

Arene-Tungsten Chemistry: Bis(arene)tungsten Hydride Derivatives; Co-condensation of Tungsten Atoms from an Electron Gun Source with Aromatic Hydrocarbons

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Summary Co-condensation of tungsten atoms from an electron gun source with benzene, toluene, or mesitylene yields bis-(arene)tungsten compounds $[(\eta\text{-C}_6\text{H}_3\text{R}_3)_2\text{W}]$ (R = H and/or Me) which are reversibly protonated by dilute acids to give the cations $[(\eta\text{-C}_6\text{H}_3\text{R}_3)_2\text{WH}]^+$ (R = H and/or Me).

PREVIOUSLY bis-(benzene)tungsten has been prepared in small quantities both by the Fischer-Hafner Al-AlCl₃ reduction procedure¹ and by the co-condensation of tungsten atoms from a hot filament with benzene.² The former synthesis is lengthy, difficult, and very inefficient (<2% yield) while the second is limited in scale by the dimensions of the filament and cannot be readily adopted as a general technique for many of the other refractory metals.

We have found that, using an electron-gun which operates up to 3.5 kW, we can readily evaporate tungsten from a 10 g sample at a rate in excess of 5 g h⁻¹ (P ca. 10⁻⁷ Torr). In fact a suitable evaporation rate for tungsten is achieved at 1.7–1.8 kW where ca. 0.8 g h⁻¹ of tungsten atoms leave the furnace. Co-condensation of the tungsten atoms generated in this way with benzene, toluene, or mesitylene at an average pressure of ca. 10⁻⁵ Torr gives the green bis-arene tungsten compounds $[\text{W}(\eta\text{-C}_6\text{H}_3\text{R}_3)_2]$ (I; R = H and/or Me).

Typically for the synthesis of (I; R = H) ca. 2.4 g of tungsten reacts with benzene (80 cm³) during a 2.5 h run giving ca. 1.4 g of the pure product (ca. 30% yield after recrystallisation from light petroleum, b.p. 30–40 °C). The other materials recovered are tungsten powder and unchanged arene, there being only traces of impurity.

It has been suggested² that electron guns are not suitable sources for atoms of highly refractory metals since electron or radiation damage of ligands or products might occur. Our observations clearly demonstrate that electron guns can provide a very clean and convenient source of tungsten atoms on a synthetically useful scale.

The photoelectron spectra of $[(\eta\text{-C}_6\text{H}_6)_2\text{W}]$ (Ia) and $[(\eta\text{-C}_6\text{H}_3\text{Me}_3)_2\text{W}]$ (Ib) have been obtained and may be assigned on the basis of an M.O. scheme which is essentially

similar to that proposed for Mo and Cr analogues.³ The first ionisation energy† [for (Ia), 5.40 eV; (Ib) 5.18 eV], from the a_{1g} (metal lone pair) orbital, is exceptionally low and thus these compounds may be classified as extremely electron rich. Furthermore in the Mo and Cr complexes ionisation from the e_{2g} orbitals (where filled metal d orbitals back donate to empty ligand orbitals) gives rise to only one band, but two distinct bands [(Ia), 6.56 and 6.99 eV; (Ib), 6.16 and 6.51 eV] occur for the tungsten analogues since spin-orbit coupling is much greater for the heavier metal.

The compounds (I) dissolve in dilute hydrochloric acid to give orange solutions and addition of PF₆⁻ precipitates the orange, diamagnetic salts $[(\eta\text{-C}_6\text{H}_3\text{R}_3)_2\text{WH}]\text{PF}_6$ (II; R = H and/or Me). This is the first example of a bis-arene complex which readily gives a stable hydride derivative as well as the usual 17e cation⁴ and constitutes a further example of the greater stability of M-H bonds of third row transition metals. The compounds (II) may be expected to adopt a 'bent' configuration. Addition of NaOH to (II) causes deprotonation and quantitative recovery of (I).

TABLE. ¹H N.m.r. and i.r. data for new bis-(arene)tungsten derivatives.

Compound ^a	δ (¹ H)	ν(W-H) ^b /cm ⁻¹
$[(\eta\text{-C}_6\text{H}_3\text{Me}_3)_2\text{W}]^c$	4.75 (6H, s, ArH) ^d , 2.03 (18H, s, Me)	—
$[(\eta\text{-C}_6\text{H}_6)_2\text{WH}]\text{PF}_6$	5.78 (12H, d, J 2, ArH) 1.07 (1H s, W ₁ 12, W-H) ^e	1870
$[(\eta\text{-C}_6\text{H}_6\text{Me})_2\text{WH}]\text{PF}_6$	5.67 (10H, m, ArH), 2.67 (6H, s, Me), 0.80 (1H, m, J _{HH} 2, ^e W ₁ 10, W-H)	1860
$[(\eta\text{-C}_6\text{H}_3\text{Me}_3)_2\text{WH}]\text{PF}_6$	5.56 (6H, d, J 2, ArH), 2.62 (18H, s, Me), -0.41 (1H, s, W ₁ 10, W-H) ^e	1875

^a Satisfactory elemental analyses have been obtained for all new compounds. ^b Nujol mull; medium intensity. ^c M⁺, m/e 424, for ¹⁸⁴W. ^d In C₆D₆. ^e In (CD₃)₂CO; J and W₁ values are in Hz.

† Ionisation energy values ±0.1 eV.

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