η-Arenetungsten Chemistry: η-Allyl, η-Butadiene, Tertiary Phosphine, and Hydrido Derivatives*

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The syntheses and properties of the new η-arenetungsten compounds [{W(η-C_6H_5Me)(η-C_3H_5)Cl}$_2$], [W(η-C_6H_5Me)(η-C_3H_5)(OCOMe)], [W(η-C_6H_5Me)(η-C_3H_5)(OCOPh)], [W(η-C_6H_5Me)(η-C_3H_5)(PPhMe_2)Cl], [W(η-C_6H_5Me)(η-C_3H_5)($PR_2CH_2CH_2PR_2$)]PF_6 (R = Me or Ph), [W(η-C_6H_5Me)(η-C_3H_5)(η-C_4H_6)]PF_6, [W(η-C_6H_5Me)(η-C_3H_5)(MeCN)$_2$]PF_6, [W(η-C_6H_5Me)(PMe_3)$_2Cl_2$H]PF_6, [W(η-C_6H_5Me)($Me_2PCH_2CH_2PMe_2$)H_2], and [W(η-C_6H_5Me)($Me_2PCH_2CH_2PMe_2$)H_3]BF_4 are described.

Bis(η-arene)molybdenum compounds have proved useful precursors for the development and study of η-arenemolybdenum derivatives as well as providing synthetic routes to monocyclopentadienylmolybdenum systems.[1-6] We are interested in transition metal compounds which have high reactivities towards hydrocarbon fragments, and inert systems such as dinitrogen. The highest occupied molecular orbitals of low-valent arene–transition metal compounds normally have high energies since the arene ligand has poor electron-acceptor properties. Indeed, the η-arene ligand is not a π-acceptor and can only accept electrons from the metal through a ligand orbital of δ symmetry with respect to the metal–ligand axis. Although the arene–transition metal system normally has high-energy electrons, as is borne out by the low ionisation potentials of many arene–metal compounds,[7] the arene–metal bond can survive intact through a wide variety of reaction conditions. Therefore, the η-arene–transition metal system can provide access to highly reactive compounds which, apart from their intrinsic interest, can provide a basis for understanding the reactivity and mechanisms of transition metal–hydrocarbon systems.

Following our study of the η-arenemolybdenum system, we set out to compare the analogous arenetungsten chemistry. Of primary concern was a suitable synthetic route to bis(η-arene)tungsten compounds and this has been established in the reaction between tungsten atoms and the arene concerned.[8] Here we describe our initial development of the chemistry of bis(η-arene)tungsten compounds.

Results

The most versatile precursors in mono-η-arenemolybdenum chemistry are the μ-chloro dimers [{Mo(η-arene)(η-C_3H_5)Cl}$_2$];[1-3] it therefore seemed appropriate to attempt to prepare the tungsten analogues.

Treatment of toluene solutions of [W(η-C_6H_5Me)$_2$] (1) with allyl chloride did not result in the formation of [{W(η-C_6H_5Me)(η-C_3H_5)Cl}$_2$] (2), but rather in oxidation of [W(η-C_6H_5Me)$_2$] to the paramagnetic cation [W(η-C_6H_5Me)$_2$]$^+$. However, when the reaction was carried out in diethyl ether a small yield of red-purple crystals of the desired [{W(η-C_6H_5Me)(η-C_3H_5)Cl}$_2$] (2) could be isolated, together with [W(η-C_6H_5Me)$_2$]Cl. When (1) was treated with RCH=CHCH_2Cl (R = Ph or Me) in diethyl ether, only the cation [W(η-C_6H_5Me)$_2$]$^+$ was formed.

Further attempts to prepare dimers analogous to (2) included the reactions of bis(η-benzene)tungsten and bis(η-mesitylene)tungsten with allyl chloride in diethyl ether. Both reactions gave only the corresponding bis(η-arene)tungsten cations.

Treatment of (2) with sodium acetate gives the η^3-acetato derivative [W(η-C_6H_5Me)(η-C_3H_5)(η^2-OCOMe)] (3) as air-sensitive red-purple crystals.

The compound [W(η-C_6H_5Me)(η-C_3H_5)(η^2-OCOMe)] (3) can be prepared directly from the reaction between (1) and allyl acetate in acetonitrile solution in good yield. A small quantity of the compound [W(η-C_6H_5Me)(η-C_3H_5)(MeCN)$_2$]PF_6 (4) was obtained as a by-product of this reaction.

Treatment of the dimers [{Mo(η-arene)(η-allyl)(μ-Cl)}$_2$] with ($AlEtCl_2$)$_2$ gives highly reactive violet solutions which further react with a variety of olefins and other donor ligands giving compounds of general class [Mo(η-arene)(η-C_3H_5)L_2]$^+$, where L is a two-electron donor.[4] Treatment of (2) with ($AlEtCl_2$)$_2$ also gives a deep violet solution, which reacts with butadiene giving the compound [W(η-C_6H_5Me)(η-C_3H_5)(η-C_4H_6)]PF_6 (6). However, attempts to synthesise the compound [W(η-C_6H_5Me)(η-C_5H_5)Cl] by treating the violet solution with cyclopentene (*cf.* the reaction found for the molybdenum analogue) were unsuccessful: no tractable products were obtained.

Treatment of [W(η-C_6H_5Me)(η-C_3H_5)(η^2-OCOMe)] (3) with ethylaluminium dichloride dimer causes slow replacement of the acetato ligand by a chloro group giving [{W(η-C_6H_5Me)(η-C_3H_5)(μ-Cl)}$_2$] (2). This indirect route to (2) provides a better overall yield [60% from (1)] than the direct reaction between (1) and allyl chloride.

Treatment of (1) with allyl benzoate in acetonitrile forms the compound [W(η-C_6H_5Me)(η-C_3H_5)(η^2-OCOPh)] (5) in good yield.

The μ-chloro bridge of [{W(η-C_6H_5Me)(η-C_3H_5)(μ-Cl)}$_2$] is readily cleaved by dimethylphenylphosphine giving the compound [W(η-C_6H_5Me)(η-C_3H_5)(PPhMe_2)Cl] (7).

Similarly, treatment of (2) with 1,2-bis(diphenylphosphino)ethane (dppe) followed by ammonium hexafluorophosphate gives the bright red compound [W(η-C_6H_5Me)(η-C_3H_5)(dppe)]PF_6 (8).

We were especially interested to prepare compounds of the type [W(η-arene)(PR_3)$_2H_2$] in order to compare their reactivity towards dinitrogen with that of the molybdenum analogues. However, the tungsten system proved to be unrewarding in this respect.

Treatment of (3) in the presence of trimethylphosphine with Na[AlH_2(OCH_2CH_2OMe)$_2$] gives a red oil; it was suspected that this was the dihydride [W(η-C_6H_5Me)(PMe_3)$_2H_2$], but it could not be purified. In an attempt to make an isolable derivative by formation of a trihydride cation, the red oil was treated with aqueous hydrochloric acid and then ammonium hexafluorophosphate. A green compound was obtained in

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* *Non-S.I. unit employed*: Torr = (101 325/760) Pa.

Table. Analytical and spectroscopic data

Compound	Colour	Analysis (%) [a] C	Analysis (%) [a] H	Hydrogen-1 n.m.r. data [b]
(2) $[\{W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(\mu\text{-}Cl)\}_2]$	Red-purple	33.8 (34.0)	3.7 [c] (3.7)	5.76—6.8, **5**, *c*, C_6H_5; 6.25, **1**, *c*, H_c; 6.95, **2**, *d*, 2 H_a or 2 H_b; 7.68, **2**, *d*, 2 H_b or 2 H_a; 8.29, **3**, *s*, Me [d]
(3) $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(\eta^2\text{-}OCOMe)]$	Deep red	38.2 (38.3)	4.25 (4.3)	5.9—6.2, **5**, *c*, C_6H_5; 6.7, **1**, *quintet* [*J* 7], H_c; 7.2, **2**, *d* [*J* 7], 2 H_b or 2 H_a; 7.45, **2**, *d* [*J* 7], 2 H_b or 2 H_a; 8.65, **3**, *s*, OCOMe; 8.8, **3**, *s*, Me [d,e]
(4) $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(MeCN)_2]PF_6$	Dark red	31.3 (30.9)	3.55 [f] (3.5)	5.05, **5**, *c*, C_6H_5; 6.35, **1**, *c*, (*apparent quintet*), H_c; 7.35, **6**, *s*, 2 MeCN; 7.65, **2**, *d* [*J* 4], 2 H_a or 2 H_b; 8.1, **3**, *s*, CMe; 8.15, **2**, *d* [*J* 5]; 2 H_b or 2 H_a [g]
(5) $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(\eta^2\text{-}OCOPh)]$	Golden	45.6 (46.6)	4.5 (4.1)	1.9, **2**, *c*, 2.9, **3**, *c*, $OCOC_6H_5$; 5.8, **5**, *c*, $\eta\text{-}C_6H_5$ 6.3, **1**, *quintet* [*J* 6], H_c; 6.9, **2**, *d* [*J* 6], 2 H_a or 2 H_b; 7.05, **2**, *d* [*J* 6], 2 H_b or 2 H_a; 8.6, **3**, *s*, CMe [d]
(6) $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(\eta\text{-}C_4H_6)]PF_6$	Yellow	33.0 (32.6)	3.8 (3.7)	4.30, **1**, *t*, H of Ph; 4.64, **3**, *c*, 2 H of Ph and H_c of η-allyl; 4.76, **2**, *d* [*J* 5.3], 2 H of Ph; 5.54, **2**, *c*, 2 H of C_4H_6; 6.83, **2**, *d* [*J* 8.4], 2 H_a; 7.17, **2**, *dd* [*J* 1.5, 9.5], 2 H of C_4H_6; 7.82, **2**, *d* [*J* 12.8], 2 H_b; 7.87, **3**, *s*, Me; 8.61, **2**, *dd* [*J* 1.1, 9.5], 2 H of C_4H_6 [g]
(7) $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(PPhMe_2)Cl]$	Deep red	44.7 (44.1)	5.3 (4.9)	2.7—3.2, **5**, *c*, PC_6H_5; 6.0—6.6, **5**, *c*, C_6H_5; 6.5—6.7, **3**, *c*, 3 H of $\eta\text{-}C_3H_5$; 8.5, **4**, *d* [*J* 7], 2 H of $\eta\text{-}C_3H_5$; 8.7, **3**, *s*, CMe; 8.85, **6**, *d* [*J*(P–H) 5], PMe_2 [d]
(8) $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(dppe)]PF_6$	Orange	50.2 (50.2)	4.4 (4.3)	2.5, **20**, *c*, 4 Ph; 4.9, **2**, *t*, 5.3, **1**, *c*, 5.5, **2**, *c*, $\eta\text{-}C_6H_5$; 6.5, **1**, *quintet* [*J* 5.5], H_c; 7.3, **4**, *c*, 2 H_a and 2 H_b; 8.2, **3**, *s*, CMe; 8.3, **2**, *c*, 8.5, **2**, *c*, 2 CH_2 [g]
(10) $[W(\eta\text{-}C_6H_5Me)(dmpe)H_2]$ [h]	Dark red	36.5 (36.4)	6.2 (6.1)	5.41—5.77, **5**, *c*, C_6H_5; 7.84, **3**, *s*, CMe; 8.31, **12**, *d* [*J*(P–H) 8.1], 2 PMe_2; 8.62, **4**, *d* [*J*(P–H) 12.6], 2 PCH_2; 17.9, **2**, *t* [*J*(P–H) 50.0], WH_2 [d]
(11) $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(dmpe)]PF_6$	Red	31.0 (31.4)	4.8 (4.7)	4.45—5.3, **5**, *c*, C_6H_5; 5.56, **1**, *quintet* [*J* 6.0], H_c; 8.18, **3**, *s*, CMe; 8.52, **6**, *d* [*J*(P–H) 8.8], 2 PMe; 8.81, **6**, *d* [*J*(P–H) 9.4], 2 PMe; 8.1—8.47, **8**, *c*, 2 PCH_2, 2 H_a and 2 H_b [i]
(12) $[W(\eta\text{-}C_6H_5Me)(dmpe)H_3]BF_4$ [j]	Yellow-green	30.5 (30.3)	4.9 (5.3)	4.5—5.4, **5**, *c*, C_6H_5; 7.81, **3**, *s*, CMe; 8.17—8.4, **12**, *c*, 2 PMe_2; 8.67, **2**, *d* [*J*(P–H) 8.4], PCH_2; 9.18, **2**, *d* [*J*(P–H) 8.5], PCH_2; 16.7, **3**, *dd* [*J*(P–H) 47.7 and 19.8], WH_3 [i]

[a] Calculated values in parentheses. [b] Given as: chemical shift (τ), **relative intensity**, *multiplicity* [*J*/Hz, for H–H coupling unless otherwise stated], assignment. [c] Cl, 12.3 (11.5)%. [d] In C_6D_6. [e] $\nu(C=O)$ of OCOMe 1 520s cm^{-1}. [f] N, 5.1 (5.15)%. [g] In $(CD_3)_2CO$. [h] $\nu(W\text{–}H)$ stretch 1 755m cm^{-1}. [i] In $(CD_3)_2SO$. [j] $\nu(W\text{–}H)$ stretch 1 859 cm^{-1}.

good yield, the crystal structure of which showed it to be the dichlorohydrido cation $[W(\eta\text{-}C_6H_5Me)(PMe_3)_2Cl_2H]PF_6$ (9).

In the hope that 1,2-bis(dimethylphosphino)ethane (dmpe) might provide a more tractable product, the reaction of (3) with dmpe and $Na[AlH_2(OCH_2CH_2OMe)_2]$ was studied. Only small yields of a highly sensitive red oil were obtained and purification was not achieved.

However, treatment of (3) with lithium triethylhydridoborate in the presence of dmpe gives small yields of highly sensitive red crystalline $[W(\eta\text{-}C_6H_5Me)(dmpe)H_2]$ (10), which could be purified by sublimation. Many attempts were made to bring about the reaction of (10) with dinitrogen, without success.

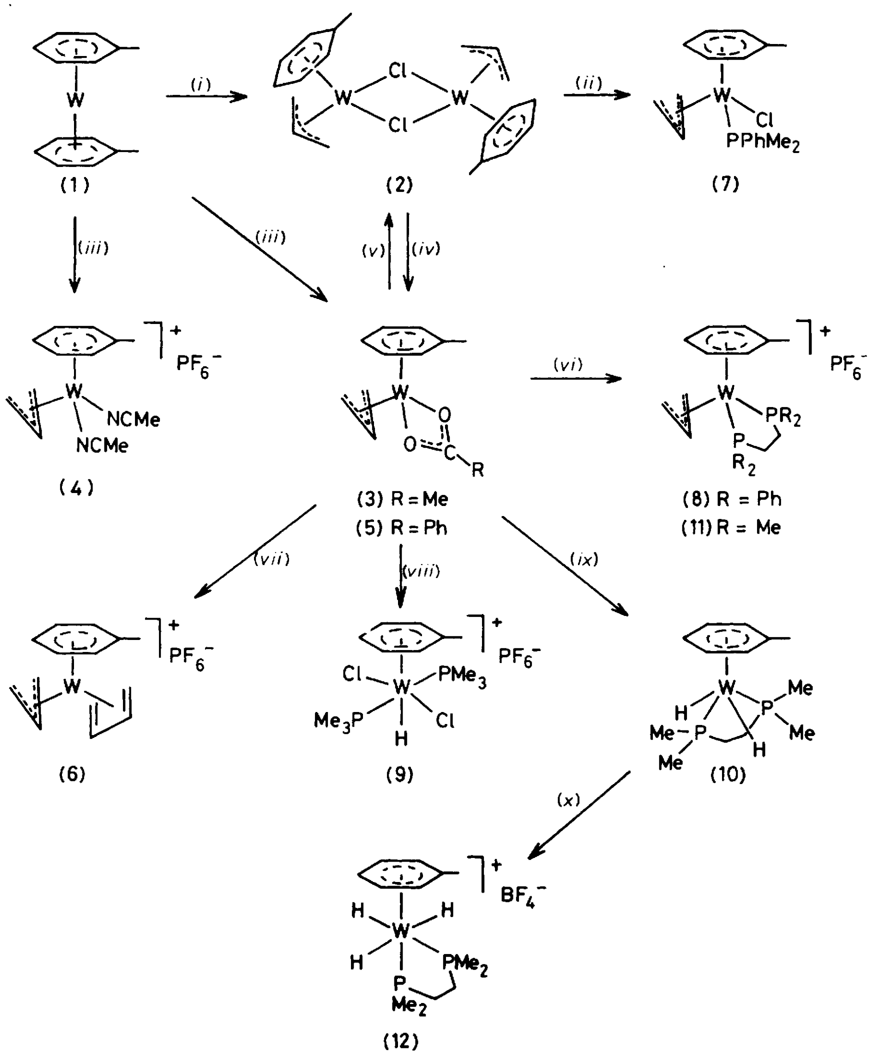
The compound $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(dmpe)]PF_6$ (11) was prepared from the reaction between $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(\eta^2\text{-}OCOMe)]$ (3) and dmpe in ethanol, and was isolated as the hexafluorophosphate salt. Reduction of (11) with sodium amalgam under dihydrogen or dinitrogen did not give tractable products.

Further attempts to prepare the tungsten analogue of $[\{Mo(\eta\text{-}arene)(dmpe)\}_2(N_2)]$ by treatment of $[\{W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)Cl\}_2]$ with n-butyl-lithium in the presence of tertiary phosphine under dinitrogen gave no evidence for the desired product.

The compound $[W(\eta\text{-}C_6H_5Me)(dmpe)H_2]$ (10) reacted with tetrafluoroboric acid giving a yellow-green compound characterised as $[W(\eta\text{-}C_6H_5Me)(dmpe)H_3]BF_4$ (12).

Discussion

The analytical and spectroscopic data which characterise compounds (2)—(8) and (10)—(12) are given in the Table. The reactions and proposed structures are shown in the Scheme. The crystal structures of the compounds $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(MeCN)_2]PF_6$ (4), $[W(\eta\text{-}C_6H_5Me)(PMe_3)_2Cl_2H]PF_6$ (9), and $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(dmpe)]PF_6$ (11) have been determined and the details have been published separately;[9,10] the structures are represented in a simple manner in the Scheme. The crystal structure of (11) is of interest in that the unit cell contains two $[W(\eta\text{-}C_6H_5Me)$-



Scheme. (*i*) Allyl chloride in Et_2O at room temperature, yield 10%; (*ii*) $PPhMe_2$ in toluene at 50 °C for 3 h, 70%; (*iii*) allyl acetate (R = Me) or allyl benzoate (R = Ph) in acetonitrile at 70 °C, 70—80%; (*iv*) sodium acetate in ethanol (R = Me); (*v*) $(AlEtCl_2)_2$ in toluene at room temperature, 80%; (*vi*) dppe (R = Ph) or dmpe (R = Me) in ethanol at 70 °C for 48 h, 80%; (*vii*) $(AlEtCl_2)_2$ in toluene, add butadiene, then aqueous NH_4PF_6, 40%; (*viii*) $Na[AlH_2(OCH_2CH_2OMe)_2]$ and PMe_3 in toluene, then aqueous HCl and aqueous NH_4PF_6, 50%; (*ix*) $Li[BHEt_3]$ and dmpe in thf, 30%; (*x*) aqueous HBF_4 in Et_2O–C_6H_5Me, 70%

(η-C_3H_5)(dmpe)]$^+$ cations which differ markedly. The disposition of the dmpe ligand is quite different in the two cations and this in turn causes substantial changes in the distances and angles of the η-toluene and η-allyl groups.[10]

The hydrogen-1 n.m.r. spectrum of (10) shows that the four methyl groups and the four hydrogens of the two methylene groups of the dmpe ligand are chemically equivalent. Therefore the compound has the *trans* configuration. The *trans* structure is also supported by the mass spectrum. This shows a complex highest mass band which can be analysed in terms of superimposed bands arising from the ions P^+, $[P - H]^+$, $[P - 2H]^+$, $[P - 3H]^+$, and $[P - 4H]^+$ {where $P = [W(\eta\text{-}C_6H_5Me)(dmpe)H_2]$} in the ratios 1 : 0.7 : 2.4 : 0.7 : 0.5, respectively. It is normally found that *cis*-oriented transition metal dihydrido systems show negligible intensity of ions arising from the loss of a single hydrogen. For example, the mass spectrum of $[W(\eta\text{-}C_5H_5)_2H_2]$ shows no bands assignable to $[W(\eta\text{-}C_5H_5)_2H]^+$.

The *trans* structure of (10) accounts for its failure to react with dinitrogen since this requires the displacement of the dihydrogen molecule and there is no simple pathway available for this reaction to proceed.

There are small but sufficient differences between the arene-molybdenum and arenetungsten systems which cause some reactions which proceed readily in high yield in one system to give poor or zero yields in the other. There is no single and simple explanation for these differences. Many of the reactions, *e.g.* the formation of (2) from (1) and allyl chloride, are clearly multi-step processes. It requires only a small difference in relative rates between competing pathways and activation energies to change the outcome of such reaction sequences.

In general it appears that the arenetungsten system is more resistant to cleavage of the arene–metal bond than is the arenemolybdenum system. This implies that the resulting tungsten intermediates might be more reactive than in the molybdenum series and hence less discriminating.

We are continuing to seek synthetic pathways *via* bis(η-arene)tungsten complexes which will enable us to develop the chemistry of low-valent tungsten.

Experimental

All preparations and manipulations were carried out *in vacuo* or under an inert atmosphere. Solvents were dried and distilled before use. I.r. spectra were determined for mulls on a Unicam SP 2000 instrument and were calibrated with polystyrene film. Hydrogen-1 n.m.r. spectra were determined with a Bruker WH 300 MHz instrument. Mass spectra were determined with an A.E.I. MS 902 instrument reconditioned and fitted with a console by Mass Spectrometry Services Ltd. The compound $[W(\eta\text{-}C_6H_5Me)_2]$ was prepared as described,[8] using a large-scale metal vapour synthesis apparatus [11] built by Dr. F. G. N. Cloke. Typically 4—7 g of $[W(\eta\text{-}C_6H_5Me)_2]$ were obtained after reaction times of 4—6 h.

Bis[(η-*allyl*)-μ-*chloro*-(η-*toluene*)*tungsten*] (2).—*Method A*. The compound $[W(\eta\text{-}C_6H_5Me)_2]$ (1) (0.3 g, 0.82 mmol) in diethyl ether (300 cm^3) was cooled to 0 °C, and allyl chloride (0.6 g, 8 mmol) was added. The mixture was kept at room temperature for 3 h and was then warmed to 30 °C for 2 h. The initially green solution developed a cloudy orange hue. The solution was filtered giving a pale red-purple filtrate which was concentrated under reduced pressure giving small red-purple needle crystals. These were collected, washed with cold diethyl ether (−20 °C) and dried *in vacuo*; yield 0.03 g (10%).

Method B. The compound $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(\eta^2\text{-}OCOMe)]$ (3) (0.4 g, 1.0 mmol) in toluene (30 cm^3) was treated with ethylaluminium dichloride dimer (0.2 g in 10 cm^3 of toluene). Within a few minutes crystals separated. The mixture was cooled to −20 °C for 4 h. The resulting crystals were collected, washed with light petroleum (b.p. 40—60 °C) (20 cm^3) and then extracted with toluene (60 cm^3). The extract was filtered and the solution was concentrated (to 10 cm^3) and cooled to −20 °C for 12 h. The resulting red crystals were collected, washed with light petroleum (b.p. 30—40 °C) and dried *in vacuo*; yield 0.28 g (80%). The compound is only slightly soluble in toluene. Solutions in acetone slowly decompose (hours). The mass spectrum (for the ^{185}W and ^{35}Cl) showed *m/z* 704 (M^+) 352 $\{[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)Cl]^+\}$, and 317 $\{[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)]^+\}$.

η-*Acetato*(η-*allyl*)(η-*toluene*)*tungsten* (3).—$[W(\eta\text{-}C_6H_5Me)_2]$ (0.5 g, 1.4 mmol) was dissolved in rigorously dried acetonitrile (150 cm^3) and warmed to 70 °C. Allyl acetate (2 cm^3, 20 mmol) was added and the mixture was warmed to 70 °C for 18 h. The initially dark green solution became deep red. The solvent was removed under reduced pressure and the red-brown residue was extracted with light petroleum (b.p. 40—60 °C) (3 × 150 cm^3). The deep red extract was filtered leaving a brown residue. The filtrate was concentrated under reduced pressure to *ca.* 20 cm^3 and cooled to −30 °C for 12 h, giving deep red crystals. These were collected, washed with light petroleum (b.p. 30—40 °C), and dried *in vacuo*; yield 0.4 g (70%). The compound is extremely sensitive to oxidation in air. It is very soluble in toluene and more polar solvents, giving thermally stable solutions.

Bis(*acetonitrile*)(η-*allyl*)(η-*toluene*)*tungsten Hexafluorophosphate* (4).—The brown residue obtained in the previous experiment was extracted with acetone, and the extract was placed on an alumina column made up in acetone. Elution with acetone gave an oily brown material. Further elution, with methanol, gave a deep red eluate, which was collected. Aqueous ammonium hexafluorophosphate was added, giving a pale red precipitate. This was collected, washed with water (2 × 5 cm^3), and dried *in vacuo*. The solid was recrystallised from acetone–ethanol (1 : 1) giving deep red crystals, which were collected, washed with water, and dried *in vacuo*; yield 0.03 g (5%).

η-*Allyl*(η²-*benzoato*)(η-*toluene*)*tungsten* (5).—The compound $[W(\eta\text{-}C_6H_5Me)_2]$ (0.25 g, 0.75 mmol) in dry acetonitrile (20 cm^3) was treated with allyl benzoate (0.15 cm^3) and the mixture was stirred at room temperature for 5 h. The initially green solution became golden yellow. The solvent was removed under reduced pressure and the residual oil was extracted with light petroleum (b.p. 30—40 °C) (2 × 50 cm^3). The filtered extract was concentrated under reduced pressure (to *ca.* 40 cm^3) and then cooled to −30 °C for 12 h. Golden crystals separated, which were collected, washed with cold (−50 °C) light petroleum (b.p. 30—40 °C) (2 × 5 cm^3) and finally dried *in vacuo*; yield 0.34 g (80%).

η-*Allyl*(η-*butadiene*)(η-*toluene*)*tungsten Hexafluorophosphate* (6).—The compound $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(\eta^2\text{-}OCOMe)]$ (3) (0.2 g, 0.5 mmol) in toluene (20 cm^3) was treated with ethylaluminium dichloride dimer (0.5 g) in toluene (2 cm^3). The initially deep red solution became deep violet. Butadiene (4 cm^3, 75 mmol) was then distilled onto the cooled solution, which was subsequently allowed to warm to room temperature. An orange oil separated from the solution, which was set aside for 2 h. The supernatant liquid was decanted from the orange oil, which was then washed with light petroleum (b.p. 100—120 °C) (2 × 20 cm^3). The oil was cooled to −10 °C, and ethanol (5 cm^3) was added dropwise. The volatile components were removed from the resulting orange oil under reduced pressure and the orange solid formed was extracted with water (2 × 10 cm^3). The extract was filtered and aqueous ammonium hexafluorophosphate was added to the filtrate, giving an orange precipitate. This was collected, washed with water (2 × 10 cm^3), and dried *in vacuo*. The product was recrystallised from acetone at −30 °C and the resulting orange crystals were washed with ethanol (2 × 2 cm^3) at −30 °C and finally dried *in vacuo*. The compound rapidly decomposed in solutions of acetone and ethanol at room temperature; yield 0.1 g (40%).

η-*Allyl*(*chloro*)(*dimethylphenylphosphine*)(η-*toluene*)-*tungsten* (7).—The compound $[W(\eta\text{-}C_6H_5Me)_2]$ (0.4 g, 1.1 mmol) in acetonitrile (20 cm^3) and allyl chloride (0.5 g, 6.0 mmol) was warmed to 50 °C for 1 h. Dimethylphenylphosphine (2.0 g, 10.7 mmol) was added and the mixture was stirred for 10 min. The solvent was removed under reduced pressure and the residue was chromatographed on an alumina column made up in light petroleum (b.p. 30—40 °C). Elution with toluene–dichloromethane (1 : 1) gave a red band which was collected, and the solvent was removed under reduced pressure. The residue was extracted with light petroleum (b.p. 30—40 °C) (2 × 20 cm^3) and the extract was filtered and concentrated (2 cm^3), giving red crystals. These were collected and dried *in vacuo*; yield *ca.* 20%.

η-*Allyl*[1,2-*bis*(*diphenylphosphino*)*ethane*](η-*toluene*)-*tungsten Hexafluorophosphate* (8).—The compound $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(\eta^2\text{-}OCOMe)]$ (3) (0.25 g, 0.7 mmol) in dry ethanol (100 cm^3) was treated with 1,2-bis(diphenylphosphino)ethane (0.5 g, 1.25 mmol), and the mixture was stirred and warmed to 70 °C for 48 h. The initially deep red solution became orange. The solvent was then removed under reduced pressure and the light orange residue was extracted with methanol. The extract was filtered and aqueous ammonium hexafluorophosphate was added, giving a red-orange precipitate. This was collected, washed with water (2 × 5 cm^3), and dried *in vacuo*. The solid was recrystallised from acetone at −30 °C giving deep orange crystals which were dried *in vacuo*; yield 0.4 g (80%).

Dichlorohydrido(η-toluene)bis(trimethylphosphine)tungsten Hexafluorophosphate (9).—The compound [W(η-C_6H_5Me)(η-C_3H_5)($η^2$-OCOMe)] (3) (0.5 g, 1.5 mmol) in toluene (50 cm^3) was treated with trimethylphosphine (1.0 g) and Na[AlH_2($OCH_2CH_2OMe)_2$] (10 cm^3 of a 70% solution in toluene); the mixture was stirred at room temperature for 2 h, then cooled, and ethanol (3 cm^3) was added slowly. The volatile components were then removed under reduced pressure and the oily pink residue was washed with light petroleum (b.p. 30—40 °C) (2 × 20 cm^3), giving a red-orange extract. This was filtered and the solvent was removed from the filtrate under reduced pressure giving a red solid. This was extracted with aqueous hydrochloric acid (1 mol dm^{-3}, 2 × 20 cm^3), giving a green solution, which was filtered. Aqueous ammonium hexafluorophosphate was added, giving a light green precipitate. This was collected, washed with water (2 × 5 cm^3), and dried *in vacuo*. It was then extracted into acetone (2—3 cm^3) and the filtered extract was cooled to −30 °C, giving a few green crystals. These were collected, washed with methanol, and dried *in vacuo*; yield 0.17 g (*ca.* 50%). The compound was characterised by crystal structure determination.

[1,2-*Bis(dimethylphosphino)ethane*]*dihydrido(η-toluene)-tungsten* (10).—The compound [{W(η-C_6H_5Me)(η-C_3H_5)(μ-Cl)}$_2$] (1.4 g, 3.7 mmol) and 1,2-bis(dimethylphosphino)ethane (0.6 g, 4 mmol) in tetrahydrofuran were treated with lithium triethylhydridoborate (1.0 g) in tetrahydrofuran (20 cm^3). The mixture was stirred at room temperature for 2 h and was then cooled to −30 °C and treated dropwise with water. The solvent was removed under reduced pressure and the residue was washed with light petroleum (b.p. 40—60 °C) (2 × 50 cm^3). The residue was transferred to a sublimation apparatus and sublimed onto a liquid-dinitrogen cooled probe at 115 °C and 10^{-3}—10^{-4} Torr for 24 h. The sublimate was extracted into light petroleum (b.p. 40—60 °C) (20 cm^3). The extracts were combined and evaporated, and the residue was resublimed at 55 °C onto a probe at 0 °C, giving the pure product as a red crystalline sublimate; yield 0.3 g (30%).

η-*Allyl*[1,2-*bis(dimethylphosphino)ethane*](η-*toluene*)-*tungsten Hexafluorophosphate* (11).—The compound [W-(η-C_6H_5Me)(η-C_3H_5)($η^2$-OCOMe)] (0.48 g, 1.3 mmol) in ethanol (40 cm^3) was treated with 1,2-bis(dimethylphosphino)ethane (0.3 cm^3) at 70 °C for 24 h. The solvent was removed under reduced pressure and the residue was extracted with methanol (40 cm^3). The solution was then filtered into an aqueous solution of ammonium hexafluorophosphate giving an orange precipitate. Further precipitation occurred as the methanol was removed under reduced pressure. The suspension was allowed to settle and the supernatant liquor was decanted. The solid residue was washed with light petroleum (b.p. 30—40 °C) (2 × 20 cm^3) and dried *in vacuo*. The compound could be recrystallised from acetone–water; yield 0.36 g (60%).

[1,2-*Bis(dimethylphosphino)ethane*]*trihydrido(η-toluene)-tungsten Tetrafluoroborate* (12).—The compound [W-(η-C_6H_5Me)(η-C_3H_5)($η^2$-OCOMe)] (0.36 g, 1.0 mmol) in toluene (20 cm^3) was treated with dmpe (1 cm^3) and then Na[AlH_2($OCH_2CH_2OMe)_2$] (70% in toluene; 3 cm^3), and the mixture was stirred at room temperature for 2 h. The mixture was cooled to −30 °C and water was added. The hydrolysed mixture was filtered and tetrafluoroboric acid–toluene–diethyl ether was added [(0.3 cm^3 of 50% solution in water) : 10 cm^3 : 20 cm^3], giving a green precipitate. This was allowed to settle and the supernatant liquor was decanted. The residual solid was washed with light petroleum (b.p. 40—60 °C) (2 × 20 cm^3) and dried *in vacuo*. It was then extracted with acetone (40 cm^3); the extract was concentrated under reduced pressure (to 15 cm^3) and water (15 cm^3) was added. Slow concentration of the solution under reduced pressure caused separation of green crystals, which were collected, washed with water, and dried *in vacuo*; yield 0.39 g (70%).

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References

1 M. L. H. Green and W. E. Silverthorn, *J. Chem. Soc., Dalton Trans.*, 1973, 301.
2 M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, *J. Chem. Soc., Dalton Trans.*, 1973, 1403.
3 M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, *J. Chem. Soc., Dalton Trans.*, 1973, 2177.
4 M. L. H. Green and J. Knight, *J. Chem. Soc., Dalton Trans.*, 1974, 311.
5 M. L. H. Green and J. Knight, *J. Chem. Soc., Dalton Trans.*, 1976, 213.
6 M. L. H. Green, J. Knight, and J. A. Segal, *J. Chem. Soc., Dalton Trans.*, 1977, 2189.
7 J. C. Green, *Struct. Bonding*, 1981, **43**, 37.
8 F. G. N. Cloke and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1981, 1938.
9 C. Couldwell, A. Gourdon, and C. K. Prout, *Acta Crystallogr., Sect. B*, 1982, **38**, 456.
10 A. Gourdon and K. Prout, unpublished work.
11 M. L. H. Green in ' Frontiers of Chemistry,' ed. K. J. Laidler, Pergamon, Oxford and New York, 1982, p. 229.

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