

η -Cycloheptatrienyl Tungsten Chemistry

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Reduction of WCl_6 with sodium amalgam in the presence of cycloheptatriene gives $[W(\eta-C_7H_7)(\eta-C_7H_9)]$, which is a precursor to the compounds $[W(\eta-C_7H_7)LX_2]$, $[W(\eta-C_7H_7)L_2X]$, where L = tertiary phosphines or acetonitrile and X = halogen, $[W(\eta-C_7H_7)(\eta-C_5H_4R)]$, R = H, Me, and $[W(\eta-C_7H_7)(\eta-C_9H_7)]$.

The chemistry of η -cycloheptatrienyl-chromium and -molybdenum compounds is well documented,¹ whilst the chemistry of η -cycloheptatrienyltungsten compounds remains relatively unexplored.²⁻⁴ Most of the known η -cycloheptatrienyl-tungsten compounds are derived from $[W(\eta-C_7H_7)(CO)_2I]$, which requires several steps to synthesise from the commercially available starting materials.³ Vacuum codeposition of tungsten atoms with cycloheptatriene gives $[W(\eta-C_7H_7)(\eta-C_7H_9)]$ **1** but no further chemistry was reported.⁴ Recently, we have discovered a one-pot gram-scale preparation of $[Mo(\eta-C_7H_7)(\eta-C_7H_9)]$ by reducing $MoCl_5$ with sodium amalgam in the presence of cycloheptatriene and demonstrated the synthetic utility of this compound.^{1e} Here, we report the extension of these synthetic pathways to tungsten.

The key step is the direct synthesis of the compound $[W(\eta-C_7H_7)(\eta-C_7H_9)]$ **1** from WCl_6 in a one-pot reaction. A mixture of tungsten hexachloride (12 g) and an excess of cycloheptatriene in tetrahydrofuran (thf) (16 cm³ in 400 cm³) was treated with sodium amalgam (4.2 g Na in 50 cm³ of Hg) at $-78^\circ C$. The mixture was stirred and allowed to warm to room temperature over 3 h and stirred for a further 3 h. The volatiles were removed under reduced pressure, then the residue was extracted with light petroleum [b.p. 40–60 $^\circ C$]. From the

petroleum extract, 3 g of pure $[W(\eta-C_7H_7)(\eta-C_7H_9)]$ **1** could be isolated as a brown solid. The yield was 27%. In contrast to the molybdenum chemistry, no $[W(\eta-C_7H_8)_2]$ could be isolated.^{1e}

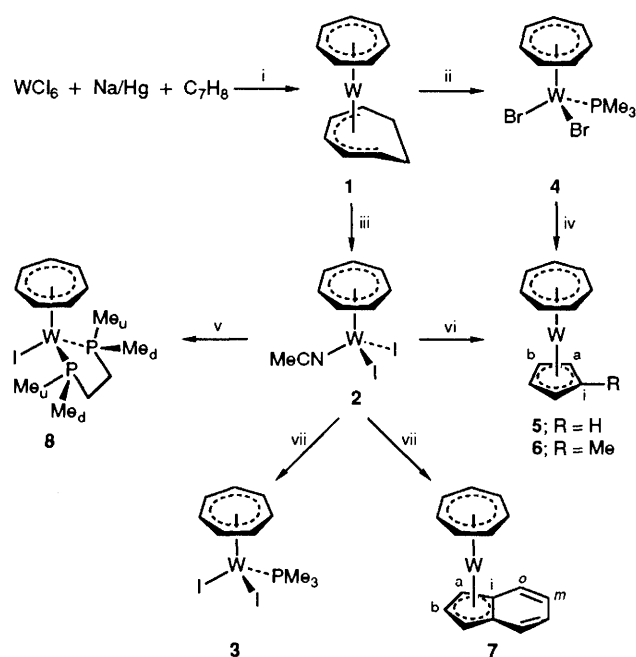
Treatment of **1** in acetonitrile with iodine gives dark-red crystalline $[W(\eta-C_7H_7)(MeCN)I_2]$ **2**, which is a reactive precursor towards new organometallic compounds of tungsten. The MeCN ligand in **2** is labile and can be displaced by PMe_3 giving red crystals of $[W(\eta-C_7H_7)(PMe_3)I_2]$ **3**. Oxidation of **1** in thf with bromine followed by addition of PMe_3 gives the compound $[W(\eta-C_7H_7)(PMe_3)Br_2]$ **4** as orange-brown crystals.

There is substantial evidence that the covalent bond formed between the $\eta-C_7H_7$ ligand and a transition metal requires three electrons from the metal. In which case the compounds **2–4** are d¹ compounds.⁵ All the room-temperature ESR spectra of dilute solution of compounds **2–4** in CD_3CN or thf exhibit a rather sharp absorption centred at $g = 1.94$ – 1.99 but no hyperfine coupling to ¹⁸³W and ³¹P was observed; lowering the temperature to 153 K only caused slight sharpening of the signals.

Treatment of **2** with sodium cyclopentadienide or sodium methylcyclopentadienide gives the compounds $[W(\eta-C_7H_7)(\eta-C_5H_4R)]$, R = H **5** or Me **6**, in good yields. Compound **6** has also been prepared by treating **4** with sodium methylcyclopentadienide. The mixed sandwich compound **5** has been previously described but the synthesis gave a low yield.⁶ Similarly, the reaction of **2** with lithium indenide affords purple crystals of $[W(\eta-C_7H_7)(\eta-C_9H_7)]$ **7**.

Reduction of **2** with sodium amalgam in the presence of $Me_2PCH_2CH_2PMe_2$ gives diamagnetic green compound $[W(\eta-C_7H_7)(Me_2PCH_2CH_2PMe_2)I]$ **8** in moderate yield.

All the new compounds **2–4** and **6–8** gave spectroscopic and analytical data in accordance with assigned structures.† The new reactions and the structures proposed are summarised in Scheme 1.



Scheme 1 Reagents and conditions: i, gradual warming from $-78^\circ C$ over 3 h in thf then at room temp. for 3 h, 27%; ii, Br_2 in thf at room temp. for 15 min then PMe_3 at room temp. for 2 h, 44%; iii, I_2 in MeCN at $80^\circ C$ for 3 h, 86%; iv, NaC_5H_4Me in thf at room temp. for 16 h, 60%; v, $Na-Hg$ and $Me_2PCH_2CH_2PMe_2$ in thf, gradual warming from $-60^\circ C$ over 2 h then at room temp. for 15 h, 22%; vi, NaC_5H_5 (or NaC_5H_4Me) in thf at room temp. for 20 h, 40% (or 80%); vii, PMe_3 in thf at room temp. for 1 h, 70%; viii, lithium indenide in thf at room temp. for 15 h, 25%

† Satisfactory microanalyses have been obtained for all new compounds.

Selected NMR data: ¹H NMR at 300 MHz, ¹³C NMR at 75.5 MHz, and ³¹P NMR at 121.4 MHz.

5: ¹H NMR (C_6D_6): δ 5.25 (s, 7 H, $\eta-C_7H_7$), 5.19 (s, 5 H, $\eta-C_5H_5$); ¹³C{¹H} NMR (C_6D_6): δ 82.5 (s, $\eta-C_5H_5$), 73.8 (s, $\eta-C_7H_7$).

6: ¹H NMR (C_6D_6): δ 5.28 (br s, 2 H, H_a or H_b), 5.21 (s, 7 H, $\eta-C_7H_7$), 5.16 (br s, 2 H, H_a or H_b), 1.76 (s, 3 H, Me); ¹³C{¹H} NMR (C_6D_6): δ 100.1 (s, C_i), 85.4 (s, C_a or C_b), 82.2 (s, C_a or C_b), 74.5 (s, $\eta-C_7H_7$), 16.0 (s, Me).

7: ¹H NMR (CD_3COCD_3): δ 7.29 [dd, $J(H-H)$ 3.0, 6.4 Hz, 2 H, H_o or H_m], 6.77 [dd, $J(H-H)$ 3.0, 6.4 Hz, 2 H, H_o or H_m], 6.08 [t, $J(H-H)$ 2.4 Hz, 1 H, H_b]; 6.02 [d, $J(H-H)$ 2.4 Hz, 2 H, H_a], 5.11 (s, 7 H, $\eta-C_7H_7$); ¹³C{¹H} NMR (C_6D_6): δ 128.4 (s, C_o or C_m), 121.2 (s, C_o or C_m), 101.8 (s, C_i), 88.9 (s, C_b), 75.9 (s, $\eta-C_7H_7$), 75.5 (s, C_a).

8: ¹H NMR ($C_6D_5CD_3$): δ 4.99 [t, $J(H-P)$ 1.9 Hz, 7 H, $\eta-C_7H_7$], 1.61 [d, $J(H-P)$ 8.0 Hz, 6 H, Me_u or Me_d], 1.12–1.36 (m, 2 H, H_u or H_d), 0.88 [d, $J(H-P)$ 7.6 Hz, 6 H, Me_u or Me_d], 0.72–0.98 (m, 2 H, H_u or H_d); ¹³C{¹H} NMR ($C_6D_5CD_3$): δ 81.0 (s, $\eta-C_7H_7$), 31.7 [virtual t, $J(C-P)$ 22.0 Hz, CH_2], 21.5 [virtual t, $J(C-P)$ 17.1 Hz, Me_u or Me_d], 17.1–18.0 (m, Me_u or Me_d); ³¹P{¹H} NMR ($C_6D_5CD_3$): δ -7.9 [s, $J(P-^{183}W)$ 346 Hz, $Me_2PCH_2CH_2PMe_2$].

Selected ESR data, **2**: $\langle g \rangle$ 1.941; line width 56 G in CD_3CN at 293 K. **3**: $\langle g \rangle$ 1.988; line width 53 G in thf at 153 K. **4**: $\langle g \rangle$ 1.943; line width 57 G in thf at 153 K.

In conclusion, we have described convenient gram-scale pathways to half-sandwich derivatives of the $W(\eta-C_7H_7)$ moiety.

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