bonding $d_{z^2}$ orbital of tungsten.[9a] The molybdenum analogue, $[Mo(\eta\text{-}C_6H_5Me)(PMe_3)_3]$, shows a first ionisation at 5.3 eV.[9b]

Compound **2** is rapidly protonated by HCl gas in a two-stage reaction in which a purple and then a yellow solid are formed. The yellow product is soluble in water and addition of ammonium hexafluorophosphate gives $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3H_2][PF_6]_2$ **3**. The $^1H$ NMR spectrum of **3** shows two distinct phosphine and hydride environments, consistent with the *mer* geometry shown in Scheme 1. Heteronuclear double-resonance experiments allow assignment of all the coupling constants. The $^2J(H_aH_b)$ coupling constant is 9.6 Hz, indicating that two classical hydride ligands are present and not a $\eta^2$-$H_2$ ligand. No coupling is observed between $H_b$ and the $^{31}P$ nucleus of the $PMe_3$ ligand *trans* to it ($P_d$). The structure of **3** has been confirmed by a single-crystal X-ray diffraction study. The molecular geometry is shown in Fig. 1, selected bond angles and distances in Table 2, and fractional atomic coordinates in Table 3. The solid-state structure is consistent with the solution NMR data; the hydride ligands were not located but space-filling models, and the P–W–P angles, suggest that the two hydrides fit *trans* to the arene-ring centroid and *trans* to P(2), giving the molecule an overall pseudo-octahedral geometry, if the η-toluene ligand is considered to occupy a single co-ordination site.

Treatment of compound **3** with 30% aqueous KOH removes one proton to give $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3H]PF_6$ **4**, as a deep purple solid which may be crystallised from dichloromethane. The analogous $BF_4^-$ salt of **4** may be prepared from $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3]$ and the weak acid $NH_4BF_4$. The monohydride $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3H]PF_6$ is stable to deprotonation by KOH at room temperature but when the temperature is raised to 70 °C deprotonation occurs regenerating **2**. Treatment of **3** with potassium hydride in tetrahydrofuran (thf) gives **2** in a clean reaction.

Comparison of the conditions required for the protonation reactions of compound **2** with those for the molybdenum analogues shows that the diprotonation of **2** occurs with weaker acids and correspondingly that the deprotonation of the dication **3** requires more forcing conditions than for the molybdenum analogue.[7]

Treatment of $[W(\eta\text{-}C_6H_5Me)_2]$ with $SiMe(CH_2PMe_2)_3$ at 200 °C for 2 d gives, after recrystallisation from pentane, the tripodal phosphine complex $[W(\eta\text{-}C_6H_5Me)\{SiMe(CH_2PMe_2)_3\}]$ **5**, in 70% yield. Complex **5** is readily protonated by $NH_4BF_4$ to give the monohydride $[W(\eta\text{-}C_6H_5Me)\{SiMe(CH_2PMe_2)_3\}H]BF_4$ **6**.

The $^1H$ NMR spectra of compounds **4** and **6** at room temperature all show resonances assignable to the η-arene and phosphine ligands as well as quartet resonances assignable to the single hydride. The $^{31}P\text{-}\{^1H\}$ NMR spectra at ambient temperature all show relatively sharp singlets. These spectra do

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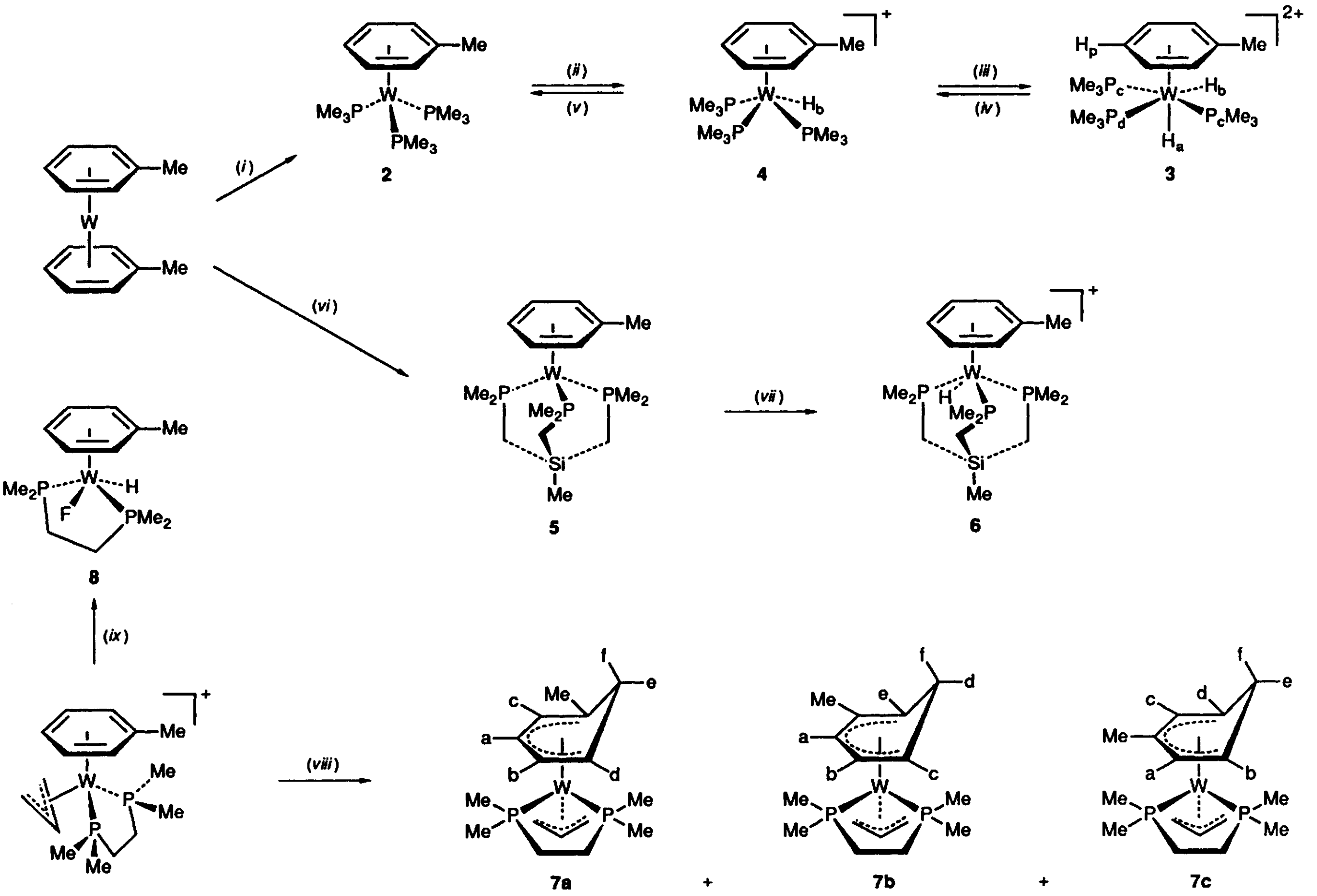
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



**Scheme 1** (*i*) $PMe_3$ (neat), sealed tube, 200 °C, 18 h, yield > 90%; (*ii*) HCl (g), light petroleum, > 90% or $NH_4BF_4$ (s), thf, 12 h, > 90%; (*iii*) HCl (g), light petroleum, > 90%; (*iv*) 30% KOH (aq.), room temperature (r.t.) > 90%; (*v*) 30% KOH (aq.), 70 °C, > 90%; (*vi*) $SiMe(CH_2PMe_2)_3$ (neat), sealed tube, 200 °C, 2 d, 70%; (*vii*) $NH_4BF_4$ (s), thf, 12 h, 75%; (*viii*) excess of $LiAlH_4$, thf, r.t., 12 h, 78%; (*ix*) (on one occasion only) excess of $LiAlH_4$, −30 °C then r.t., 1 h

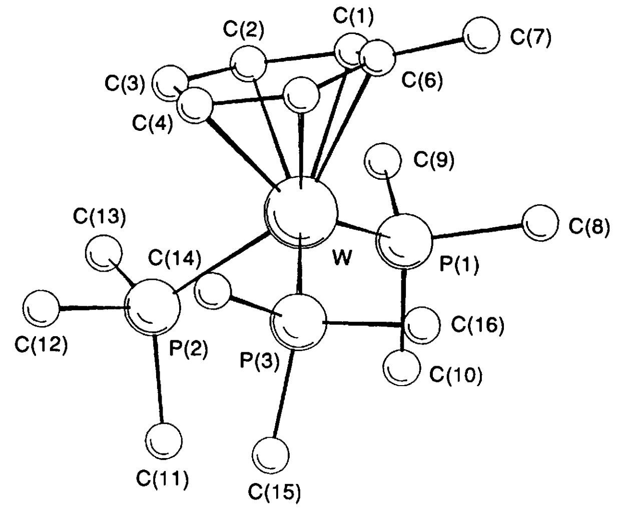


**Fig. 1** Molecular structure of $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3H_2][PF]_2$ **3**. Hydrogen atoms bonded to W were not located. Other hydrogen atoms and $PF_6^-$ anions omitted for clarity

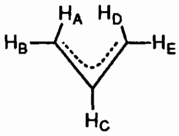
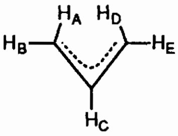
not allow one unambiguously to distinguish between a symmetrical pseudo-trigonal-bipyramidal ground state (approximate $C_{3v}$ symmetry) or a highly fluxional pseudo-square-based pyramidal structure (approximate $C_s$ symmetry as illustrated in Scheme 1). To our knowledge, the cation $[W(\eta\text{-}C_5Me_5)Me_4]^+$ is the only crystallographically characterised $[M(\eta\text{-hydrocarbyl})(ligand)_4]$ species which possesses local $C_{3v}$ symmetry at the metal centre.[10]

We have studied the reaction between the previously described compound $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(dmpe)]$ (dmpe = $Me_2PCH_2CH_2PMe_2$) and $LiAlH_4$. Treatment of $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(dmpe)]PF_6$ with $LiAlH_4$ in thf gave a pale yellow solid $[W(\eta^5\text{-}C_6H_6Me)(\eta\text{-}C_3H_5)(dmpe)]$ **7**. The infrared spectrum shows a band at 2745 $cm^{-1}$, which suggests the presence of a $C\text{-}H_{exo}$ group.[11,12] The $^{31}P\text{-}\{^1H\}$ NMR spectrum indicates an isomeric mixture. For example there are three pairs of doublets with associated $^{183}W$ satellites, each pair assignable to a co-ordinated dmpe ligand in which the phosphorus atoms of the dmpe ligands are inequivalent. This inequivalence suggests that, as found for the analogous molybdenum compounds $[Mo(\eta\text{-}C_6H_6R)(\eta\text{-}C_3H_5)L_2]$ [R = H or Bu; $L_2$ = dmpe, dppe ($Ph_2PCH_2CH_2PPh_2$), or 2,5-dithiahexane] there is no plane of symmetry through the molecules of the three isomers present and that ring rotation does not occur on the NMR time-scale.[11]

The $^1H$ NMR spectrum of the isomeric mixture is extremely complex and a substantial assignment was only possible with the aid of phosphorus-decoupled phase-sensitive double-quantum-filtered $^1H$–$^1H$ correlation spectroscopy (COSY) together with $^1H\text{-}\{^1H,^{31}P\}$ NMR spectra. These spectra identified three distinct coupling networks which may be assigned to methylcyclohexadienyl groups arising from nucleophilic addition of hydride at the *ortho* (**7a**), *meta* (**7b**) or *para* (**7c**) positions (Scheme 1) of the η-toluene ligand. The data show the isomers to be in the approximate ratio 1:2:4. There is no evidence for addition of the $H^-$ to the *ipso*-ring carbon.

It has been observed in the molybdenum analogues of compound **7**, namely $[Mo(\eta\text{-}C_6H_6R)(\eta\text{-}C_3H_5)L_2]$ (R = H or Bu; $L_2$ = dmpe, dppe, or 2,5-dithiahexane), and elsewhere,[11] that the protons at the 4 position of a η-cyclohexadienyl ligand are

**Table 1** Analytical and spectroscopic data

| Compound | Colour | Analysis (%)[a] | | NMR data[b] (δ) |
|---|---|---|---|---|
| | | C | H | |
| **2** $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3]$ | Orange | 37.9<br>(38.1) | 6.8<br>(7.0) | $^{1}$H: 3.75 (2 H, br t, *ortho* or *meta*), 3.58 (3 H, m, *para* and *meta* or *ortho*), 2.19 (3 H, s, MePh), 1.35 (27 H, m, MeP)<br>$^{13}$C: 78.9 (s, *ipso*), 73.5 (d, *ortho* or *meta*), 70.8 (d, *para*), 63.9 (d, *meta* or *ortho*), 28.9 (q, MeP), 21.9 (q, $C_6H_5Me$)<br>$^{31}$P: 16.3 (s) |
| **3** $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3H_2][PF_6]_2$ | Yellow | 24.2<br>(24.1) | 4.6<br>(4.6) | $^{1}$H [$(CD_3)_2CO$]: 6.7 (1 H, m, *para*), 6.1 (4 H, m, *ortho* and *meta*), 3.5 [1 H, br q, $J(H_aP_c) = 58$, $J(H_aP_d) = 40.8$, $J(H_aH_p) = 2$, $J(H_aH_b) = 9.6$, $WH_a$], 2.1 (18 H, d, $J_{PH} = 12$, 2 × $PMe_3$), 2.6 (3 H, s, MePh), 1.9 (9 H, d, $J_{PH} = 12$, $PMe_3$), −4.5 [1 H, br t, $J(H_bP_c) = 38$, $J(H_bP_d) = 0$, $J(H_bH_a) = 9.6$, $WH_b$]<br>$^{13}$C ($D_2O$):[c] 122.9 (s, *ipso*), 116.9 (d, *para*), 90.8 (d, *ortho* or *meta*), 89.7 (d, *ortho* or *meta*), 25.3 (qd, $MeP_c$), 22.7 [qd, $Me_3P_d$], 21.5 (q, $C_6H_5Me$)<br>$^{31}$P ($D_2O$):[c] −34.5 (2, d, $J_{PP} = 23.5$, $P_c$), −45.4 (1 t, $J_{PP} = 23.5$, $P_d$) |
| **4** $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3H][PF_6]$ | Purple | 29.8<br>(29.5) | 5.3<br>(5.5) | $^{1}$H [$(CD_3)_2CO$]: 4.6 (4 H, m, *ortho* and *meta*), 4.4 (1 H, m, *para*), 2.1 (3 H, s, $J_{HH} = 1.3$, $C_6H_5Me$), 1.9 (27 H, m, $PMe_3$), −4.7 (1 H, q, $J_{PH} = 55.8$, WH)<br>$^{31}$P [$(CD_3)_2CO$]: −36.6 (s, $J_{PW} = 283$) |
| **5** $[W(\eta\text{-}C_6H_5Me)\{SiMe(CH_2PMe_2)_3\}]$ | Orange | 37.3<br>(37.6) | 6.4<br>(6.5) | $^{1}$H: 3.82 (2 H, br m, *ortho* or *meta*), 3.75 (2 H, m, *meta* or *ortho*), 3.68 (1 H, m, *para*), 2.25 (3 H, s, $C_6H_5Me$), 1.45 (18 H, vct, $Me_2P$), 0.85 (6 H, m, $PCH_2$), −0.05 (3 H, s, SiMe)<br>$^{31}$P: −32.8 (s, $J_{PW} = 395$) |
| **6** $[W(\eta\text{-}C_6H_5Me)\{SiMe(CH_2PMe_2)_3\}H][BF_4]$ | Purple | 31.7<br>(32.2) | 6.4<br>(5.8) | $^{1}$H [$(CD_3)_2CO$]: 5.1 (2 H, m, *ortho* or *meta*), 5.0 (2 H, m, *meta* or *ortho*), 4.75 (1 H, m, *para*), 2.8 (3 H, s, $C_6H_5Me$), 2.1 (18 H, vct, $PMe_2$), 1.3 (6 H, br s, $PCH_2$), 0.0 (3 H, s, SiMe), −7.6 (1 H, q, $J_{HW} = 46$, WH)<br>$^{31}$P [$(CD_3)_2CO$]: −33.3 (s, $J_{WP} = 260$) |
| **7a** $[W(\eta^5\text{-}C_6H_6Me)(\eta^3\text{-}C_3H_5)(dmpe)]$[d] | Off-white | 41.00<br>(41.05) | 6.35<br>(6.4) | $^{1}$H (500 MHz): 5.77 (1 H, t, $J_{HH} = 7.5$, $H_a$), 4.18 (1 H, m, $H_b$), 3.8 (1 H, m, $H_f$), 3.38 (1 H, d, $J_{HH} = 5.0$, $H_c$), 2.4 (1 H, m, $H_e$), 1.95 (3 H, s, Me), 1.93 (1 H, m, $H_d$)<br>$^{13}$C: 97.7 (CH, $C_a$), 97.6 (CH, $C_c$), 78.4 (CH, $C_b$), 29.5 ($CH_2$, $C_{e/f}$), 26.3 (ring Me), 25.2 (CH, $C_d$)<br>$^{31}$P (202 MHz): 15.05 (d, $J_{PP} = 8.3$, $J_{PW} = 303$), 7.78 (d, $J_{PP} = 8.3$, $J_{PW} = 224$) |
| **7b** $[W(\eta^5\text{-}C_6H_6Me)(\eta^3\text{-}C_3H_5)(dmpe)]$[d]<br><br> | | | | $^{1}$H (500 MHz): 5.68 (1 H, d, $J_{HH} = 5.3$, $H_a$), 4.18 (1 H, q, $J_{HH} = 6.0$, $H_b$), 3.8 (1 H, m, $H_f$), 2.90 (1 H, m, $H_C$), 2.40 (1 H, m, $H_e$), 2.27 (1 H, m, $H_d$), 1.96 (1 H, m, $H_c$), 1.72 (3 H, s, Me), 1.15 (1 H, dq, $H_E$), 0.80 (1 H, m, $H_B$), 0.29 (1 H, m, $H_D$), 0.20 (1 H, dd, $J_{HH} = 1.7, 3.5$, $H_A$)<br>$^{13}$C: 99.3 (CH, $C_a$), 76.0 (CH, $C_b$), 30.6 ($CH_2$, $C_{b/f}$), 30.5 (CH, $C_e$), 25.0 (CH, $C_c$), 19.6 (ring Me)<br>$^{31}$P (202 MHz): 13.93 (d, $J_{PP} = 8.4$, $J_{PW} = 305$), 7.06 (d, $J_{PP} = 8.4$, $J_{PW} = 224$) |
| **7c** $[W(\eta^5\text{-}C_6H_6Me)(\eta^3\text{-}C_3H_5)(dmpe)]$[d]<br><br> | | | | $^{1}$H (500 MHz): 4.02 (1 H, dt, $H_e$), 3.8 (1 H, m, $H_f$), 3.66 (1 H, d, $J_{HH} = 6.4$, $H_g$), 2.75 (1 H, m, $H_C$), 2.68 (1 H, m, $H_d$), 2.4 (1 H, m, $H_b$), 2.4 (3 H, s, Me), 1.95 (1 H, m, $H_c$), 1.35 (2 H, 2 × m, $H_B$, $H_E$), 0.55 (1 H, m, $H_A$), 0.4 (1 H, m, $H_D$)<br>$^{13}$C: 96.7 (CH, $C_g$), 77.3 (CH, $C_e$), 29.6 ($CH_2$, $C_{f/b}$), 27.6 (CH, $C_d$), 25.0 (CH, $C_c$), 22.1 (ring Me)<br>$^{31}$P (202 MHz): 14.95 (d, $J_{PP} = 7.4$, $J_{PW} = 302$), 7.39 (d, $J_{PP} = 7.4$, $J_{PW} = 225$) |
| **8** $[W(\eta\text{-}C_6H_5Me)(dmpe)H(F)]$ | Red | | | $^{1}$H: 4.33 (2 H, td, $J_{HH} = 5$, $J_{FH} = 2.2$, *meta*), 4.17 (2 H, t, $J_{FH} = 2.2$, *ortho*), 3.00 (1 H, t, $J_{FH} = 5.4$, *para*), 1.80 (3 H, d, $J_{FH} = 0.79$, $C_6H_5Me$), 1.50 (6 H, m, MeP), 1.41 (6 H, m, MeP), −4.80 (1 H, td, $J_{PH} = 56$, $J_{FH} = 23$, WH)<br>$^{31}$P: 24 [d, $J_{PF} = 66$, $J_{PW} = 139.3$)<br>$^{19}$F (282 MHz): 158 (1 F, t, $J_{FP} = 67$) |
| **9** $[W(\eta\text{-}C_6H_5Me)(dmpe)_2][PF_6]_2$ | Green | 25.7<br>(26.3) | 4.6<br>(4.6) | $^{1}$H [$(CD_3)_2SO$]: 6.18 (1 H, t, $J_{HH} = 5.3$, *para*), 5.5 (4 H, m, *ortho* and *meta*), 2.28 (4 H, br s, $PCH_2$), 2.15 (3 H, s, $C_6H_5Me$), 1.84 (16 H, br s, PMe and $PCH_2$), 1.65 (12 H, s, PMe) |

[a] Given as Found (Calculated). [b] Unless otherwise stated all spectra are recorded at 293 K in $C_6D_6$ with $^{1}$H at 300 MHz, $^{13}$C at 75.43 MHz and $^{31}$P at 121.5 MHz; *J* in Hz; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, vct = virtual coupled triplet and br = broad. [c] As the chloride salt. [d] Approximate ratio of isomers **7a**:**7b**:**7c** = 1:2:4.

strongly deshielded (the methylene is taken as position 1). Accordingly, the bands at δ 5.77 and 5.68 in the spectrum of **7** are assigned to the 4 hydrogens of **7a** and **7b**. In the spectrum associated with isomer **7a** the doublet at δ 3.38 is assigned to the proton labelled c (see Scheme 1 for labelling system) which is consistent with the methyl group being located in the 6 position of the ring. The two geminal protons f and e of the methylene unit show a mutual coupling constant of 10 Hz, the largest of the

**Table 2** Selected bond lengths (Å) and angles (°) for [W(η- $C_6H_5$-Me)$(PMe_3)_3H_2][PF_6]_2$ **3** with estimated standard deviations (e.s.d.s) in parentheses. Cent refers to the computed η-$C_6H_5Me$ ring centroid

| | | | |
|---|---|---|---|
| W–P(1) | 2.503(4) | W–P(2) | 2.537(3) |
| W–P(3) | 2.506(3) | W–C(1) | 2.29(2) |
| W–C(2) | 2.31(1) | W–C(3) | 2.40(1) |
| W–C(4) | 2.33(2) | W–C(5) | 2.28(1) |
| W–C(6) | 2.41(1) | P(1)–C(8) | 1.83(2) |
| P(1)–C(9) | 1.82(2) | P(1)–C(10) | 1.87(2) |
| P(2)–C(11) | 1.82(2) | P(2)–C(12) | 1.81(2) |
| P(2)–C(13) | 1.86(2) | P(3)–C(14) | 1.81(1) |
| P(3)–C(15) | 1.82(2) | P(3)–C(16) | 1.81(1) |
| P–F(average) | 1.59 | W(1)–Cent | 1.87 |
| | | | |
| P(2)–W–P(1) | 90.3(1) | P(3)–W–P(1) | 126.7(1) |
| P(3)–W–P(2) | 91.7(1) | C (8)–P(1)–W | 111.3(7) |
| C(9)–P(1)–W | 117.9(7) | C(9)–P(1)–C(8) | 101.5(10) |
| C(10)–P(1)–W | 116.3(7) | C(10)–P(1)–C(8) | 106.0(13) |
| C(10–P(1)–C(9) | 102.2(9) | C(11)–P(2)–W | 119.8(7) |
| C(12)–P(2)–W | 113.8(6) | C1(2)–P(2)–C(11) | 100.4(12) |
| C(13)–P(2)–W | 114.2(6) | C(13)–P(2)–C(11) | 101.8(9) |
| C(13)–P(2)–C(12) | 104.7(10) | C(14)–P(3)–W | 119.7(6) |
| C(15)–P(3)–W | 117.6(6) | C(15)–P(3)–C(14) | 99.8(8) |
| C(16)–P(3)–W | 111.2(5) | C(16)–P(3)–C(14) | 103.2(8) |
| C(16)–P(3)–C(15) | 103.2(9) | Cent–W–P(1) | 114.6 |
| Cent–W–P(2) | 114.1 | Cent–W–P(3) | 112.9 |
| F–P–F (*cis*, average) | 90.0 | F–P–F (*trans*, average) | 180.0 |

**Table 3** Fractional atomic coordinates for [W(η-$C_6H_5Me)(PMe_3)_3$-$H_2][PF_6]_2$ **3** with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| W | 0.198 28(3) | 0.147 51(2) | 0.101 56(2) |
| P(1) | 0.205 3(4) | 0.110 7(2) | −0.020 1(2) |
| P(2) | 0.311 8(2) | 0.059 9(2) | 0.138 5(2) |
| P(3) | 0.311 2(2) | 0.225 5(1) | 0.156 3(2) |
| C(1) | 0.031(1) | 0.140 5(7) | 0.076(2) |
| C(2) | 0.058(1) | 0.085 8(8) | 0.114(1) |
| C(3) | 0.093(1) | 0.093 5(8) | 0.181(1) |
| C(4) | 0.113(1) | 0.149 8(8) | 0.206(1) |
| C(5) | 0.089(1) | 0.203 7(7) | 0.166 3(9) |
| C(6) | 0.038(1) | 0.198 8(8) | 0.103(1) |
| C(7) | 0.001(1) | 0.254 6(8) | 0.067(1) |
| C(8) | 0.165(3) | 0.170 2(9) | −0.079 6(9) |
| C(9) | 0.124(2) | 0.047 1(8) | −0.044 4(9) |
| C(10) | 0.331(2) | 0.084(1) | −0.052(1) |
| C(11) | 0.439(1) | 0.054 7(9) | 0.104(1) |
| C(12) | 0.337(2) | 0.059(1) | 0.229 6(9) |
| C(13) | 0.261(1) | −0.018 0(6) | 0.119(1) |
| C(14) | 0.299(1) | 0.241 7(8) | 0.247 1(8) |
| C(15) | 0.446(1) | 0.212 5(8) | 0.151(1) |
| C(16) | 0.296(2) | 0.300 2(7) | 0.117 1(9) |
| P(4) | 0.266 9(2) | 0.125 0(2) | 0.425 8(2) |
| F(1) | 0.183 5(6) | 0.104 6(4) | 0.479 4(4) |
| F(2) | 0.350 3(6) | 0.145 4(4) | 0.372 2(4) |
| F(3) | 0.227 6(6) | 0.193 7(3) | 0.429 7(5) |
| F(4) | 0.306 1(6) | 0.056 4(3) | 0.421 9(5) |
| F(5) | 0.191 4(6) | 0.111 6(4) | 0.364 5(4) |
| F(6) | 0.342 4(6) | 0.138 4(4) | 0.487 1(4) |
| P(5) | 0.500 0 | 0.417 2(2) | 0.250 0 |
| F(7) | 0.500 0 | 0.490 1(3) | 0.250 0 |
| F(8) | 0.500 0(9) | 0.417 2(2) | 0.331 4(3) |
| F(9) | 0.380 9(4) | 0.417 2(2) | 0.250 0(9) |
| F(10) | 0.500 0 | 0.344 2(3) | 0.250 0 |
| P(6) | 0.000 0 | 0.373 8(3) | 0.250 0 |
| F(11) | −0.066 9(9) | 0.373 8(3) | 0.317 4(5) |
| F(12) | 0.069 6(5) | 0.322 2(3) | 0.282 4(4) |
| F(13) | 0.069 6(5) | 0.425 4(3) | 0.282 3(4) |

system. The coupling network for **7b** is similar. The doublet resonance at δ 5.68 is assigned to proton a which is consistent with the presence of a methyl group in the 5 position of the ring. Again a geminal mutual coupling constant of 10 Hz is observed between the methylene protons (f and d). Assignment of the cyclohexadienyl system of **7c** begins by noting the presence of a further multiplet at δ *ca.* 3.8 (overlapping with those of **7a** and **7b**) containing a geminal coupling constant of 10 Hz, and which we may assign to f. Further assignment is straightforward. We note that no coupling from the protons in either the 2 or the 6 positions to the f proton of the methylene is observed in either **7a**, **7b** or **7c**. This must be attributed to a Karplus angle of *ca.* 90°. We cannot assign the f resonance further than to say that it is due to either the *endo* or the *exo* proton (the latter choice is illustrated in Scheme 1).

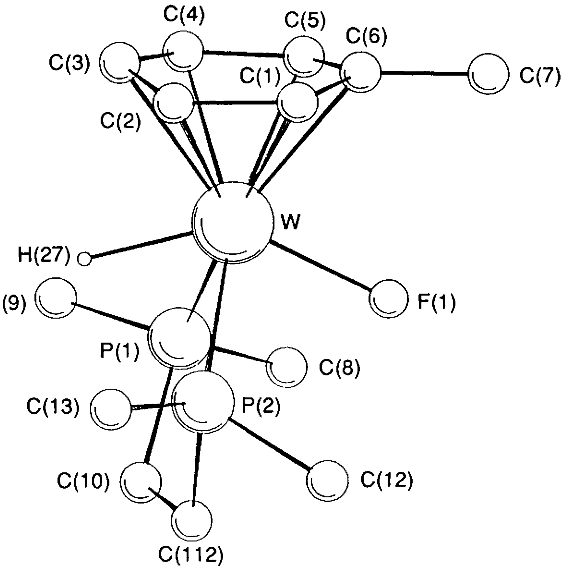


**Fig. 2** Molecular structure of [W(η-$C_6H_5Me$)(dmpe)H(F)] **8**. Hydrogen atoms bonded to carbon atoms omitted for clarity

In the COSY spectrum and the $^1H$ and $^{13}C$ NMR spectra of the isomers **7** there are bands which may be identified readily with the presence of two asymmetric η-allyl groups, as shown in Table 1. The most deshielded bands at δ 2.90 and δ 2.75 are assigned to the central (methine) protons of **7b** and **7c** respectively, on the basis of their integrals. The allyl protons of **7a** could not be located in the COSY spectrum, presumably due to a combination of severe overlap and low intensity. The $^1H$ resonances due to the $CH_2$ and Me groups of the dmpe ligands have also not been assigned, the resonances due to all three isomers being essentially coincident in the regions δ 1.3–0.8 ($CH_2$), 0.7–0.3 (Me) and 1.25–1.0 (Me).

The $^{13}C$ NMR spectrum of the isomers **7** was assigned with the aid of the $^{13}C$–$^1H$ heteronuclear shift correlation spectrum and edited $^{13}C$-{$^1H$} distortionless enhancements by polarisation transfer (DEPT) spectra. Again, the resonances due to the $CH_2$ and $CH_3$ groups of the dmpe ligands could not be assigned due to severe overlap of resonances.

In the course of a synthesis of compound **7** we isolated an unexpected product. After hydrolysis of the excess of $LiAlH_4$ red crystals of [W(η-$C_6H_5Me$)(dmpe)H(F)] **8** were obtained. The $^1H$ NMR spectrum of **8** shows a triplet of doublets ($J_{PH}$ = 56, $J_{FH}$ = 23 Hz) assigned to the hydride at δ = −4.80. Compound **8** was further characterized by single-crystal X-ray diffraction. The molecular structure of **8** is shown in Fig. 2, selected bond lengths and angles in Table 4 and fractional atomic coordinates in Table 5. The hydride ligand was located from a Fourier difference synthesis in a position *trans* to the fluoride ligand and its isotropic thermal parameter and fractional atomic coordinates could be successfully refined. One of the methylenic carbons of the dmpe ligand was disordered over two sites and only the major conformer is shown in Fig. 2. The structure may essentially be described as a four-legged piano-stool geometry, with the chelating dmpe ligand spanning two *trans* sites.

**Table 4** Selected bond lengths (Å) and angles (°) for [W(η-$C_6H_5$Me)(dmpe)H(F)] **8** with e.s.d.s in parentheses.* Cent refers to the computed η-$C_6H_5$Me ring centroid

| | | | |
|---|---|---|---|
| W–P(1) | 2.420(2) | W–P(2) | 2.418(2) |
| W–F | 2.044(3) | W–C(1) | 2.302(6) |
| W–C(2) | 2.208(7) | W–C(3) | 2.331(6) |
| W–C(4) | 2.244(7) | W–C(5) | 2.253(6) |
| W–C(6) | 2.374(6) | W–H(27) | 1.79(2) |
| P(1)–C(8) | 1.815(6) | P(1)–C(9) | 1.804(8) |
| P(1)–C(10) | 1.827(7) | P(2)–C(12) | 1.809(9) |
| P(2)–C(13) | 1.816(8) | P(2)–C(111) | 1.824(8) |
| P(2)–C(112) | 1.828(9) | C(1)–C(2) | 1.45(1) |
| C(1)–C(6) | 1.395(9) | C(2)–C(3) | 1.40(1) |
| C(3)–C(4) | 1.40(1) | C(4)–C(5) | 1.41(1) |
| C(5)–C(6) | 1.428(9) | C(6)–C(7) | 1.49(1) |
| C(10)–C(111) | 1.510(8) | C(10)–C(112) | 1.505(9) |
| C(111)–C(112) | 1.00(2) | W–Cent | 1.79 |
| | | | |
| P(2)–W–P(1) | 80.02(6) | F–W–P(1) | 81.3(1) |
| F–W–P(2) | 80.3(1) | H(27)–W–P(1) | 64.1(22) |
| H(27)–W–P(2) | 71.0(20) | H(27)–W–F(1) | 137.8(21) |
| C(8)–P(1)–W | 118.4(2) | C(9)–P(1)–W | 119.0(3) |
| C(9)–P(1)–C(8) | 102.5(4) | C(10–P(1)–W | 111.5(2) |
| C(10)–P(1)–C(8) | 101.5(4) | C(10)–P(1)–C(9) | 101.4(5) |
| C(12)–P(2)–W | 118.0(3) | C(13)–P(2)–W | 120.1(3) |
| C(13)–P(2)–C(12) | 101.3(4) | C(111)–P(2)–W | 110.0(3) |
| C(111)–P(2)–C(12) | 110.4(5) | C(111)–P(2)–C(13) | 94.4(5) |
| C(112)–P(2)–W | 112.3(5) | C(112)–P(2)–C(12) | 82.9(6) |
| C(112)–P(2)–C(13) | 116.1(7) | C(111)–C(10)–P(1) | 114.1(6) |
| C(112–C(10)–P(1) | 115.0(8) | C(10)–C(111)–P(2) | 111.4(6) |
| C(10)–C(112)–P(2) | 111.4(7) | Cent–W–F | 115.1 |
| Cent–W–P(1) | 138.2 | Cent–W–P(2) | 138.3 |
| Cent–W–H(27) | 106.9 | | |

* The occupancy factors of C(111) and C(112) are 0.62 and 0.38 respectively.

**Table 5** Fractional atomic coordinates for [W(η-$C_6H_5$Me)(dmpe)-H(F)] **8** with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| W | 0.020 49(2) | 0.137 22(1) | 0.135 50(1) |
| P(1) | 0.183 5(2) | 0.184 5(1) | 0.056 27(8) |
| P(2) | 0.057 1(2) | 0.276 3(1) | 0.181 67(9) |
| F | −0.088 8(3) | 0.205 5(2) | 0.068 3(2) |
| C(1) | −0.143 9(7) | 0.084 4(4) | 0.200 5(3) |
| C(2) | −0.022 6(8) | 0.067 5(5) | 0.232 6(4) |
| C(3) | 0.064 1(8) | 0.015 2(4) | 0.198 3(5) |
| C(4) | 0.049 4(8) | −0.001 8(4) | 0.126 9(4) |
| C(5) | −0.064 9(6) | 0.018 2(3) | 0.093 3(4) |
| C(6) | −0.165 2(6) | 0.054 5(4) | 0.132 9(4) |
| C(7) | −0.286 9(7) | 0.072 6(5) | 0.097 2(5) |
| C(8) | 0.143 1(7) | 0.200 2(4) | −0.035 2(3) |
| C(9) | 0.328 2(8) | 0.125 6(7) | 0.050 7(5) |
| C(10) | 0.241 9(9) | 0.288 3(5) | 0.080 5(4) |
| C(12) | −0.061 (1) | 0.355 9(4) | 0.165 4(5) |
| C(13) | 0.086(1) | 0.290 9(6) | 0.274 6(4) |
| C(111)[a] | 0.212 3(8) | 0.313 5(7) | 0.155 0(5) |
| C(112)[b] | 0.151(2) | 0.340 8(8) | 0.122 4(9) |
| H(27) | 0.176(3) | 0.142(4) | 0.171(3) |

[a] Occupancy factor 0.62. [b] Occupancy factor 0.38.

The mechanism of formation of compound **8** is unknown, and could not be investigated as the preparation was not reproducible. However we note that fluoride abstraction from $PF_6^-$ and $BF_4^-$ has occasionally been observed[13] and protonation of [W($PMe_3$)$_4$($\eta^2$-$CH_2PMe_2$)H] with either HF or $HPF_6$ gives the salts [W($PMe_3$)$_4$F(H)$_2$($H_2O$)]X (X = F or $PF_6$).[14] Further, the protonation of [Mo($PMe_2Ph$)$_4$$H_4$] with $HBF_4$ gives [{Mo($PMe_2Ph$)$_3$$H_2$}$_2$(μ-$F_3$)][15] and fluoride-ion abstraction from [Zr(η-$C_5H_5$)$_2$Me(thf)]$PF_6$ gives rise to [Zr(η-$C_5H_5$)$_2$Me(F)].[16]

It was observed that solutions of compound **7** slowly turned orange when exposed to sunlight. Photolysis of a $C_6D_6$ solution of **7** in an NMR tube caused the solution to become deep red after several hours. The $^1H$ NMR spectrum of the solution indicated the presence of [W(η-$C_6H_5$Me)(dmpe)$H_2$] by comparison with an authentic sample.[3] When [W(η-$C_6H_5$Me)$_2$]-$PF_6$ was stirred for 24 h at 40 °C with dmpe a green solution was formed together with a grey solid. The green solution was shown to consist of [W(η-$C_6H_5$Me)$_2$] by comparison with an authentic sample. Extraction of the grey residue with acetone followed by chromatography on alumina gave a red solution which could be recrystallised from liquid $SO_2$–$CH_2Cl_2$ to give green needles of [W(η-$C_6H_5$Me)(dmpe)$_2$][$PF_6$]$_2$ **9**. This complex is presumably formed by disproportionation of the starting material in the presence of excess of the chelating diphosphine.

The reactions and new compounds are shown in Scheme 1.

## Experimental

Except where otherwise stated all reactions and manipulations were carried out under dinitrogen using standard Schlenk or glove-box techniques. Dinitrogen was purified by passage through a column containing 4 Å molecular sieves and Fluka BTS catalyst. All solvents were thoroughly deoxygenated before use by repeated pumping followed by admission of dinitrogen. Solvents were pre-dried over molecular sieves and distilled from suitable drying agents before use. Toluene and light petroleum (b.p. 100–120 °C) were dried over molten sodium, benzene and tetrahydrofuran over molten potassium; diethyl ether and light petroleum (b.p. 40–60 °C) over sodium–potassium alloy (3:1 w/w), and dichloromethane over $P_2O_5$. Deuteriated solvents for NMR spectroscopy were stored in Young's ampoules over activated molecular sieves [except $D_2O$ and $(CD_3)_2CO$] and transferred either by vacuum distillation or by glass pipette in a glove-box.

Proton, $^{31}P$ and $^{13}C$ NMR spectra were acquired on Brüker spectrometers at 500, 202.4 and 125.8 MHz (AM-500), at 300, 121.4 and 75.5 MHz (AM-300 and WH-300) or at 250, 101.2 and 62.9 MHz (AM-250), $^{19}F$ NMR spectra at 282 MHz on a Brüker WH-300 spectrometer. Two-dimensional spectra were obtained using standard Brüker software on AM-300 or AM-500 spectrometers. One-dimensional $^1H$-{$^{31}P$} spectra were acquired on an AM-300 in inverse mode using a Brüker BFX-5 fast switching unit or on an AM-300 spectrometer using an external broad-band $^{31}P$ decoupler, two-dimensional [$^1H$–$^1H$]-{$^{31}P$} spectra on either AM-250 or AM-300 spectrometers using an external broad-band $^{31}P$ decoupler. Proton and $^{13}C$ spectra were calibrated internally relative to residual protio-solvent ($^1H$) or solvent ($^{13}C$) resonances and reported relative to tetramethylsilane; $^{19}F$ and $^{31}P$ spectra were referenced externally and chemical shifts are reported relative to $(CF_3)_2CO$ and $PO(OMe)_3$, downfield shifts being taken as positive.

Infrared spectra were run as KBr discs or Nujol mulls using either a Unicam SP 2000 or a Mattson Polaris spectrometer. Mass spectra were recorded on an AEI MS 902 spectrometer updated with a data-handling system supplied by Mass Spectroscopy Services. Elemental analyses were carried out by the analytical service of this laboratory, or, in the case of very air-sensitive samples, by Analytische Laboratorien, Elbach, Germany.

The compounds [W(η-$C_6H_5$Me)$_2$] and [W(η-$C_6H_6$)$_2$] were prepared by metal-atom synthesis using an electron gun operating in the positive hearth mode as previously described.[2] The phosphines $PMe_3$,[17] dmpe,[18] and SiMe($CH_2PMe_2$)$_3$[19] were prepared by the published procedures.

*Preparations.*—[W(η-$C_6H_5$Me)($PMe_3$)$_3$] **2**. The compound [W(η-$C_6H_5$Me)$_2$] (2.8 g, 7.6 mmol) was transferred into a glass ampoule and an excess of trimethylphosphine (*ca.* 20 cm$^3$) condensed onto the solid under reduced pressure. The ampoule was sealed and placed in a steel pressure tube filled with light petroleum (b.p. 40–60 °C) and heated to 200 °C for 18 h giving an orange solution. After removal of the excess of phosphine the residue was extracted with thf. The extract was filtered and pumped to dryness. The orange residue was extracted with light petroleum (b.p. 40–60 °C, 3 × 30 $cm^3$). The solution was concentrated under reduced pressure and cooled to –20 °C for 2 h to give orange crystals. The crystals were filtered off cold, washed with cold light petroleum and dried *in vacuo*. Yield: 3.6 g (93%).

$[W(\eta\text{-}C_6H_5Me)(PMe_3)_3H_2][PF_6]_2$ **3**. A solution of the compound $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3]$ (0.5 g, 0.99 mmol) in light petroleum (b.p. 40–60 °C, 30 $cm^3$) was treated with hydrogen chloride gas. A purple solid was formed initially, which then turned yellow. The colourless light petroleum layer was decanted off and the yellow solid washed with light petroleum ether (b.p. 40–60 °C, 3 × 30 $cm^3$). The solid was dried under reduced pressure and dissolved in deoxygenated water. An aqueous solution of $NH_4PF_6$ was added to the extract and a yellow precipitate was obtained. This was filtered off, washed with water and extracted into acetone. The extract was filtered and recrystallised from water–acetone giving yellow crystals. Yield: 0.75 g (95%).

$[W(\eta\text{-}C_6H_5Me)(PMe_3)_3H]PF_6$. A solution of the compound $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3]$ (0.5 g, 0.99 mmol) in light petroleum (b.p. 40–60 °C, 30 $cm^3$) was treated with hydrogen chloride gas giving a yellow precipitate as before (see above). The clear supernatant was decanted and the solid washed with light petroleum (b.p. 40–60 °C, 2 × 20 $cm^3$) and dried *in vacuo*. Dissolution of the solid in deoxygenated water and dropwise addition of 30% aqueous KOH gave a purple solution. Addition of $NH_4PF_6$ gave a purple solid which was separated and recrystallised from dichloromethane. Yield: 0.6 g (93%).

$[W(\eta\text{-}C_6H_5Me)(PMe_3)_3H]BF_4$. A solution of the compound $[W(\eta\text{-}C_6H_5Me)(PMe_3)_3]$ (0.5 g, 0.99 mmol) in thf was added to solid $NH_4BF_4$ (32 mg, 1 mmol) and the mixture was stirred for 12 h. A purple solid was produced, the colourless supernatant was decanted and the solid dried *in vacuo*. The solid was recrystallised from acetone. Yield: 0.6 g (93%).

$[W(\eta\text{-}C_6H_5Me)\{SiMe(CH_2PMe_2)_3\}]$ **5**. The compound $[W(\eta\text{-}C_6H_5Me)_2]$ (0.42 g, 1.13 mmol) was placed in a thick-walled glass ampoule and neat $SiMe(CH_2PMe_2)_3$ (0.6 g, 2.25 mmol) added. The sealed ampoule was placed in a steel pressure tube, filled with toluene, and heated at 200 °C for 2 d, giving an orange solution. This was washed from the ampoule with light petroleum (b.p. 40–60 °C, 20 $cm^3$) and the volatiles removed under reduced pressure. The excess of silane was removed by sublimation to a cold-finger at –196 °C. The residue was extracted into light petroleum (b.p. 40–60 °C, 20 $cm^3$), filtered and cooled to –80 °C giving green crystals identified as $[W(\eta\text{-}C_6H_6Me)_2]$; the supernatant was decanted and reduced in volume to *ca.* 10 $cm^3$. Further cooling to –80 °C gave orange crystals which were isolated and washed with a little cold light petroleum. Yield: 400 mg (70%).

$[W(\eta\text{-}C_6H_5Me)\{SiMe(CH_2PMe_2)_3\}H]BF_4$ **6**. A solution of the compound $[W(\eta\text{-}C_6H_5Me)\{SiMe(CH_2PMe_2)_3\}]$ (0.18 g, 0.33 mmol) in thf (20 $cm^3$) was added to an excess of solid $NH_4BF_4$ and the mixture stirred for 12 h. The orange solution slowly turned purple. The solution was filtered and the volatiles removed under reduced pressure. The residue was extracted with thf (10 $cm^3$) and the soluble portion reduced in volume to 5 $cm^3$. Cooling to –80 °C for 12 h afforded purple crystals, which were collected, washed with a small quantity of cold thf and dried *in vacuo*. Yield: 0.14 g (75%).

$[W(\eta^5\text{-}C_6H_6Me)(\eta^3\text{-}C_3H_5)(dmpe)]$ **7**. A suspension of the compound $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(dmpe)]PF_6$ (0.5 g, 0.8 mmol) in dry thf (30 $cm^3$) was stirred at room temperature with an excess of $LiAlH_4$ (0.1 g, 2.6 mmol) for 12 h, after which time all the orange solid had reacted. The solvent was removed under reduced pressure to give a grey-white solid. This was extracted with light petroleum (b.p. 40–60 °C, 3 × 30 $cm^3$) with vigorous shaking giving a pale yellow solution which was filtered and the solvent removed under reduced pressure. The residue was extracted with light petroleum (b.p. 40–60 °C) to give a pale yellow solution. On concentrating to 5–10 $cm^3$ the solution showed a slight orange colour (due to the presence of photodecomposition products) and was cooled to –20 °C for 30 min affording an off-white solid with an orange impurity which was washed away at –78 °C with light petroleum (b.p. 40–60 °C) until the washings were colourless. Yield: 0.3 g (78%).

$[W(\eta\text{-}C_6H_5Me)(dmpe)H(F)]$, **8**. The salt $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(dmpe)]PF_6$ (0.4 g, 0.6 mmol) was suspended in dry thf (30 $cm^3$) at –30 °C. An excess of $LiAlH_4$ (0.2 g, 5.2 mmol) was added, also as a suspension in thf. The solution was stirred and allowed to warm to room temperature while being stirred for 1 h. After cooling to –78 °C, deoxygenated water was added to hydrolyse the excess of $LiAlH_4$. The product was extracted with benzene giving an orange solution and a white sticky precipitate. The orange solution was filtered, the solvent removed under reduced pressure and stored under argon for a few days. Over this period it became red. The red compound was extracted with light petroleum (b.p. 40–60 °C, 50 $cm^3$) giving a deep red solution which was concentrated and cooled to –20 °C giving air-sensitive red crystals. This reaction was not reproducible (see text). All subsequent attempts to repeat this synthesis yielded $[W(\eta^5\text{-}C_6H_6Me)(\eta^3\text{-}C_3H_5)(dmpe)]$.

$[W(\eta\text{-}C_6H_5Me)(dmpe)_2][PF_6]_2$ **9**. The salt $[W(\eta\text{-}C_6H_5Me)_2]PF_6$ (1 g, 1.9 mmol) was suspended in neat dmpe (8 g, 53.3 mmol). The mixture was warmed to 40 °C for 2 d after which time the yellow solid had changed to dark grey and a green solution had formed. The green solution was filtered and the residue washed with light petroleum (b.p. 40–60 °C, 6 × 15 $cm^3$). The solid was dried *in vacuo* and then washed with water. The residues were dissolved in acetone and the extract concentrated to about one third of its original volume and passed through a chromatography column packed with deactivated neutral alumina as an acetone slurry. The column was deoxygenated and eluted with acetone giving three bands. The first fraction yielded a red-orange solid (still impure), the second a yellow oil which was discarded and the third a grey-red dichroic solution which gave green crystals. The first fraction was chromatographed a second time but decomposed on the column. The pale green crystals were recrystallised from $SO_2(l)$–$CH_2Cl_2$. As the $SO_2$ evaporated, green needles separated. Yield: *ca.* 100 mg (6%).

*X-Ray Crystal Structure Determinations of Compounds* **3** *and* **8**.—Crystal data, data-collection and -processing parameters are given in Table 6. In each case a crystal was sealed in a Lindemann glass capillary and transferred to the goniometer head of an Enraf–Nonius CAD4 diffractometer. Unit-cell parameters were calculated from the setting angles of 25 carefully centred reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections.

The data were corrected for Lorentz and polarisation effects and an empirical absorption correction[20] based on azimuthal scan data was applied. Equivalent reflections were merged and systematically absent reflections rejected. The heavy-atom positions were determined from Patterson syntheses. Subsequent Fourier difference syntheses revealed the positions of other non-hydrogen atoms. The crystals of compound **3** contained one $PF_6$ anion on a general position and two half $PF_6$ anions lying on the two-fold axis at 0, *y*, 0.25. Non-hydrogen atoms were refined with anisotropic thermal parameters by least-squares procedures, with the exception of the $PF_6$ atoms of compound **3** which were refined subject to soft restraints[21] to conserve the octahedral symmetry. One of the methylene carbon atoms of the dmpe ligand of compound **8** was resolved as two peaks in the difference map [C(111) and C(112)] indicating site disorder. The site occupation factors were refined as 0.62 and 0.32 respectively for equivalent isotropic thermal

**Table 6** Crystallographic data and experimental conditions for compounds **3** and **8**[a]

| Compound | **3** | **8** |
|---|---|---|
| Formula | $C_{16}H_{37}F_{12}P_5W$ | $C_{13}H_{26}FP_2W$ |
| $M$ | 796.17 | 447.17 |
| Crystal size/mm | 0.2 × 0.15 × 0.30 | 0.5 × 0.38 × 0.30 |
| Space group | *Pbcn* | *Pbca* |
| $a$ Å | 13.322(2) | 10.623(1) |
| $b$ Å | 21.471(3) | 15.948(2) |
| $c$ Å | 19.475(3) | 19.086(3) |
| $U$ | 5570 | 3233.5 |
| $D_c$/g cm$^{-3}$ | 1.903 | 1.83 |
| $F(000)$ | 3240 | 1736 |
| μ/cm$^{-1}$ | 46.04 | 74.85 |
| Total data collected | 7301 | 4246 |
| No. of observations $[I > 3\sigma(I)]$ | 3503 | 2016 |
| $R_{merge}$ | 0.032 | 0.015 |
| No. of parameters | 331 | 158 |
| Weighting coefficients | 23.2, −6.40, 15.4 | 6.03, −5.24, 4.71, −1.04 |
| Maximum residual peak in final difference map/e Å$^{-3}$ | 1.4 | 0.83 |
| Final residuals $R,R'$[b] | 0.075, 0.082 | 0.025, 0.029 |

[a] Details in common: crystal system, orthorhombic; $\alpha, \beta, \gamma = 90°$; $Z = 8$; Mo-K$\alpha$ radiation ($\lambda = 0.710\ 69$ Å); $\theta_{max} = 25°$; scan mode $\omega$–$2\theta$; $\omega$ scan width $0.6 + 0.35 \tan\theta$; Chebyshev weighting scheme. [b] $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}}$.

parameters and then fixed. Atoms C(111) and C(112) were then refined isotropically with soft restraints on the bonds to C(10) and P(2) respectively. Disorder in the methylene linkages of co-ordinated dmpe ligands have been observed elsewhere.[22] Hydrogen atoms were placed in estimated positions (C–H 1.00 Å) with an isotropic thermal parameter of 0.080 Å$^2$ and refined riding on their supporting carbon atoms. For compound **8** the hydride ligand was located from Fourier difference syntheses and its fractional coordinates and isotropic thermal parameter were refined. A Chebyshev weighting scheme[23] was applied, and the data were corrected for the effects of anomalous dispersion and isotropic extinction (*via* an overall isotropic extinction parameter[24]) in the final stages of refinement.

All crystallographic calculations were performed using the CRYSTALS suite[25] on either a Vax 11/750 or Micro Vax 3800 computer in the Chemical Crystallography Laboratory, Oxford. Scattering factors were taken from the usual sources.[26]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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