Further Evidence for 1,2-Hydrogen Shift Equilibria in the Bis(η-cyclopentadienyl)methyltungsten System

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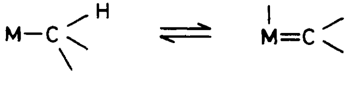
Trimethylphosphine reacts with $[W(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)Me]PF_6$ (1) to give $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2PMe_3)Me]PF_6$ (8) which decomposes thermally to $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_3)H]PF_6$ (9). Thermal equilibrium between (9) and $[W(\eta\text{-}C_5H_5)_2(PMe_3)Me]PF_6$ (11) has been demonstrated. Methyldiphenylphosphine with $[W(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)Me]PF_6$ (1) gives the complex $[W(\eta\text{-}C_5H_5)_2(CH_2PMePh_2)H]PF_6$ (10), then $[W(\eta\text{-}C_5H_5)_2(PMePh_2)Me]PF_6$ (12). The products of the reaction of a 1 : 1 mixture of $[W(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)Me]PF_6$ (1) and the CD_3 analogue with PMe_2Ph show that intermolecular hydrogen/deuterium scrambling does not occur. Exchange of the PMe_2Ph group by PMe_3 has been shown in $[W(\eta\text{-}C_5H_5)_2(CH_2PMePh_2)H]PF_6$ (10). A mechanism for the reactions involving reversible 1,2-hydrogen shift equilibria of the tungsten–methyl system is discussed.

The shift of a hydrogen attached to the α-carbon of a transition metal alkyl ligand to the transition metal forming a metal–carbene–hydrido-system has been postulated to occur in a number of the reactions of transition metal alkyls.[1–3] The first and most substantial evidence for the occurrence in a homogeneous system of a 1,2-hydrogen shift as a reversible equilibrium process (see below) arose from the study of the reactions of the bis(η-cyclopentadienyl)methyltungsten derivatives $[W(\eta\text{-}C_5H_5)_2LMe]^+$ [L = η-C_2H_4 (1), SMe_2 (2), or I^- (3)] with the tertiary phosphine PMe_2Ph.[4,5]



Treatment of (1) with PMe_2Ph gave rise to the sequence of reaction products $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2PMe_2Ph)Me]PF_6$ (4), then $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_2Ph)H]PF_6$ (5), and finally the thermally most stable product $[W(\eta\text{-}C_5H_5)_2(PMe_2Ph)Me]PF_6$ (6). In marked contrast, treatment of (1) with PPh_3 gave only the compound $[W(\eta\text{-}C_5H_5)_2(PPh_3)Me]PF_6$ (7). These reaction sequences are illustrated in the Scheme.

Here we describe further studies of the bis(η-cyclopentadienyl)methyltungsten compounds with the tertiary phosphines PMe_3 and $PMePh_2$ which were carried out in order to establish the factors which influence the outcome of the reaction between (1) and tertiary phosphines and also to reinforce the earlier studies. There has been a communication describing some of this work.[6]

Results and Discussion

Treatment of the compound $[W(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)Me]PF_6$ (1) with PMe_3 at room temperature in acetone solution gives the expected compound $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2PMe_3)Me]PF_6$ (8). When an acetone solution of (8) was refluxed for 5 d ethylene was evolved and the hydrido-compound $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_3)H]PF_6$ (9) formed in essentially quantitative yield.

When (1) in acetone was treated with $PMePh_2$ at room temperature, after 2 d compound $[W(\eta\text{-}C_5H_5)_2(CH_2PMePh_2)H]PF_6$ (10) was formed. When solutions of (9) or (10) in acetone were heated at 70 °C they underwent steady conversion to the compounds $[W(\eta\text{-}C_5H_5)_2(PMe_3)Me]PF_6$ (11) and $[W(\eta\text{-}C_5H_5)_2(PMePh_2)Me]PF_6$ (12) respectively. The reactions were monitored by ^1H n.m.r. spectroscopy which showed that (9) was converted to an equilibrium mixture of (9) and (11) over a period of 14 d whereas (10) was converted quantitatively to (12) after only 24 h at 65 °C.

A pure sample of (11) was prepared by treatment of $[W(\eta\text{-}C_5H_5)_2(PMe_3)Br]PF_6$ (13) or $[W(\eta\text{-}C_5H_5)_2(PMe_3)I]PF_6$ (14) with $MgCH_3Br$. Compound (13) was initially prepared by the following sequence of reactions: $[W(\eta\text{-}C_5H_5)_2(SMe_2)Br]PF_6$ was treated with PMe_3 followed by crystallisation from aqueous acetone. This reaction gave only a small yield of (13) and the major product was the hydroxo-compound $[W(\eta\text{-}C_5H_5)_2(PMe_3)(OH)]PF_6$ (15). This could be partially converted to (13) by treatment with lithium bromide in acetone. It was subsequently found that (13) was readily prepared by direct reaction between $[W(\eta\text{-}C_5H_5)_2Br_2]$ and PMe_3 followed by addition of aqueous ammonium hexafluorophosphate. In a similar manner (14) was prepared in high yield by direct reaction between $[W(\eta\text{-}C_5H_5)_2I_2]$ and PMe_3.

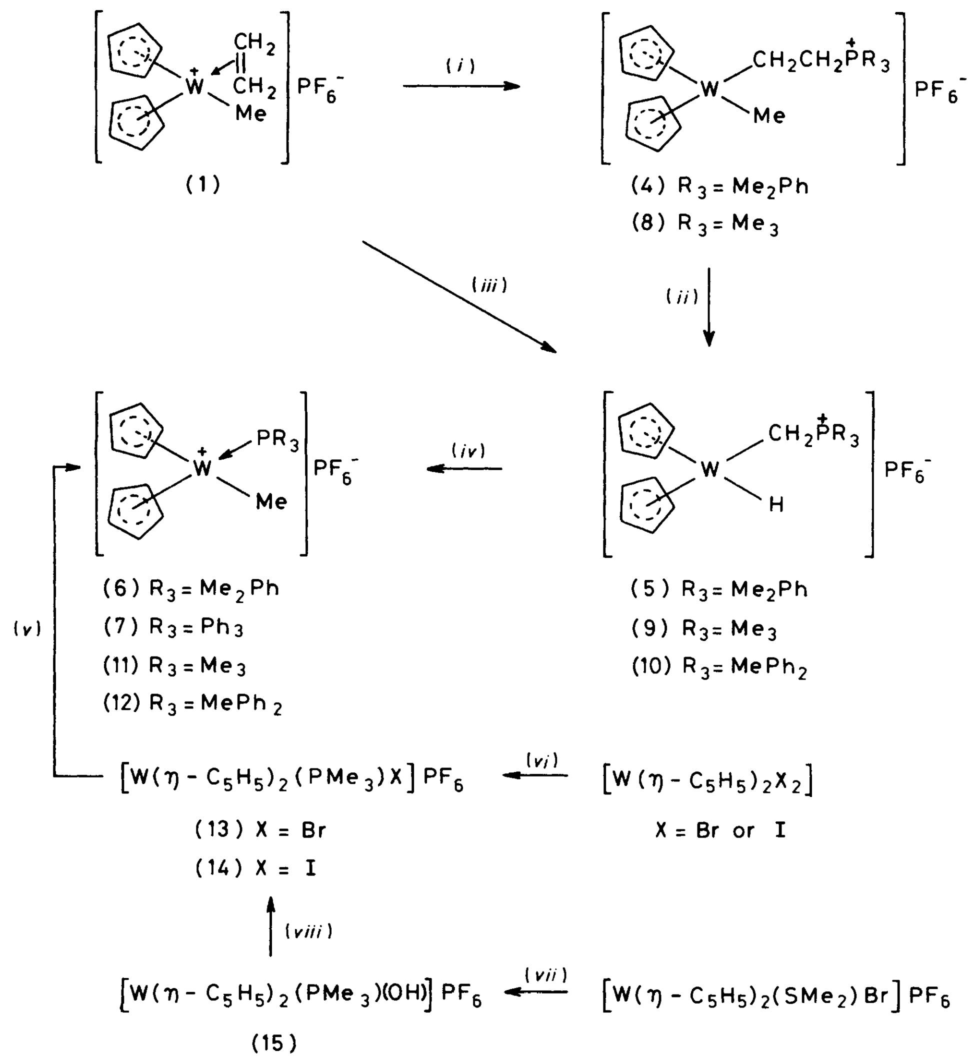
Thermolysis of pure (11) in acetone at 70 °C for 20 d gave a mixture of (9) and (11) in the *same* ratio as found for the thermolysis of a pure sample of (9), namely 72 : 28 for (9) : (11); this shows that solutions (9) and (11) are in thermal equilibrium.

The thermal decomposition of acetone solutions of the compounds $[W(\eta\text{-}C_5H_5)_2(CH_2PR_3)H]PF_6$ [R_3 = Me_3 (9), Me_2Ph (5), and $MePh_2$ (10)] at 70 °C gave the corresponding methyl derivatives $[W(\eta\text{-}C_5H_5)_2(PR_3)Me]PF_6$ and was monitored by ^1H n.m.r. spectroscopy. The data clearly showed the rates of decomposition to occur in the sequence PPh_3 (*ca.* 6 h) > $PMePh_2$ (*ca.* 24 h) > PMe_2Ph (*ca.* 72 h) > PMe_3 (*ca.* 300 h).

In view of these marked differences in conversion rates it was decided to see whether it was possible to trap-out intermediates. Thus a solution of (10) in acetone was treated with an excess of PMe_3 at 70 °C. The reaction was monitored by ^1H n.m.r. spectroscopy which showed a steady formation of (9) and after 3 d the solution contained (9) (41%), (11) (11%), and (10) (48%).

Similarly, treatment of (10) with PMe_2Ph gave $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_2Ph)H]PF_6$ (5) as the first formed product (*ca.* 40%). In contrast, treatment of (9) with $PMePh_2$ at 70 °C for 6 d gave only a small quantity (10% conversion) of (11) and none of the compound (10) was detected in the mixture.

The perdeuteriomethyl compound $[W(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)(CD_3)]PF_6$ (1d), prepared as previously described,[5] together with an equimolar amount of the undeuteriated analogue (1) in acetone was treated with an excess of PMe_2Ph at 70 °C. The ^1H n.m.r. spectrum was monitored at intervals for 14 d. The products were found to be only $[W(\eta\text{-}C_5H_5)_2(PMe_2Ph)Me]PF_6$ (6) and $[W(\eta\text{-}C_5H_5)_2(PMe_2Ph)(CD_3)]PF_6$. There was no evidence in the n.m.r. spectrum for the formation of any

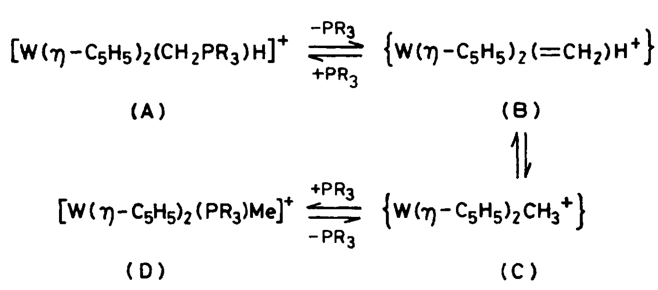


Scheme. (*i*) PMe_3 in acetone, r.t., 12 h, yield 65%; (*ii*) heat in acetone, 70 °C, 48 h, 51%; (*iii*) PMe_3 or $PMePh_2$ in acetone, r.t., 48 h; (*iv*) heat in acetone, 70 °C, duration depends on PR_3; (*v*) MgMeBr in Et_2O, 15 h, r.t., then 1 h at 50 °C, 60%; (*vi*) PMe_3 in acetone, 70 °C, 7 h, X = Br (80%) or I (40%); (*vii*) PMe_3 in acetone, 70 °C, 3 h, then NH_4PF_6(aq), 59%; (*viii*) LiBr in acetone, 70 °C, 4.5 h, 15%

partially deuteriated methyl derivatives. For example, the group CH_2D would have been detected from the presence of side-bands on the CH_3 band arising from H/D coupling [typical values for J(H–D) in transition metal–methyl systems are *ca.* 10 Hz].[7] The absence of hydrogen–deuterium exchange in the above reaction is entirely consistent with an *intramolecular* mechanism, as was previously proposed for the conversion of (5) to (6).[4,5]

An exploratory reaction was carried out between (1) and 1,2-bis(dimethylphosphino)ethane; the first formed product was the compound $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2PMe_2CH_2CH_2PMe_2)Me]PF_6$ (16). Thermal decomposition of acetone solutions of (16) gave a complex mixture of products (^1H n.m.r.) which was not further investigated.

The data characterising the new compounds (8)—(16) are given in the Table and in the Experimental section.



The above observations are entirely consistent with a mechanism for interconversion of the compounds $[W(\eta\text{-}C_5H_5)_2(CH_2PR_3)H]^+$ to $[W(\eta\text{-}C_5H_5)_2(PMe_3)Me]^+$ *via* the following sequence. It is clear from the approximate rate data above that the rate of dissociation of the compounds (A) decreases with increasing alkylation of PR_3. Also that the equilibrium between the compounds (A) and (D) shifts towards (A) with increasing alkylation of PR_3.

There have been several recent observations where reactions of α-hydrogens of transition metal–hydrocarbon systems have been invoked. For example, a remarkable abstraction of an α-hydrogen in preference to the normal β-hydrogen abstraction has been observed by Gladsyz and co-workers[8] in the compound $[Re(\eta\text{-}C_5H_5)(NO)(PPh_3)Et]$. Also, Holmes and Schrock[9] have evidence for a reversible 1,2-hydrogen shift

Table. Analytical and spectroscopic data

		Analysis[a] (%)		Selected	
Compound	Colour	C	H	i.r. data[b]	Hydrogen-1 n.m.r. data[c]
(8) $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2PMe_3)Me]PF_6$	Yellow-orange	33.6 (33.2)	4.7 (4.5)		5.39, **10**, *s*, $(\eta\text{-}C_5H_5)_2$; 7.50, **2**, *c*, CH_2P; 8.13, **9**, *d*[*J*(P-H) 14.0], Me_3; 9.47, **2**, *c*, WCH_2; 10.14, **3**, *s*, WMe[d]
(9) $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_3)H]PF_6$	Yellow	32.0 (31.6)	4.6 (4.2)	1 918m[e]	5.16, **10**, *s*, $(\eta\text{-}C_5H_5)_2$; 8.50, **9**, *d* [*J*(P-H) 13.0], Me_3; 9.27, **2**, *d*[*J*(P-H) 13.5], CH_2; 22.78, **1**, *d*[*J*(P-H) 9.5], WH[d]
(10) $[W(\eta\text{-}C_5H_5)_2(CH_2PMePh_2)H]PF_6$	Yellow	43.0 (42.8)	3.5 (3.7)	1 917m[e]	2.35—2.60, **10**, *c*, Ph_2, 5.27, **10**, *s*, $(\eta\text{-}C_5H_5)_2$; 7.59, **3**, *d*[*J*(P-H) 13.5], PMe; 8.29, **2**, *d*[*J*(P-H) 12.5], CH_2; 22.65, **1**, *d*[*J*(P-H) 9.0], WH[d]
(11) $[W(\eta\text{-}C_5H_5)_2(PMe_3)Me]PF_6$	Orange	31.0 (30.6)	4.1 (4.0)		4.65, **10**, *d*[*J*(P-H) 1.83], $(\eta\text{-}C_5H_5)_2$; 8.24, **9**, *d*[*J*(P-H) 9.5], Me_3; 9.74, **3**, *d*[*J*(P-H) 8.0], WMe[d]
(12) $[W(\eta\text{-}C_5H_5)_2(PMePh_2)Me]PF_6$	Red-orange	42.5 (42.8)	3.9 (3.7)		2.4—2.6, **10**, *c*, Ph_2; 4.89, **10**, *d*[*J*(P-H) 2.5], $(\eta\text{-}C_5H_5)_2$; 7.93, **3**, *d*[*J*(P-H) 9.0), PMe; 9.35, **3**, *d*[*J*(P-H) 6.5], WMe[d]
(13) $[W(\eta\text{-}C_5H_5)_2(PMe_3)Br]PF_6$	Red-purple	25.0 (25.4)	2.9 (3.1)		4.32, **10**, *d*[*J*(P-H) 1.72], $(\eta\text{-}C_5H_5)_2$; 8.10, **9**, *d*[*J*(P-H) 10.5], PMe_3[d]
(14) $[W(\eta\text{-}C_5H_5)_2(PMe_3)I]PF_6$	Purple	24.6 (23.6)	2.9 (2.9)[f]		4.23, **10**, *d*[*J*(P-H) 1.83], $(\eta\text{-}C_5H_5)_2$; 7.99, **9**, *d*[*J*(P-H) 10.5], PMe_3[d]
(15) $[W(\eta\text{-}C_5H_5)_2(PMe_3)(OH)]PF_6$	Red	27.8 (28.3)	3.6 (3.6)	3 600[g]	4.44, **10**, *d*[*J*(P-H) 1.67], $(\eta\text{-}C_5H_5)_2$; 8.27, **9**, *d*[*J*(P-H) 10.5], PMe_3[d]
(16) $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2PMe_2CH_2CH_2PMe_2)Me]PF_6$	Orange	34.4 (35.0)	5.0 (5.1)		5.35, **10**, *s*, $(\eta\text{-}C_5H_5)_2$; 7.3—7.7, 8.0—8.4, 9.2—9.6, **8**, *complex*, $4(CH_2)$; 8.09, **6**, *d*[*J*(P-H) 13.83], $-PMe_2-$; 8.91, **6**, *d*[*J*(P-H) 2.83], PMe_2; 10.15, **3**, *s*, Me[d]

[a] Calculated values are given in parentheses. [b] Measured as Nujol mulls; values in cm^{-1}. [c] Given as chemical shift(τ), **relative intensity**, *multiplicity* (*J* in Hz), assignment, *etc.* [d] In $(CD_3)_2CO$. [e] ν(W-H). [f] I = 19.8 (19.2%). [g] ν(O-H).

between a tungsten–carbene system and the corresponding tungsten–carbyne-hydrido-compound.

Thus it appears that, as we proposed elsewhere [7] the ability of suitable metal centres to take part in α-hydrogen activation leading to reversible 1,2-hydrogen shifts is quite a *general phenomenon*.

A theoretical discussion of the 1,2-hydrogen shift in transition metal alkyls by Hoffmann and co-workers [10] has indicated the process to be allowed and favourable.

The normal requirements for a metal–hydrocarbon system to take part in 1,2-hydrogen shifts are that the metal centre should be electronically unsaturated, *i.e.* there should be a 16-electron environment (or fewer) about the metal, and also that two of these electrons should be of essentially d^2 character. However, if in any particular system the carbene ligand resulting from a 1,2-shift bonds to the metal in a manner analogous to that of a carbon monoxide ligand, *i.e.* as a formal two-electron donor, then the requirement for a d^2 system is removed.

It also seems probable that methyl groups attached to transition metal centres which have a 16-electron environment (or fewer) will not show in the ground state a local C_{3v} symmetry for the $M-CH_3$ grouping but there will be a distortion such that one hydrogen will be moved towards the metal centre. We are presently carrying out studies to test this proposal. The reason for such a distortion would lie in the tendency of the C–H bond to interact with the electronically unsaturated metal centre; similar intermolecular C–H to metal interactions have been observed in some dinuclear systems involving distorted bridging methyl groups.[11,12]

Experimental

All reactions and manipulations were carried out under nitrogen or *in vacuo*. All solvents were thoroughly dried and distilled before use. Chromatography was carried out using alumina oxide (100—120 mesh) supplied by East Anglia Chemicals Ltd. Celite 545 was supplied by Koch-Light Ltd. Microanalyses were by A. Bernhardt or by the microanalytical laboratory of this department. Infrared spectra were recorded as mulls on a Perkin-Elmer 457 instrument and were calibrated with polystyrene film. Hydrogen-1 n.m.r. spectra were determined using a Bruker WH-90, JNM-PMX 0, or Bruker WH-300 spectrometer. Mass spectra were recorded on an A.E.I. M.S. 9 spectrometer. Gas–liquid chromatography (g.l.c.) was carried out on a Pye 104 chromatograph using a 10% KCl–alumina column. The compounds $[W(\eta\text{-}C_5H_5)_2X_2]$ (X = Cl, Br, or I) [13] $[W(\eta\text{-}C_5H_5)_2Me(I)]$ (3),[14] $[W(\eta\text{-}C_5H_5)_2MeH]$,[15] $[W(\eta\text{-}C_5H_5)(SMe_2)Br]PF_6$,[16] and $[W(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)Me]PF_6$ (1) [17] were prepared as previously described.

Bis(η-*cyclopentadienyl*)*hydrido*[(*trimethylphosphonio*)*methylide*]*tungsten Hexafluorophosphate*.—(*i*) *From* $[W(\eta\text{-}C_5H_5)_2Me(I)]$. The compound $[W(\eta\text{-}C_5H_5)_2Me(I)]$ (1.0 g, 2.21 mmol) in acetone (100 cm^3) was treated with trimethylphosphine (0.5 g, 6.6 mmol) and the mixture refluxed for 17 h. After cooling the orange solution was filtered and kept at room temperature (r.t.) for 2 d giving yellow crystals of the *iodide salt*. These were collected, washed, and dried *in vacuo* (yield 0.5 g, 43%). The corresponding hexafluorophosphate salt was prepared by addition of aqueous ammonium hexafluorophosphate to an aqueous solution of the iodide salt. It was recrystallised from methanol as yellow-orange crystals.

(*ii*) *From* [W(η-C_5H_5)$_2$($CH_2CH_2PMe_3$)Me]PF_6.—The compound [W(η-C_5H_5)$_2$($CH_2CH_2PMe_3$)Me]PF_6 (1.1 g, 1.9 mmol) in acetone (150 cm^3) was refluxed for 5 d. The solution was filtered and the solvent removed under reduced pressure. The residue was extracted with acetone and passed through a short alumina column. The solvent was removed from the resulting yellow acetone eluate and the residue extracted with methanol. Concentration under reduced pressure and cooling gave the pure product as before (yield 0.48 g, 46%).

Bis(η-*cyclopentadienyl*)*methyl*[2-(*trimethylphosphonio*)-*ethylide*]*tungsten Hexafluorophosphate* (8).—The compound [W(η-C_5H_5)$_2$(η-C_2H_4)Me]PF_6 (1.5 g, 2.99 mmol) in acetone (100 cm^3) was treated with trimethylphosphine (0.23 g, 3.03 mmol). The initial yellow solution began to change to orange within a few minutes. After 12 h the solvent was removed under reduced pressure, the residue was washed with light petroleum (b.p. 30—40 °C) and then extracted with acetone. The extract was filtered through an alumina bed and ethanol added to the filtrate. Concentration and cooling gave the product as yellow-orange crystals (yield 1.12 g, 65%).

Bis(η-*cyclopentadienyl*)*hydrido*[(*methyldiphenylphosphonio*)-*methylide*]*tungsten Hexafluorophosphate* (10).—(*i*) *From* [W(η-C_5H_5)$_2$Me(I)]. The compound [W(η-C_5H_5)$_2$Me(I)] (1.0 g, 2.21 mmol) in acetone (100 cm^3) was treated with methyldiphenylphosphine (1.3 g, 6.50 mmol) and the mixture refluxed for 36 h. The solvent was removed under reduced pressure and the oily residue washed with light petroleum (b.p. 30—40 °C) to remove excess of the tertiary phosphine. The residue was extracted with ethanol–water (1 : 1) (100 cm^3) and aqueous ammonium hexafluorophosphate was added to the orange extract giving an orange-yellow precipitate. This was collected, washed with water, and dried *in vacuo*. It was then recrystallised from acetone–methanol giving red-orange needles which were collected, washed with methanol, and dried *in vacuo* (yield 0.89 g, 60%).

(*ii*) *From* [W(η-C_5H_5)$_2$(η-C_2H_4)Me]PF_6. The compound [W(η-C_5H_5)$_2$(η-C_2H_4)Me]PF_6 (0.5 g, 1 mmol) in acetone (100 cm^3) was treated with methyldiphenylphosphine (1.0 g, 5 mmol) at r.t. for 48 h. The reaction mixture was treated as above except that the final recrystallisation was from ethanol (yield 0.34 g, 51%).

Bromobis(η-*cyclopentadienyl*)(*trimethylphosphine*)*tungsten Hexafluorophosphate* (13).—The compound [W(η-C_5H_5)$_2Br_2$] (1.5 g, 3.16 mmol) in acetone (75 cm^3) was treated with trimethylphosphine (0.25 g, 3.29 mmol) and the mixture warmed to 70 °C for 7 h. The solvent was removed under reduced pressure and the resulting brown-green residue washed with light petroleum (b.p. 30—40 °C) (3 × 15 cm^3). The residue was extracted with acetone–water (4 : 1) giving a red-purple solution which was chromatographed on an alumina column made up in light petroleum (b.p. 30—40 °C). Elution with acetone–water (4 : 1) gave a red-purple band which was collected and aqueous ammonium hexafluorophosphate added to give a red-purple precipitate. This was crystallised from tetrahydrofuran giving red-purple crystals which were collected and dried *in vacuo* (yield 80%). The compound [W(η-C_5H_5)$_2$(PMe_3)I]PF_6 was prepared in a similar manner starting from the di-iodo-compound [W(η-C_5H_5)$_2I_2$] (yield 40%).

Bis(η-*cyclopentadienyl*)*hydroxo*(*trimethylphosphine*)*tungsten Hexafluorophosphate* (15).—The compound [W(η-C_5H_5)$_2$-(SMe_2)Br]PF_6 (3.5 g, 5.8 mmol) in acetone (75 cm^3) was treated with trimethylphosphine (1.4 g, 18.4 mmol) and the mixture stirred at 70 °C for 3 h. The initially purple solution became red. The solvent was removed under reduced pressure giving a red-brown solid which was washed with light petroleum (b.p. 30—40 °C). The residue was then extracted with dichloromethane and the resulting red solution separated from a residual red-orange solid. The insoluble residue was extracted with acetone and water was added. Slow concentration of the solution gave red needles of the compound (15) (yield 59%). Addition of aqueous ammonium hexafluorophosphate to the dichloromethane soluble fraction, followed by separation of the resulting solid and crystallisation from acetone–water, gave the compound [W(η-C_5H_5)$_2$(PMe_3)Br]PF_6 whose synthesis is described above (yield 5%).

Bis(η-*cyclopentadienyl*)*methyl*(*trimethylphosphine*)*tungsten Hexafluorophosphate* (11).—The compound [W(η-C_5H_5)$_2$-(PMe_3)Br]PF_6 (0.5 g, 0.81 mmol) in tetrahydrofuran (60 cm^3) was treated with methylmagnesium bromide (10 cm^3 of a 1.5 mol dm^{-3} solution; 15 mmol) in diethyl ether. The reaction mixture was stirred at r.t. for 15 h and then warmed to *ca.* 50 °C for 1 h. The solvent was removed from the resulting red-orange solution and the residue cooled to *ca.* −100 °C and ethanol was added. The mixture was allowed to warm to r.t. whereupon the solvent was removed under reduced pressure. Dichloromethane (100 cm^3) and water (50 cm^3) were added and the red organic layer was separated *via* filtration through a Celite bed. The solvent was removed under reduced pressure giving orange microcrystals. These were recrystallised from dichloromethane at −20 °C giving orange crystals which were collected and dried *in vacuo* (yield 0.27 g, 60%). Compound (11) could be similarly prepared in 58% yield starting from the compound [W(η-C_5H_5)$_2$(PMe_3)I]PF_6.

Bis(η-*cyclopentadienyl*){2-[(2-*dimethylphosphinoethyl*)-*dimethylphosphonio*]*ethylide*}*methyltungsten Hexafluorophosphate*.—The compound [W(η-C_5H_5)$_2$(η-C_2H_4)Me]PF_6 (1.0 g, 2 mmol) in acetone (40 cm^3) was treated with 1,2-bis(dimethylphosphino)ethane (0.3 g, 2 mmol) and the mixture stirred at r.t. for 15 h giving an orange solution. The solvent was removed under reduced pressure and the resulting orange solid washed with light petroleum (b.p. 40—60 °C) (3 × 15 cm^3) to remove any excess of tertiary phosphine. The residue was dissolved in a minimum volume of acetone and chromatographed on an alumina column made up in light petroleum (b.p. 30—40 °C). Elution with tetrahydrofuran–acetone (1 : 1) gave a yellow band which was collected and the solvent was removed under reduced pressure. The resulting orange-yellow solid was crystallised from ethanol as orange crystals. These were collected and dried *in vacuo* (yield 60%).

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