The Synthesis of Electron-rich η-Cyclopentadienyl Trimethylphosphine Complexes of Tungsten

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The new compounds $W(\eta^4\text{-}C_5H_5R)(PMe_3)_3H_2$, (R = H, $CHPh_2$), $[W(\eta\text{-}C_5H_5)(PMe_3)_3H_2][BF_4]$, $W(\eta\text{-}C_5H_4R)(PMe_3)_3H$, $W(\eta\text{-}C_5H_5)(PMe_3)_2H_3$, and $W(\eta\text{-}C_5H_4R)(PMe_3)H_5$ (R = H, Et) are described; $W(\eta\text{-}C_5H_4Et)(PMe_3)_3H$ reacts with C_5H_6 under photolysis to give the mixed-ring compound $W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Et)H_2$.

Mono(η-cyclopentadienyl)–tertiary phosphine compounds have an extensive and varied chemistry[1] and recently have been relevant to important reactions such as alkane carbon–hydrogen bond activation,[2,3] and Ziegler–Natta catalysis.[4] Mono(η-cyclopentadienyl) complexes of tungsten[5] are mainly restricted to those containing carbonyl or nitrosyl as co-ligands and this results in the formation of comparatively low energy tungsten centres. We recently described the formation of $W(\eta\text{-}C_5H_5)(PMe_3)H_5$ (**1**) from tungsten atoms, cyclopentane, and PMe_3[6] and here we describe a more convenient synthesis of (**1**) and of related compounds from the readily available trimethylphosphine–polyhydride complexes $W(PMe_3)_3H_6$,[7] $W(PMe_3)_4H_4$,[7,8] and $W(PMe_3)_5H_2$.[8]

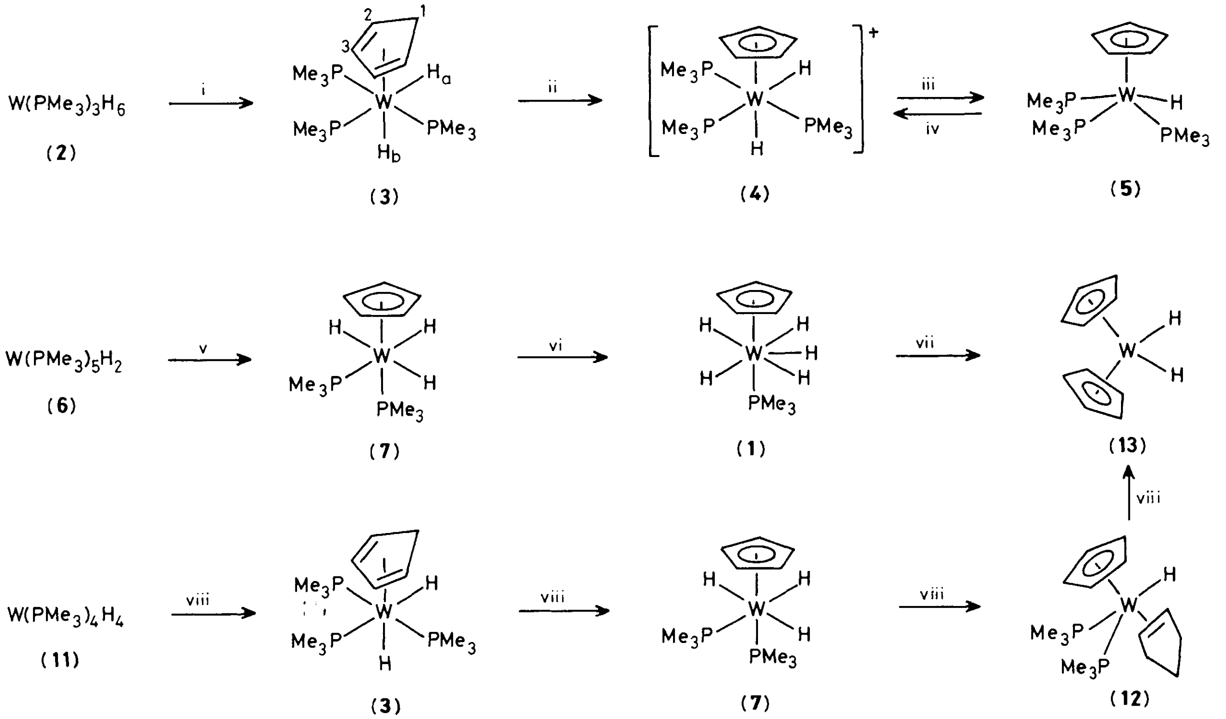
The complex $W(PMe_3)_3H_6$ (**2**) reacts with cyclopentadiene at 60 °C to give the diene–dihydrido compound $W(\eta^4\text{-}C_5H_6)(PMe_3)_3H_2$ (**3**) as pale yellow crystals in 65% isolated yield. The compound (**3**) represents the first example of an (η^4-cyclopentadiene)tungsten compound.

Protonation of (**3**) with $HBF_4\cdot Et_2O$ results in loss of H_2 and formation of the η-cyclopentadienyl compound $[W(\eta\text{-}C_5H_5)(PMe_3)_3H_2][BF_4]$ (**4**) in good yield. Presumably the formation of (**4**) involves an intramolecular migration of the *endo* hydrogen from the η-cyclopentadiene ligand of (**3**). Compound (**4**) is readily deprotonated by KH to give $W(\eta\text{-}C_5H_5)(PMe_3)_3H$ (**5**), which may be reprotonated by HBF_4 to give (**4**).

$W(PMe_3)_5H_2$ (**6**) reacts with cyclopentadiene to give $W(\eta\text{-}C_5H_5)(PMe_3)_2H_3$ (**7**).[6] Photolysis (in borosilicate apparatus with a 500 Watt medium pressure Hg lamp) of (**7**) under dihydrogen (2 atm) gives (**1**) in *ca.* 60% isolated yield. The sequence (**6**)–(**7**)–(**1**) gives the most convenient syntheses for (**7**) and (**1**).

The compound $W(\eta\text{-}C_5H_4Et)(PMe_3)_3H$ (**8**) has been synthesised from $W(PMe_3)_3H_6$ (**2**) and spiro[2.4]hepta-4,6-diene.[9] This compound reacts with H_2 (2 atm) under photolysis giving $W(\eta\text{-}C_5H_4Et)(PMe_3)H_5$ (**9**) in 45% isolated yield. The ^1H n.m.r. spectrum of the reaction mixture shows bands assignable to $W(\eta\text{-}C_5H_4Et)(PMe_3)_2H_3$ (**10**) at an intermediate stage of reaction.

In a separate study the photolysis of $W(PMe_3)_4H_4$ (**11**) with cyclopentadiene was monitored by ^1H n.m.r. spectroscopy. The data show the following products to be formed sequentially: (**3**), $W(\eta\text{-}C_5H_5)(PMe_3)_2H_3$ (**7**), $W(\eta\text{-}C_5H_5)(\eta^2\text{-}C_5H_8)(PMe_3)_2H$ (**12**),[6] and finally $W(\eta\text{-}C_5H_5)_2H_2$ (**13**).[10]



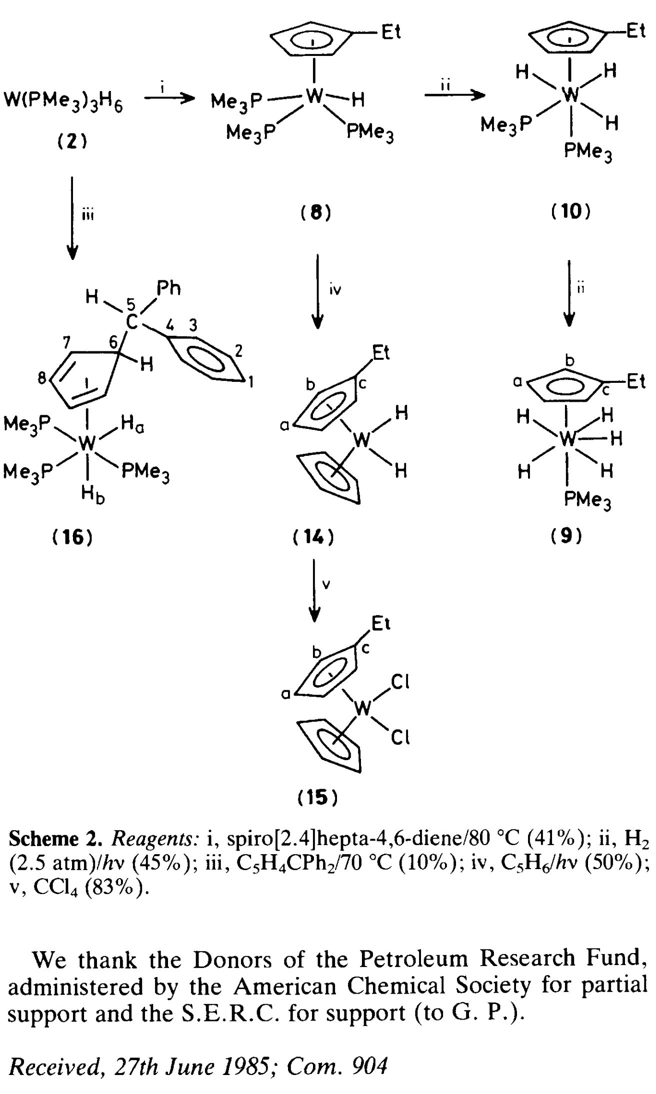
Scheme 1. *Reagents:* i, C_5H_6/80 °C (65%); ii, $HBF_4\cdot Et_2O$ (42%); iii, KH (21%); iv, $HBF_4\cdot Et_2O$ (63%); v, C_5H_6/65 °C (16%); vi, H_2 (2.5 atm)/*hν* (61%); vii, C_5H_6/110 °C; viii, C_5H_6/*hν*.

Compound (**13**) is also formed by the thermal reaction of (**1**) or the photochemical reaction of (**3**) with cyclopentadiene.

The photolysis of (**8**) with cyclopentadiene gives the mixed-ring metallocene dihydride $W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Et)H_2$ (**14**) which reacts with CCl_4 to give the dichloride $W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Et)Cl_2$ (**15**). Both reactions occur in good yield and therefore provide a convenient entry to mixed-ring metallocene derivatives of tungsten.

The reaction of $W(PMe_3)_3H_6$ with 6,6-diphenylfulvene, $C_5H_4CPh_2$, occurs with reduction of the exocyclic-double bond giving the diphenylmethylcyclopentadiene derivative $W(\eta^4\text{-}C_5H_5CHPh_2)(PMe_3)_3H_2$ (**16**).

The new compounds (**3**), (**4**), (**5**), (**9**), (**14**), (**15**), and (**16**) have been characterised by microanalysis, mass spectroscopy, and detailed n.m.r. studies.† The proposed structures are shown in Schemes 1 and 2.



Scheme 2. *Reagents:* i, spiro[2.4]hepta-4,6-diene/80 °C (41%); ii, H_2 (2.5 atm)/*hν* (45%); iii, $C_5H_4CPh_2$/70 °C (10%); iv, C_5H_6/*hν* (50%); v, CCl_4 (83%).

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† *Characterising data* [δ, *J* in Hz, δ_P in p.p.m. relative to external $P(O)(OMe_3)$].

(**3**) $W(\eta^4\text{-}C_5H_6)(PMe_3)_3H_2$ ^1H n.m.r. ($[^2H_6]$benzene) 5.61 [1H, m, H_{exo} or H_{endo}], 3.98 [2H, br.s, 2 H_3 or 2 H_2], 3.38 [1H, d, J(H–H) 7.2, H_{endo} or H_{exo}], 1.53 [2H, br.s, 2 H_2 or 2 H_3], 1.38 [18H, d, J(P–H) 6.5, 2 PMe_3], 1.25 [9H, d, J(P–H) 6.8, PMe_3], −1.18 [1H, br.q, J_q(P–H) 45.0, W–H_b], −4.62 [1H, br., W–H_a]; ^{13}C n.m.r. ($[^2H_6]$benzene) 63.5 [d, J(C–H) 176, 2 C_3 or 2 C_2], 48.6 [tq, J_t(C–H) 127, J_q(P–C) 5, CH_2], 31.1 [d, J(C–H) 159, 2 C_2 or 2 C_3], 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, 1 PMe_3]; $^{31}P\{^1H\}$ n.m.r. ($[^2H_6]$benzene) −30.3 [2P, d, J(P–P) 12, J(P–W) 227, 2 PMe_3], −33.6 [1P, t, J(P–P) 12, J(P–W) 237, 1 PMe_3].

(**4**) $[W(\eta\text{-}C_5H_5)(PMe_3)_3H_2][BF_4]$ ^1H n.m.r. ($[^2H_4]$MeOH) 4.83 [5H, t, J 1.8, C_5H_5], 1.66 [27H, d, J(P–H) 10.5, 3PMe_3], 0.70 [1H, dq, J_d(H–H) 8.4, J_q(P–H) 50.0, W–H], −6.45 [1H, tt, J_d(P–H) 8.4, J_d(H–H) 8.4, J_t(P–H) 39.8, W–H]; ^{13}C n.m.r. ($[^2H_4]$MeOH) 83.3 [dt, ^1J_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]; $^{31}P\{^1H\}$ n.m.r. ($[^2H_4]$MeOH) −33.4 [2P, d, J(P–P) 16, J(P–W) 214, 2 PMe_3], −39.1 [1P, t, J(P–P) 16, J(P–W) 237, 1 PMe_3].

(**5**) $W(\eta\text{-}C_5H_5)(PMe_3)_3H$ ^1H n.m.r. ($[^2H_6]$benzene) 4.39 [5H, s, C_5H_5], 1.43 [27H, m (virtual multiplet), J'(P–H) 5.7, 3 PMe_3], −10.61 [1H, q, J(P–H) 48.2, J(W–H) 46.0, W–H]; ^{13}C n.m.r. ($[^2H_6]$benzene) 78.2 [d, C_5H_5], 33.2 [qm, 3 PMe_3]; $^{31}P\{^1H\text{-Me}\}$ n.m.r. ($[^2H_6]$benzene) −31.4 [d, J(P–H) 48.2, J(P–W) 335, 3 PMe_3].

(**9**) $W(\eta\text{-}C_5H_4Et)(PMe_3)H_5$ ^1H n.m.r. ($[^2H_6]$benzene) 4.93 (2H, m, 2H_a or 2 H_b], 4.78 [2H, m, 2 H_b or 2 H_a], 2.39 [2H, q, J(H–H) 7.4, CH_2], 1.46 [9H, d, J(P–H) 9.8, PMe_3], 1.07 [3H, t, J(H–H) 7.4, CH_2CH_3], −3.71 [5H, d, J(P–H) 42.2, J(W–H) 42.8, 5W–H]; ^{13}C n.m.r. ($[^2H_6]$benzene) 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) 35.5, PMe_3], 23.2 [t, CH_2], 16.1 [q, CH_2CH_3]; $^{31}P\{^1H\text{-Me}\}$ n.m.r. ($[^2H_6]$benzene) −22.4 [sextet, J(P–W) 47, PMe_3].

(**14**) $W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Et)H_2$ ^1H n.m.r. ($[^2H_6]$benzene) 4.51 [2H, s, 2 H_a or 2 H_b], 4.37 [5H, s, C_5H_5], 4.17 [2H, s, 2 H_b or 2 H_a], 2.46 [2H, q, J(H–H) 7.5, CH_2], 1.17 [3H, t, J(H–H) 7.5, CH_2CH_3], −11.81 [2H, s, J(W–H) 74.4, 2W–H]; ^{13}C n.m.r. ($[^2H_6]$benzene) 103.8 [s, C_c], 74.0 [d, J(C–H) 177, 2 C_a or 2 C_b], 72.0 [dt, J_d(C–H) 180, J_t(C–H) 6, C_5H_5], 67.1 [d, J(C–H) 186, 2 C_b or 2 C_a], 63.5 [t, J(C–H) 128, CH_2], 15.9 [q, J(C–H) 126, CH_2CH_3].

(**15**) $W(\eta\text{-}C_5H_4Et)(\eta\text{-}C_5H_5)Cl_2$ ^1H n.m.r. ($[^2H_6]Me_2SO$) 5.57 [5H, s, C_5H_5], 5.54 [2H, m, 2 H_a or 2 H_b], 5.12 [2H, m, 2 H_b or 2 H_a], 2.34 [2H, q, J(H–H) 7.5, CH_2], 1.09 [3H, t, J(H–H) 7.5, CH_3].

(**16**) $W(\eta^4\text{-}C_5H_5CHPh_2)(PMe_3)_3H_2$ ^1H n.m.r. ($[^2H_6]Me_2CO$) 7.36—7.18 [10H, m, 2 Ph], 5.35 [1H, s, H_5 or H_6], 4.82 [4H, m, 2 H_7 and 2 H_8], 1.75 [9H, d, J(P–H) 7.9, PMe_3], 1.55 [18H, d, J(P–H) 8.9, 2 PMe_3], 1.01 [1H, m, W–H_b], *ca.* 1.0 [1H, located by double resonance, H_6 or H_5], −5.84 [1H, dddt, J_d(H–H) 1.0, ^2J_d(H_a–H_b) 9.5, J_d(P–H) 7.0, J_t (P–H) 35.5, W–H_a]; ^{13}C n.m.r. ($[^2H_6]Me_2CO$) 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]; $^{31}P\{^1H\}$ n.m.r. ($[^2H_6]Me_2CO$) −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].