New η-Cycloheptatrienyl Tungsten Compounds and the Intercalation of $[M(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$ (M = Mo or W) into ZrS_2†

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The compound $[W(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **1** is formed in gram quantities by reduction of WCl_6 with sodium amalgam in the presence of cycloheptatriene. The compound **1** with iodine in acetonitrile gives $[W(\eta\text{-}C_7H_7)(MeCN)I_2]$ **2** and this reacts with PMe_3 forming $[W(\eta\text{-}C_7H_7)(PMe_3)I_2]$. Oxidation of **1** with bromine in acetonitrile yields $[W(\eta\text{-}C_7H_7)(MeCN)Br_2]$ and with bromine in tetrahydrofuran followed by addition of PMe_3 gives $[W(\eta\text{-}C_7H_7)(PMe_3)Br_2]$. Reduction of **2** with sodium amalgam in the presence of 1,2-bis(dimethylphosphino)ethane (dmpe) affords $[W(\eta\text{-}C_7H_7)(dmpe)I]$. Compound **2** also reacts with $Na(C_5H_4R)$ (R = H or Me) and lithium indenide to give the mixed-sandwich compounds $[W(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4R)]$ (R = H or Me) and $[W(\eta\text{-}C_7H_7)(\eta\text{-}C_9H_7)]$ respectively. The sandwich compounds $[M(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$ (M = Mo or W) and ZrS_2 form the intercalates $\{ZrS_2[M(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]_x\}$.

The chemistry of η-cycloheptatrienyl–molybdenum compounds has been studied extensively,[1,2] whilst the chemistry of η-cycloheptatrienyl–tungsten compounds remain relatively unexplored.[2,3] Most of the known η-cycloheptatrienyl derivatives of tungsten are derived from $[W(\eta\text{-}C_7H_7)(CO)_2I]$, which requires several steps to synthesise from the commercially available starting materials.[3a] Another drawback of this route is the difficulty in removing the carbonyl ligands of $[W(\eta\text{-}C_7H_7)(CO)_2I]$ and the products derived from this compound usually contain at least one carbonyl ligand. The codeposition of tungsten atoms with cycloheptatriene gives $[W(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **1** but no further chemistry was reported.[4] This route is restrictive because it requires the apparatus for metal vapour synthesis, which is not available in most laboratories. The compound $[W(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ has been prepared from WCl_6 in a one-pot reaction by a reductive method.[5] However, the extremely low yield (1.4%) of this reaction limits further investigation of the chemistry. In the preceding paper, we have reported a one-pot gram-scale preparation of $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ by reducing $MoCl_5$ with sodium amalgam in the presence of cycloheptatriene and demonstrated the synthetic utilities of this compound.[1f] Here we report the extension of these synthetic pathways to tungsten. A preliminary report of part of this work has appeared.[3d]

Results and Discussion

The compound $[W(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **1** was prepared by reduction of WCl_6 in tetrahydrofuran (thf) with sodium amalgam in the presence of an excess of cycloheptatriene. Large scale preparations using 12 g of WCl_6 gave 3 g of the product **1** (27% yield).

The formation of $[W(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **1** may proceed through the intermediate $[W(\eta\text{-}C_7H_8)_2]$. However, in contrast to the corresponding molybdenum chemistry,[1f] this compound could not be isolated. Possibly, the intramolecular hydrogen migration for $[W(\eta\text{-}C_7H_8)_2]$ is faster than that for $[Mo(\eta\text{-}C_7H_8)_2]$.[1b]

When the reddish brown suspension of **1** in acetonitrile was treated with 1 equivalent of iodine the colour darkened gradually. Heating this mixture to 80 °C for 3 h gave a bright red solution from which air-stable dark red crystals of $[W(\eta\text{-}C_7H_7)(MeCN)I_2]$ **2** were obtained in 86% yield. The characterising data for **2** and for all the other new compounds described herein are presented in Table 1 and the reactions and proposed structures are shown in Scheme 1.

The microanalytical data for compound **2** are consistent with the proposed stoichiometry. The fast atom bombardment (FAB) mass spectrum of **2** showed the presence of the parent cation M^+. The IR spectrum exhibited bands at 2280m and 2310m cm^{-1} assignable to the co-ordinated MeCN ligand, and 813vs cm^{-1} which is characteristic of the $\eta\text{-}C_7H_7$ group.[5] The structure for **2** is proposed by analogy with the molecular structure of the molybdenum congener $[Mo(\eta\text{-}C_7H_7)(MeCN)I_2]$, which has been determined.[2h]

The solution EPR spectrum of compound **2** is consistent with the presence of one unpaired electron and shows a rather broad signal at $g = 1.941$ with linewidth = 56 G without hyperfine splitting due to tungsten.

Treatment of **1** with 1 equivalent of bromine in acetonitrile gave a mixture of products from which a small amount of $[W(\eta\text{-}C_7H_7)(MeCN)Br_2]$ **3** could be isolated as green microcrystals. The IR spectrum of compound **3** showed bands characteristic of the $\eta\text{-}C_7H_7$ ring (818 cm^{-1}) and MeCN ligand (2279 and 2308 cm^{-1}). The room-temperature solid-state EPR spectrum of **3** exhibited a very broad signal at $g = 1.927$. Due to the limited amount of sample, this compound was not further characterised.

Treatment of **1** with 1 equivalent of bromine in thf followed by addition of 1 equivalent of PMe_3 led to the isolation of orange-brown crystals of compound **4** in 44% yield. The stoichiometry of **4** was confirmed by microanalysis and the mass spectrum (FAB) showed bands at m/z 509 (M^+) and 430 (M − Br). Bands at 816vs, 946vs and 962vs cm^{-1} in the IR spectrum of **4** were consistent with the presence of $\eta\text{-}C_7H_7$ and PMe_3 ligands, respectively. The solution EPR spectrum of complex **4** in thf at 153 K also displayed a rather broad signal at $g = 1.943$ with linewidth = 57 G. No hyperfine splitting was observed.

The tungsten complex $[W(\eta\text{-}C_7H_7)(MeCN)I_2]$ **2** is similar to $[Mo(\eta\text{-}C_7H_7)(MeCN)I_2]$;[1f] it is highly reactive and is a precursor to other η-cycloheptatrienyl tungsten derivatives. For example, **2** reacts with 1 equivalent of PMe_3 giving red crystals of $[W(\eta\text{-}C_7H_7)(PMe_3)I_2]$ **5** in good yield. This compound is

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† *Non-SI units employed:* mmHg ≈ 133 Pa, G = 10^{-4} T, emu = SI × $10^6/4\pi$, $\mu_B \approx 9.274\,02 \times 10^{-24}$ J T^{-1}.

Table 1 Analytical and spectroscopic data

		Analysis[a] (%)			
Compound	Colour	C	H	Other	Spectroscopic data[b]
2	Dark red	18.7 (19.0)	1.8 (1.8)	N 2.5 (2.5) I 45.1 (44.5)	EPR (CD_3CN): g_{iso} = 1.941, linewidth = 56 G Mass spectrum (FAB): *m/z* 570 (M^+) IR: ν(C≡N) 2280m, 2310m
3	Green				EPR (solid): g_{iso} = 1.927, linewidth = 630 G IR: ν(C≡N) 2279m, 2308m
4	Orange brown	23.9 (23.5)	3.1 (3.2)	I 31.8 (31.3)	EPR (thf, 153 K): g_{iso} = 1.943, linewidth = 57 G Mass spectrum (FAB): *m/z* 509 (M^+), 430 (M − Br) IR: ν(P–C) 946vs, 962vs
5	Red	20.2 (19.9)	2.7 (2.7)	I 42.5 (42.0)	EPR (thf, 153 K): g_{iso} = 1.988, linewidth = 53 G IR: ν(P–C) 940vs, 956vs
6	Green	29.0 (28.3)	4.2 (4.2)	I 23.4 (23.0)	^1H NMR:[c] 4.99 [t, *J*(H–P) 1.9, 7 H, η-C_7H_7], 1.61 [d, *J*(H–P) 8.0, 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, 6 H, Me_u or Me_d], 0.72–0.98 (m, 2 H, H_u or H_d) ^{13}C-{^1H} NMR:[c] 81.0 (s, η-C_7H_7), 31.7 [vt, *J*(C–P) 22.0, CH_2], 21.5 [vt, *J*(C–P) 17.1, Me_u of Me_d], 17.1–18.0 (m, Me_u or Me_d) ^{31}P-{^1H} NMR:[c] −7.9 [s, *J*(P–^{183}W) 346.0 dmpe] Mass spectrum (EI): *m/z* 552 (M^+), 402 (M − dmpe) IR: ν(P–C) 941vs
7	Dark brown				^1H NMR: 5.25 (s, 7 H, η-C_7H_7), 5.19 (s, 5 H, η-C_5H_5) ^{13}C-{^1H} NMR: 82.5 (η-C_5H_5), 73.8 (η-C_7H_7)
8	Dark brown	44.2 (44.1)	4.0 (4.0)		^1H NMR: 5.28 (br s, 2 H, H_a or H_b), 5.21 (s, 7 H, η-C_7H_7), 5.16 (br s, 2 H, H_a or H_b), 1.76 (s, 3 H, Me) ^{13}C-{^1H} NMR: 100.1 (C_i), 85.4 (C_a or C_b), 82.2 (C_a or C_b), 74.5 (η-C_7H_7), 16.0 (Me)
9	Purple	49.4 (49.3)	3.6 (3.6)		^1H NMR:[d] 7.29 [dd, *J*(H–H) 3.0, 6.4, 2 H, H_o or H_m], 6.77 [dd, *J*(H–H) 3.0, 6.4, 2 H, H_o or H_m], 6.08 [t, *J*(H–H) 2.4, 1 H, H_b], 6.02 [d, *J*(H–H) 2.4, 2 H, H_a], 5.11 (s, 7 H, η-C_7H_7) ^{13}C-{^1H} NMR: 128.4 (C_o or C_m), 121.2 (C_o or C_m), 101.8 (C_i), 88.9 (C_b), 75.9 (η-C_7H_7), 75.5 (C_a)

[a] Calculated values given in parentheses. [b] The NMR spectra were obtained at room temperature in [$^2H_6$]benzene unless stated otherwise; data given as chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br s = broad signal, vt = virtual triplet), coupling constant (Hz), relative intensity, and assignment; for virtual triplet, *J* is the apparent coupling constant. For labelling of atoms see Scheme 1. The EPR spectra were recorded at room temperature unless stated otherwise. The IR spectra (cm^{-1}) were recorded in KBr discs. For mass spectra, the *m/z* values quoted are based on the most abundant isotope of each element. The bands show the predicted isotope patterns. [c] In [$^2H_8$]toluene. [d] In [$^2H_6$]acetone.

stable in air and was characterised by microanalysis and IR spectroscopy. The IR spectrum of **5** is very similar to that of **4**.

The room-temperature EPR spectrum of compound **5** in thf exhibited a rather broad absorption centred at g = 1.988 with linewidth = 60 G but no hyperfine coupling to ^{183}W and ^{31}P was observed; lowering the temperature to 153 K only caused slight sharpening of the signal (linewidth = 53 G).

The 17-electron compounds **2**–**5** are all air-stable in the solid state, but solutions in air decompose gradually.

Compounds **2**, **4** and **5** show interesting magnetic properties. They behave as one-dimensional antiferromagnets with *J* values ranging from −7.4 to −10.5 K (for a one-dimensional Heisenberg model) or from −13.4 to −17.5 K (for a one-dimensional Ising model) as described elsewhere.[2h]

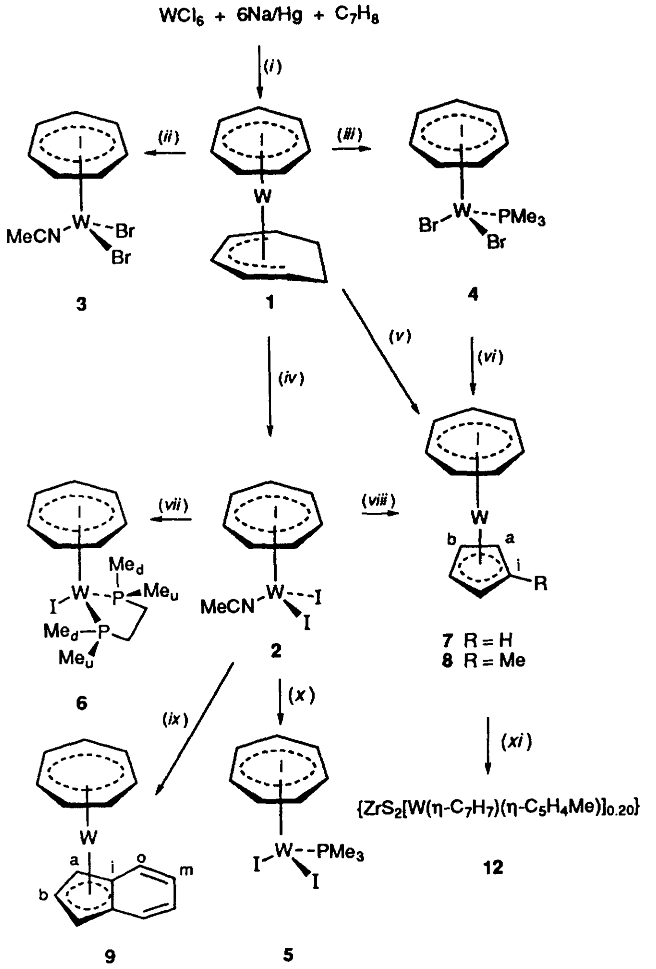
Reduction of [W(η-C_7H_7)(MeCN)I_2] **2** with 1 equivalent of sodium amalgam in the presence of 1 equivalent of $Me_2PCH_2CH_2PMe_2$ (dmpe) in thf led to the formation of diamagnetic [W(η-C_7H_7)(dmpe)I] **6** as a green solid. This compound is air sensitive both in the solid state and in solution, and was characterised by the spectroscopic data in Table 1.

The reaction between [W(η-C_7H_7)(MeCN)I_2] **2** and an excess of Na(C_5H_5) in thf afforded dark brown crystals of [W(η-C_7H_7)(η-C_5H_5)] **7** in 40% yield. Alternatively, the compound **7** could be prepared by treating [W(η-C_7H_7)(η-C_7H_9)] **1** with 1 equivalent of iodine in thf, followed by the treatment of an excess of Na(C_5H_5). The isolated yield of this reaction was 14%. It was reported that the reaction between **1** and Na(C_5H_5) did not lead to the isolation of pure **7**; only mass spectral evidence could be obtained for its presence.[4] Hence, oxidation with iodine is crucial in the displacement of the η-C_7H_9 ring in **1**. The compound **7** was prepared previously from WCl_6 but this synthesis gave an extremely low yield (1.4%).[5] It was claimed that **7** did not dissolve in common organic solvents, thus no NMR data could be obtained.[5] However, we found that **7** is soluble in the solvents light petroleum (b.p. 40–60 °C), benzene and dichloromethane, and the ^{1}H and ^{13}C NMR spectra give bands unambiguously assignable to η-C_7H_7 and η-C_5H_5 ligands.

Table 2 Carbon-13 NMR data for [M(η-C_7H_7)(η-C_5H_5)]

	δ_C			
Compound	C_5H_5	C_7H_7	Solvent	Ref.
M = Cr	75.4	86.9	CS_2	7
Mo	83.8	80.0	C_6D_6	7
W	82.5	73.8	C_6D_6	This work

It is well documented that ^{13}C NMR chemical shifts of cyclic olefins strongly depend on the charge on the carbon atoms of the compounds; an increase in the negative charge gives rise to an upfield shift of the ^{13}C resonance, indicating an increase in the shielding of the carbon atoms.[6] Table 2 summarises the ^{13}C NMR data of the compounds [M(η-C_7H_7)(η-C_5H_5)] (M = Cr, Mo or W). It can be seen that for the chromium compound the signal at higher field is due to the C_5 ring, while for the molybdenum and tungsten compounds it is due to the C_7 ring. This may suggest that in the chromium compound the electron density of the carbon atoms of the C_5 ring is larger than that of the C_7 ring which is in accord with the X-ray photoelectron spectroscopy studies,[8] while the reverse is true for the molybdenum and tungsten compounds. The electron density of the C_7 ring-carbons may increase down the group as indicated by the chemical shifts of the C_7 ring. A similar trend is



Scheme 1 Reagents and conditions: (*i*) gradual warming from −78 °C over 3 h in thf then at room temperature (r.t.) for 3 h, 27%; (*ii*) Br_2 in MeCN at 80 °C for 4 h; (*iii*) Br_2 in thf at r.t. for 15 min then PMe_3 at r.t. for 2 h, 44%; (*iv*) I_2 in MeCN at 80 °C for 3 h, 86%; (*v*) I_2 in thf at 60 °C for 2 h then $Na(C_5H_5)$ [or $Na(C_5H_4Me)$] at r.t. for 16 h, 14% (or 50%); (*vi*) $Na(C_5H_4Me)$ in thf at r.t. for 16 h, 60%; (*vii*) Na/Hg and dmpe in thf, gradual warming from −60 °C over 3 h then at r.t. for 15 h, 22%; (*viii*) $Na(C_5H_5)$ [or $Na(C_5H_4Me)$] in thf at r.t. for 20 h, 40% (or 80%); (*ix*) lithium indenide in thf at r.t. for 15 h, 25%; (*x*) PMe_3 in thf at r.t. for 1 h, 70%; (*xi*) ZrS_2 in toluene at 120 °C for 5 d

Table 3 Half-wave potentials ($E_{\frac{1}{2}}$/V) of [M(η-C_7H_7)(η-C_5H_4R)] and [M(η-C_7H_7)(η-C_9H_7)] *vs.* SCE

Compound	M = Mo	W
[M(η-C_7H_7)(η-C_5H_5)]$^{+/0}$	−0.60	−0.77
[M(η-C_7H_7)(η-C_5H_4Me)]$^{+/0}$	−0.63	−0.79
[M(η-C_7H_7)(η-C_9H_7)]$^{+/0}$	−0.48	−0.66

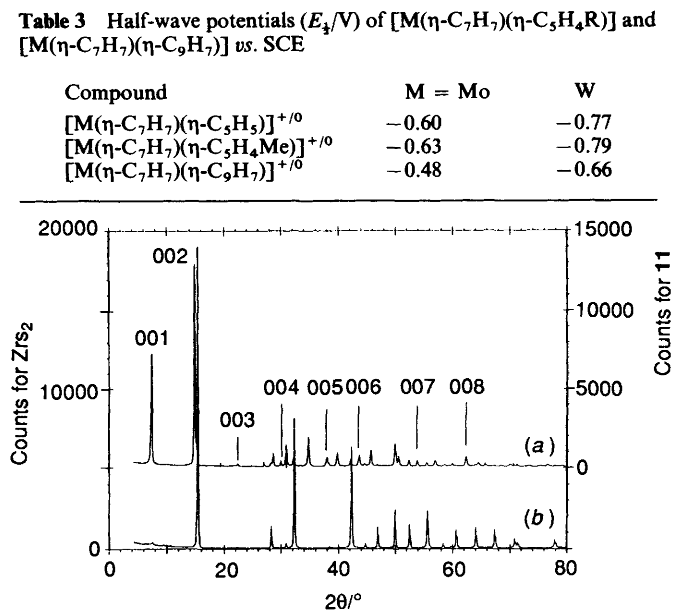


Fig. 1 X-Ray powder diffraction patterns of (*a*) **11** and (*b*) ZrS_2

not observed in the ^1H NMR data. This may be due to the fact that the interpretation of the ^1H NMR spectrum is complicated by local magnetic anisotropies and shieldings which are of less importance in ^{13}C NMR spectroscopy.[9]

Treatment of [W(η-C_7H_7)(MeCN)I_2] **2** with an excess of $Na(C_5H_4Me)$ in thf gave dark brown crystals of [W(η-C_7H_7)(η-C_5H_4Me)] **8** in 80% yield. The dibromo compound [W(η-C_7H_7)(PMe_3)Br_2] **4** could also be used instead of **2** to prepare compound **8** in 60% yield. As an alternative pathway to prepare **8**, the compound [W(η-C_7H_7)(η-C_7H_9)] **1** was treated with 1 equivalent of iodine in thf, then the resulting mixture was reacted with an excess of $Na(C_5H_4Me)$ to give the compound **8** in 50% yield.

Treatment of [W(η-C_7H_7)(MeCN)I_2] **2** with an excess of lithium indenide in thf gave a dark brown solution from which purple crystals of [W(η-C_7H_7)(η^5-C_9H_7)] **9** were isolated in 25% yield.

The electrochemistry of compounds **7**–**9** has been studied by cyclic voltammetry. The data tabulated in Table 3, which also includes the half-wave potentials of the molybdenum analogues[1f] for comparison, show **7**–**9** undergo one fully reversible oxidation. We note that the tungsten complexes are more reducing than their molybdenum congeners and that on changing the pentahapto-ring from η-cyclopentadienyl to η-indenyl ligand the compounds become less reducing. Chemical oxidation of **7** with iodine to the corresponding monocation [W(η-C_7H_7)(η-C_5H_5)]$^+$ has been reported previously.[5]

It has been shown that neutral electron-rich organometallic sandwich compounds which form stable cations can intercalate into layered transition-metal dichalcogenides.[10] The electrochemical data (Table 3) show the compounds [M(η-C_7H_7)(η-C_5H_4R)] (M = Mo or W, R = H or Me) may be classed as electron rich and that they form cations stable to isolation. The intercalation of [Cr(η-C_7H_7)(η-C_5H_5)] into ZrS_2 has been reported and the resulting intercalate {ZrS_2[Cr(η-C_7H_7)(η-C_5H_5)]$_{0.25}$} has a lattice expansion of 6.17 Å.[10a] Therefore we were interested to study the intercalation of [M(η-C_7H_7)(η-C_5H_4Me)] (M = Mo or W) into ZrS_2.

Treatment of zirconium disulfide powder with an excess of [Mo(η-C_7H_7)(η-C_5H_4Me)] **10** in toluene at 120 °C resulted in intercalation of the sandwich compound; thorough washing of the resulting solid with toluene gave a brown compound of stoichiometry {ZrS_2[Mo(η-C_7H_7)(η-C_5H_4Me)]$_{0.22}$} **11**. The intercalation reaction was assumed complete when no lines due to starting material were observed in the X-ray powder diffraction pattern. The stoichiometry of the intercalate was determined by microanalysis which also confirmed that the C:H ratio remains unchanged upon intercalation.

Similarly, treatment of zirconium disulfide powder with [W(η-C_7H_7)(η-C_5H_4Me)] **8** in toluene at 120 °C led to the formation of a dull black solid which was thoroughly washed with toluene and then dried *in vacuo*. Powder X-ray diffraction of this black solid showed that intercalation had occurred. Microanalysis gave the stoichiometry {ZrS_2[W(η-C_7H_7)(η-C_5H_4Me)]$_{0.20}$} **12** and confirmed the expected C:H ratio.

Fig. 1 shows the X-ray diffraction patterns of ZrS_2 and the intercalate **11**, which is typical. Because of disorder in the *ab* plane characteristic of such intercalation compounds,[11] only 00*l* lines could be indexed. From the measured *c* axis of the intercalate and the *c* axis of the host lattice (5.83 Å for ZrS_2), the lattice expansion (Δc) which occurs on intercalation of **10** and **8** into the van der Waals gap of the host lattice was obtained. The indexing as well as observed and calculated *d* spacings are given in Table 4. The cell parameters for **11** and **12** together with those for the chromium analogue are listed in Table 5. It is interesting that both the stoichiometry (*x*) and the lattice expansion (Δc) decrease down the group.

Table 4 X-Ray powder data for **11** and **12**

	11		**12**	
hkl	d_{obs}/Å	d_{calc}/Å	d_{obs}/Å	d_{calc}/Å
001	11.7464	11.7435	11.8250	11.8310
002	5.9608	5.9186	5.9270	5.9202
003	3.9510	3.9564	3.9693	3.9479
004	2.9782	2.9713	2.9786	2.9613
005	2.3639	2.3790	2.3699	2.3692
006	1.9822	1.9837	1.9672	1.9745
007	1.7011	1.7010	1.6885	1.6925
008	1.4899	1.4889	1.4840	1.4810

Table 5 Cell parameters for $\{ZrS_2[M(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4R)]_x\}$

Guest	*x*	*c*/Å	Δ*c*/Å	Ref.
$[Cr(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$	0.25	36.0(2)*	6.17(7)	10(*a*)
$[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$	0.22	11.93(1)	6.10(1)	This work
$[W(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$	0.20	11.85(2)	6.02(2)	This work

* The *c* axis was tripled.

The EPR spectrum of a solid sample of **11** showed a signal at $g = 1.98$ (linewidth = 60 G) at room temperature. No hyperfine splitting due to molybdenum or hydrogen was observed. In contrast, the room-temperature solid-state EPR spectrum of the intercalate **12** showed no signal, however, on cooling to 26 K, a broad signal at $g = 1.95$ (linewidth = 210 G) appeared.

The magnetic susceptibility of the intercalate **11** was measured in the temperature range 6–125 K at 2 and 3 T using a superconducting quantum interference device (SQUID) magnetometer. The data were field independent. As shown in Fig. 2, the magnetic susceptibility of **11** can be fitted by the Curie–Weiss expression, $\chi_M = C/(T - \theta)$ with $C = 0.043$ emu K mol^{-1} and $\theta = -2.4$ K, yielding an effective moment $\mu_{eff} = 0.58\ \mu_B$. If we assume that all of the sandwich compound **10** converts to the corresponding cation in the formation of the intercalate **11** and only the guest is contributing to the susceptibility, then by using the spin-only formula and the observed stoichiometry, the expected value of μ_{eff} should be 0.80 μ_B. On this basis, we estimate the percentage of ionisation of **10** in the formation of **11** to be 53%.

The magnetic property of **12** was also studied in the temperature range 6–180 K at 1, 2 and 3 T. The data were field independent and could be fitted with the Curie–Weiss expression $[\chi_M = C/(T - \theta)]$ with $C = 0.049$ emu K mol^{-1} and $\theta = -5.2$ K. As shown in Fig. 3, the effective moment has a steady value of 0.061 μ_B at higher temperatures. The percentage of ionisation of **8** in the formation of intercalate **12** was estimated to be 65%. This value is higher than that of the molybdenum analogue, which suggests that the least tightly bound electron in $[W(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$ can be removed more readily than in $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$. This result is consistent with the electrochemical measurements.

In conclusion, we have developed convenient pathways to half-sandwich derivatives of the $W(\eta\text{-}C_7H_7)$ moiety. The reactions and structures proposed for the new compounds are shown in Scheme 1. The intercalation of $[M(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$ (M = Mo or W) into ZrS_2 has also been described.

Experimental

General.—All manipulations and reactions were performed using either standard Schlenk-line techniques under an atmosphere of dinitrogen or in an inert atmosphere dry box containing dinitrogen. Dinitrogen was purified by passage over a BTS catalyst and 5 Å molecular sieves. Solvents were pre-dried by standing over 5 Å molecular sieves and then distilled under an atmosphere of dinitrogen from potassium (tetrahydrofuran), sodium (toluene), calcium hydride (acetonitrile) or sodium–potassium alloy [light petroleum (b.p. 40–60 °C)]. Deuteriated solvents for NMR studies were stored in Young's ampoules and transferred by pipette in the dry box. Powdered ZrS_2 was prepared as described.[10b] The preparation of **1**, **2**, **4**, **5**[2h] and **10**[1f] have been described elsewhere.

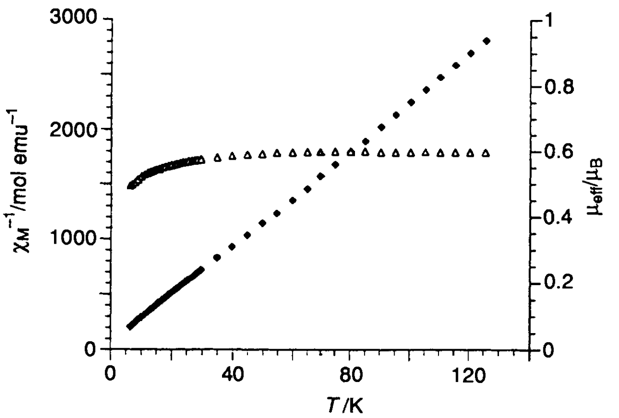


Fig. 2 Inverse molar magnetic susceptibility (◆) and effective moment (△) as a function of temperature for **11**

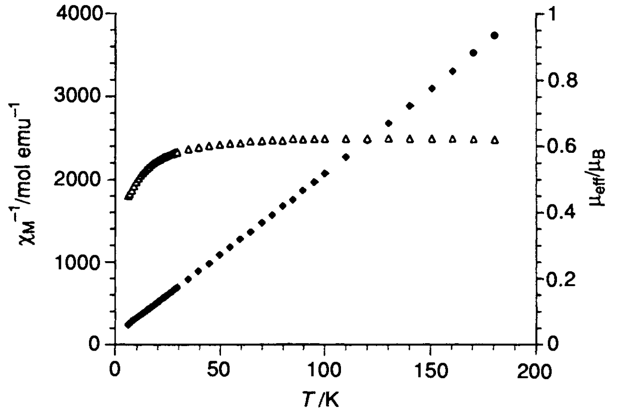


Fig. 3 Inverse molar magnetic susceptibility (◆) and effective moment (△) as a function of temperature for **12**

The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Brüker AM 300 spectrometer (^1H, 300; ^{13}C, 75.43; ^{31}P, 121.44 MHz). Spectra were referenced internally using the residue solvent (^1H) and solvent (^{13}C) resonances relative to tetramethylsilane ($\delta = 0$), or externally using trimethyl phosphate $[PO(OMe)_3]$ in D_2O (^{31}P). All chemical shifts are quoted in δ and coupling constants in Hertz (Hz). The EPR spectra were obtained using an X-band Varian spectrometer and an Oxford Instruments cryostat or a Brüker ESP 300 spectrometer. The field was calibrated using 1,1-diphenyl-2-picrylhydrazyl. The samples were prepared under an atmosphere of dinitrogen and recorded in quartz tubes fitted with a Young's Teflon stopcock. Infrared spectra were recorded on a Perkin Elmer 1510 FT interferometer or a Mattison Instruments Polaris Fourier transform spectrometer as KBr pellets. Electron impact (EI) mass spectra were obtained on an AEI MS 302 mass spectrometer and mass spectra (FAB) were measured by the SERC mass spectrometry service, University College, Swansea. Microanalyses were performed by the Microanalytical Department of the Inorganic Chemistry Laboratory.

Cyclic voltammograms were recorded in the three-electrode configuration with a platinum disc working electrode, a platinum gauze auxiliary electrode, and a silver wire pseudo-reference electrode in MeCN–0.1 mol dm^{-3} $[NBu_4][PF_6]$. The potentials were referenced to the ferrocenium–ferrocene couple at +0.355 V relative to the saturated calomel electrode (SCE), and the reversibility was judged by comparison of ΔE_p at various scan rates with that of the ferrocenium–ferrocene internal standard.[12]

Powder X-ray diffraction data were obtained using Cu-Kα radiation (40 kV, 30 mA) on a Philips PW 1710 powder diffractometer. Lattice parameters were obtained by least-squares analysis of the peak positions.

The magnetic susceptibility data were collected on a Cryogenics Consultants SCU 500 SQUID magnetometer in conjunction with a Lakeshore DRC-91C temperature controller. The susceptibilities were corrected for the intrinsic diamagnetism of the sample container and the diamagnetism of the electronic cores of the constituent atoms.

Syntheses.—$[W(\eta\text{-}C_7H_7)(dmpe)I]$ **6**. A mixture of $[W(\eta\text{-}C_7H_7)(MeCN)I_2]$ **2** (0.43 g, 0.75 mmol) and 1,2-bis(dimethylphosphino)ethane (1.2 cm^3 of a 0.1 g cm^{-3} solution in toluene, 0.80 mmol) in thf (50 cm^3) was cooled to −60 °C. Then Na/Hg [18 mg of Na (0.78 mmol) in *ca.* 0.5 cm^3 of Hg] was added with vigorous stirring. The mixture was allowed to warm to room temperature over 3 h, then it was stirred at room temperature for a further 15 h. After filtration, the residue was washed with thf (10 cm^3). The combined thf solution was evaporated to dryness and the residue was extracted with toluene (3 × 15 cm^3). Removal of the volatiles in the extract gave the product as a green solid. An analytically pure sample was obtained from sublimation [*ca.* 130 °C (10^{-4} mmHg)]. Yield, 91 mg (22%).

$[W(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ **7**. (*a*) A mixture of $[W(\eta\text{-}C_7H_7)(MeCN)I_2]$ **2** (0.11 g, 0.19 mmol) and $Na(C_5H_5)$ (0.07 g, 0.79 mmol) in thf (15 cm^3) was stirred at room temperature for 20 h. After removing the volatiles *in vacuo*, the residue was extracted with light petroleum (b.p. 40–60 °C) (2 × 20 cm^3). The extract was concentrated to *ca.* 15 cm^3 and then cooled to −80 °C to give the product as dark brown crystals. Yield, 26 mg (40%).

(*b*) To a solution of $[W(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **1** (1.3 g, 3.5 mmol) in thf (70 cm^3) was slowly added a solution of iodine (0.9 g, 3.5 mmol) in thf (70 cm^3). Precipitation occurred immediately and the resulting brown suspension was heated at 60 °C for 2 h. It was then transferred to a Schlenk vessel containing $Na(C_5H_5)$ (1.2 g, 13.6 mmol). The mixture was stirred at room temperature for 16 h. The volatiles were then removed *in vacuo* and the residue was extracted with light petroleum (b.p. 40–60 °C) (3 × 20 cm^3). The extract was concentrated to *ca.* 30 cm^3 then cooled to −80 °C to afford the product as dark brown microcrystals. Yield, 0.17 g (14%).

$[W(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$ **8**. (*a*) A mixture of $[W(\eta\text{-}C_7H_7)(MeCN)I_2]$ **2** (0.15 g, 0.26 mmol) and $Na(C_5H_4Me)$ (0.11 g, 1.08 mmol) in thf (20 cm^3) was stirred at room temperature for 20 h. After removing the volatiles *in vacuo*, the residue was extracted with light petroleum (b.p. 40–60 °C) (3 × 20 cm^3). The extract was concentrated to *ca.* 15 cm^3 and then cooled to −80 °C to give the product as dark brown crystals. Yield, 74 mg (80%).

(*b*) A mixture of $[W(\eta\text{-}C_7H_7)(PMe_3)Br_2]$ **4** (0.20 g, 0.39 mmol) and $Na(C_5H_4Me)$ (0.15 g, 1.47 mmol) in thf (30 cm^3) was stirred at room temperature for 16 h. The mixture was evaporated to dryness and then the residue was extracted with light petroleum (b.p. 40–60 °C) (3 × 20 cm^3). The extract was concentrated to *ca.* 15 cm^3 and then cooled to −80 °C to afford the product as dark brown microcrystals. Yield, 83 mg (60%).

(*c*) To a solution of $[W(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **1** (0.28 g, 0.76 mmol) in thf (30 cm^3) was slowly added a solution of iodine (0.19 g, 0.75 mmol) in thf (30 cm^3). The resulting brown suspension was heated at 60 °C for 2 h, then it was transferred to a Schlenk vessel containing $Na(C_5H_4Me)$ (0.17 g, 1.66 mmol). The mixture was stirred at room temperature for 16 h. The volatiles were then removed *in vacuo* and the residue was extracted with light petroleum (b.p. 40–60 °C) (2 × 20 cm^3). The extract was cooled to −80 °C to afford the desired product. Yield, 0.13 g (50%).

$[W(\eta\text{-}C_7H_7)(\eta\text{-}C_9H_7)]$ **9**. A mixture of $[W(\eta\text{-}C_7H_7)(MeCN)I_2]$ **2** (0.15 g, 0.26 mmol) and lithium indenide (0.10 g, 0.82 mmol) in thf (20 cm^3) was stirred at room temperature for 15 h. After removing the volatiles *in vacuo*, the residue was extracted with light petroleum (b.p. 40–60 °C) (3 × 15 cm^3) to give a purple solution which was filtered, concentrated to *ca.* 15 cm^3, and then cooled to −80 °C. The purple crystals formed were recrystallised from light petroleum (b.p. 40–60 °C). Yield, 26 mg (25%).

$\{ZrS_2[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]_{0.22}\}$ **11**. A mixture of $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$ **10** (0.20 g, 0.75 mmol) and powdered ZrS_2 (0.22 g, 1.42 mmol) in toluene (2 cm^3) was heated at 120 °C with stirring for 4 d. The mixture was allowed to settle then decanted. The residue was washed with toluene (4 × 10 cm^3) then dried *in vacuo*.

$\{ZrS_2[W(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]_{0.20}\}$ **12**. A mixture of $[W(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$ **8** (0.3 g, 0.85 mmol) and powdered ZrS_2 (0.3 g, 1.93 mmol) in toluene (3 cm^3) was heated at 120 °C with stirring for 5 d. The mixture was allowed to settle then decanted. The residue was washed with toluene (4 × 10 cm^3) then dried *in vacuo*.

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