η-1,2,4,6-Tetramethylcycloheptatrienyl Molybdenum Chemistry

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Treatment of $[Mo(CO)_6]$ with 1,3,5,7-tetramethylcycloheptatriene in octane gives a mixture of $[Mo(\eta^6\text{-}C_7H_4Me_4\text{-}1,3,5,7)(CO)_3]$ **1**, $[Mo(\eta^6\text{-}C_7H_4Me_4\text{-}1,2,4,6)(CO)_3]$ **2** and $[Mo(\eta^6\text{-}C_7H_4Me_4\text{-}1,3,4,6)(CO)_3]$ **3**. The compounds **2** and **3** arise as a result of sequential 1,5-shifts of the 7-*endo*-hydrogen atom of the initially formed **1**. Hydride abstraction from compounds **1**–**3** by $[CPh_3][BF_4]$ gives $[Mo(\eta^7\text{-}C_7H_3Me_4\text{-}1,2,4,6)(CO)_3][BF_4]$ **4**. Compound **4** reacts with LiCl to yield $[Mo(\eta^7\text{-}C_7H_3Me_4\text{-}1,2,4,6)(CO)_2Cl]$ **5** which reacts with 1 equivalent of $Me_2PCH_2CH_2PMe_2$ (dmpe) to give $[Mo(\eta^3\text{-}C_7H_3Me_4\text{-}1,2,4,6)(dmpe)(CO)_2Cl]$ **7**. This is fluxional due to trigonal twist rearrangement and 1,2-shift of metal around the C_7 ring. Photolysis of **7** in toluene produces $[Mo(\eta^7\text{-}C_7H_3Me_4\text{-}1,2,4,6)(dmpe)Cl]$ **9**. Treatment of **4** with toluene affords the mixed-sandwich compound $[Mo(\eta^6\text{-}C_6H_5Me)(\eta^7\text{-}C_7H_3Me_4\text{-}1,2,4,6)][BF_4]$ **10** which yields $[Mo(\eta^7\text{-}C_7H_3Me_4\text{-}1,2,4,6)(CH_3COCHCOCH_3)(PPh_3)]$ **11** upon treatment with sodium pentane-2,4-dionate and triphenylphosphine.

Many studies of pentamethylcyclopentadienyl transition-metal derivatives show that ring methylation can have a considerable influence on the structure and properties of η-cyclopentadienyl metal compounds.[1] Recently, considerable progress has been made in the development of η-cycloheptatrienyl–transition metal chemistry.[2–4] However, the chemistry of highly ring-substituted η-cycloheptatrienyl analogues remains virtually unexplored. Here we describe the syntheses and reactions of 1,2,4,6-tetramethylcycloheptatrienyl derivatives of molybdenum.

Results and Discussion

A mixture of $[Mo(CO)_6]$ and 1,3,5,7-tetramethylcycloheptatriene in octane was heated at 140 °C for 17 h to give a red suspension. A small amount of tetrahydrofuran (thf) was also added to the reaction mixture to rinse down the sublimed $[Mo(CO)_6]$ along the Schlenk wall as it refluxed. Removal of the volatiles of the red suspension followed by extraction with light petroleum (b.p. 40-60 °C) gave an orange-red solution. Cooling the solution at −20 °C produced orange crystals which were characterised as the compound $[Mo(\eta^6\text{-}C_7H_4Me_4\text{-}1,3,5,7)(CO)_3]$ **1**. Characterising data for **1** and for all other new compounds described below are given in Table 1. The mother-liquor was filtered, concentrated and cooled again to yield some further red crystals which were shown by ^1H NMR spectroscopy to be an inseparable mixture of $[Mo(\eta^6\text{-}C_7H_4Me_4\text{-}1,2,4,6)(CO)_3]$ **2** and $[Mo(\eta^6\text{-}C_7H_4Me_4\text{-}1,3,4,6)(CO)_3]$ **3** (Scheme 1).

The *exo* isomer was assigned to the compound **1** on the basis of the coupling constant between H_f and H_g of 8.4 Hz which is in good agreement with Karplus's predicted value for an *exo* isomer.[5] The coupling constant should be around 4 Hz for an *endo* isomer.

Pauson and co-workers[6] reported that the 7-*endo* hydrogen atom of substituted cycloheptatriene complexed to metal was able to migrate in a 1,5-shift manner. On this basis, the formation of **2** and **3** may be ascribed to a series of sequential [1,5] hydrogen migrations in the initially formed compound **1**. The above assumption was tested by heating a solution of pure compound **1** in octane at 120 °C for 10 h. The ^1H NMR spectrum of the resulting solution showed that it contains the compounds **1**, **2** and **3** in the ratio 6:2.5:1 respectively. This ratio is close to that found in the initial reaction (Scheme 1). The ratio may represent the equilibrium distribution of compounds **1**, **2** and **3**. Pauson and co-workers[6] also reported that substituents in the 1 position might hinder the formation of the proposed transition state. As a result, compounds having 1- and 6-substitution did not undergo further rearrangement. Thus, the presence of compounds **2** and **3** only but not of other isomers of **1** is understandable.

Treatment of **1** with $[CPh_3][BF_4]$ in dichloromethane at 60 °C for 32 h gave the tetramethylcycloheptatrienyl molybdenum compound $[Mo(\eta^7\text{-}C_7H_3Me_4\text{-}1,2,4,6)(CO)_3][BF_4]$ **4** in 38% yield and 15% of **1** was recovered. The reaction requires more vigorous conditions than for the unsubstituted analogue.[7] The reaction between $[CPh_3][BF_4]$ and a mixture of **1**, **2** and **3** (2:3:1) in dichloromethane at 60 °C for 7 h also afforded compound **4**. The yield was 86% and 67% of **1** was recovered. These results showed that **2** and **3** underwent hydride elimination much more readily than **1**. Probably, the 7-*exo*-methyl group of **1** hinders the approach of the bulky $[CPh_3]^+$ cation.

The ^1H NMR spectrum of **4** in $[^2H_6]$acetone gave four singlets at δ 6.43, 6.22, 2.80 and 2.71 with relative intensity 2:1:6:6 assignable to the $\eta^7\text{-}C_7H_3Me_4\text{-}1,2,4,6$ group. The ^{13}C NMR spectrum exhibited four absorptions at δ 118.6, 116.6, 103.3 and 101.3 for the ring carbons and two absorptions at δ 26.2 and 25.0 for the methyl groups. These results clearly indicated the presence of a mirror plane in the molecule. These ^1H and ^{13}C NMR spectra are typical for all the other $Mo(\eta^7\text{-}C_7H_3Me_4\text{-}1,2,4,6)$ complexes described below.

An orange solution of **4** in acetone was treated with 1 equivalent of LiCl giving dark green crystals of $[Mo(\eta^7\text{-}C_7H_3Me_4\text{-}1,2,4,6)(CO)_2Cl]$ **5** in good yield. The carbonyl stretching frequencies of **5** are lower than that of the unsubstituted analogue by about 40 cm^{-1}. Predictably, the enhancement of electron density in the metal centre due to the four methyl groups increases the extent of back-bonding and decreases the ν(CO). Similar results have been obtained for the compounds **1** and **4**. The electron impact (EI) mass spectrum of **5** did not show a parent M^+ peak, but peaks at *m*/*z* 592 and 280 (M − 2CO) occurred in high intensity. The former peak may correspond to the species $[Mo_2(\eta^7\text{-}C_7H_3Me_4\text{-}1,2,4,6)_2Cl_3]$ **6** formed by recombination reactions in the spectrometer. A similar result was observed for the mass spectra of the complexes $[Mo(\eta^7\text{-}C_7H_7)(CO)_2X]$ (X = Cl, Br or I).[8]

We attempted to prepare the compound **6** independently

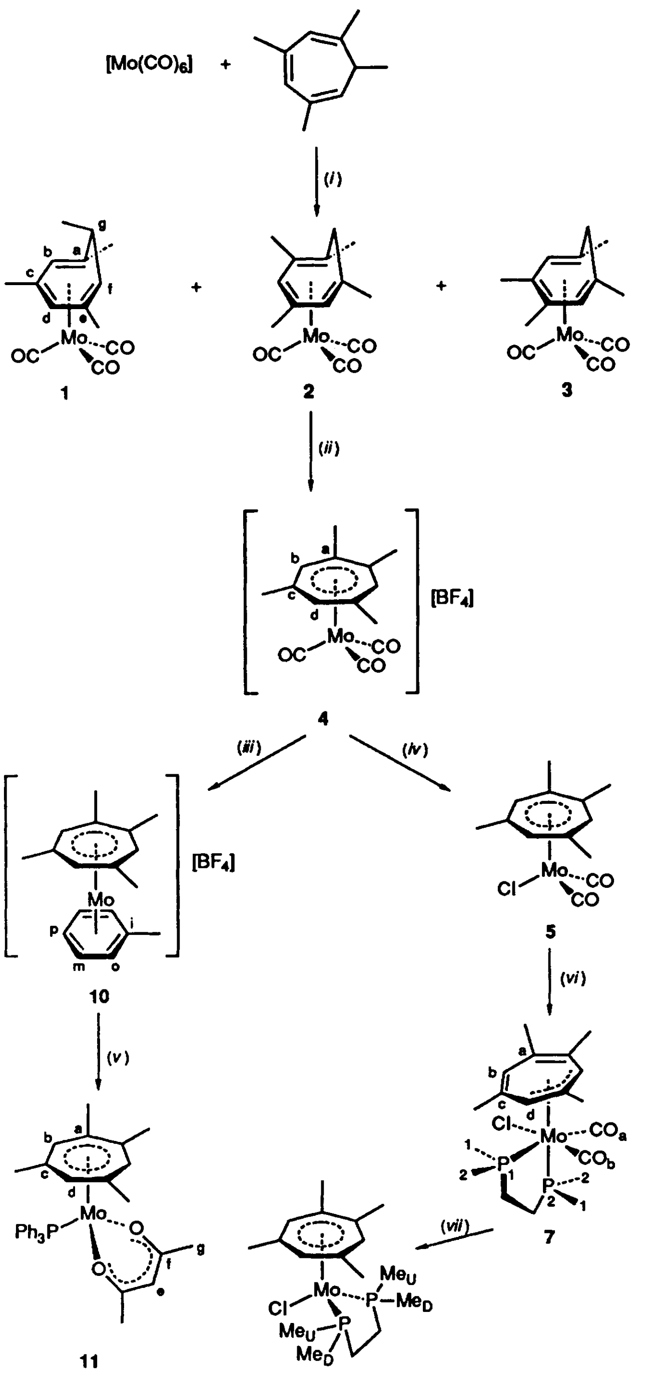
Table 1 Analytical[a] and spectroscopic data

Compound	Colour	Spectroscopic data[b]
1 C, 51.0 (51.2); H, 5.1 (4.9)	Orange	^{1}H NMR[c]: 5.17 (s, 1 H, H$_b$ or H$_d$), 4.17 (s, 1 H, H$_b$ or H$_d$), 3.24 [dd, *J*(H–H) 8.4, 1.4, 1 H, H$_f$], 2.24–2.20 (m, 1 H, H$_g$), 1.95 (s, 3 H, Me$_a$, Me$_c$ or Me$_e$), 1.67 (s, 3 H, Me$_a$, Me$_c$ or Me$_e$), 1.55 (s, 3 H, Me$_a$, Me$_c$ or Me$_e$), −0.04 [d, *J*(H–H) 7.0, 3 H, Me$_g$] ^{13}C-{^{1}H} NMR[c,d]: 112.3 (C$_c$ or C$_e$), 109.7 (C$_c$ or C$_e$), 100.7 (C$_b$ or C$_d$), 100.5 (C$_b$ or C$_d$), 90.6 (C$_a$), 66.4 (C$_f$), 38.7 (C$_g$), 26.62 (Me$_a$, Me$_c$, Me$_e$ or Me$_g$), 26.57 (Me$_a$, Me$_c$, Me$_e$ or Me$_g$), 26.0 (Me$_a$, Me$_c$, Me$_e$ or Me$_g$), 24.0 (Me$_a$, Me$_c$, Me$_e$ or Me$_g$) IR: ν(CO) 1870, 1958 Mass spectrum (EI): *m/z* 330 (M^+), 302 (*M* − CO), 274 (*M* − 2CO), 244 (*M* − 3CO), 148 ($C_7H_4Me_4$)
2[e] C, 51.8 (51.2); H, 4.9 (4.9)	Bright red	^{1}H NMR[c]: 5.24 (s, 1 H, H$_c$ or H$_e$), 4.34 (s, 1 H, H$_c$ or H$_e$), 2.04 (s, 1 H, H$_{g\text{-}exo}$ or H$_{g\text{-}endo}$), 1.92 (s, 4 H, H$_{g\text{-}exo}$ or H$_{g\text{-}endo}$ and Me$_a$, Me$_b$, Me$_d$ or Me$_f$), 1.73 (s, 3 H, Me$_a$, Me$_b$, Me$_d$ or Me$_f$), 1.53 (s, 3 H, Me$_a$, Me$_b$, Me$_d$ or Me$_f$), 1.49 (s, 3 H, Me$_a$, Me$_b$, Me$_d$ or Me$_f$) ^{13}C-{^{1}H} DEPT NMR[c]: 102.2 (C$_c$ or C$_e$), 101.7 (C$_c$ or C$_e$), 39.0 (C$_g$), 27.1 (Me$_a$, Me$_b$, Me$_d$ or Me$_f$), 25.7 (Me$_a$, Me$_b$, Me$_d$ or Me$_f$), 25.1 (Me$_a$, Me$_b$, Me$_d$ or Me$_f$), 23.4 (Me$_a$, Me$_b$, Me$_d$ or Me$_f$)
3[e] C, 51.8 (51.2); H, 4.9 (4.9)	Bright red	^{1}H NMR[c,f]: 4.48 (s, 2 H, H$_b$), 1.87 (s, 7 H, H$_{g\text{-}exo}$ or H$_{g\text{-}endo}$ and Me$_a$ or Me$_c$), 1.52 (s, 6 H, Me$_a$ or Me$_c$)
4 C, 40.7 (40.6); H, 3.6 (3.7)	Orange-red	^{1}H NMR[g]: 6.43 (s, 2 H, H$_b$), 6.22 (s, 1 H, H$_d$), 2.80 (s, 6 H, Me$_a$ or Me$_c$), 2.71 (s, 6 H, Me$_a$ or Me$_c$) ^{13}C-{^{1}H} NMR[g]: 210.7 (CO), 118.6 (C$_a$ or C$_c$), 116.6 (C$_a$ or C$_c$), 103.3 (C$_b$), 101.3 (C$_d$), 26.2 (Me$_a$ or Me$_c$), 25.0 (Me$_a$ or Me$_c$) IR: ν(CO) 1864, 1928, 2007, 2055 Mass spectrum (FAB): *m/z* 413 (M^+), 329 ($M - BF_4$), 301 ($M - BF_4 - CO$), 273 ($M - BF_4 - 2CO$), 245 ($M - BF_4 - 3CO$), 147 ($C_7H_3Me_4$)
5 C, 46.8 (46.7); H, 4.3 (4.5)[h]	Dark green	^{1}H NMR[c]: 4.60 (s, 2 H, H$_b$), 3.88 (s, 1 H, H$_d$), 1.90 (s, 6 H, Me$_a$ or Me$_c$), 1.76 (s, 6 H, Me$_a$ or Me$_c$) ^{13}C-{^{1}H} NMR[c]: 221.4 (CO), 109.0 (C$_a$ or C$_c$), 101.4 (C$_a$ or C$_c$), 98.7 (C$_b$), 93.0 (C$_d$), 26.1 (Me$_a$ or Me$_c$), 23.2 (Me$_a$ or Me$_c$) IR: ν(CO) 1913, 1929, 1980 Mass spectrum (EI): *m/z* 592, 280 (*M* − 2CO)
7 C, 46.8 (47.1); H, 6.5 (6.5)[i]	Red	^{1}H NMR[g]: 5.32 (br s, 2 H, H$_b$), 4.80 [vt, *J*(H–P) 1.7, 1 H, H$_d$], 2.02 (s, 6 H, Me$_a$ or Me$_c$), 1.97 (s, 6 H, Me$_a$ or Me$_c$), 1.62 [d, *J*(H–P) 7.5, 12 H, Me], 1.55 (br s, 4 H, CH$_2$) ^{1}H NMR[j]: 5.42 (br s, 2 H, H$_b$), 4.92 (br s, 1 H, H$_d$), 2.08 (s, 6 H, Me$_a$ or Me$_c$), 2.01 (s, 6 H, Me$_a$ or Me$_c$), 1.55–1.25 (m, 2 H, H^1 or H^2), 1.29 [d, *J*(H–P) 8.6, 6 H, Me^1 or Me^2], 1.09 [d, *J*(H–P) 7.3, 6 H, Me^1 or Me^2], 1.18–0.88 (m, 2 H, H^1 or H^2) ^{13}C-{^{1}H} NMR[k]: 229.6 [dd, *J*(C–P) 20.8, 25.6, CO$_a$], 225.5 [vt, *J*(C–P) 11.0, CO$_b$], 129.9 (br s, C on C$_7$ ring), 104.3 (br s, C on C$_7$ ring), 78.6 (br s, C on C$_7$ ring), 28.6 [d, *J*(C–P) 16.2 CH$_2$], 28.3 [d, *J*(C–P) 16.2, CH$_2$], 26.4–24.4 (Me on C$_7$ ring), 14.7 [d, *J*(C–P) 20.3, PMe], 14.5 [d, *J*(C–P) 26.4, PMe], 13.3 [d, *J*(C–P) 29.1, PMe], 10.3 [d, *J*(C–P) 14.4, PMe] ^{31}P-{^{1}H} NMR[l]: 30.2 [d, *J*(P–P) 18.6, P^1 or P^2], 14.6 [d, *J*(P–P) 18.6, P^1 or P^2] IR: ν(CO) 1828, 1910 Mass spectrum (EI): *m/z* 593, 430 (*M* − 2CO), 280 (*M* − 2CO − dmpe), 147 ($C_7H_3Me_4$)
9 —	Green	^{1}H NMR[c]: 4.81 (br s, 2 H, H$_b$), 4.55 (br s, 1 H, H$_d$), 2.40 (s, 6 H, Me$_a$ of Me$_c$), 2.17 (s, 6 H, Me$_a$ of Me$_c$), 1.34 [d, *J*(H–P) 7.9, 6 H, Me$_U$ or Me$_D$], 1.30–1.12 (m, 2 H, H$_U$ or H$_D$), 0.94 [d, *J*(H–P) 8.1, 6 H, Me$_U$ or Me$_D$], 0.82–0.56 (m, 2 H, H$_U$ or H$_D$) ^{13}C-{^{1}H} DEPT NMR[c]: 91.1 (s, C$_b$), 82.7 (s, C$_d$), 27.6 [vt, *J*(C–P) 20.4, CH$_2$], 26.3 (s, Me$_a$ or Me$_c$), 23.9 (s, Me$_a$ or Me$_c$), 17.1 [vt, *J*(C–P) 9.7, Me$_U$ or Me$_D$], 12.8 [vt, *J*(C–P) 12.0, Me$_U$ or Me$_D$] ^{31}P-{^{1}H} NMR[c]: 31.4 (dmpe)
10 C, 51.1 (51.2); H, 5.6 (5.5)	Pale green	^{1}H NMR[g]: 6.22–6.16 (m, 4 H, H$_o$ and H$_m$), 6.10–6.06 (m, 1 H, H$_p$), 5.89 (s, 2 H, H$_b$), 5.82 (s, 1 H, H$_d$), 2.49 (s, 6 H, Me$_a$ or Me$_c$), 2.46 (s, 6 H, Me$_a$ or Me$_c$), 2.25 (s, 3 H, Me) ^{13}C-{^{1}H} NMR[g]: 113.7 (C$_i$), 100.0 (C$_o$ or C$_m$), 99.7 (C$_a$ or C$_c$), 99.2 (C$_a$ or C$_c$), 98.8 (C$_o$ or C$_m$), 97.7 (C$_p$), 91.2 (C$_b$), 89.1 (C$_d$), 25.2 (Me$_a$ or Me$_c$), 24.2 (Me$_a$ or Me$_c$), 20.4 (Me) Mass spectrum (FAB): *m/z* 337 ($M - BF_4$)
11 —	Red	^{1}H NMR[g]: 7.54–7.26 (m, 15 H, Ph), 5.41 (s, 1 H, H$_e$), 5.16 (br s, 1 H, H$_d$), 5.02 (br s, 2 H, H$_b$), 2.23 (s, 6 H, Me$_a$ or Me$_c$), 2.18 (s, 6 H, Me$_a$ or Me$_c$), 2.04 (s, 6 H, H$_g$) ^{13}C-{^{1}H} NMR[g]: 187.4 (s, C$_f$), 138.2 [d, *J*(C–P) 11.6, Ph], 134.5 (s, Ph), 134.3 (s, Ph), 132.7 (s, C$_e$), 129.7 (s, Ph), 129.5 (s, Ph), 129.4 (s, Ph), 99.4 (s, C$_a$ or C$_c$), 96.4 (s, C$_a$ or C$_c$), 91.9 (s, C$_b$), 87.2 (s, C$_d$), 27.7 (s, Me$_a$, Me$_c$ or Me$_g$), 27.6 (s, Me$_a$, Me$_c$ or Me$_g$), 25.5 (s, Me$_a$, Me$_c$ or Me$_g$) ^{31}P-{^{1}H} NMR[g]: −8.4 (s, PPh$_3$) Mass spectrum (FAB): *m/z* 344 ($M - PPh_3$), 147 ($C_7H_3Me_4$)

[a] Calculated values given in parentheses. [b] The NMR spectra were obtained at room temperature unless stated otherwise; data given as chemical shift (δ) [multiplicity (*J* in Hz), relative intensity, and assignment] where s = singlet, d = doublet, t = triplet, m = multiplet, br s = broad signal, vt = virtual triplet. The IR spectra (cm^{-1}) were recorded in KBr discs. [c] In [^{2}H$_6$]benzene. [d] Carbonyl absorptions not observed. [e] An inseparable mixture of **2** and **3**. [f] A band due to another H$_{g\text{-}exo}$ or H$_{g\text{-}endo}$ was not observed. [g] In [^{2}H$_6$]acetone. [h] Cl 10.6 (10.6)%. [i] Cl 7.4 (7.3)%. [j] In [^{2}H$_8$]toluene at 323 K. [k] In [^{2}H$_6$]acetone at 233 K. [l] In [^{2}H$_6$] acetone at 230 K.

by refluxing a mixture of **4** with trimethylsilyl chloride in thf for 7 h.[8] The resulting deep green suspension was evaporated to dryness, then the residue was extracted with toluene. The ^{1}H NMR spectrum of the resulting green product showed that the toluene extract contained compound **5**. No compound **6** could be isolated.

Addition of 1 equivalent of $Me_2PCH_2CH_2PMe_2$ (dmpe) to a solution of **5** in toluene gave a red solution from which the compound [Mo(η^3-C$_7$H$_3$Me$_4$-1,2,4,6)(dmpe)(CO)$_2$Cl] **7** could be isolated in good yield. The related compound [Mo(η^3-C$_7$H$_7$)(dppe)(CO)$_2$Cl] (dppe = $Ph_2PCH_2CH_2PPh_2$) **8** has been prepared similarly.[9]



Scheme 1 *Reagents and conditions*: (*i*) in octane–thf at 140 °C for 17 h [1 (53); 2 (21); 3 (8%)]; (*ii*) from 1, $[CPh_3][BF_4]$ in CH_2Cl_2 at 60 °C for 32 h (38%); from a mixture of 1, 2 and 3 (2:3:1), $[CPh_3][BF_4]$ in CH_2Cl_2 at 60 °C for 7 h (86%); (*iii*) in toluene at 125 °C for 27 h (88%); (*iv*) LiCl in acetone at room temperature (r.t.) for 1 h (74%); (*v*) sodium pentane-2,4-dionate and PPh_3 in MeOH at 60 °C for 6 h (40%); (*vi*) dmpe in toluene at r.t. for 2 h (83%); (*vii*) *hv* in toluene at r.t. for 1 h (*ca.* 50%)

It has been shown that some trihapto-cycloheptatrienyl complexes have extensive fluxional behaviour. The compound $[Mo(\eta^3\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)(CO)_2]$ undergoes 1,2-shift of the metal group around the cycloheptatrienyl ring so that only one resonance due to the $\eta\text{-}C_7H_7$ protons is observed in the ^1H NMR spectrum at room temperature.[10] Whiteley and co-workers[9] reported that the compound 8 underwent a trigonal twist process which interconverted the two P-donor atoms (Fig. 1).[9] The variable-temperature NMR spectra of 7 manifest that it has both fluxional properties. Thus the low-temperature (230 K) ^{31}P NMR spectrum of 7 exhibits a doublet of doublet pattern which shows that the two phosphorus atoms are inequivalent. The signals broaden at higher temperature and finally coalesce at 313 K. The $\Delta G^\ddagger$ of this trigonal twist rearrangement was estimated to be 53.3 kJ mol^{-1}.

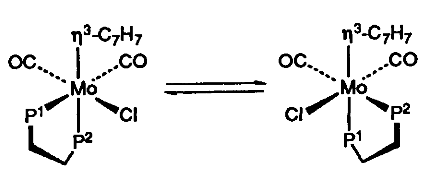


Fig. 1 The trigonal twist rearrangement proposed for $[Mo(\eta^3\text{-}C_7H_7)(dppe)(CO)_2Cl]$

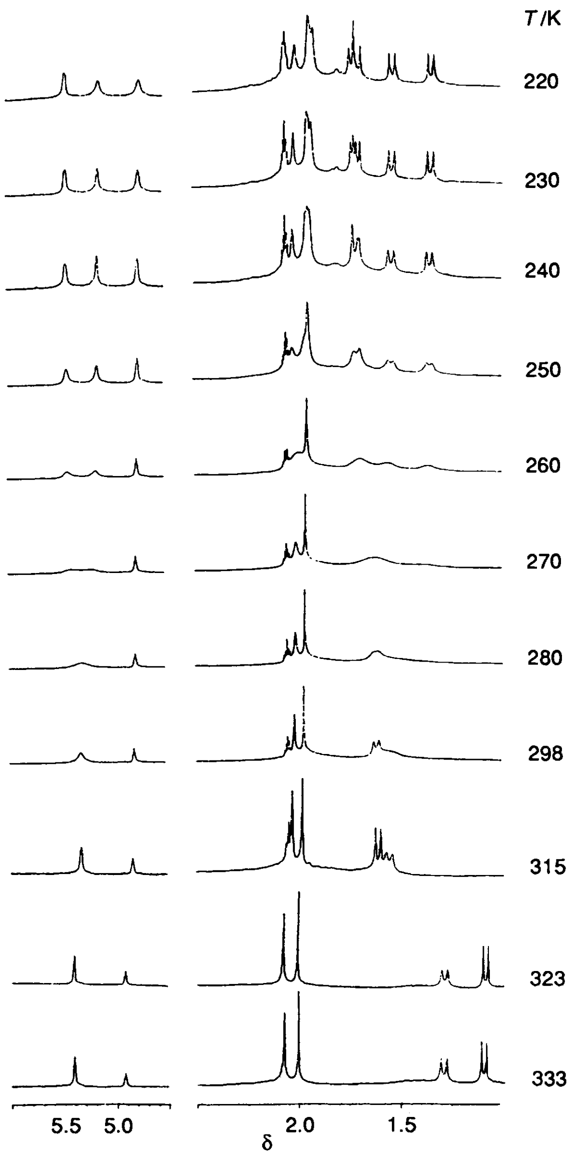


Fig. 2 Variable-temperature ^1H NMR spectra of 7 in $[^2H_6]$acetone (220–315 K) or $[^2H_8]$toluene (323–333 K): * indicates solvent

Fig. 2 shows the variable-temperature ^1H NMR spectra of 7 in $[^2H_6]$acetone (220–315 K) or $[^2H_8]$toluene (323–333 K). At the higher temperature (323 K), two doublets at δ 1.29 and 1.09 and two multiplets at *ca.* δ 1.4 and 1.0 are observed which may be assigned to the methyl and methylene groups in the dmpe ligand respectively. The presence of two methyl signals and two methylene signals reflects that a fast exchange process is operating which interconverts the two P-donor atoms. The remaining four signals may be assigned to the η^3-$C_7H_3Me_4$-1,2,4,6 group. The simplicity of this pattern clearly indicates that another averaging process occurs on the C_7 ring. The rearrangement may involve 1,2-shift of the Mo atom about the cycloheptatrienyl ring as described previously.[10] Moreover, the fast trigonal twist rearrangement produces a pseudo-mirror plane across the C_7 ring so that only four signals arise for this ligand. Changing the solvent to [$^2H_6$]acetone shifts the two methyl absorptions downfield and reduces the separation between them. At the lower temperature, the methyl absorptions overlap to become a broad signal which splits into four doublets at 230 K. Two of the doublets overlap at 220 K. The four doublets may be assigned to the four methyl groups in the dmpe ligand. The positions of the methylene absorptions are partially obscured due to their low intensity. The broad signal at δ 5.3 also splits into two signals of equal intensity at the lower temperature. It is worth noting that the two cycloheptatrienyl methyl absorptions broaden at different rates and both of them split into two signals at 240–250 K. The downfield signal broadens much faster than the upfield one and gives two signals with larger separation. The three broad signals for the cycloheptatrienyl protons and four broad signals for the methyl groups on the C_7 ring indicate that the pseudo-mirror plane is removed at low temperature due to the slow trigonal twist process. However, the 1,2-shift of the Mo atom around the C_7 ring is still occurring even at 220 K.

The IR and low-temperature ^{13}C NMR spectra of **7** provide further evidence for the proposed structure. The IR spectrum of **7** in a KBr disc shows two almost equally intense carbonyl stretching absorptions suggesting that the two carbonyl groups are *cis* to each other.[11] The ^{13}C NMR spectrum of **7** in [$^2H_6$]acetone at 233 K exhibits a virtual triplet at δ 225.5 with average coupling constant 11 Hz and a virtual doublet of doublets at δ 229.6 with coupling constants 21 and 26 Hz. It was reported that the carbonyls *trans* to phosphorus showed a larger ^{31}P–^{13}C coupling than those oriented *cis* to phosphorus.[12] Thus the former band may be assigned to CO_b which is *cis* to both phosphorus atoms while the latter may be assigned to CO_a which is *cis* to one phosphorus atom but *trans* to the other.[9]

A parent-ion M^+ peak could not be detected in the EI mass spectrum of **7**, but peaks at *m/z* 593 (**6**$^+$), 430 (M − 2CO), 280 (M − 2CO − dmpe) and 147 (η^7-$C_7H_3Me_4$) occurred with high intensity.

Heating a solution of **7** in toluene at 110 °C for 8 h gave a pale green solution from which only a mixture of unidentified products was obtained. However, photolysis of a solution of **7** in toluene at room temperature for 1 h gave the oily green product [Mo(η^7-$C_7H_3Me_4$-1,2,4,6)(dmpe)Cl] **9**. Compound **9** was characterised by ^1H, ^{13}C and ^{31}P NMR spectroscopy. Attempts to purify **9** by recrystallisation and sublimation were not successful. This reaction has not been reported for the unsubstituted analogue.

The mixed-sandwich compound [Mo(η^6-C_6H_5Me)(η^7-$C_7H_3Me_4$-1,2,4,6)][BF_4] **10** was prepared by heating a suspension of **4** in toluene. It has been shown that the unsubstituted analogue of **10**, namely [Mo(η^6-C_6H_5Me)(η^7-C_7H_7)][PF_6] is an excellent precursor of half-sandwich Mo(η^7-C_7H_7) compounds.[13] For example, it reacts with LiCl or ROH (R = Me or Et) to give the binuclear compounds [Mo_2(η^7-C_7H_7)$_2$$Cl_3$] or [$Mo_2$($\eta^7$-$C_7H_7$)$_2(OR)_3$][$PF_6$] (R = Me or Et) respectively.[13a] However, the reactions of **10** with LiCl or PhOH failed to give the corresponding products and a significant amount of starting material **10** was recovered in both cases.

The reaction between **10** and benzenethiol afforded the binuclear thiolato-bridged complex [Mo_2(η^7-$C_7H_3Me_4$-1,2,4,6)$_2$(μ-SPh)$_3$][BF_4] in excellent yield.[14] Treatment of **10** with sodium pentane-2,4-dionate and PPh_3 in MeOH gave a brown suspension from which compound **11** was isolated. Satisfactory microanalysis could not be obtained for this compound, but the fast atom bombardment (FAB) mass spectrum exhibited signals at *m/z* 344 (M − PPh_3) and 147 ($C_7H_3Me_4$). This together with the ^1H, ^{13}C and ^{31}P spectra suggested **11** to be [Mo(η^7-$C_7H_3Me_4$-1,2,4,6)($CH_3COCHCOCH_3$)(PPh_3)].

It has been demonstrated that the compound [Mo(η^7-C_7H_7)(η^5-C_7H_9)] can be prepared readily by reducing $MoCl_5$ with sodium amalgam in the presence of cycloheptatriene.[4a] However, treatment of a thf suspension of $MoCl_5$ and 1,3,5,7-tetramethylcycloheptatriene with 5 equivalents of sodium amalgam failed to yield any tractable organometallic products.

In conclusion, the reactions and structures proposed for the new compounds are shown in Scheme 1. The chemistry for the most part is closely similar to that of Mo(η-C_7H_7) analogues. However, the mixed-ring cation **10** is clearly less reactive than [Mo(η^6-C_6H_5Me)(η^7-C_7H_7)]$^+$.

Experimental

All manipulations and reactions were carried out using standard Schlenk-line techniques under an atmosphere of dinitrogen which was purified by passage over 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 (thf)], sodium (toluene), 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. Molybdenum hexacarbonyl was used as received (Aldrich) and 1,3,5,7-tetramethylcycloheptatriene was prepared as described.[15] Ultraviolet photolyses were performed using a Hanovia 500 W low-pressure mercury lamp with the sample contained in a quartz ampoule.

Proton, ^{31}P and ^{13}C NMR spectra were recorded on a Brüker AM 300 spectrometer (^1H, 300; ^{31}P, 121.44; ^{13}C, 75.43 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 Hz. Infrared spectra were recorded on a Perkin Elmer 1510 FT interferometer or a Perkin Elmer 457 grating spectrometer, on which spectra below 400 cm^{-1} were obtained. Mass spectra were measured by the SERC mass spectrometry service, University College, Swansea. Microanalyses were performed by the Microanalytical Department of the Inorganic Chemistry Laboratory.

Reaction of Molybdenum Hexacarbonyl with 1,3,5,7-*Tetramethylcycloheptatriene*.—A mixture of [Mo(CO)$_6$] (1 g, 3.8 mmol), 1,3,5,7-tetramethylcycloheptatriene (0.67 g, 4.5 mmol), octane (15 cm^3) and thf (5 cm^3) was heated at 140 °C for 17 h. The resulting deep red solution was evaporated to dryness, then the residue was extracted with light petroleum (b.p. 40–60 °C) (2 × 30 cm^3). Cooling the extract at −20 °C gave orange needle crystals of [Mo(η^6-$C_7H_4Me_4$-1,3,5,7)(CO)$_3$] **1** which were collected by filtration. The crystals were then washed with cold light petroleum (b.p. 40–60 °C) (5 cm^3) and dried *in vacuo*. Yield 0.66 g (53%). The filtrate was concentrated to *ca.* 20 cm^3, then cooled at −20 °C to give red crystals of [Mo(η^6-$C_7H_4Me_4$-1,2,4,6)(CO)$_3$] **2** (0.26 g, 21%) and [Mo(η^6-$C_7H_4Me_4$-1,3,4,6)(CO)$_3$] **3** (0.10 g, 8%) as an inseparable mixture.

Preparations. [Mo(η^7-$C_7H_3Me_4$-1,2,4,6)(CO)$_3$][BF_4] **4**. (*a*) A mixture of [Mo(η^6-$C_7H_4Me_4$-1,3,5,7)(CO)$_3$] **1** (3.94 g, 12 mmol) and triphenylcarbenium tetrafluoroborate (3.96 g, 12 mmol) in CH_2Cl_2 (50 cm^3) was heated at 60 °C for 32 h. After removing the volatiles, the residue was extracted with light petroleum (b.p. 40–60 °C) (3 × 30 cm^3). The insoluble material was extracted with acetone (3 × 25 cm^3). The volatiles were removed and the ^1H NMR spectrum of the residue showed that it contained the starting [Mo(η^6-$C_7H_4Me_4$-1,3,5,7)(CO)$_3$]

(0.61 g). The acetone solution was concentrated to *ca.* 30 cm^3 then cooled at -80 °C to afford the product as orange-red crystals. Yield 1.6 g (38% based on unrecovered starting material).

(*b*) A mixture of [Mo(η^6-$C_7H_4Me_4$-1,3,5,7)(CO)$_3$] **1**, [Mo(η^6-$C_7H_4Me_4$-1,2,4,6)(CO)$_3$] **2** and [Mo(η^6-$C_7H_4Me_4$-1,3,4,6)(CO)$_3$] **3** (1.4 g, 4.3 mmol) in 2:3:1 ratio was treated with triphenylcarbenium tetrafluoroborate (1.5 g, 4.5 mmol) in CH_2Cl_2 (25 cm^3) at 60 °C for 7 h. The volatiles were then removed *in vacuo* and the residue was extracted with light petroleum (b.p. 40–60 °C) (2 × 30 cm^3). The insoluble material was then extracted with acetone (2 × 20 cm^3). The light petroleum was evaporated to dryness and the ^{1}H NMR spectrum of the residue showed that it contained [Mo(η^6-$C_7H_4Me_4$-1,3,5,7)(CO)$_3$] (0.31 g). The acetone solution was cooled at -80 °C to produce red crystals which were filtered off and then dried *in vacuo*. Yield 1.2 g (87% based on unrecovered starting material).

[Mo(η^7-$C_7H_3Me_4$-1,2,4,6)(CO)$_2$Cl] **5**. A mixture of [Mo(η^7-$C_7H_3Me_4$-1,2,4,6)(CO)$_3$][BF$_4$] **4** (0.50 g, 1.21 mmol) and LiCl (52 mg, 1.23 mmol) in acetone (20 cm^3) was stirred at room temperature for 1 h, then the volatiles were removed *in vacuo*. The residue was extracted with toluene (2 × 25 cm^3). Concentration followed by cooling at -80 °C gave dark green crystals which were collected by filtration and dried *in vacuo*. Yield 0.3 g (74%).

[Mo(η^3-$C_7H_3Me_4$-1,2,4,6)(CO)$_2$(dmpe)Cl] **7**. To a solution of [Mo(η^7-$C_7H_3Me_4$-1,2,4,6)(CO)$_2$Cl] **5** (50 mg, 0.15 mmol) in toluene (10 cm^3) was added a solution of 1,2-bis(dimethylphosphino)ethane in toluene (0.22 cm^3 of a 0.1 g cm^{-3} solution, 0.15 mmol). The colour changed from green to bright red during the course of the reaction. After stirring for 2 h at room temperature, the volatiles were removed *in vacuo* and the red oily material was extracted with light petroleum (b.p. 40–60 °C) (2 × 20 cm^3). After filtration, the red filtrate was cooled at -20 °C to give red needle crystals which were collected by filtration and dried *in vacuo*. Yield 60 mg (83%).

[Mo(η^7-$C_7H_3Me_4$-1,2,4,6)(dmpe)Cl] **9**. A solution of [Mo-(η^3-$C_7H_3Me_4$-1,2,4,6)(CO)$_2$(dmpe)Cl] **7** (40 mg, 0.08 mmol) in toluene (20 cm^3) was photolysed for 1 h at room temperature. The resulting green solution was evaporated to dryness to give the product in an oily form containing a small amount of impurities. Yield *ca.* 50%.

[Mo(η^6-C_6H_5Me)(η^7-$C_7H_3Me_4$-1,2,4,6)][BF$_4$] **10**. A suspension of [Mo(η^7-$C_7H_3Me_4$-1,2,4,6)(CO)$_3$][BF$_4$] **4** (0.65 g, 1.57 mmol) in toluene (80 cm^3) was heated at 125 °C for 27 h. After removing the volatiles *in vacuo*, a green solid was obtained which was essentially pure. Recrystallisation from acetone–thf mixture furnished the pure product as pale green crystals. Yield 0.58 g (88%).

[Mo(η^7-$C_7H_3Me_4$-1,2,4,6)($CH_3COCHCOCH_3$)(PPh$_3$)] **11**. A mixture of pentane-2,4-dione (30 mg, 0.3 mmol) and sodium ethoxide (18 mg, 0.26 mmol) in methanol (10 cm^3) was stirred at room temperature for 30 min. Then the solution was transferred to another Schlenk flask containing PPh$_3$ (62 mg, 0.24 mmol) and [Mo(η^6-C_6H_5Me)(η^7-$C_7H_3Me_4$-1,2,4,6)][BF$_4$] **10** (0.1 g, 0.24 mmol). The mixture was heated at 60 °C for 6 h to give a brown suspension. The suspension was then evaporated to dryness and the residue was extracted with light petroleum (b.p. 40–60 °C) (4 × 25 cm^3). The light petroleum solution was concentrated to *ca.* 20 cm^3 and then cooled at -80 °C to afford the product as red crystals. Yield 58 mg (40%).

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