Synthesis and Reactions of η-Cycloheptatrienyl Derivatives of Molybdenum *

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An improved route to [Mo(η-C_7H_7)(η-C_7H_9)] **2** has been found which involves the reduction of $MoCl_5$ with sodium amalgam in the presence of cycloheptatriene followed by thermolysis. Compound **2** can be oxidised with a half equivalent of iodine or tetrafluoroboric acid forming the corresponding cation [Mo(η-C_7H_7)(η-C_7H_9)]$^+$ **3**, which reacts with ethanol or an excess of iodine to yield the binuclear cations [(η-C_7H_7)Mo(μ-X)$_3$Mo(η-C_7H_7)]$^+$ (X = OEt **4** or I **5** respectively). Treatment of **2** with 1 equivalent of iodine, bromine or an excess of $PhICl_2$ in the presence of a weak co-ordinating solvent or σ-donor affords the 17-electron compounds [Mo(η-C_7H_7)LX_2] [L = tetrahydrofuran (thf), MeCN, PPh_3, PMe_3 or Et_2S; X = Cl, Br or I). Treatment of [Mo(η-C_7H_7)(MeCN)I_2] **11** with [NBu_4]I gives [NBu_4][Mo(η-C_7H_7)I_3] **18** and reduction of **11** with sodium amalgam in the presence of 1,2-bis(dimethylphosphino)ethane (dmpe), 1,2-bis(diphenylphosphino)ethane (dppe) or PMe_3 gives [Mo(η-C_7H_7)(dmpe)I] **19**, [Mo(η-C_7H_7)(dppe)I] **20** or [Mo(η-C_7H_7)(PMe_3)$_2$I] **13**, respectively. Compound **11** also reacts with Na(C_5H_4R) (R = H or Me) or lithium indenide to yield the mixed-sandwich compounds [Mo(η-C_7H_7)(η-C_5H_4R)] (R = H **21** or Me **22**) or [Mo(η-C_7H_7)(η-C_9H_7)] **23**. The crystal structures of [NBu_4][Mo(η-C_7H_7)I_3] **18** and [Mo(η-C_7H_7)(η-C_5H_4Me)] **22** have been determined. Compound **22** reacts with 1 equivalent of tetracyanoethene (tcne) to give the electron-transfer complex [Mo(η-C_7H_7)(η-C_5H_4Me)][tcne] **24** while compound **21** reacts with 1 equivalent of 7,7,8,8-tetracyanoquinodimethane (tcnq) to yield [Mo(η-C_7H_7)(η-C_5H_5)]$_2$[tcnq] **25**.

The chemistry of the η-cycloheptatrienyl–transition metal system, M(η-C_7H_7), has been relatively little studied compared with the M(η-C_6H_6) and M(η-C_5H_5) systems.[1] Recent studies have shown that, like the η-C_5H_5 group, the η-C_7H_7 group normally acts as a robust, non-labile ligand. However the latter differs markedly from the η-cyclopentadienyl system since it requires three electrons from the metal centre in the formation of the covalent metal–ligand bond rather than only the single electron required from the metal by the η-C_5H_5 group.[2a,3b] Also, the seven-electron donor η-C_7H_7 ring has a larger cone angle (θ = 154°) than the five-electron donor η-C_5H_5 ring (θ = 110°).[2a] Therefore, the chemistry of the η-C_7H_7–metal derivatives should be extensive but significantly different from that of η-C_5H_5–metal compounds.

A substantial barrier to the development of η-cycloheptatrienyl–transition metal chemistry has been the difficulty of finding convenient synthetic routes. However, considerable progress has been made in the development of η-cycloheptatrienyl chemistry of Group 4 and 5 metals in our laboratory.[2,3] Here we report new and substantially improved routes to η-cycloheptatrienyl–molybdenum derivatives. Related η-cycloheptatrienyl–tungsten chemistry is described in the following paper.[4] Part of this work has been communicated.[5]

Results and Discussion

A suspension of $MoCl_5$ in tetrahydrofuran (thf) was treated with an excess of cycloheptatriene at −80 °C giving a greenish-yellow suspension. Five equivalents of sodium amalgam were then added with stirring and the mixture was allowed to warm to room temperature. During the course of the reaction, the colour of the mixture changed gradually from greenish yellow to brown, and then to deep green. After removing the volatiles and then extracting the residue with light petroleum (b.p. 40–60 °C), a deep green solution was obtained from which green microcrystals were separated. The ^1H NMR spectrum of these microcrystals showed that they were a mixture of [Mo(η-C_7H_8)$_2$] **1** and [Mo(η-C_7H_7)(η-C_7H_9)] **2** in 1.7:1 ratio (Scheme 1). Previously, these compounds were available only by a metal vapour synthesis route.[6]

It has been reported that the compound [Mo(η-C_7H_8)$_2$] **1** is thermally unstable and isomerises quantitatively on heating to give the compound [Mo(η-C_7H_7)(η-C_7H_9)] **2**.[6a] Thus it is reasonable to suggest that compound **1** is initially formed in the above reaction, but a portion of it isomerises to **2**. In fact, heating the green microcrystalline product at 70 °C for 2 h gave pure **2** as dark red microcrystals. The above reduction reaction can be performed in a large scale. Typically, 10.0 g of $MoCl_5$ gave 4.0 g of [Mo(η-C_7H_7)(η-C_7H_9)] **2** (39% yield).

Reduction of [$MoCl_4$(thf)$_2$][7] in thf at −60 °C with 4 equivalents of sodium amalgam in the presence of cycloheptatriene produced a mixture of [Mo(η-C_7H_8)$_2$] **1** and [Mo(η-C_7H_7)(η-C_7H_9)] **2** in 3:2 ratio in 46% yield.

Treatment of compound **2** in toluene or thf with a half equivalent of iodine gave a light orange precipitate which was insoluble in all non-polar solvents. The light orange solid was dissolved in deionised water and rapid addition of [NH_4][PF_6] afforded lilac crystals of [Mo(η-C_7H_7)(η-C_7H_9)][PF_6] **3a** which could be recrystallised from acetone–light petroleum (b.p. 40–60 °C). The analytical and spectroscopic data for **3a** and for all other new compounds described below are given in Table 1 and are not discussed further unless the interpretation is not straightforward.

In an attempt to protonate compound **2** with $HBF_4{\cdot}Et_2O$, the unexpected product [Mo(η-C_7H_7)(η-C_7H_9)][BF_4] **3b** was isolated in 62% yield. This compound has been prepared

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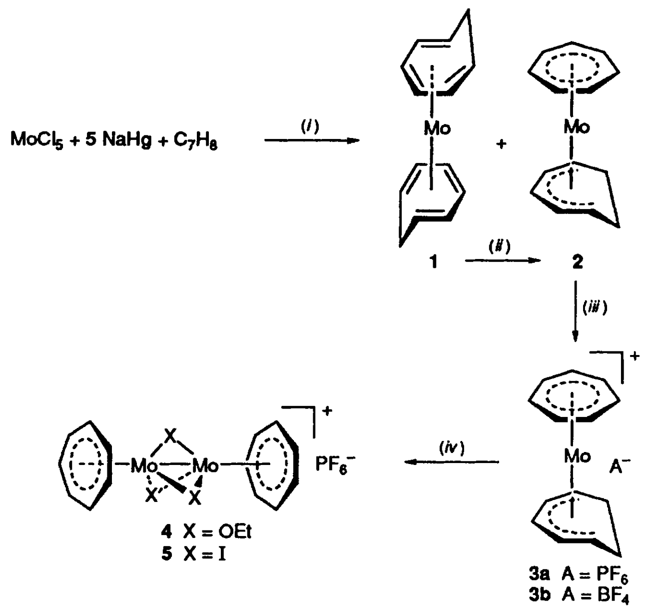
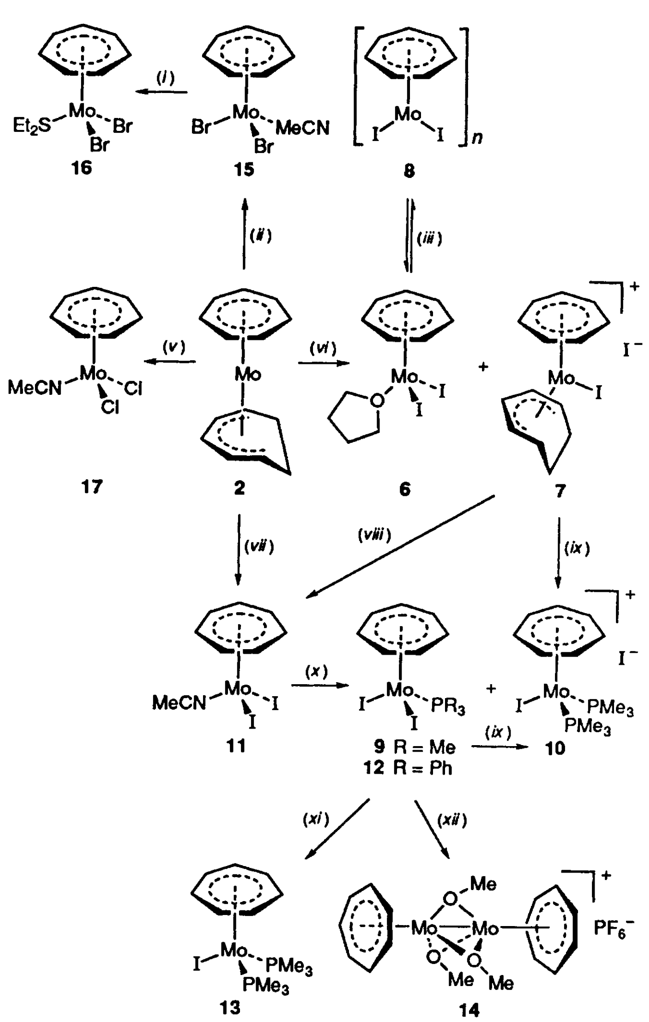
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

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}.



Scheme 1 Reagents and conditions: (*i*) gradual warming from -78 °C over 3 h in thf then at room temperature (r.t.) for 2 h, 59%, **1**:**2** = 1.7:1; (*ii*) at 70 °C for 2 h, quantitative; (*iii*) for A = PF_6, I_2 in toluene, then $[NH_4][PF_6]$ in water, 42%; for A = BF_4, HBF_4 in Et_2O, 62%; (*iv*) for X = OEt, EtOH at 50 °C for 10 min, 52%; for X = I, I_2 in thf, 96%



Scheme 2 Reagents and conditions: (*i*) Et_2S in Et_2O at 40 °C for 3 h, 78%; (*ii*) Br_2 in thf, then MeCN, 54%; (*iii*) at 35 °C for 10 min, 98%; (*iv*) thf; (*v*) $PhICl_2$ in toluene at r.t. for 1 h, then MeCN, 54%; (*vi*) I_2 in thf at 50 °C for 30 min, 65% **6** and 30% **7**; (*vii*) I_2 in MeCN at 50 °C for 1 h, 71%; (*viii*) from **6**, MeCN at 50 °C for 10 min, quantitative; from **7**, MeCN at 50 °C for 40 min, 91%; (*ix*) PMe_3; (*x*) for R = Me, PMe_3 in thf at r.t. for 3 h, 79%; for R = Ph, PPh_3 in acetone at 60 °C for 4 h, 85%; (*xi*) $LiAlH_4$ in toluene at r.t. for 15 h, 30%; (*xii*) NaOMe and $[NH_4][PF_6]$ in MeOH at r.t. for 10 min, 55%

previously by oxidation of **2** with $AgBF_4$.[6a] It appears therefore that **2** has a strong tendency to behave as a reducing agent rather than a base. The paramagnetic 17-electron cation of **3a** and **3b** is rapidly decomposed by air in solution and in the solid state.

When compound **3a** was dissolved in ethanol, the initial lilac solution rapidly turned green. After chromatographic separation, green crystals of $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}OEt)_3Mo(\eta\text{-}C_7H_7)][PF_6]$ **4** were obtained.

Treatment of **3a** with an excess of iodine in thf gave brick red microcrystalline $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}I)_3Mo(\eta\text{-}C_7H_7)][PF_6]$ **5** in excellent yield. These binuclear compounds have been described previously, but were only available from lengthy procedures.[8] A series of thiolato-bridged η-cycloheptatrienyl molybdenum complexes $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}SR)_3Mo(\eta\text{-}C_7H_7)][BF_4]$ (R = Et, Pr, Bu, Ph or CH_2Ph) has also been prepared by treating **3b** with thiols RSH.[9] These reactions show the ease with which nucleophiles react with $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]^+$ to displace the η-C_7H_9 group. Indeed solutions of this compound in halogenocarbon solvents are unstable and decompose slowly.

Treatment of compound **2** with 1 equivalent of iodine in thf yielded a red-purple precipitate in a red-green dichroic solution. The precipitate was separated. Concentration of the red-green solution gave crimson crystals of $[Mo(\eta\text{-}C_7H_7)(thf)I_2]$ **6**, a new complex in the previously unreported class of $[Mo(\eta\text{-}C_7H_7)LX_2]$ compounds. This compound, although air-stable, is thermally unstable, losing thf even at room temperature. It may be stored without decomposition at -20 °C but repeated microanalysis gave a stoichiometry corresponding to $[Mo(\eta\text{-}C_7H_7)(thf)_{0.33}I_2]$. The electron impact (EI) mass spectrum showed an ion at *m*/*z* 759 which corresponds to the dimeric species $[Mo_2(\eta\text{-}C_7H_7)_2I_3]^+$ formed by recombination reactions in the spectrometer, and peaks at *m*/*z* 443 and 316 which are attributed to the fragments $[Mo(\eta\text{-}C_7H_7)I_2]^+$ and $[Mo(\eta\text{-}C_7H_7)I]^+$ respectively. The compound **6** was unambiguously characterised by X-ray crystal structure determination and these results have been reported elsewhere.[10] As noted above, the other product of this reaction was a red-purple crystalline insoluble material **7**. The microanalysis was consistent with the stoichiometry $Mo(C_7H_7)(C_7H_9)I_2$ and the field desorption (FD) mass spectrum showed a peak at *m*/*z* 443 which could be assigned to $[Mo(\eta\text{-}C_7H_7)I_2]^+$. The IR spectrum showed a very strong band at 795 cm^{-1} which is characteristic of a η-C_7H_7 group.[11] In view of the remarkable similarity in the IR spectrum of **7** with that of $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]I$, the red-purple compound is tentatively assigned as $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)I]I$ **7** (Scheme 2).

Heating compound **6** under mild conditions caused a rapid darkening of the crimson crystals giving a black solid **8** for which the elemental analyses for C, H and I corresponded to the stoichiometry $Mo(\eta\text{-}C_7H_7)I_2$. The IR spectrum showed an intense band at 808 cm^{-1} assignable to a η-C_7H_7 ligand. Dissolution of **8** in thf was found to slowly regenerate **6** quantitatively. A polymeric structure is thus proposed for the black solid **8**.

When the compounds **6** or **7** were treated with an excess of PMe_3 in thf, a mixture of 17-electron compounds $[Mo(\eta\text{-}C_7H_7)(PMe_3)I_2]$ **9** and $[Mo(\eta\text{-}C_7H_7)(PMe_3)_2I]I$ **10** was obtained. Compound **9** can be converted to compound **10** by further reaction with PMe_3, thus **9** is believed to be the initially formed product of this reaction.

Both compounds **6** and **8** dissolved readily in MeCN giving a red-green dichroic solution from which purple crystals of $[Mo(\eta\text{-}C_7H_7)(MeCN)I_2]$ **11** were isolated. Heating compound

Table 1 Analytical and spectroscopic data

		Analysis[a] (%)			
Compound	Colour	C	H	Other	Spectroscopic data[b]
3a	Lilac	39.4 (39.5)	3.8 (3.8)		EPR (CD_2Cl_2): g_{iso} = 2.00, A^{Mo} = 42 G, linewidth = 19 G Mass spectrum (FD): m/z 282 (M^+)
6	Crimson	21.5 (21.5)	1.9 (2.1)[c]		EPR (thf): g_{iso} = 2.01, A^{Mo} = 45 G, linewidth = 21 G Mass spectrum (EI): m/z 759 $\{[Mo_2(\eta\text{-}C_7H_7)_2I_3]^+\}$, 443 ($M$ − thf), 316 (M − thf − I)
7	Red-purple	31.6 (31.5)	3.0 (3.0)	I 44.2 (47.3)	Mass spectrum (FD): m/z 443 $\{[Mo(\eta\text{-}C_7H_7)I_2]^+\}$
8	Black	19.6 (19.1)	1.6 (1.6)	I 55.6 (57.6)	IR: ν(η-C_7H_7) 808vs
9	Red	23.2 (23.2)	3.1 (3.1)	I 49.7 (49.1)	EPR (thf): g_{iso} = 2.06, linewidth = 49 G Mass spectrum (EI): m/z 519 (M^+), 443 (M − PMe_3) IR: ν(P–C) 957vs
10	Orange	25.8 (26.3)	4.4 (4.3)	I 42.5 (42.8)	EPR[d]: $g_{\parallel}$ = 1.99, $g_{\perp}$ = 2.05, linewidth = 50 G
11	Purple	22.5 (22.4)	2.1 (2.1)	N 2.9 (2.9) I 53.1 (52.7)	EPR (thf): g_{iso} = 2.02, A^{Mo} = 46 G, linewidth = 20 G IR: ν(C≡N) 2270m
12	Dark grey	43.1 (42.7)	3.1 (3.2)	Mo 13.2 (13.6) I 36.4 (36.1)	Mass spectrum (EI): m/z 443 (M − PPh_3), 316 (M − PPh_3 − I)
13	Green	33.5 (33.5)	5.5 (5.4)	I 29.0 (27.2)	^1H NMR: 4.74 [t, J(H–P) 2.2, 7 H, η-C_7H_7], 1.05 [vt, J(H–P) 3.3, 18 H, PMe_3] ^{13}C-$\{^1H\}$ NMR: 86.6 (s, η-C_7H_7), 20.8 [vt, J(C–P) 12.1, PMe_3] ^{31}P-$\{^1H\}$ NMR: −24.5 (s, PMe_3) IR: ν(P–C) 941vs, 951(sh)
15	Orange	27.7 (27.9)	2.4 (2.6)	N 3.6 (3.6) Br 41.9 (41.2)	EPR (MeCN): g_{iso} = 2.00, A^{Mo} = 47 G, linewidth = 18 G IR: ν(C≡N) 2273m
16	Orange-yellow	30.2 (30.2)	3.9 (3.9)	Mo 22.1 (21.9) Br 36.4 (36.6)	Mass spectrum (EI): m/z 615 $\{[Mo_2(\eta\text{-}C_7H_7)_2Br_3]^+\}$
17	Orange	36.0 (36.1)	3.3 (3.4)	N 4.7 (4.7) Cl 23.6 (23.7)	EPR (CD_3CN): g_{iso} = 1.97, A^{Mo} = 45 G, linewidth = 14 G IR: ν(C≡N) 2287m
18	Purple	34.1 (34.1)	5.4 (5.4)	N 1.7 (1.7) I 49.1 (47.8)	EPR (thf): g_{iso} = 2.04, A^{Mo} = 46 G, linewidth = 22 G
19	Green	34.0 (33.6)	5.1 (5.0)	I 28.4 (27.3)	^1H NMR: 4.81 [t, J(H–P) 2.2, 7 H, η-C_7H_7], 1.61 [d, J(H–P) 7.9, 6 H, Me_u or Me_d], 1.19–1.34 (m, 2 H, H_u or H_d), 0.78 [d, J(H–P) 7.1, 6 H, Me_u or Me_d], 0.53–0.75 (m, 2 H, H_u or H_d) ^{13}C-$\{^1H\}$ NMR: 86.0 (s, η-C_7H_7), 28.4 [vt, J(C–P) 20.6, CH_2], 21.7 [vt, J(C–P) 14.6, Me_u or Me_d], 15.6 [vt, J(C–P) 9.8, Me_u or Me_d] ^{31}P-$\{^1H\}$ NMR: 19.9 (s, dmpe) Mass spectrum (EI): m/z 466 (M^+), 339 (M − I)
20	Green				^1H NMR: 7.88 [t, J(H–H) 8.3, 4 H, Ph], 7.00–7.24 (m, 16 H, Ph), 4.91 [t, J(H–P) 1.9, 7 H, η-C_7H_7], 2.40–2.62 (m, 2 H, H_u or H_d), 1.73–2.00 (m, 2 H, H_u or H_d) ^{13}C-$\{^1H\}$ NMR: 141.4 [d, J(C–P) 27.0, Ph], 127.6–134.8 (Ph), 87.3 (s, η-C_7H_7), 27.2 [vt, J(C–P) 19.4, CH_2] ^{31}P-$\{^1H\}$ NMR: 53.5 (s, dppe)
22	Green				^1H NMR: 4.90 (s, 7 H, η-C_7H_7), 4.80 [t, J(H–H) 1.8, 2 H, H_a or H_b], 4.66 [t, J(H–H) 1.8, 2 H, H_a or H_b], 1.75 (s, 3 H, Me) ^{13}C-$\{^1H\}$ NMR: 101.7 (C_i), 86.6 (C_a or C_b), 83.7 (C_a or C_b), 80.8 (η-C_7H_7), 14.6 (Me) Mass spectrum (EI): m/z 268 (M^+)
23	Purple	62.6 (63.6)	4.6 (4.7)		^1H NMR:[e] 7.38 [dd, J(H–H) 3.0, 6.4, 2 H, H_o or H_m], 6.78 [dd, J(H–H) 3.0, 6.4, 2 H, H_o or H_m], 5.50 [d, J(H–H) 2.6, 2 H, H_a], 5.38 [t, J(H–H) 2.6, 1 H, H_b], 4.75 (s, 7 H, η-C_7H_7) ^{13}C-$\{^1H\}$ NMR:[e] 127.8 (C_o or C_m), 121.4 (C_o or C_m), 103.3 (C_i), 91.2 (C_b), 82.7 (η-C_7H_7), 78.6 (C_a) Mass spectrum (EI): m/z 304 (M^+)
24	Purple	57.7 (57.9)	3.3 (3.6)	N 13.8 (14.2)	EPR (solid): g_{iso} = 1.995, linewidth = 50 G IR: ν(C≡N) 2160s, 2171s, 2192m
25	Dark green	57.3 (61.0)	3.6 (4.0)	N 7.5 (7.9)	EPR (CH_2Cl_2): g_{iso} = 1.982, linewidth = 25 G IR: ν(C≡N) 2104s, 2150s

[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, vt = virtual triplet), coupling constant (Hz), relative intensity, and assignment; for virtual triplet, J is the apparent coupling constant. For labelling of atoms see the Schemes. The EPR spectra were recorded at room temperature. 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] Calculated for $[Mo(\eta\text{-}C_7H_7)(thf)_{0.33}I_2]$. [d] In dimethyl sulfoxide. [e] In [$^2H_6$]acetone.

7 in MeCN also led to the formation of **11**. A further and improved route to **11** is the oxidation of $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **2** with iodine in MeCN from which compound **11** can be isolated in 71% yield. The compound **11** is more thermally robust than **6** and is stable indefinitely at 50 °C and is air- and water-stable in solid and solution. The compounds **9** and **11** exhibit interesting antiferromagnetic behaviour and their magnetic properties, together with the crystal structure of **11**, have been described elsewhere.[12]

The MeCN ligand in **11** is labile and, for example, can be displaced by PMe_3 at room temperature giving compound **9** in good yield. However, the reaction between **11** and PPh_3

requires more forcing conditions. Thus, **11** was treated with a large excess of PPh_3 in acetone at 60 °C yielding [Mo(η-C_7H_7)(PPh_3)I_2] **12**. Interestingly this reaction did not produce the disubstituted product [Mo(η-C_7H_7)(PPh_3)$_2$I]I despite the large excess of PPh_3 employed in the reaction.

In an attempt to prepare hydride complexes such as [Mo(η-C_7H_7)(PMe_3)H_3], compound **9** was treated with an excess of $LiAlH_4$ in toluene. However the unexpected product [Mo(η-C_7H_7)(PMe_3)$_2$I] **13** was obtained, in 30% yield. The reaction of **9** in a methanol solution of NaOMe in the presence of [NH_4][PF_6] gave green crystals of the known complex [(η-C_7H_7)Mo(μ-OMe)$_3$Mo(η-C_7H_7)][PF_6] **14**.[8a]

Oxidation of [Mo(η-C_7H_7)(η-C_7H_9)] **2** with 1 equivalent of bromine in thf followed by addition of MeCN gave the compound [Mo(η-C_7H_7)(MeCN)Br_2] **15**. A suspension of **15** was treated with diethyl sulfide in diethyl ether at 40 °C and the suspension changed colour from a mid orange to a lighter shade. A freshly prepared sample, analysed immediately after preparation was found to give excellent C, H and Br analyses for the formulation [Mo(η-C_7H_7)(Et_2S)Br_2] **16**. Samples of **16** were unstable and slowly thermally decomposed by evolving Et_2S at room temperature.

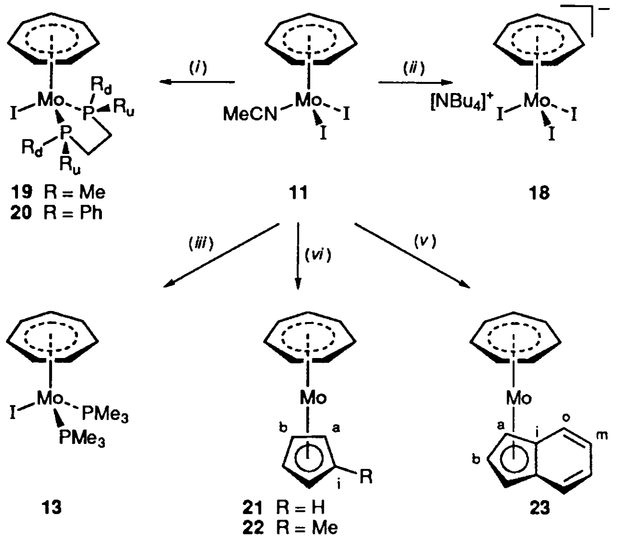
The dichloro analogue of **11** and **15**, namely [Mo(η-C_7H_7)(MeCN)Cl_2] **17**, was prepared by treating compound **2** with an excess of $PhICl_2$ in toluene; the resulting brown precipitate was recrystallised from MeCN giving orange crystals of **17** in 54% yield.

The magnetic susceptibility of compound **17** was measured in the temperature range 6–290 K at 1 T using a superconducting quantum interference device (SQUID) magnetometer. In contrast to its analogues **9** and **11** the compound **17** did not show antiferromagnetic interactions.[12] The susceptibility data are displayed in Fig. 1. It can be seen that the susceptibility rises with decreasing temperature and the data can be fitted by the Curie–Weiss expression [$\chi_M = C/(T - \theta)$] with a Curie constant C = 0.30 emu K mol^{-1} and a Weiss constant $\theta = -0.5$ K, yielding an effective moment (μ_{eff} = 1.55 μ_B) which is consistent with the existence of one $S = \frac{1}{2}$ spin. The effective moment is lower than the value of 1.71 μ_B calculated on the basis of the spin-only formula: $\mu_{eff}{}^2 = g^2[S(S + 1)]$ where g is taken from the EPR data.

The compound [Mo(η-C_7H_7)(MeCN)I_2] **11** is an excellent precursor to other η-cycloheptatrienyl molybdenum derivatives. As mentioned, the MeCN ligand is labile and can be displaced by σ donors, such as PMe_3 and PPh_3. It can also be displaced by weak anionic nucleophiles, such as iodide ion. Thus treatment of the compound **11** with 1 equivalent of tetrabutylammonium iodide in acetone at room temperature gave a purple solid which was soluble in thf. Slow diffusion of diethyl ether into the thf solution gave large purple crystals of [NBu_4][Mo(η-C_7H_7)I_3] **18** (Scheme 3).

These crystals were suitable for structure determination by X-ray diffraction. Diffraction analysis revealed that crystals of **18** consist of discrete cations and anions; there is no significant intermolecular non-bonded contacts. Both the cation and anion have crystallographically imposed mirror symmetry. Perspective views of the anion [Mo(η-C_7H_7)I_3]$^-$ with atom numbering scheme are given in Fig. 2, selected bond lengths and angles are shown in Table 2, and atomic coordinates for non-hydrogen atoms are given in Table 3.

The anion [Mo(η-C_7H_7)I_3]$^-$ has a typical three-legged piano stool structure with the η-C_7H_7 ligand bonded symmetrically to the metal. The Mo–C distances range from 2.21(1)–2.236(8) Å (mean 2.222 Å), which are comparable with



Scheme 3 Reagents and conditions: (*i*) for R = Me, Na/Hg and dmpe in toluene, gradual warming from −60 °C over 3 h then at r.t. for 20 h, 61%; for R = Ph, Na/Hg and dppe in toluene, gradual warming from −60 °C over 3 h then at r.t. for 14 h, 65%; (*ii*) [NBu_4]I in acetone at r.t. for 12 h, 77%; (*iii*) Na/Hg and PMe_3 in toluene, gradual warming from −60 °C over 3 h then at r.t. for 15 h, 82%; (*iv*) for R = H, Na(C_5H_5) in thf at r.t. for 16 h, 65%; for R = Me, Na(C_5H_4Me) in thf at r.t. for 15 h, 85%; (*v*) lithium indenide in thf at r.t. for 12 h, 64%

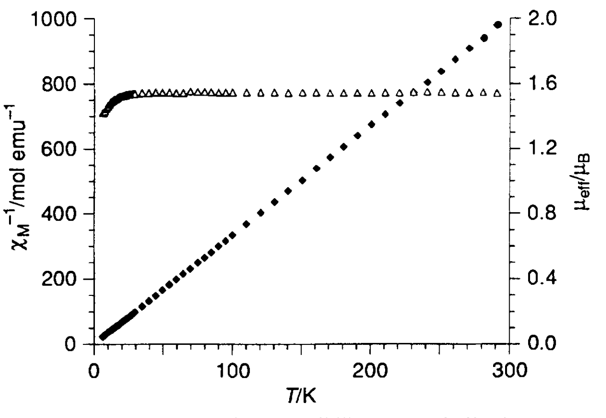


Fig. 1 Inverse molar magnetic susceptibility (◆) and effective moment (△) as a function of temperature for complex **17**

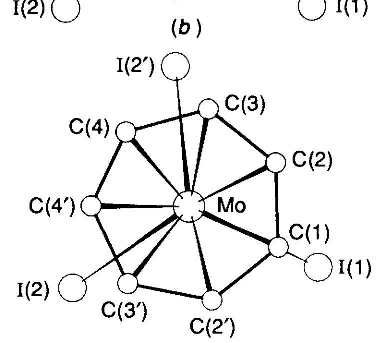


Fig. 2 The structure and labelling scheme for the [Mo(η-C_7H_7)I_3]$^-$ anion (the primed atoms are generated from the asymmetric unit using the mirror plane). (*a*) A general view; (*b*) a projection on the C_7-ring plane

Table 2 Selected bond lengths (Å) and angles (°) for $[NBu_4][Mo(\eta\text{-}C_7H_7)I_3]$ **18**

Mo–I(1)	2.8386(9)	C(1)–C(2)	1.36(2)
Mo–I(2)	2.8394(7)	C(2)–C(3)	1.34(2)
Mo–C(1)	2.22(1)	C(3)–C(4)	1.34(2)
Mo–C(2)	2.21(1)	C(4)–C(4′)	1.32(2)
Mo–C(3)	2.22(1)	Mo–C_7(centroid)	1.598
Mo–C(4)	2.236(8)	Mo–C_7(plane)	1.597
I(1)–Mo–I(2)	87.47(2)	C_7(centroid)–Mo–I(1)	127.9
I(2)–Mo–I(2′)	86.33(3)	C_7(centroid)–Mo–I(2)	127.0

Table 3 Fractional atomic coordinates for $[NBu_4][Mo(\eta\text{-}C_7H_7)I_3]$ **18***

Atom*	*X/a*	*Y/b*	*Z/c*
Mo	0.073 21(4)	0.2500	−0.044 70(5)
I(1)	0.018 29(4)	0.2500	0.123 28(4)
I(2)	0.184 59(3)	0.079 09(4)	0.005 71(3)
N	0.244 8(5)	0.2500	0.291 6(5)
C(1)	−0.053 5(8)	0.2500	−0.074(1)
C(2)	−0.023 8(9)	0.356(2)	−0.095 6(9)
C(3)	0.040(1)	0.118(1)	−0.140 7(8)
C(4)	0.089 9(6)	0.308(1)	−0.177 5(5)
C(5)	0.198 8(4)	0.144 6(7)	0.261 0(5)
C(6)	0.234 3(6)	0.026 9(8)	0.277 3(6)
C(7)	0.175 4(9)	−0.069(1)	0.256 6(9)
C(8)	0.109(1)	−0.075(1)	0.315(1)
C(9)	0.326 6(6)	0.2500	0.255 7(8)
C(10)	0.333 2(8)	0.2500	0.162 1(9)
C(11)	0.415(2)	0.2500	0.132(1)
C(12)	0.432(2)	0.2500	0.057(4)
C(13)	0.255 2(7)	0.2500	0.386 5(6)
C(14)	0.184 2(9)	0.2500	0.436 3(9)
C(15)	0.200(1)	0.2500	0.527 3(9)
C(16)	0.141(2)	0.2500	0.584(2)

* Atoms N and C(5)–C(16) correspond to the cation $[NBu_4]^+$

those in the 17-electron compounds $[Mo(\eta\text{-}C_7H_7)(thf)I_2]$ [2.23(2)–2.29(2) Å, mean 2.25 Å],[10] $[Mo(\eta\text{-}C_7H_7)(MeCN)I_2]$ [2.258(5)–2.280(5), mean 2.268 Å][12] and $[Mo(\eta\text{-}C_7H_7)(acac)(H_2O)]^+$ (acac = acetylacetonate) [2.248(6)–2.291(8), mean 2.265 Å][13] and they are, on average, shorter than the corresponding values observed in the 18-electron compounds $[Mo(\eta\text{-}C_7H_7)(CO)_2X]$ (X = Cl, mean 2.307 Å; X = Br, mean 2.321 Å)[14] and $[Mo(\eta\text{-}C_7H_7)(CO)_2(\sigma\text{-}C_6F_5)]$ (mean 2.318 Å).[15] However, the Mo–I bond lengths of 2.8386(9) and 2.8394(7) Å are significantly longer than those in $[Mo(\eta\text{-}C_7H_7)(thf)I_2]$ [2.800(2)–2.829(2) Å][10] and $[Mo(\eta\text{-}C_7H_7)(MeCN)I_2]$ [2.8003(4) and 2.8210(4) Å].[12]

The paramagnetic nature of compound **18** was determined by magnetic susceptibility measurements. The data were collected in the temperature range 6–180 K at 1 and 3 T. Both sets of data could be fitted with the Curie–Weiss expression $[\chi_M = C/(T - \theta)]$ with a Curie constant $C = 0.31$ emu K mol^{-1} and a Weiss constant $\theta = -1.2$ K. The effective magnetic moment of 1.57 μ_B corresponds to one unpaired electron per formula unit.

Treatment of $[Mo(\eta\text{-}C_7H_7)(MeCN)I_2]$ **11** with 1 equivalent of sodium amalgam in the presence of 1 equivalent of $Me_2PCH_2CH_2PMe_2$ (dmpe) gave diamagnetic $[Mo(\eta\text{-}C_7H_7)(dmpe)I]$ **19** as a green solid. This air-sensitive compound could be purified by sublimation. The ^1H NMR spectrum of **19** showed a triplet at δ 4.81 with coupling constant ^3J(H–P) 2.2 Hz assignable to the $\eta\text{-}C_7H_7$ protons, two doublets at δ 1.61 and 0.78 assignable to two sets of methyl groups, 'up' and 'down', and two multiplets at δ 1.19–1.34 and δ 0.53–0.75 assignable to two sets of methylene protons. These data are markedly different from those of the complexes $[M(\eta\text{-}C_7H_7)(dmpe)Cl]$ (M = Ti[2a] or Zr[2c]). Firstly, the coupling between the ring protons and the diphosphine was not observed for M = Zr, and only barely resolved for M = Ti. Secondly, for both of these compounds, the ^1H NMR signals for the dmpe ligand were very broad at room temperature. This was explained by a reversible dissociation of a M–P bond. The well resolved triplet for the ring protons and well separated doublets for the methyl groups in the spectrum of **19** clearly indicate that a dissociative process is less significant in this complex. This may suggest that the Mo–P bond in **19** is stronger than the Ti–P and Zr–P bonds in related complexes.

Reduction of **11** with 1 equivalent of sodium amalgam in the presence of 1 equivalent of $Ph_2PCH_2CH_2PPh_2$ (dppe) gave the previously described diamagnetic $[Mo(\eta\text{-}C_7H_7)(dppe)I]$ **20** in 65% yield. The ^1H NMR spectrum of **20** showed a well resolved triplet at δ 4.91 with coupling constant ^3J(H–P) 1.9 Hz which was attributed to the $\eta\text{-}C_7H_7$ ligand. This signal was not observed in the spectrum reported previously.[16]

The reaction of **11** with 1 equivalent of sodium amalgam in the presence of 2 equivalents of PMe_3 in toluene provides an improved route to $[Mo(\eta\text{-}C_7H_7)(PMe_3)_2I]$ **13** and this air-sensitive compound was isolated as green crystals in 82% yield.

Treatment of compound **11** with an excess of sodium cyclopentadienide in thf gave the known[11,17] mixed-sandwich compound $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ **21** in 65% yield. This compound was prepared previously from $MoCl_5$[11] or $[MoCl_3(thf)_3]$[17] in low yield. Treatment of **11** with an excess of sodium methylcyclopentadienide in thf gave a good yield of the new compound $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$ **22**. This compound is extremely air-sensitive and as a result, satisfactory microanalytical data could not be obtained. It has been characterised, however, by NMR spectroscopy and an X-ray crystal structure determination.

The molecular structure and atom labelling scheme for **22** are shown in Fig. 3, the selected bond lengths and angles are given in Table 4, and the atomic coordinates in Table 5. The molybdenum is sandwiched between the five- and seven-membered rings, which are both planar within the experimental error. The carbon C(6) bends out of the best C_5 plane by 4.01° away from the Mo atom. The two rings are essentially parallel and the angle subtended at molybdenum by the two ring centroids is 179.72°. As shown in Fig. 3(*b*), the arrangement of the two rings of **22** deviates from the ideally eclipsed conformation which is found for $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ (M = Ti[18] or V[19]).

The reaction between compound **11** and an excess of lithium indenide in thf resulted in the formation of a purple suspension from which purple crystals of $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_9H_7)]$ **23** were isolated. The ^1H NMR spectrum of the purple crystals in $[^2H_6]$benzene showed a very broad signal at *ca.* δ 5 for the C_5 and C_7 ring protons which may be due to the presence of paramagnetic impurities. Recrystallisation of the crude product twice from light petroleum (b.p. 40–60 °C) gave a well resolved ^1H NMR spectrum in $[^2H_6]$acetone.

Sandwich compounds almost invariably undergo electron-transfer reactions,[20] hence it is not unexpected that compounds **21**–**23** were found to be redox active. Cyclic voltammetric studies showed that **21**–**23** undergo one fully reversible oxidation. The data are listed in Table 6 which also includes the half-wave potentials of related sandwich compounds for comparison. 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.[24] Chemical oxidation of **21** with iodine to give the corresponding cation has been reported previously.[11]

There has been considerable interest in electron-transfer complexes C^+A^-, where C is a reducing sandwich compound containing $\eta\text{-}C_5H_5$ and/or η-arene ligands and A is a polycyano electron acceptor, since they can exhibit interesting magnetic and electrical properties.[25] The compounds **21** and **22** were available readily and are electron rich, thus we have explored their corresponding electron-transfer complexes.

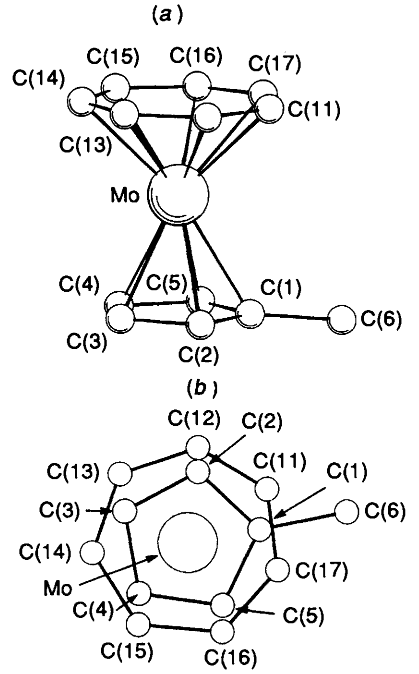


Fig. 3 Molecular structure of [Mo(η-C_7H_7)(η-C_5H_4Me)] **22**. (*a*) A general view; (*b*) a projection of the molecule perpendicular to the molecular axis

Table 4 Selected bond lengths (Å) and angles (°) for [Mo(η-C_7H_7)(η-C_5H_4Me)] **22**

Mo–C(1)	2.334(4)	C(1)–C(2)	1.417(7)
Mo–C(2)	2.312(5)	C(1)–C(5)	1.409(7)
Mo–C(3)	2.306(5)	C(1)–C(6)	1.497(7)
Mo–C(4)	2.304(5)	C(2)–C(3)	1.393(8)
Mo–C(5)	2.317(5)	C(3)–C(4)	1.393(8)
Mo–C(11)	2.255(5)	C(4)–C(5)	1.417(7)
Mo–C(12)	2.246(5)	C(11)–C(12)	1.357(9)
Mo–C(13)	2.269(5)	C(11)–C(17)	1.36(1)
Mo–C(14)	2.247(5)	C(12)–C(13)	1.381(9)
Mo–C(15)	2.247(5)	C(13)–C(14)	1.391(9)
Mo–C(16)	2.243(6)	C(14)–C(15)	1.42(1)
Mo–C(17)	2.241(6)	C(15)–C(16)	1.42(1)
Mo–C_5(centroid)	1.982	C(16)–C(17)	1.39(1)
Mo–C_7(centroid)	1.583		
C_5(centroid)–Mo–C_7(centroid)	179.72		
C_5(centroid)–C(1)–C(6)	85.99		

Table 5 Fractional atomic coordinates for [Mo(η-C_7H_7)(η-C_5H_4Me)] **22**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo	0.773 78(3)	0.013 11(4)	0.047 39(3)
C(1)	0.703 5(4)	−0.114 5(6)	−0.150 2(4)
C(2)	0.823 7(4)	−0.083 5(7)	−0.114 0(5)
C(3)	0.885 0(5)	−0.176 9(7)	−0.006 7(5)
C(4)	0.805 9(5)	−0.266 3(6)	0.027 0(5)
C(5)	0.693 3(5)	−0.228 4(6)	−0.062 0(5)
C(6)	0.608 2(6)	−0.050(1)	−0.266 1(5)
C(11)	0.706 4(6)	0.276 7(7)	0.009 5(6)
C(12)	0.823 8(6)	0.283 8(6)	0.063 7(6)
C(13)	0.900 7(5)	0.205 2(7)	0.169 9(6)
C(14)	0.876 3(7)	0.091 1(8)	0.247 2(5)
C(15)	0.766 3(9)	0.033 4(8)	0.238 6(7)
C(16)	0.656 5(7)	0.077(1)	0.146 6(9)
C(17)	0.633 2(5)	0.186 9(9)	0.046 4(7)

Table 6 Electrochemical potentials of selected sandwich compounds *vs.* SCE

Compound	$E_{\frac{1}{2}}$/V	Ref.
[Mo(η-C_7H_7)(η-C_5H_5)] **21**$^{+/0}$	−0.60	This work
[Mo(η-C_7H_7)(η-C_5H_4Me)] **22**$^{+/0}$	−0.63	This work
[Mo(η-C_7H_7)(η-C_9H_7)] **23**$^{+/0}$	−0.48	This work
[Mo(η-C_7H_7)(η-C_7H_9)] **2**$^{+/0}$	+0.17	6(*a*)
[Mo(η-C_7H_8)$_2$] **1**$^{+/0}$	−0.08	6(*a*)
[Mo(η-C_6H_6)$_2$]$^{+/0}$	−0.71	21
[Cr(η-C_5H_5)$_2$]$^{+/0}$	−0.67	22
[Co(η-C_5H_5)$_2$]$^{+/0}$	−0.94	23

Treatment of [Mo(η-C_7H_7)(η-C_5H_4Me)] **22** with a stoichiometric amount of tetracyanoethene (tcne) in thf resulted in a spontaneous precipitation and addition of diethyl ether gave a black solid which was extracted with dichloromethane. Purple crystals were obtained by cooling a saturated dichloromethane solution. Microanalyses correspond to the 1 : 1 electron-transfer complex [Mo(η-C_7H_7)(η-C_5H_4Me)][tcne] **24**.

The IR spectrum of **24** showed three bands assignable to C≡N stretching vibrations at 2160s, 2171s and 2192m cm^{-1}. These are characteristic for the dimeric dianion [tcne]$_2^{2-}$.[26] A related electron-transfer complex [Cr(η-C_6H_6)$_2$][tcne], which has a structure which consists of linear chains of $\cdots D^+A_2^{2-}D^+D^+A_2^{2-}D^+\cdots$ (D = donor; A = acceptor), has been reported.[26]

Since the dimeric dianion [tcne]$_2^{2-}$ is diamagnetic, only one signal due to the cation should be observed in the solid-state EPR spectrum of **24**. As expected, the spectrum showed an isotropic signal with $g = 1.995$ and linewidth = 50 G. No hyperfine splitting was observed. This *g* value is in good agreement with the value of 1.997 found for [Mo(η-C_7H_7)(η-C_5H_4Me)][PF_6].[27]

It has been reported that the solution EPR spectrum of [Cr(η-C_6H_6)$_2$][tcne] gives two isotropic signals at $g = 2.001$ and 1.896 characteristic of [tcne]$^-$ and [Cr(η-C_6H_6)$_2$]$^+$; thus, [tcne]$^-$ and not [tcne]$_2^{2-}$ is present in solution.[26] The EPR spectrum of **24** in dichloromethane also revealed the presence of [Mo(η-C_7H_7)(η-C_5H_4Me)]$^+$ and [tcne]$^-$. However, the *g* values of these ions are so close to each other that the two signals overlap, as shown in Fig. 4.

The molar magnetic susceptibility of **24** was measured in the temperature range 6–300 K at 0.2 T using a SQUID magnetometer. As shown in Fig. 5, the compound obeys the Curie–Weiss law [$\chi_M = C/(T - \theta)$] with $C = 0.35$ emu K mol^{-1} and $\theta = -3.1$ K, yielding an effective moment $\mu_{eff} = 1.67\ \mu_B$. The value of μ_{eff} indicates that only one $S = \frac{1}{2}$ radical per formula unit is contributing to the susceptibility. This is consistent with the structure possessing $S = 0$ [tcne]$_2^{2-}$ and $S = \frac{1}{2}$[Mo(η-C_7H_7)(η-C_5H_4Me)]$^+$. The effective moment is close to the value of 1.73 μ_B calculated on the basis of the spin-only formula.

Based on these results, it is likely that solid-state structure of **24** also consists of linear chains of $\cdots D^+A_2^{2-}D^+D^+A_2^{2-}D^+\cdots$. Unfortunately, attempts to grow single crystals of compound **24** were unsuccessful.

A stirred suspension of 7,7,8,8-tetracyanoquinodimethane (tcnq) in acetonitrile was treated with 1 molar equivalent of [Mo(η-C_7H_7)(η-C_5H_5)] **21** in dichloromethane, giving a green solution and a small amount of precipitate. Filtration followed by layering with diethyl ether led to the isolation of a dark green solid. The IR spectrum displayed strong absorptions at 2104 and 2150 cm^{-1} which suggested the presence of the dianion [tcnq]$^{2-}$.[28] Microanalyses for nitrogen and hydrogen were consistent with the values calculated for the 2 : 1 electron-transfer complex [Mo(η-C_7H_7)(η-C_5H_5)]$^+_2$[tcnq]$^{2-}$ **25**, but the carbon content was 3.7% lower than expected. Attempts to purify **25** by recrystallisation from dichloromethane or acetonitrile, by layering with diethyl ether onto a dichloromethane solution or by diffusion of diethyl ether into a dichloromethane solution were unsuccessful. Thus no satisfactory magnetic data could be obtained. However, the ambient

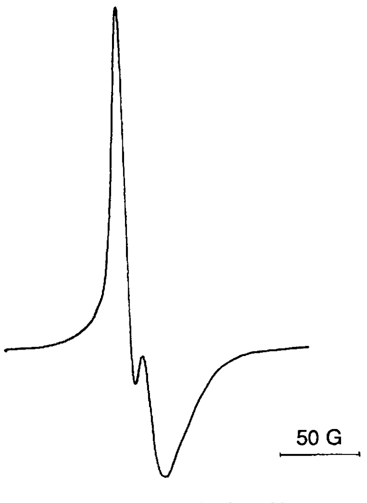


Fig. 4 EPR spectrum of complex **24** in CH_2Cl_2 at room temperature

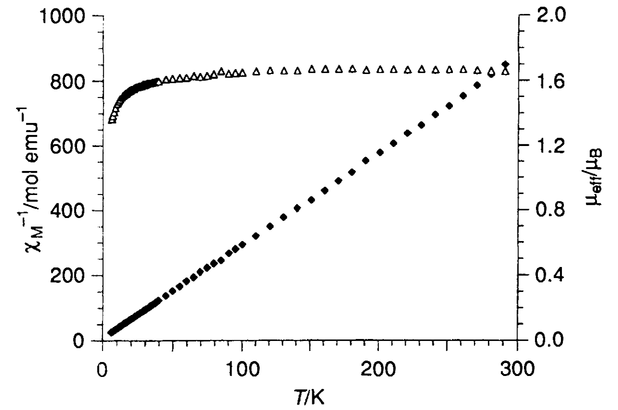


Fig. 5 Inverse molar magnetic susceptibility (◆) and effective moment (△) as a function of temperature for complex **24**

temperature solid-state EPR spectrum of **25** exhibited an absorption centred at $g = 1.982$ with a linewidth of 36 G. This was assigned to the cation $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]^+$ whilst the dianion $[tcnq]^{2-}$ has $S = 0$. In solution, the signal sharpened slightly (linewidth = 25 G). No hyperfine splitting was observed in both spectra.

In conclusion, we have developed convenient pathways to half-sandwich derivatives of the $Mo(\eta\text{-}C_7H_7)$ moiety, many of which will themselves be synthons for the further development of the η-cycloheptatrienyl molybdenum chemistry. The reactions and structures proposed for the new compounds are shown in Schemes 1-3.

Experimental

General.—All manipulations and reactions were carried out 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 predried by standing over 5 Å molecular sieves and then distilled under an atmosphere of dinitrogen from potassium (tetrahydrofuran), sodium [toluene, light petroleum (b.p. 100–120 °C)], calcium hydride (acetonitrile), phosphorus pentaoxide (dichloromethane) or sodium–potassium alloy [light petroleum (b.p. 40–60 °C) and diethyl ether]. Deuteriated solvents for NMR studies were stored in Young's ampoules and transferred by pipette in the dry box. Cycloheptatriene (tech., Aldrich) was distilled before use. $MoCl_5$ and tcnq were used as received (Aldrich). Tetracyanoethene was sublimed prior to use and $[MoCl_4(thf)_2]$[7] and $PhICl_2$[29] were prepared as described. The preparation of **2** from $MoCl_5$, **11** from **2** and **9** from **11** have been described elsewhere.[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 (δ = 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. 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. Mass spectra were obtained on an AEI MS 302 mass spectrometer. Microanalyses were performed by the Microanalytical Department of the Inorganic Chemistry Laboratory.

Cyclic voltammetry measurements were carried out using an Oxford Instruments potentiostat and recorded on a Rikadenki X-Y chart recorder. The cell used comprised a vacuum-tight chamber fitted with inlets for a platinum disc working electrode, a platinum gauze auxiliary electrode, and a silver wire pseudo-reference electrode. Typically, experiments were carried out using *ca.* 15 cm^3 of *ca.* 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate in acetonitrile solution containing *ca.* 2 mg of sample under dinitrogen at ambient temperature.

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.—$[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **2**. (*a*) From $MoCl_5$ as described in ref. 12. We note that $MoCl_5$ reacts with thf therefore the cold thf (−20 °C) was added to $MoCl_5$ which was cooled by liquid nitrogen. Then this was warmed to −80 °C before addition of cycloheptatriene and Na/Hg as described.[12] These precautions can be neglected by using the molybdenum(IV) compound $[MoCl_4(thf)_2]$ as the starting material.

(*b*) A mixture of $[MoCl_4(thf)_2]$ (4.9 g, 12.8 mmol) and cycloheptatriene (9 cm^3) in thf (100 cm^3) was cooled to −60 °C, then Na/Hg [1.2 g of Na (52.2 mmol) in 20 cm^3 of Hg] was added slowly. The mixture was stirred vigorously and allowed to warm gradually to room temperature over 3 h. The mixture was kept stirring for a further 3 h at room temperature then the volatiles were removed *in vacuo*. The residue was extracted with light petroleum (b.p. 40–60 °C) (3 x 40 cm^3). The combined extract was then cooled to −80 °C and green microcrystals separated. The ^1H NMR spectrum showed it to be a mixture of $[Mo(\eta\text{-}C_7H_8)_2]$ **1** and $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **2** in 3:2 ratio. The green microcrystals were heated at 70 °C for 2 h to give the product **2** as dark red microcrystals. Yield, 1.9 g (54%).

$[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)][PF_6]$ **3a**. A solution of iodine (0.64 g, 2.5 mmol) in toluene (75 cm^3) was added slowly to a deep red solution of $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **2** (1.40 g, 5.0 mmol) in toluene (30 cm^3) causing immediate precipitation of a light coloured material. The precipitate was allowed to settle and the supernatant was filtered off. The precipitate was washed with diethyl ether (30 cm^3) and dried *in vacuo* giving a light orange powder. This was dissolved in hot deionised water (450 cm^3) then it was filtered rapidly. An excess of $[NH_4][PF_6]$ was added immediately to the filtrate causing precipitation of the lilac complex **3a**. This was separated and then recrystallised from acetone–light petroleum (b.p. 40–60 °C) (1:1). Yield, 0.89 g (42%).

$[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)][BF_4]$ **3b**. An excess of an $HBF_4 \cdot Et_2O$ solution was added dropwise to a solution of [Mo(η-

$C_7H_7)(\eta$-$C_7H_9)]$ **2** (0.25 g, 0.9 mmol) in diethyl ether (50 cm^3) causing immediate precipitation of a light coloured material. The precipitate was allowed to settle and the supernatant was filtered off. The precipitate was washed with diethyl ether (40 cm^3) and dried *in vacuo*. The crude product was recrystallised from hot thf. Yield, 0.20 g (62%).

$[(\eta$-$C_7H_7)Mo(\mu$-$OEt)_3Mo(\eta$-$C_7H_7)][PF_6]$ **4**. A mixture of $[Mo(\eta$-$C_7H_7)(\eta$-$C_7H_9)][PF_6]$ **3a** (0.40 g, 0.94 mmol) in ethanol (100 cm^3) was heated at 50 °C for 10 min yielding a green solution. The solution was concentrated under reduced pressure and then chromatographed on an alumina column using acetone as eluent. A green band developed which was collected. Ethanol was added to the green eluate and the mixture was concentrated *in vacuo* and green crystals of **4** formed. The crystals were collected by filtration, washed with diethyl ether (20 cm^3) and then dried *in vacuo*. Yield, 0.16 g (52%).

$[(\eta$-$C_7H_7)Mo(\mu$-$I)_3Mo(\eta$-$C_7H_7)][PF_6]$ **5**. Compound $[Mo(\eta$-$C_7H_7)(\eta$-$C_7H_9)][PF_6]$ **3a** (0.40 g, 0.94 mmol) was suspended in thf (150 cm^3). A solution of iodine in thf was added dropwise with stirring until the iodine colour failed to disappear from the reaction solution. All the lilac crystals of **3a** were converted to a brick red powder. The supernatant liquor was filtered off and the residual powder was washed with diethyl ether (20 cm^3) and dried *in vacuo*. Yield, 0.41 g (96%).

$[Mo(\eta$-$C_7H_7)(thf)I_2]$ **6** *and* $[Mo(\eta$-$C_7H_7)(\eta$-$C_7H_9)I]I$ **7**. A solution of iodine (0.88 g, 3.5 mmol) in thf (50 cm^3) was slowly added to a solution of $[Mo(\eta$-$C_7H_7)(\eta$-$C_7H_9)]$ **2** (0.98 g, 3.5 mmol) in thf (40 cm^3) causing immediate precipitation. The mixture was heated at 50 °C for 30 min to yield a red-green dichroic solution and purple microcrystals. After filtration, the purple crystals of $[Mo(\eta$-$C_7H_7)(\eta$-$C_7H_9)I]I$ **7** were collected, washed with diethyl ether (20 cm^3) and then dried *in vacuo*. Yield, 0.56 g (30%). The red-green dichroic filtrate was concentrated under reduced pressure to *ca*. 50 cm^3. On cooling to −20 °C, crimson crystals of $[Mo(\eta$-$C_7H_7)(thf)I_2]$ **6** were deposited and were collected by filtration. The product was dried over a flow of dinitrogen at −20 °C. Yield, 1.17 g (65%).

$[\{Mo(\eta$-$C_7H_7)I_2\}_n]$ **8**. Crimson crystals of $[Mo(\eta$-$C_7H_7)(thf)I_2]$ **6** (0.30 g, 0.6 mmol) were heated at 35 °C *in vacuo* over a period of 10 min. There was a rapid colour change through purple to black. The resultant black powder was maintained under reduced pressure for a further 30 min then was washed with light petroleum (b.p. 40–60 °C) and dried *in vacuo*. Yield, 0.25 g (98%).

$[Mo(\eta$-$C_7H_7)(PMe_3)I_2]$ **9** *and* $[Mo(\eta$-$C_7H_7)(PMe_3)_2I]I$ **10**. (*a*) To a red-green dichroic solution of $[Mo(\eta$-$C_7H_7)(thf)I_2]$ **6** (0.35 g, 0.68 mmol) in thf (70 cm^3) was added an excess of PMe_3 (0.5 cm^3). The solution was concentrated to *ca*. 50 cm^3 under reduced pressure to deposit crude $[Mo(\eta$-$C_7H_7)(PMe_3)_2I]I$ **10** as orange powder. This was separated and recrystallised from acetone. The red-green dichroic filtrate was mixed with toluene (15 cm^3) then concentrated to *ca*. 40 cm^3 under reduced pressure. On standing, red crystals of $[Mo(\eta$-$C_7H_7)(PMe_3)I_2]$ **9** were deposited which were separated and recrystallised from thf.

(*b*) The compound PMe_3 (0.5 cm^3) was added to a purple suspension of $[Mo(\eta$-$C_7H_7)(\eta$-$C_7H_9)I]I$ **7** (0.25 g, 0.47 mmol) in thf (150 cm^3). The mixture was heated at 50 °C to give a red-green dichroic solution and an orange powder. The supernatant was filtered off the solid and then evaporated to dryness under reduced pressure. The resulting oily purple solid was washed with light petroleum (b.p. 40–60 °C) (20 cm^3) and dried *in vacuo* to yield an oil free purple solid of crude $[Mo(\eta$-$C_7H_7)(PMe_3)I_2]$ **9**, which was recrystallised from thf. The orange powder left was washed with diethyl ether (20 cm^3) and dried *in vacuo*. The product $[Mo(\eta$-$C_7H_7)(PMe_3)_2I]I$ **10** was purified by recrystallisation from acetone.

$[Mo(\eta$-$C_7H_7)(MeCN)I_2]$ **11**. (*a*) Crimson $[Mo(\eta$-$C_7H_7)(thf)I_2]$ **6** (0.35 g, 0.68 mmol) or black $[\{Mo(\eta$-$C_7H_7)I_2\}_n]$ **8** (0.30 g) were dissolved in acetonitrile (70 cm^3). The mixture was heated at 50 °C for 10 min, then concentrated to *ca*. 40 cm^3 under reduced pressure. On cooling to −20 °C, purple crystals of **11** were deposited which were separated, washed with light petroleum (b.p. 40–60 °C) and then dried *in vacuo*. Overall yields of these reactions were essentially quantitative.

(*b*) A suspension of $[Mo(\eta$-$C_7H_7)(\eta$-$C_7H_9)I]I$ **7** (0.40 g, 0.75 mmol) in acetonitrile (100 cm^3) was heated at 50 °C for 40 min. This gave a very dark red-green dichroic solution above an orange-buff coloured insoluble solid. After filtration, the filtrate was concentrated and cooled at −20 °C to give **11** as purple crystals. Yield, 0.33 g (91%).

$[Mo(\eta$-$C_7H_7)(PPh_3)I_2]$ **12**. A mixture of $[Mo(\eta$-$C_7H_7)(MeCN)I_2]$ **11** (0.30 g, 0.62 mmol) and a large excess of PPh_3 in acetone (150 cm^3) was heated at 60 °C for 4 h. The mixture was concentrated to *ca*. 70 cm^3 and deposited dark grey-green crystals which were separated, washed with diethyl ether (2 × 50 cm^3) and dried *in vacuo*. Yield, 0.37 g (85%).

$[Mo(\eta$-$C_7H_7)(PMe_3)_2I]$ **13**. (*a*) A mixture of $[Mo(\eta$-$C_7H_7)(PMe_3)I_2]$ **9** (0.25 g, 0.48 mmol) and an excess of $LiAlH_4$ in toluene (150 cm^3) was stirred at room temperature for 15 h, then it was filtered through a bed of Celite. The filtrate was evaporated to dryness then light petroleum (b.p. 100–120 °C) (150 cm^3) was added to the solid residue. After stirring at 50 °C for 15 min, a green extract was produced which was filtered. The extract was concentrated to *ca*. 20 cm^3 under reduced pressure and cooled to −20 °C giving light green platelets. The crystals were collected by filtration and dried *in vacuo*. Yield, 0.07 g (30%).

(*b*) A mixture of $[Mo(\eta$-$C_7H_7)(MeCN)I_2]$ **11** (0.24 g, 0.5 mmol) and PMe_3 (0.1 cm^3, 1 mmol) in toluene (30 cm^3) was cooled to −60 °C. Then Na/Hg [12 mg of Na (0.5 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 toluene (10 cm^3). The combined toluene solution was evaporated to dryness to give the product as green microcrystals. Yield, 0.19 g (82%).

$[(\eta$-$C_7H_7)Mo(\mu$-$OMe)_3Mo(\eta$-$C_7H_7)][PF_6]$ **14**. To a pale red suspension of $[Mo(\eta$-$C_7H_7)(PMe_3)I_2]$ **9** (0.15 g, 0.29 mmol) and $[NH_4][PF_6]$ (0.10 g, 0.61 mmol) in methanol was added an excess of sodium methoxide in methanol. The suspension turned yellow-green rapidly. After stirring at room temperature for 10 min, the mixture was evaporated to dryness *in vacuo* and the residue was extracted with acetone (50 cm^3). The extract was concentrated to *ca*. 10 cm^3 and cooled to −20 °C. Green crystals of **14** were deposited which were separated and dried *in vacuo*. Yield, 0.05 g (55%).

$[Mo(\eta$-$C_7H_7)(MeCN)Br_2]$ **15**. A solution of bromine (1.1 g, 7 mmol) in thf (75 cm^3) was added dropwise to a red solution of $[Mo(\eta$-$C_7H_7)(\eta$-$C_7H_9)]$ **2** (2.0 g, 7 mmol) in thf (50 cm^3). There was immediate precipitation of a creamy solid which became orange as more bromine solution was added. The solution was filtered off the orange solid. This was then dissolved in hot acetonitrile (150 cm^3) and the solution was concentrated to *ca*. 100 cm^3 under reduced pressure. On standing a copious amount of orange crystals of **15** were deposited which were separated and dried *in vacuo*. Yield, 1.5 g (54%).

$[Mo(\eta$-$C_7H_7)(Et_2S)Br_2]$ **16**. A suspension of $[Mo(\eta$-$C_7H_7)(MeCN)Br_2]$ **15** (0.25 g, 0.64 mmol) in diethyl ether–diethyl sulfide (1 : 1) was heated at 40 °C for 3 h. A slow colour change from red-orange to yellow-orange was observed in the solid while the solution changed from colourless to slightly yellow. The crystals were collected by filtration, washed with diethyl ether (50 cm^3) and then dried *in vacuo*. Yield, 0.21 g (78%).

$[Mo(\eta$-$C_7H_7)(MeCN)Cl_2]$ **17**. A yellow suspension of $PhICl_2$ (0.45 g, 1.6 mmol) in toluene (15 cm^3) was added to a red solution of $[Mo(\eta$-$C_7H_7)(\eta$-$C_7H_9)]$ **2** (0.2 g, 0.7 mmol) in toluene (15 cm^3). Precipitation occurred immediately. The mixture was stirred at room temperature for 1 h then filtered. The residue was extracted with MeCN (20 cm^3) to give a brown solution. The extract was then cooled to −20 °C to afford the product as orange microcrystals. The filtrate was concentrated and cooled again to give a second crop of product. Combined yield, 0.12 g (54%).

$[NBu_4][Mo(\eta\text{-}C_7H_7)I_3]$ **18**. A mixture of $[Mo(\eta\text{-}C_7H_7)(MeCN)I_2]$ **11** (0.10 g, 0.21 mmol) and tetrabutylammonium iodide (0.08 g, 0.21 mmol) in acetone (10 cm^3) was stirred at room temperature for 12 h. The volatiles were removed *in vacuo* then the residue was extracted with thf (10 cm^3) giving a purple solution. Diethyl ether diffused slowly into the thf solution over a few days to deposit the product as large purple crystals. Yield, 0.13 g (77%).

$[Mo(\eta\text{-}C_7H_7)(dmpe)I]$ **19**. A mixture of $[Mo(\eta\text{-}C_7H_7)(MeCN)I_2]$ **11** (0.24 g, 0.5 mmol) and 1,2-bis(dimethylphosphino)ethane (0.8 cm^3 of a 0.1 g cm^{-3} solution in toluene, 0.5 mmol) in toluene (30 cm^3) was cooled to −60 °C. Then Na/Hg [12 mg of Na (0.5 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 20 h. After filtration, the residue was washed with toluene (20 cm^3). The combined toluene solution was evaporated to dryness to give a green solid which was purified by sublimation [*ca.* 160 °C (0.02 mmHg)]. Yield, 0.14 g (61%).

$[Mo(\eta\text{-}C_7H_7)(dppe)I]$ **20**. A mixture of $[Mo(\eta\text{-}C_7H_7)(MeCN)I_2]$ **11** (0.24 g, 0.5 mmol) and 1,2-(diphenylphosphino)ethane (0.20 g, 0.5 mmol) in toluene (30 cm^3) was cooled to −60 °C. Then Na/Hg [12 mg of Na (0.5 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 14 h. After filtration, the residue was washed with toluene (10 cm^3). The combined toluene solution was stripped to dryness to afford the product as a green solid. Yield, 0.23 g (65%).

$[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ **21**. A mixture of $[Mo(\eta\text{-}C_7H_7)(MeCN)I_2]$ **11** (0.12 g, 0.25 mmol) and $Na(C_5H_5)$ (0.09 g, 1.02 mmol) in thf (25 cm^3) was stirred at room temperature for 16 h. After removing the volatiles *in vacuo*, the residue was extracted with light petroleum (b.p. 40–60 °C) (3 × 20 cm^3). The combined extract was concentrated to *ca.* 15 cm^3 then cooled to −80 °C to give the product as brown crystals. Yield, 41 mg (65%).

$[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$ **22**. A mixture of $[Mo(\eta\text{-}C_7H_7)(MeCN)I_2]$ **11** (0.18 g, 0.37 mmol) and $Na(C_5H_4Me)$ (0.15 g, 1.47 mmol) in thf (30 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 × 20 cm^3). The combined extract was concentrated to *ca.* 15 cm^3 then cooled to −80 °C to give the product as green crystals. Yield, 85 mg (85%).

$[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_9H_7)]$ **23**. A mixture of $[Mo(\eta\text{-}C_7H_7)(MeCN)I_2]$ **11** (0.12 g, 0.25 mmol) and lithium indenide (0.09 g, 0.74 mmol) in thf (20 cm^3) was stirred at room temperature for 12 h. After removing the volatiles *in vacuo*, the residue was extracted with light petroleum (b.p. 40–60 °C) (4 × 25 cm^3) to give a purple solution. The combined extract was concentrated to *ca.* 25 cm^3 then cooled to −80 °C. The purple crystals formed were separated and recrystallised again from light petroleum (b.p. 40–60 °C). Yield, 48 mg (64%).

$[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)][tcne]$ **24**. A solution of tetracyanoethene (0.12 g, 0.94 mmol) in thf (5 cm^3) was added to a solution of $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$ **22** (0.25 g, 0.94 mmol) in thf (20 cm^3). Precipitation occurred immediately and the solution darkened. The mixture was stirred at room temperature for *ca.* 15 min, then diethyl ether (30 cm^3) was layered. After 2 d, some black solid was formed which was collected by filtration. The black solid was extracted with dichloromethane (3 × 10 cm^3) to give a dark red solution. The solution was concentrated and cooled to −80 °C to give the product as purple crystals. Yield, 0.12 g (32%).

$[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]_2[tcnq]$ **25**. A solution of $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ **21** (70 mg, 0.28 mmol) in dichloromethane (10 cm^3) was added to a suspension of 7,7,8,8-tetracyanoquinodimethane (57 mg, 0.28 mmol) in acetonitrile (10 cm^3). A green solution with a small amount of precipitate was formed. The mixture was stirred at room temperature for *ca.* 15 min then it was filtered. Diethyl ether (40 cm^3) was layered onto the filtrate and the mixture was allowed to stand for a few days to give the product as a dark green solid. Yield, 50 mg (51%).

Crystal Structure Determinations of Compounds **18** *and* **22**.—Crystal data, data collection and processing parameters are given in Table 7. The general procedure was as follows. A crystal was mounted in a Lindemann tube (0.7 mm) under dinitrogen and sealed with a small flame. This was transferred to the goniometer head of an Enraf-Nonius CAD4 diffracto-

Table 7 Crystal data, data collection and processing parameters for $[NBu_4][Mo(\eta\text{-}C_7H_7)I_3]$ **18** and $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$ **22**

	18	**22**
Formula	$C_{23}H_{43}I_3MoN$	$C_{13}H_{14}Mo$
M	810.26	266.19
Crystal size/mm	0.20 × 0.22 × 0.84	0.30 × 0.40 × 0.50
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma*	$P2_1/c$
a/Å	17.137(2)	12.512(10)
b/Å	11.365(1)	8.018(7)
c/Å	15.943(1)	11.521(12)
β/°	90.0	112.82(8)
U/Å^3	3105.2	1065.2
Z	4	4
D_c/g cm^{-3}	1.73	1.66
μ/cm^{-1}	33.74	11.58
F(000)	1556	536
Total data collected	3528	2689
No. of observations	1967 [$I > 4\sigma(I)$]	1446 [$I > 3\sigma(I)$]
R(merge)	0.013	0.086
No. of variables	145	128
Observations/variables	13.6	11.3
Weighting coefficients	11.7, −6.00, 9.15	25.1, −33.9, 27.0, −11.1, 4.13
Max./min. peaks in final difference map/e Å^{-3}	0.57, −0.63	0.61, −0.03
R^a	0.035	0.035
R'^b	0.041	0.039

[a] $R = \Sigma(|F_o - F_c|)/\Sigma|F_o|$. [b] $R' = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{\frac{1}{2}}$.

meter. Unit cell parameters were calculated from the setting angles of 25 carefully centred reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections. The data were collected at room temperature using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) and an ω–2θ scan mode (θ_{max} = 25°).

The data were corrected for Lorentz and polarisation effects and an empirical absorption correction [30] based on azimuthal scan data was applied. For both structures the heavy atom positions were revealed by direct methods. Subsequent Fourier difference syntheses revealed the positions of other non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares procedures. Hydrogen atoms were placed in estimated positions with fixed isotropic thermal parameters. For **18**, they were included in the refinement with the fixed positional parameters. For **22** they were refined riding their supporting carbon atoms. On this stage, the empirical absorption correction using the DIFABS [31] program was applied. A Chebyshev weighting scheme [32] was applied and the data were corrected for the effects of anomalous dispersion and isotropic extinction (*via* an overall isotropic extinction parameter [33]) in the final stages of refinement. All crystallographic calculations were performed using the CRYSTALS suite [34] on a MicroVAX 3800 computer in the Chemical Crystallography Laboratory, Oxford. Neutral atom scattering factors were taken from the usual sources.[35]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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