η-Arene and η-Cyclohexadiene Tungsten Chemistry: New Synthetic Routes to Tertiary Phosphine–Hydride Derivatives

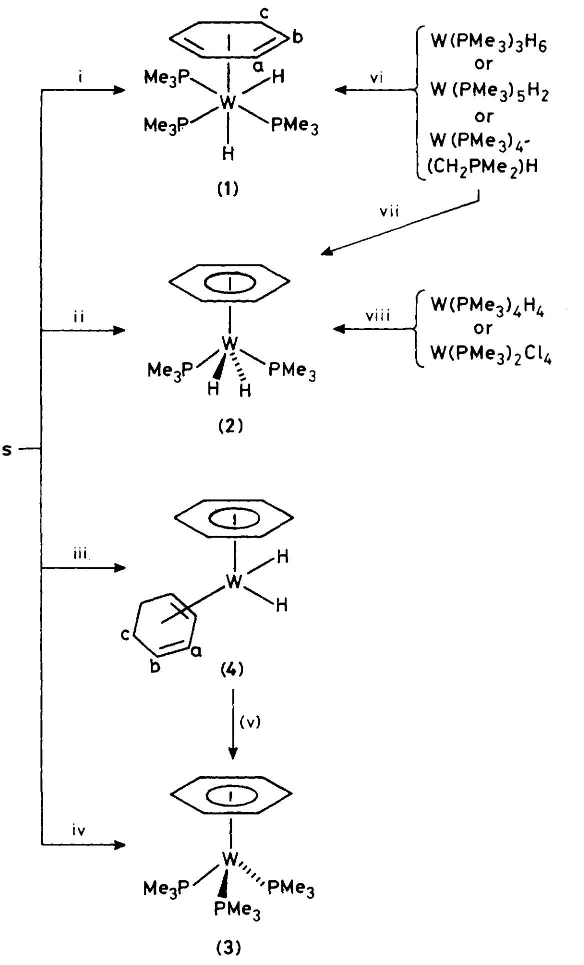
Malcolm L. H. Green and Gerard Parkin

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K.

Convenient syntheses of $W(\eta\text{-}C_6H_8)(PMe_3)_3H_2$ and $W(\eta\text{-}C_6H_6)(PMe_3)_2H_2$ are described; these compounds, together with $W(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)H_2$, $W(\eta\text{-}PhMe)(PMe_3)_2H_2$, $W(\eta\text{-}PhMe)(Me_2PCH_2CH_2PMe_2)H_2$, and $W(\eta\text{-}C_6H_6)(PMe_3)_3$ have been synthesized using either tungsten atoms or by the reductive labilization of an η-PhMe ring of $W(\eta\text{-}PhMe)_2$ using potassium metal.

It is clear from the existing studies on the (η-arene)tungsten system[1—3] that there can be expected to be an extensive and varied chemistry for high-energy, half sandwich (η-arene)tungsten compounds. The common precursors to this chemistry are bis(η-arene)tungsten compounds. These are difficult to prepare by normal synthetic methods[4] and otherwise require metal vapour synthesis techniques.[5] Here we describe a new route to (η-arene) and (η-cyclohexadiene)tungsten compounds using readily available tungsten–tertiary phosphine compounds as precursors. Further examples of (η-arene)tungsten chemistry are also described, including displacement of one or two of the toluene rings from bis(η-toluene)tungsten by tertiary phosphine and hydride ligands.

The compounds $W(PMe_3)_5H_2$, $W(PMe_3)_4H_4$, and $W(PMe_3)_3H_6$ are readily available.[6] Treatment of $W(PMe_3)_5H_2$ {or $W(PMe_3)_3H_6$} with cyclohexa-1,3-diene gives pale brown crystals of $W(\eta\text{-}1,3\text{-}C_6H_8)(PMe_3)_3H_2$ (**1**), in 80% yield. Transition metal diene hydride compounds are comparatively rare and some compounds may be better described as agostic η-allyl compounds.[7] However, n.m.r. studies on (**1**) show it to have the diene–dihydride structure,



Scheme 1. *Reagents:* i, C_6H_{10}–PMe_3 (10 : 1); ii, C_6H_{10}–PMe_3 (10 : 1) or 1,3-C_6H_8–PMe_3 (10 : 1); iii, C_6H_{10} or 1,3-C_6H_8; iv, C_6H_6–PMe_3 (5 : 1); v, PMe_3 at 55 °C; vi, 1,3-C_6H_8 at 60 °C and for $W(PMe_3)_4(CH_2PMe_2)H$, either 1,3- or 1,4-C_6H_8 at 60 °C in benzene; vii, For $W(PMe_3)_4(CH_2PMe_2)(H)$, 1,3- or 1,4-C_6H_8 at 60 °C in benzene; viii, For $W(PMe_3)_4H_4$, 1,3-C_6H_8, *hν* in pentane; for $W(PMe_3)_2Cl_4$, 1,3-C_6H_8, Na(K) alloy in pentane.

thus providing further evidence that the tendency to form the agostic compound decreases with the heavier members of the transition metals.[7] The compound $W(\eta\text{-}C_6H_6)(PMe_3)_2H_2$ (**2**) may be conveniently prepared in *ca.* 30% yield by photolysis of $W(PMe_3)_4H_4$ in the presence of cyclohexa-1,3-diene using a medium-pressure mercury lamp. Alternatively, reduction of $W(PMe_3)_2Cl_4$[8] in the presence of cyclohexa-1,3-diene using Na(K) alloy also gives (**2**) in *ca.* 30% yield. The reaction between $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ and cyclohexa-1,3-diene or cyclohexa-1,4-diene gives (**1**) and (**2**) in the ratio 4 : 1.

Photolysis of (**1**) forms a mixture of (**2**) and $W(\eta\text{-}C_6H_6)(PMe_3)_3$ (**3**) (*ca.* 1 : 1 molar ratio); in the presence of H_2, $W(PMe_3)_3H_6$ is also formed.

Co-condensation of tungsten atoms with a mixture of cyclohexene and trimethylphosphine (10 : 1) gives a mixture of the compounds $W(\eta\text{-}1,3\text{-}C_6H_8)(PMe_3)_3H_2$ (**1**), and $W(\eta\text{-}C_6H_6)(PMe_3)_2H_2$ (**2**) from which (**1**) can be isolated as pale brown crystals (*ca.* 5%). When tungsten atoms are co-condensed with a mixture of cyclohexa-1,3-diene and trimethylphosphine (10 : 1) three products are formed: (**2**), $W(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)H_2$ (**4**), and a third compound which has not been isolated but the ^1H n.m.r. spectrum suggests to be the hydrido compound $W(\eta\text{-}C_6H_7)(\eta\text{-}C_6H_8)(PMe_3)H$ (**5**). Co-condensation of tungsten atoms with benzene–trimethylphosphine (5 : 1) gives the expected new compound $W(\eta\text{-}C_6H_6)(PMe_3)_3$ (**3**), which is isolated as orange crystals (*ca.* 15%). Thus, the sequence of reactions of tungsten atoms and PMe_3–C_6H_x mixtures where x = 12,[9] 10, 8, and 6 shows how the products are related to the degree of unsaturation in the cyclic hydrocarbon. If the reactant hydrocarbon contains *n* saturated carbon atoms then the products are consistent with a transfer of up to *n* hydrogens from the ligand to the metal. Similarly, co-condensation of W atoms with cyclohexa-1,3-diene or cyclohexene gives the compound $W(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)H_2$ (**4**) as pale yellow crystals in *ca.* 10% yield. Solutions of (**4**) decompose at room temperature but in the presence of PMe_3 at 55 °C, (**3**) can be obtained.

Previous studies of the chemistry of bis(η-arene)tungsten compounds have shown that thermal replacement of one η-arene ring required strongly forcing conditions.[10] We have found that η-toluene ring substitution of bis(η-toluene)tungsten (**6**) proceeds readily in the presence of potassium films. Thus, stirring tetrahydrofuran solutions of (**6**) containing trimethylphosphine in the presence of a potassium film at room temperature gives $W(\eta\text{-}PhMe)(PMe_3)_2H_2$ (**7**) in *ca.* 50% yield. When the same reaction is carried out at 50 °C and in the presence of dihydrogen (2 atm) then the products are a mixture (n.m.r.) of (**7**), $W(\eta\text{-}PhMe)(PMe_3)_3$,[10] $W(PMe_3)_4H_4$, and $W(PMe_3)_3H_6$. Similarly, reaction of $W(\eta\text{-}PhMe)_2$ and 1,2-bis(dimethylphosphino)ethane (dmpe) with a potassium film in tetrahydrofuran gives the compound $W(\eta\text{-}PhMe)(dmpe)H_2$.[1] We assume that this labilization of the (η-PhMe) ring occurs owing to the reduction of $W(\eta\text{-}PhMe)_2$ by potassium leading to population of metal–ring antibonding orbitals. The reactions are described in Scheme 1, and structures are proposed on the basis of detailed n.m.r. studies.† With the exception of (**5**), all the new compounds

---

† *Characterising Data* (coupling constants in Hz): (**1**) $W(\eta\text{-}C_6H_8)(PMe_3)_3H_2$, ^1H n.m.r. in C_6D_6: 3.85 (br., 2H, 2H of $\eta\text{-}C_6H_8$), 2.54 (d, $J_{H\text{-}H}$ 8.7, 2H, 2H of $\eta\text{-}C_6H_8$), 2.20 (br., 2H, 2H of $\eta\text{-}C_6H_8$), 1.75 (d, $J_{H\text{-}H}$ 8.7, 2H, 2H of $\eta\text{-}C_6H_8$), 1.35 (d, $J_{P\text{-}H}$ 7.4, 18H, 2PMe$_3$), 1.28 (d, $J_{P\text{-}H}$ 6.6, 9H, PMe$_3$), −1.53 (m, W–H), and −5.55 (br., W–H); $^{31}P\{^1H\}$ n.m.r. in C_7D_8: −30.87 (d, $J_{P\text{-}P}$ 14.3, $J_{P\text{-}W}$ 220, 2PMe$_3$) and −32.14 (t, $J_{P\text{-}P}$ 14.3, $J_{P\text{-}W}$ 242, 1PMe$_3$); $^{31}P\{^1H\text{-}Me\}$ n.m.r. in C_7D_8: −30.87 (dt) and − 32.14 (tt); ^{13}C n.m.r. in C_7D_8: 68.34 (d, $J_{C\text{-}H}$ 168.4, C_a or C_b), 47.59 (d, $J_{C\text{-}H}$ 141.7, C_b or C_a), 28.76 (t, $J_{C\text{-}H}$ 124.8, C_c), 26.70 (dq, $J_{P\text{-}C}$ 26.9, $J_{C\text{-}H}$ 126.8, 2PMe$_3$), and 26.20 (poorly resolved dq, $J_{P\text{-}C}$ 26.8, PMe$_3$); *m/z* 494 (M^+). (**2**) $W(\eta\text{-}C_6H_6)(PMe_3)_2H_2$ ^1H n.m.r. in C_6D_6: 4.19 (quintet, $J_{P\text{-}H}$ 1.1, $J_{H\text{-}H}$ 1.1, 6H, C_6H_6), 1.59 (d, $J_{P\text{-}H}$ 7.3, 18H, 2PMe$_3$), and −6.15 (t, $J_{P\text{-}H}$ 48.1, $J_{W\text{-}H}$ 48.9, 2H, 2W–H); $^{31}P\{^1H\}$ in C_6D_6: 31.2 (s, $J_{P\text{-}W}$ 277); $^{31}P\{^1H\text{-}Me\}$: 31.2 (t); *m/z* 416 (M^+). (**3**) $W(\eta\text{-}C_6H_6)(PMe_3)_3$, ^1H n.m.r. in C_6D_6: 3.62 (q, $J_{P\text{-}H}$ 2.2, 6H, C_6H_6) and 1.31 (virtually coupled triplet, $J'_{P\text{-}H}$ 5.6, 27H, 3PMe$_3$); *m/z* 490 (M^+). (**4**) $W(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)H_2$, ^1H n.m.r. in C_6D_6: 5.49 (m, 2H, 2H of C_6H_8), 4.13 (s, 6H, C_6H_6), 3.12 (m, 2H, 2H of C_6H_8), 2.29 (m, 2H, 2H of C_6H_8), 1.19 (m, 2H, 2H of C_6H_8), and −7.98 (s, $J_{W\text{-}H}$ 70, 2H, 2W–H); $^{13}C\{^1H$, off-resonance$\}$ in C_6D_6: 84.50 (d, C_6H_6), 81.45 (d, C_a or C_b), 52.19 (d, C_b or C_a), and 28.80 (t, C_c); *m/z* 342 (M^+ − 2H). (**5**) $W(\eta\text{-}C_6H_7)(\eta\text{-}C_6H_8)(PMe_3)H$, ^1H n.m.r. in C_6D_6: 5.50 (m, 1H), 5.27 (m, 1H), 5.02 (m, 1H), 4.67 (m, 1H), 3.90 (m, 1H), 3.76 (m, 1H), 2.80 (m, 2H), 2.30 (m, 3H), and 2.07 (m, 4H), (15H of $\eta\text{-}C_6H_7$ and $\eta\text{-}C_6H_8$); 1.20 (d, $J_{P\text{-}H}$ 10, 9H, PMe$_3$); −5.53 (d, $J_{P\text{-}H}$ 40, $J_{W\text{-}H}$ 40, 1H, W–H). (**7**) $W(\eta\text{-}PhMe)(PMe_3)_2H_2$, ^1H n.m.r. in C_6D_6: 4.38 (m, 2H, 2H of Ph), 4.33 (m, 2H, 2H of Ph), 4.02 (m, 1H, 1H of Ph), 1.87 (s, 3H, Ph*Me*), 1.61 (d, $J_{P\text{-}H}$ 7.3, 18H, 2PMe$_3$), and −6.30 (t, $J_{P\text{-}H}$ 48.1, $J_{W\text{-}H}$ 52, 2H, 2W–H); $^{31}P\{^1H\}$ in C_6D_6: −30.9 (s, $J_{P\text{-}W}$ 284); $^{31}P\{^1H\text{-}Me\}$ in C_6D_6: −30.9 (t); *m/z* 430 (M^+).

(**1**), (**2**), (**3**), (**4**), and (**7**) have been characterised by microanalysis and mass spectroscopy.

We thank the S.E.R.C. for a grant (to G. P.) and the Donors of the Petroleum Research Fund administered by the American Chemical Society for partial support.

Received, 4th March 1985; Com. 291

References

1 W. E. Silverthorn, *Adv. Organomet. Chem.*, 1975, **13**, 47.
2 P. R. Brown, F. G. N. Cloke, M. L. H. Green, and N. J. Hazel, *J. Chem. Soc., Dalton Trans.*, 1983, 1075.
3 R. Davis and L. A. P. Kane-Maguire, in 'Comprehensive Organometallic Chemistry,' Vol. 3, Pergamon, Oxford, 1982, p. 1321.
4 E. O. Fischer, F. Scherer, and H. O. Stahl, *Chem. Ber.*, 1960, **93**, 2065.
5 F. G. N. Cloke and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1981, 1938.
6 M. L. H. Green, G. Parkin, C. Mingqin, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1984, 1400; K. W. Chiu, R. A. Jones, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse, and K. M. Abdul Malik, *J. Chem. Soc., Dalton Trans*, 1981, 1204; M. B. Hursthouse, D. Lyons, M. Thornton-Pett, and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1983, 476.
7 M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, **250**, 395.
8 E. Carmona, J. M. Marin, M. L. Poveda, R. D. Rogers, and J. L. Atwood, *J. Organomet. Chem.*, 1982, **238**, C63.
9 M. L. H. Green, D. O'Hare, and G. Parkin, *J. Chem. Soc., Chem. Commun.*, 1985, 356.
10 M. L. H. Green, F. G. N. Cloke, and J. J. Martin-Polo, unpublished observations.