Synthesis, Structure and Reactivity of Tri- and Penta-hapto-bonded Cycloheptadienyl Complexes of Molybdenum†

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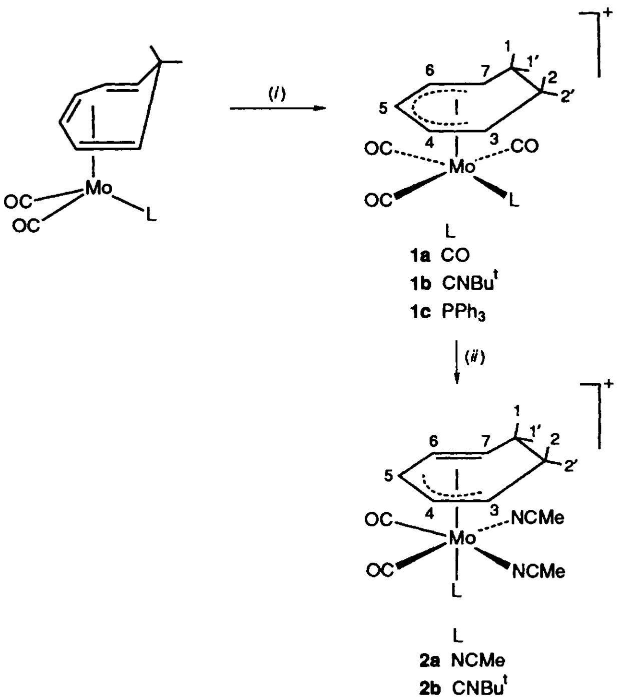
Protonation by $HBF_4 \cdot Et_2O$ of the cycloheptatriene complexes $[Mo(CO)_2L(\eta^6\text{-}C_7H_8)]$ in the presence of CO has yielded the cycloheptadienyl products $[Mo(CO)_3L(\eta^5\text{-}C_7H_9)][BF_4]$ (L = CO **1a**, CNBu^t **1b** or PPh_3 **1c**); subsequent treatment of **1a** or **1b** with acetonitrile afforded the trihapto-bonded complexes $[Mo(CO)_2L(NCMe)_2(\eta^3\text{-}C_7H_9)]^+$ (L = NCMe **2a** or CNBu^t **2b**). Reaction of **2a** with sodium cyclopentadienide Na(cp) gives $[Mo(CO)_2(\eta^3\text{-}C_7H_9)(cp)]$ **3** for which an X-ray structural characterisation confirmed the trihapto-bonding mode of the cycloheptadienyl ligand. The monodentate ligands PPh_3 and CNBu^t react in a 2:1 ratio with **2a** to give $[Mo(CO)_2L_2(\eta^5\text{-}C_7H_9)]^+$ (L = PPh_3 **4a** or CNBu^t **4b**) and chelate ligands L–L react with **2a** to give $[Mo(CO)_2(L\text{–}L)(\eta^5\text{-}C_7H_9)]^+$ (L = $Ph_2PCH_2PPh_2$ **5**, 2,2′-bipyridyl **6**, cyclohexa-1,3-diene **7** or norborna-2,5-diene **8**). The crystal structure of **5** reveals a highly asymmetric molecule in which the carbonyl carbon and phosphorus donor atoms exhibit significant deviation from a common basal plane.

The variable hapticity of dienyl ligands and the interconversion of η^5, η^3 and σ bonding modes are of importance both for an understanding of organometallic reaction mechanisms and for potential catalytic applications. The extensive reports on hapticity interconversions in 'closed', cyclic dienyl ligands[1] and 'open', acyclic pentadienyl groups[2] have been reviewed but, by contrast, the analogous chemistry of 'open' pentadienyls, constrained within a closed ring such as cyclohexadienyl[3] or cycloheptadienyl,[4–7] is surprisingly underdeveloped in view of the promise of some fascinating comparative chemistry. Thus, whilst the 'open' dienyl system of the cycloheptadienyl ligand (like its 'open', acyclic pentadienyl counterparts) might be expected to undergo hapticity interconversions more readily than 'closed' analogues such as the cyclopentadienyl or indenyl ligand (which have no break in the dienyl conjugation), cycloheptadienyl ligands are constrained to a rigid 'U' conformation irrespective of the hapticity of the dienyl system, but acyclic pentadienyl ligands exhibit considerable conformational flexibility which may further facilitate hapticity variations. Our interest in hapticity changes of the cycloheptatrienyl ligand in complexes of Mo and W[8–10] led us to consider the chemistry of related cycloheptadienyl complexes[11–14] and this paper describes the first examples of $\eta^5 \longleftrightarrow \eta^3$ hapticity interconversions in cycloheptadienylmolybdenum chemistry together with a versatile synthetic route to a wide range of half-sandwich cycloheptadienylmolybdenum complexes. Representative examples of complexes with η^3- or η^5-bonded cycloheptadienyl ligands have been structurally characterised so inviting comparison with analogous cycloheptatrienyl and acyclic pentadienyl derivatives.

Results and Discussion

Treatment of CH_2Cl_2 solutions of the cycloheptatriene complexes $[Mo(CO)_2L(\eta^6\text{-}C_7H_8)]$ (L = CO, CNBu^t or PPh_3) with $HBF_4 \cdot Et_2O$ in the presence of a vigorous stream of carbon monoxide affords the new η^5-bonded cycloheptadienyl complexes $[Mo(CO)_3L(\eta^5\text{-}C_7H_9)][BF_4]$ [L = CO **1a**, CNBu^t **1b** or PPh_3 **1c** (Scheme 1)]. Details of the characterisation of these and subsequently described compounds are given in Tables 1 (microanalytical, infrared and mass spectroscopic data) and 2 (^{1}H and ^{13}C NMR data). The ^{1}H and ^{13}C NMR data establish typical chemical shifts for a cycloheptadienyl ligand bonded η^5 to molybdenum; thus in the ^{13}C NMR spectra the five pentadienyl carbons lie in the approximate range δ 110–90 whilst ^{1}H NMR spectra exhibit three separate environments for the pentadienyl protons and two resonances corresponding to *exo*/*endo* protons attached to sp^3 carbons of the cycloheptadienyl ring. A feature of the FAB mass spectra common to these and many of the subsequently described complexes is the successive loss of 28 then 30 mass units from the molecular ion; the loss of 30 units may be explained by the combined loss of CO



Scheme 1 *Reagents and conditions:* (*i*) L = CO, CNBu^t or PPh_3, $HBF_4 \cdot Et_2O$ + CO in CH_2Cl_2; (*ii*) L = CO or CNBu^t, stirred in MeCN

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

Table 1 Microanalytical, infrared and mass spectroscopic data

	Analysis (%)[a]			Infrared[b] (cm^{-1})	
Complex	C	H	N	ν(CO)	Mass spectral data[c]
1a	34.0 (34.0)	2.5 (2.3)		2112, 2065, 2008	303 (M^+), 275 ($[M - CO]^+$), 245 ($[M - 2CO - 2H]^+$)
1b	40.1 (40.6)	4.0 (4.1)	3.0 (3.2)	2070, 2014 (sh), 1991[d]	358 (M^+), 330 ($[M - CO]^+$), 300 ($[M - 2CO - 2H]^+$)
1c	53.8 (54.0)	4.1 (3.85)		2059s, 2018w, 1964s	537 (M^+), 509 ($[M - CO]^+$), 451 ($[M - 3CO - 2H]^+$)
2a	39.4 (39.6)	4.0 (3.9)	8.9 (9.2)	1958, 1877[e,f]	g
2b	43.2 (43.5)	4.9 (4.8)	8.6 (8.5)	1957, 1880[e,h]	413 (M^+), 385 ($[M - CO]^+$), 330 ($[M - CNBu^t]^+$)
3	54.5 (54.2)	4.2 (4.5)		1938, 1856[i]	313 (M^+), 284 ($[M - CO]^+$), 254 ($[M - 2CO - 2H]^+$)
4a	62.8 (63.1)	4.8 (4.6)		1980, 1908	771 (M^+), 509 ($[M - PPh_3]^+$), 451 ($[M - 2CO - PPh_3 - 2H]^+$)
4b	45.9 (45.7)	5.6 (5.4)	5.7 (5.6)	2030, 1963[j]	413 (M^+), 385 ($[M - CO]^+$), 355 ($[M - 2CO - 2H]^+$)
5	56.9 (56.9)	4.3 (4.3)		2014, 1924	631 (M^+), 573 ($[M - 2CO - 2H]^+$)
6	47.3 (46.7)	3.6 (3.5)	5.7 (5.7)	1988, 1922	403 (M^+), 345 ($[M - 2CO - 2H]^+$)
7	43.9 (43.7)	4.1 (4.1)		2046, 2008	327 (M^+)
8	44.9 (45.3)	4.2 (4.0)		2037, 1990	339 (M^+)

[a] Calculated values in parentheses. [b] Solution spectra in CH_2Cl_2 unless stated otherwise; s = strong, w = weak and sh = shoulder. [c] By FAB mass spectroscopy, m/z values based on ^{98}Mo. [d] ν(C≡N) 2196 cm^{-1}, [e] In MeCN. [f] ν(C≡N) (Nujol) 2347, 2319 and 2290 cm^{-1}. [g] Satisfactory spectrum not obtained. [h] ν(C≡N) (Nujol) (NCMe) 2285, ($CNBu^t$) 2191 cm^{-1}. [i] ν(CO) (hexane) 1955 and 1882 cm^{-1}. [j] ν(C≡N) 2186 and 2165 cm^{-1}.

from the metal centre and two hydrogens from the cycloheptadienyl ligand. The complexes **1** are analogues of a series of previously reported tungsten derivatives $[W(CO)_3L(\eta^5\text{-}C_7H_9)]^+$ [L = PPh_3, $P(OMe)_3$, *etc.*] obtained by direct protonation of $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ in the presence of L;[12] however, this route is not applicable to the synthesis of the corresponding cycloheptadienylmolybdenum complexes.[11]

The tetracarbonyl complex **1a** is only very sparingly soluble in CH_2Cl_2 and acetone and attempts to obtain NMR spectra in CD_3CN suggested that it reacts with this solvent; a synthetic study was therefore undertaken. When $[Mo(CO)_4(\eta^5\text{-}C_7H_9)]^+$ was stirred at ambient temperature in acetonitrile CO was evolved and the η^3-bonded complex $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_9)][BF_4]$ **2a** was isolated in high yield. The formation of **2a** from **1a** defines the first example of $\eta^5 \longrightarrow \eta^3$ ring slip in cycloheptadienyl complexes of the Group 6 transition metals, moreover the formation of $[Co(CO)_2(PPh_3)(\eta^3\text{-}C_7H_9)]$ from $[Co(PPh_3)_2(\eta^5\text{-}C_7H_9)]$[6] is the only well established precedent for $\eta^5 \longleftrightarrow \eta^3$ hapticity interconversion of the cycloheptadienyl ligand.

The formulation $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_9)]^+$ provides two comparisons of interest. First, the reaction of $[\{Mo(CO)_3(\eta^5\text{-}C_9H_7)\}_2]$ (*Mo–Mo*) (C_9H_7 = indenyl) with $Ag[BF_4]$ in MeCN[15] affords $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)]^+$ and not $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_9H_7)]^+$ so supporting the view that the cycloheptadienyl ligand is more susceptible to $\eta^5 \longrightarrow \eta^3$ ring slip than is the indenyl ligand, in spite of the well established 'indenyl effect'.[1] Secondly the η^3-cycloheptadienyl complex **2a** is a direct analogue of the cycloheptatrienylmolybdenum complex $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)]^+$ that we have reported previously,[9] but whilst $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)]^+$ exists as an equilibrium mixture with $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_7)]^+$ in acetonitrile, we have obtained no evidence for the formation of $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_7H_9)]^+$ from **2a**.

The NMR spectroscopic data for complex **2a** define characteristic spectra for an η^3-bonded cycloheptadienyl ligand. The ^1H NMR spectrum was assigned with the aid of $[^1H\text{–}^1H]$COSY (correlation spectroscopy) and $^1H\text{–}^1H$ double-irradiation experiments and may be compared with data for $[Co(CO)_2(PPh_3)(\eta^3\text{-}C_7H_9)]$[6] and $[W(CO)_2(\eta^3\text{-}C_7H_9)(\eta^5\text{-}C_5H_4Me)]$.[16] A $[^1H\text{–}^{13}C]$HETCOR (heteronuclear correlation) experiment was employed to establish assignments in the ^{13}C NMR spectrum of **2a** for which no comparable data are available in the literature; characteristic features of the spectrum are the two unco-ordinated alkene carbons with chemical shifts around δ 130 and the three co-ordinated allyl carbons with chemical shifts in an approximate range δ 85–75. The ambient-temperature ^1H and ^{13}C NMR spectra of **2a** were both well defined with no evidence for a fluxional process leading to interconversion of the metal-co-ordinated carbons of the cycloheptadienyl ring, although such a process has been described for $[Co(CO)_2(PPh_3)(\eta^3\text{-}C_7H_9)]$[17] and is well established for η^3-bonded cycloheptatrienyl complexes of molybdenum.[18] The infrared spectrum of **2a** in the carbonyl stretching region exhibits a pattern typical of *cis* carbonyl ligands[19] and on this basis the isomer of **2a** illustrated in Scheme 1 is suggested as the preferred molecular geometry. A comparison of the wavenumbers of the carbonyl stretching frequencies for the η^3-cycloheptadienyl complex **2a** [ν(CO)(NCMe) 1958 and 1877 cm^{-1}] and the analogous η^3-cycloheptatrienyl complex[9] $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)]^+$ [ν(CO)(NCMe) 1960 and 1887 cm^{-1}] reveals a close correspondence, but bands for the η^3-cycloheptatrienyl complex are to high wavenumber relative to the analogous η^3-cycloheptadienyl derivative; subsequent studies have shown this to be a general feature which may reflect an enhanced ability of the conjugated diene unit of $\eta^3\text{-}C_7H_7$ ligands to withdraw electron density from the metal centre by comparison with the single 'ene' system of the η^3-cycloheptadienyl ligand.

The conversion of the η^5-cycloheptadienyl complex **1a** into the η^3-cycloheptadienyl product **2a** *via* reaction with NCMe prompted an investigation of the analogous reactions of $[Mo(CO)_3L(\eta^5\text{-}C_7H_9)]^+$ (L = $CNBu^t$ or PPh_3). When $[Mo(CO)_3(CNBu^t)(\eta^5\text{-}C_7H_9)]^+$ **1b** was dissolved in acetonitrile a colour change from yellow to red-brown accompanied

Table 2 Proton and ^{13}C NMR spectral data

Complex	^{1}H NMR (δ)[a]	^{13}C NMR (δ)[a]
1a[b]	7.58 (m, 1 H, H^5), 6.12 (m, 2 H, H^3, H^7), 5.99 (m, 2 H, H^4, H^6), 2.76, 2.53 (m, 4 H, $H^{1,1'}$, $H^{2,2'}$)	
1b[c]	6.78 (m, 1 H, H^5), 5.47 (m, 2 H, H^4, H^6), 5.31 (m, 2 H, H^3, H^7), 2.34, 2.23 (m, 4 H, $H^{1,1'}$, $H^{2,2'}$), 1.69 (s, 9 H, CNBu^t)	219.3, 213.9 (CO), 141.8 (*C*NCMe$_3$), 100.7, 100.4 (C^3, C^4, C^6, C^7), 96.5 (C^5), 62.1 (CN*C*Me$_3$), 32.8 (C^1, C^2), 30.2 (CNC*Me*$_3$)
1c	7.57, 7.31 (m, 15 H, Ph), 6.14 (m, 1 H, H^5), 5.26 (m, 2 H, H^4, H^6), 5.22 (m, 2 H, H^3, H^7), 2.37, 2.21 (m, 4 H, $H^{1,1'}$, $H^{2,2'}$)	219.4, 219.2 (CO), 133.2, 133.0, 132.2, 130.1, 130.0 (Ph), 108.2, 102.4, 99.1 (C^{3-7}), 34.7 (C^1, C^2)
2a[d]	6.14 [m, 1 H, H^6 $J(H^6-H^7)$ 11, $J(H^5-H^6)$ 6], 5.40 (m, 1 H, H^7), 5.01 (m, 1 H, H^5), 4.92 (m, 1 H, H^3), 4.19 [m, 1 H, H^4, $J(H^4-H^5)$ 6, $J(H^3-H^4)$ 7], 2.57 (m, 1 H, $H^{2'}$), 2.10, 2.01 (m, 2 H, H^2, $H^{1'}$), 1.43 (m, 1 H, H^1)	224.8, 223.2 (CO), 131.6 (C^6), 130.4 (C^7), 82.2 (C^5), 80.5 (C^3), 70.0 (C^4), 30.8, 28.6 (C^1, C^2)
2b[d]	6.17 [m, 1 H, H^6, $J(H^6-H^7)$ 10], 5.54 (m, 1 H, H^7), 5.37 (m, 1 H, H^5), 5.09 (br, 1 H, H^3), 4.65 [m, 1 H, H^4, $J(H^4-H^5)$ 7, $J(H^3-H^4)$ 7], 2.57 (m, 1 H, $H^{2'}$), 2.15 (m, 2 H, $H^{1'}$, H^2), 1.57 (m, 1 H, H^1), 1.68 (s, 9 H, CNCMe$_3$)	223.1, 220.5 (CO), 148.1 (*C*NCMe$_3$), 130.3, 130.1 (C^6, C^7), 89.2, 83.2, 81.7 (C^{3-5}), 59.5 (CN*C*Me$_3$), 30.2, 27.8 (C^1, C^2), 29.1 (CNC*Me*$_3$)
3	5.97 [m, 1 H, H^6, $J(H^6-H^7)$ 11], 5.27 (s, 5 H, C_5H_5), 5.12 (m, 1 H, H^7), 4.40 (m, 1 H, H^3), 4.13 (m, 2 H, H^4, H^5), 2.35 (m, 1 H, H^2), 2.06 (m, 2 H, $H^{2'}$, H^1), 1.46 (m, 1 H, $H^{1'}$)	239.3, 237.2 (CO), 131.7 (C^6), 124.9 (C^7), 92.4 (C_5H_5), 66.2 (C^5), 65.3 (C^3), 55.7 (C^4), 29.7 (C^2), 28.8 (C^1)
4a[e]	7.54 (br, 30 H, Ph), 5.30 (m, 1 H, H^5), 5.17 (m, 2 H, H^4, H^6), 4.82 (m, 2 H, H^3, H^7), 1.75, 1.22 (m, 4 H, $H^{1,1'}$, $H^{2,2'}$)	229.0 [t, CO, J(P–C) 24], 133.4–129.3 (Ph), 104.2, 100.4, 99.2 (C^{3-7}), 33.9 (C^1, C^2)
4b[f]	6.38 (m, 1 H, H^5), 5.33 (m, 2 H, H^4, H^6), 4.75 (m, 2 H, H^3, H^7), 2.07 (m, 4 H, $H^{1,1'}$, $H^{2,2'}$), 1.60 (s, 18 H, CNCMe$_3$)	218.7 (CO), 150.5 (*C*NCMe$_3$), 104.0, 99.0, 92.3 (C^{3-7}), 60.7 (CN*C*Me$_3$), 33.2 (C^1, C^2), 30.2 (CNC*Me*$_3$)
5[g]	7.86–7.20, 6.60 (m, 20 H, Ph), 5.98 (m, 1 H, H^5), 5.45 (m, 1 H, H^4), 5.23 (m, 1 H, H^7), 4.68 (m, 2 H, H^6, CH_2 of dppm), 4.27 (m, 1 H, CH_2 of dppm) 4.00 (m, 1 H, H^3), 2.57 (m, 1 H), 2.12 (m, 2 H), 1.85 (m, 1 H), ($H^{1,1'}$, $H^{2,2'}$)	225.1, 222.8 (br, CO), 135.2–130.2 (Ph), 106.5, 102.5, 100.4, 99.9, 82.3 (C^{3-7}), 43.6 [t, CH_2 of dppm, J(P–C) 26], 33.5, 32.3 (C^1, C^2)
6[h]	9.38 (m, 1 H), 8.92 (m, 1 H) ($H^{A,A'}$), 8.66 (m, 1 H), 8.58 (m, 1 H) ($H^{D,D'}$), 8.37 (m, 1 H), 8.15 (m, 1 H), ($H^{C,C'}$), 7.91 (m, 1 H), 7.56 (m, 1 H) ($H^{B,B'}$), 6.16 (m, 1 H, H^5), 5.75 (m, 1 H, H^4), 4.70 (m, 1 H, H^6), 4.65 (m, 1 H, H^7), 4.03 (m, 1 H, H^3), 2.06, 1.41 (4 H, $H^{1,1'}$, $H^{2,2'}$)	243.2, 234.7 (CO), 156.9, 153.6 ($C^{A,A'}$), 155.2, 154.0 ($C^{E,E'}$), 140.7, 139.4 ($C^{C,C'}$), 128.5, 126.9 ($C^{B,B'}$), 125.0, 124.6 ($C^{D,D'}$), 113.8, 111.8, 98.1, 91.9, 82.3 (C^{3-7}), 34.3, 27.1 (C^1, C^2)
7[i]	6.54 (m, 1 H, H^5), 6.44 (m, 1 H, H^4), 5.64 (m, 1 H, H^6), 5.30 (m, 1 H, H^7), 4.57 (m, 1 H, H^3), 2.74, 2.50, 2.20–2.00 (m, 4 H, $H^{1,1'}$, $H^{2,2'}$), 6.02 (m, 1 H), 5.59 (m, 1 H) (H^D, H^E), 4.34 (m, 1 H), 4.06 (m, 1 H), (H^C, H^F), 2.27, 2.20–2.00 (4 H, $H^{A,A'}$, $H^{B,B'}$)	218.5, 214.9 (CO), 107.0, 104.1, 101.2, 100.0, 95.8, 81.8, 78.9, 78.5, 73.3 (C^{3-7}, C^{C-F}), 37.5, 27.9, 25.9, 23.7 (C^1, C^2, C^A, C^B)
8[i]	6.60 (m, 1 H, H^5), 6.00 (m, 2 H), 5.91 (m, 1 H), (H^3, H^4, H^6), 4.47 (m, 1 H, H^7), 2.46 (m, 2 H, $H^{2,2'}$), 1.98 (m, 2 H, $H^{1,1'}$), 4.69 (m, 1 H), 4.59 (m, 2 H), 3.87 (m, 1 H) [$H^{C,C'}$, $H^{D,D'}$, $J(H^C-H^{C'})$ or $J(H^D-H^{D'})$ 4, 5], 3.56 (m, 2 H, $H^{B,B'}$), 1.18 (s, 2 H, $H^{A,A'}$)	219.1, 215.1 (CO), 115.0, 109.2, 103.9, 99.7, 79.8, 76.1, 75.6, 60.8, 57.9 (C^{3-7}, $C^{C,C'}$, $C^{D,D'}$), 47.7, 46.2, 40.9, 34.3, 30.4 (C^1, C^2, C^A, $C^{B,B'}$)

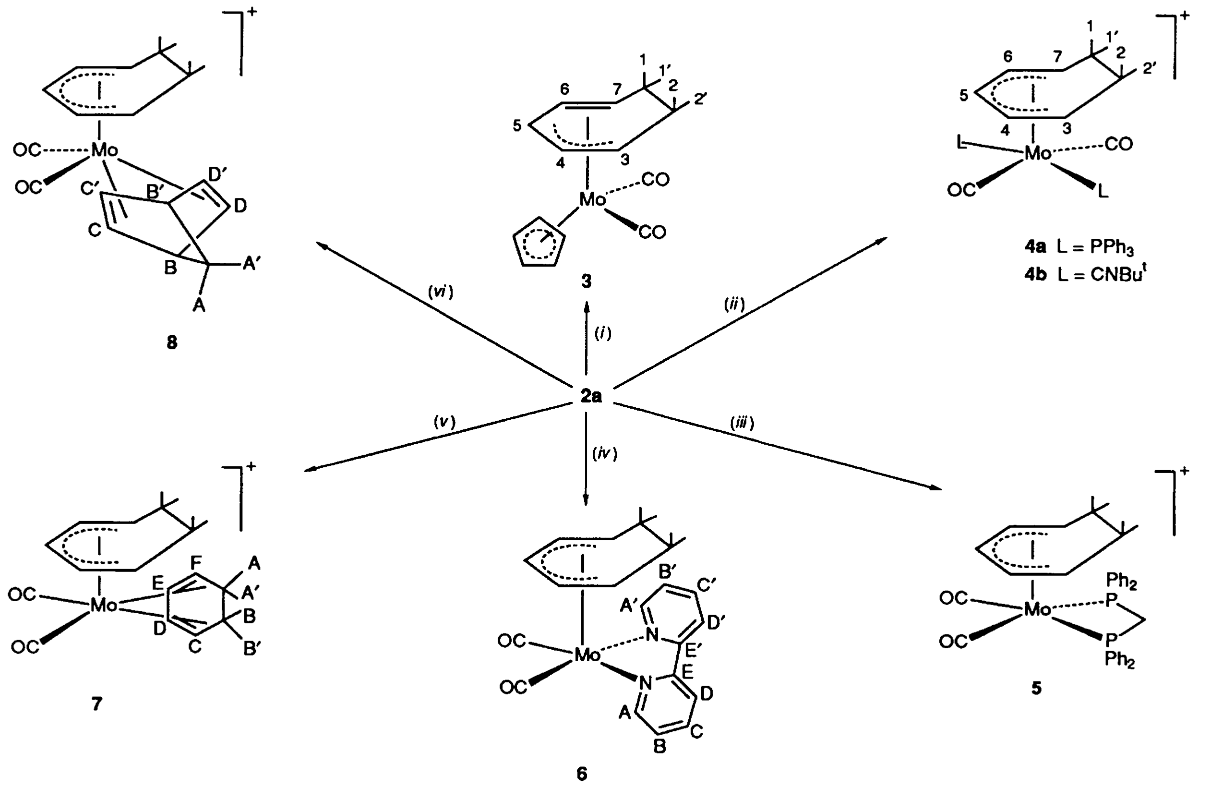
[a] 300 MHz ^{1}H NMR spectra, 75 MHz ^{13}C NMR spectra; s = singlet, t = triplet, m = multiplet, br = broad; chemical shifts downfield from SiMe$_4$, coupling constants in Hz, in CDCl$_3$ solution unless otherwise stated; numbering as in Schemes 1 and 2. [b] In $(CD_3)_2CO$. [c] ^{13}C NMR spectrum in CD_2Cl_2 (−40 °C). [d] In CD_3CN. [e] ^{31}P NMR spectrum, signal downfield from H_3PO_4 [δ 50.7 (s)]. [f] Data for minor isomer (CDCl$_3$): ^{1}H, δ 6.29 (m, 1 H, H^5), 5.21 (m, 2 H, H^4, H^6), and 4.96 (m, 2 H, H^3, H^7); ^{13}C δ 225.5 (CO), 149.7 (*C*NCMe$_3$); 100.4, 100.2, 96.7 (C^{3-7}), 60.2 (CN*C*Me$_3$) and 32.7 (C^1, C^2). [g] In CD_2Cl_2, ^{1}H at (−90 °C), ^{13}C at (−20 °C); ^{31}P (−60 °C), AB doublet of doublets, δ −5.37, −7.11, J(P–P) 75 Hz; (20 °C), δ −5.2 (s). [h] In CD_2Cl_2. [i] In CD_2Cl_2 (−40 °C).

the formation of $[Mo(CO)_2(CNBu^t)(NCMe)_2(\eta^3\text{-}C_7H_9)]^+$ **2b**; its infrared spectrum is consistent with a *cis* arrangement of carbonyl ligands but further discrimination between several possible isomeric configurations was not achieved. By contrast, treatment of $[Mo(CO)_3(PPh_3)(\eta^5\text{-}C_7H_9)]^+$ **1c** with acetonitrile led to an incompletely characterised product mixture of which the predominant component was phosphine-free **2a**. The relative stability of $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_9)]^+$ **2a** with respect to loss of NCMe and reversion to an η^5-bonded cycloheptadienyl product $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_7H_9)]^+$ has already been referred to; indeed **2a** can be recrystallised from CH_2Cl_2 without significant loss although prolonged exposure to CH_2Cl_2 does result in decomposition. However in CH_2Cl_2 the isocyanide derivative **2b** rapidly changes to a new complex with ν(CO)(CH_2Cl_2) 2001 and 1947 cm^{-1}, tentatively formulated as $[Mo(CO)_2(CNBu^t)(NCMe)(\eta^5\text{-}C_7H_9)]^+$ {*cf.* $[Mo(CO)_2(CNBu^t)(PPh_3)(\eta^5\text{-}C_7H_9)]^+$,[20] ν(CO)($CH_2Cl_2$) 2007 and 1939 cm^{-1}}. So far attempts to isolate and characterise fully $[Mo(CO)_2(CNBu^t)(NCMe)(\eta^5\text{-}C_7H_9)]^+$ have been unsuccessful but on redissolving in acetonitrile **2b** is reformed.

Organometallic acetonitrile complexes are generally useful synthetic precursors to a wide range of products *via* displacement of relatively labile acetonitrile ligands[15] and the convenient, high-yield synthesis of **2a** led to the development of an extensive substitution chemistry (Scheme 2). Two basic reaction types have been observed: acetonitrile displacement with retention of an η^3-bonded cycloheptadienyl ligand, and acetonitrile displacement with reversion to an η^5-bonded C_7H_9 ligand, although the latter reaction type is predominant.

Reaction of complex **2a** with sodium cyclopentadienide Na(cp) afforded the neutral η^3-cycloheptadienyl complex $[Mo(CO)_2(\eta^3\text{-}C_7H_9)(cp)]$ **3** (Scheme 2) which was isolated in low yield as a yellow solid following purification by column chromatography. The NMR spectroscopic data for **3**, including the ^{13}C NMR spectrum which was assigned with the aid of a [^{1}H–^{13}C]HETCOR experiment, are consistent with those obtained for the η^3-cycloheptadienyl complexes **2a** and **2b** but, in contrast to **2a**, our efforts to obtain crystals of **3**, suitable for a single-crystal X-ray diffraction study, met with success. The crystallographic characterisation of $[Mo(CO)_2(\eta^3\text{-}C_7H_9)(cp)]$ provides a confirmation of the ^{13}C NMR spectroscopic diagnosis of the trihapto-bonding mode of the cycloheptadienyl ligand and moreover, to our knowledge, represents the first example of a structural corroboration of an η^3-bonded C_7H_9 ligand. Selected derived bond lengths and angles for **3** are presented in Table 3 and a view of the molecule, together with the atomic numbering scheme adopted, is shown in Fig. 1. Fig. 1 also illustrates the high thermal motion at atoms C(3), C(4) and C(5) in the cycloheptadienyl ring and, in consideration of this, the apparent chair configuration of the ring must be viewed with caution.

The molecular geometry of complex **3** closely resembles that of a series of related complexes $[Mo(CO)_2(\eta^3\text{-R})(cp)]$ (R = C_3H_5[22] or C_7H_7[23]) and $[Mo(CO)_2(\eta^3\text{-}C_5H_7)(\eta^5\text{-}C_9H_7)]$



Scheme 2 *Reagents and conditions:* (*i*) Na(cp) in thf; (*ii*) 2 equivalents of PPh_3 or $CNBu^t$ in CH_2Cl_2; (*iii*) dppm in CH_2Cl_2; (*iv*) 2,2′-bipyridyl in CH_2Cl_2; (*v*) cyclohexa-1,3-diene in CH_2Cl_2; (*vi*) norborna-2,5-diene in CH_2Cl_2

Table 3 Selected bond lengths (Å) and angles (°) for complex **3**

Mo–C(1)	2.200(4)	C(1)–C(2)	1.374(7)
Mo–C(2)	2.364(5)	C(1)–C(7)	1.361(7)
Mo–C(7)	2.376(4)	C(2)–C(3)	1.434(11)
Mo–C(8)	1.931(4)	C(3)–C(4)	1.272(16)
Mo–C(9)	1.923(5)	C(4)–C(5)	1.341(15)
Mo–C(10)	2.285(4)	C(5)–C(6)	1.505(12)
Mo–C(11)	2.316(4)	C(6)–C(7)	1.496(7)
Mo–C(12)	2.365(4)	C(10)–C(11)	1.355(7)
Mo–C(13)	2.359(4)	C(10)–C(14)	1.402(7)
Mo–C(14)	2.311(4)	C(11)–C(12)	1.350(7)
O(8)–C(8)	1.155(4)	C(12)–C(13)	1.372(7)
O(9)–C(9)	1.160(5)	C(13)–C(14)	1.390(7)
C(1)–Mo–C(2)	34.8(2)	C(1)–Mo–C(7)	34.3(2)
C(1)–Mo–C(8)	107.2(2)	C(1)–Mo–C(9)	106.6(2)
C(1)–Mo–C(10)	147.3(2)	C(1)–Mo–C(11)	122.9(2)
C(1)–Mo–C(12)	92.8(2)	C(1)–Mo–C(13)	90.7(2)
C(1)–Mo–C(14)	120.1(3)	C(2)–Mo–C(7)	61.0(2)
C(8)–Mo–C(9)	82.1(2)	C(8)–Mo–C(10)	98.2(2)
C(9)–Mo–C(10)	96.8(2)	Mo–C(1)–C(2)	79.1(3)
Mo–C(1)–C(7)	79.9(3)	C(2)–C(1)–C(7)	123.3(5)
Mo–C(2)–C(1)	66.1(3)	Mo–C(2)–C(3)	120.3(5)
C(1)–C(2)–C(3)	126.5(6)	C(2)–C(3)–C(4)	128.8(9)
C(3)–C(4)–C(5)	131(1)	C(4)–C(5)–C(6)	124.1(8)
C(5)–C(6)–C(7)	119.5(5)	Mo–C(7)–C(1)	65.7(2)
Mo–C(7)–C(6)	122.3(3)	C(1)–C(7)–C(6)	125.1(5)
Mo–C(8)–O(8)	177.7(4)	Mo–C(9)–O(9)	177.3(4)

(C_5H_7 = pentadienyl[24]), with the η^3-cycloheptadienyl ligand aligned *exo* and the two carbonyls located below the terminal allyl carbons C(2) and C(7). In solution, infrared spectroscopic studies suggest that the cycloheptatrienyl complex $[Mo(CO)_2(\eta^3\text{-}C_7H_7)(cp)]$ exhibits *exo–endo* conformational isomerism (four carbonyl stretching frequencies are observed in cyclohexane[18]) but the hexane solution infrared spectrum of **3** shows only two carbonyl bands indicating that **3** has a strong preference for one conformation in solution.

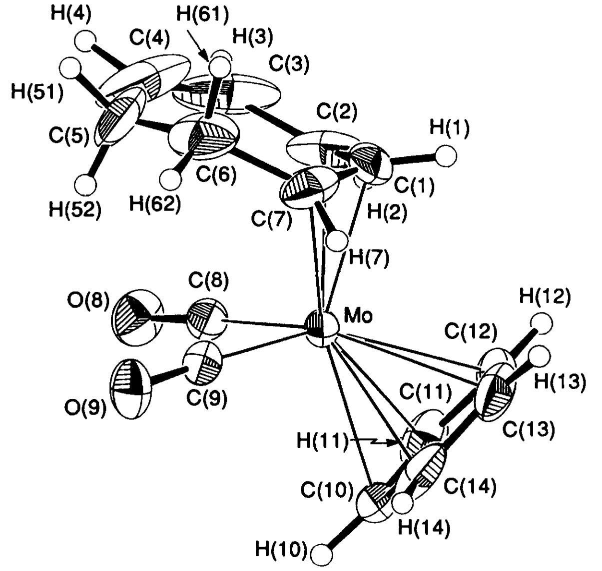


Fig. 1 An ORTEP[21] plot of the molecular structure of complex **3** showing the crystallographic numbering scheme

The remaining ligand-substitution reactions of $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_9)]^+$ **2a** that we have investigated lead to half-sandwich complexes in which the C_7H_9 ligand reverts to η^5 hapticity. Treatment of **2a** with 2 equivalents of monodentate ligands L in CH_2Cl_2 at room temperature rapidly affords products of the type $[Mo(CO)_2L_2(\eta^5\text{-}C_7H_9)]^+$ (L = PPh_3 **4a** or $CNBu^t$ **4b**); an alternative, albeit low-yield preparation of **4a** involves protonation of $[Mo(CO)_2(PPh_3)(\eta^6\text{-}C_7H_8)]$ in the presence of PPh_3. The relative intensities of infrared-active carbonyl stretching frequencies are consistent with a *trans* geometry[19] for **4a** and spectroscopic data, including ^{31}P NMR, indicate the presence of a single form; in general the spectroscopic data accord with data typical for η^5-cycloheptadienyl

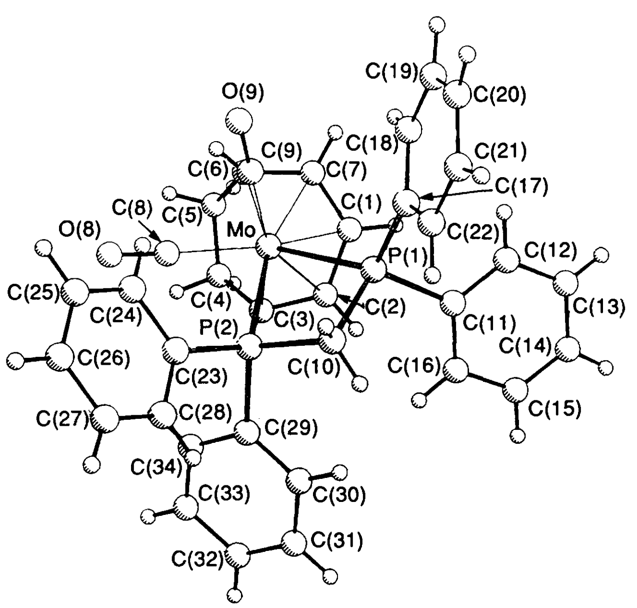


Fig. 2 The molecular structure of complex **5** showing the crystallographic numbering scheme

Table 4 Selected bond lengths (Å) and angles (°) for complex **5**

Mo–P(1)	2.520(2)	Mo–P(2)	2.479(1)
Mo–C(1)	2.326(7)	Mo–C(2)	2.310(6)
Mo–C(3)	2.454(6)	Mo–C(6)	2.344(6)
Mo–C(7)	2.309(7)	Mo–C(8)	2.021(8)
Mo–C(9)	1.946(6)	P(1)–C(10)	1.833(6)
P(1)–C(11)	1.816(6)	P(1)–C(17)	1.805(6)
P(2)–C(10)	1.823(7)	P(2)–C(23)	1.822(6)
P(2)–C(29)	1.820(5)	O(8)–C(8)	1.136(7)
O(9)–C(9)	1.158(7)	C(1)–C(2)	1.43(1)
C(1)–C(7)	1.38(1)	C(2)–C(3)	1.38(1)
C(3)–C(4)	1.51(1)	C(4)–C(5)	1.48(1)
C(5)–C(6)	1.52(1)	C(6)–C(7)	1.41(1)
P(1)–Mo–P(2)	67.55(5)	P(1)–Mo–C(1)	82.2(2)
P(2)–Mo–C(1)	130.7(2)	C(1)–Mo–C(2)	36.0(3)
C(1)–Mo–C(3)	63.5(3)	C(1)–Mo–C(6)	63.6(3)
C(1)–Mo–C(7)	34.8(3)	C(1)–Mo–C(8)	130.3(2)
C(1)–Mo–C(9)	117.0(3)	Mo–P(1)–C(10)	95.6(2)
Mo–P(1)–C(11)	122.3(2)	Mo–P(1)–C(17)	121.3(2)
C(10)–P(1)–C(11)	108.1(3)	C(10)–P(1)–C(17)	105.0(3)
C(11)–P(1)–C(17)	102.6(3)	Mo–P(2)–C(10)	97.3(2)
Mo–P(2)–C(23)	123.3(2)	Mo–P(2)–C(29)	118.4(2)
C(10)–P(2)–C(23)	105.4(3)	C(10)–P(2)–C(29)	108.0(3)
C(23)–P(2)–C(29)	102.9(3)	Mo–C(1)–C(2)	71.4(4)
Mo–C(1)–C(7)	72.0(4)	C(2)–C(1)–C(7)	124.0(7)
C(1)–C(2)–C(3)	127.0(7)	C(2)–C(3)–C(4)	124.6(7)
C(3)–C(4)–C(5)	118.1(6)	C(4)–C(5)–C(6)	115.9(6)
C(5)–C(6)–C(7)	123.6(7)	C(1)–C(7)–C(6)	123.6(8)
Mo–C(8)–O(8)	178.6(6)	Mo–C(9)–O(9)	175.5(6)
P(1)–C(10)–P(2)	99.0(3)		

complexes as established for **1a**–**1c**. The preferred geometry of the isocyanide derivative **4b** is less clear and ^{1}H and ^{13}C NMR spectroscopic studies indicate the presence of two isomers in an approximate ratio of 3 : 1 as determined from ^{1}H NMR integrals.

A series of bidentate chelate ligands also reacts readily with complex **2a** in CH_2Cl_2 to give products of the type [Mo(CO)$_2$(L–L)(η^5-C_7H_9)]$^+$ [L–L = $Ph_2PCH_2PPh_2$ (dppm) **5**, 2,2′-bipyridyl (bipy), cyclohexa-1,3-diene (chd) **7** or norborna-2,5-diene (nbd) **8**]. Spectroscopic data, including where appropriate ^{31}P NMR, for complexes **5**–**8** are detailed in Tables 1 and 2 and the numbering scheme for the NMR data is given in Scheme 2. The complex assignments of ^{1}H NMR data for **6**–**8** were made with the aid of [^{1}H–^{1}H]COSY and ^{1}H–^{1}H double-irradiation experiments and for **6** by comparison with reference spectra for the bipyridyl ligand.[25]

In principle complexes **5**–**8** might adopt a square-based pyramidal structure in which the carbonyl ligands are constrained to a *cis* geometry. However the related 'open' pentadienyl complex [Mo(CO)$_2$(dppe)(η^5-C_5H_7)]$^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$) exhibits a distorted structure in which the phosphorus-to-pentadienyl plane distances differ significantly.[26] An additional point of concern involves the NMR spectroscopic data for complexes **5**–**8**; essentially all spectra, including the ^{31}P NMR spectrum of **5**, are temperature dependent and limiting low-temperature spectra, which, with the exception of **6**, were obtained only by cooling to at least −20 °C, reveal asymmetric molecules as evidenced by the separate signals for each individual carbon/hydrogen of the C_7H_9 ring. Asymmetry is also apparent from ^{1}H and ^{13}C NMR signals of the dppm, bipy, chd and nbd ligands, and moreover variable-temperature ^{31}P NMR studies on **5** reveal an AB doublet of doublets pattern at −20 °C which coalesces to a singlet at +20 °C. Examples of inequivalence of all proton and carbon environments in an η^5-bonded cycloheptadienyl ring have been described previously and were attributed to a high barrier to rotation of the co-ordinated metal fragment with respect to the C_7H_9 ligand.[13]

Although the spectroscopic data determined for complexes **5**–**8** are most consistent with an η^5-bonded cycloheptadienyl ligand there are some aspects, notably the range of chemical shifts in ^{1}H and ^{13}C NMR spectra, which do not accord with complexes **1a**–**1c**. Therefore to provide a confirmation of the η^5-bonding mode of the cycloheptadienyl ligand in complexes **5**–**8** and to investigate the origin of the asymmetry established by NMR spectra, we set out to characterise structurally one example by an X-ray diffraction study. In the event the dppm complex **5** was selected for crystallographic characterisation because a knowledge of its molecular geometry permits comparison with the acyclic pentadienyl analogue[26] [Mo(CO)$_2$(dppe)(η^5-C_5H_7)]$^+$.

The molecular configuration of [Mo(CO)$_2$(dppm)(η^5-C_7H_9)]$^+$ **5** (and the crystallographic numbering scheme adopted) is illustrated in Fig. 2 and important bond lengths and angles are presented in Table 4. The structure confirms the proposed η^5-bonding mode of the cycloheptadienyl ring which is folded about the planes defined by C(3)–C(2)–C(1)–C(7)–C(6) and C(6)–C(5)–C(4)–C(3) (interplanar angle 133.4°); the fold angle corresponds closely to that reported for [FeMe(CO){P(OPh)$_3$}(η^5-C_7H_9)].[5] Both **5** and the acyclic pentadienyl complex [Mo(CO)$_2$(dppe)(η^5-C_5H_7)]$^+$ exhibit a significant deviation of the ligand arrangement at the metal centre away from a square-based pyramidal structure and this is most apparent when comparisons of non-bonded ligand-to-pentadienyl plane distances are made. For **5** the distances of the carbonyl carbons from the plane of the pentadienyl carbons in the cycloheptadienyl ring are 1.92 Å for C(8) and 2.93 Å for C(9) whilst the phosphorus-to-plane of ring distances are 3.04 Å for P(1) and 3.64 Å for P(2). For the pentadienyl complex [Mo(CO)$_2$(dppe)(η^5-C_5H_7)]$^+$ the distances between the phosphorus atoms of the dppe ligand and the pentadienyl plane are reported as 2.205 and 3.302 Å. A second structural similarity between **5** and [Mo(CO)$_2$(dppe)(η^5-C_5H_7)]$^+$ is the asymmetric orientation of the carbonyl and P-donor ligands with respect to the pentahapto-bonded ligand; this is clearly apparent for the cycloheptadienyl complex in Fig. 2. Whilst both complexes are asymmetric, the ligand orientations with respect to the η^5-bonded ligand are not identical. In **5** one of the carbonyl carbons C(8) is located directly below the carbon–carbon bond C(4)–C(5) of the cycloheptadienyl ring, whilst P(1) lies approximately under the central dienyl carbon C(1). By contrast, the solid-state ligand orientation observed for [Mo(CO)$_2$(dppe)(η^5-C_5H_7)]$^+$ comprises a phosphorus atom directly below the plane of the open face of the pentadienyl ligand and a carbonyl carbon located below the central pentadienyl carbon of the C_5H_7 ligand.

The low-temperature ^1H, ^{13}C and ^{31}P NMR data for complex **5** may be rationalised if it is assumed that the preferred low-temperature solution conformation corresponds to that adopted in the solid state. At higher temperatures a fluxional process or processes must operate which average out the cycloheptadienyl ring resonances in the ^1H and ^{13}C NMR spectra and the phosphorus environments in the ^{31}P NMR spectrum. Similar temperature-dependent NMR behaviour has been observed[26] for the pentadienyl complex $[Mo(CO)_2(dppe)(\eta^5-C_5H_7)]^+$ and, in view of the structural similarities, it is possible that the fluxional processes suggested for $[Mo(CO)_2(dppe)(\eta^5-C_5H_7)]^+$ are also valid for **5**.

The 2,2′-bipyridyl complex **6** is exceptional in that the ^1H and ^{13}C NMR spectra, which reveal the inequivalence of all cycloheptadienyl ring environments, are already well resolved at ambient temperature. Interestingly the acyclic pentadienyl analogue of **6** is formulated as $[Mo(CO)_2(bipy)(\textit{syn}-\eta^3-C_5H_7)][BF_4]$, a species with a trihapto-bonded pentadienyl ligand and a σ-co-ordinated BF_4 anion.[27] In the case of **6** the spectroscopic data suggest and an X-ray crystallographic study[28] confirms that the cycloheptadienyl ligand is bonded pentahapto and therefore **6** and $[Mo(CO)_2(bipy)(\textit{syn}-\eta^3-C_5H_7)][BF_4]$ provide an example of contrasting hapticity preferences of cycloheptadienyl and pentadienyl ligands. However subsequent studies[4,20] have revealed that the cycloheptadienyl complex **6** does undergo facile addition of ligands L (L = NCMe, PMe_3 or $CNBu^t$) at the metal centre accompanied by $\eta^5 \longrightarrow \eta^3$ ring slip of the cycloheptadienyl ligand to give products of formulation $[Mo(CO)_2L(bipy)(\eta^3-C_7H_9)]^+$.

The successful syntheses of the diene complexes **7** and **8** demonstrate the ability of $[Mo(CO)_2(NCMe)_3(\eta^3-C_7H_9)]^+$ to react with both conjugated and non-conjugated dienes. Although cycloheptatrienylmolybdenum complexes of any diene are unknown, **7** and **8** have close analogues in indenylmolybdenum chemistry.[15] As with the indenyl analogue, two conformational isomers must be considered as possible structures for the cyclohexa-1,3-diene complex **7**; spectroscopic data do not allow a distinction, but the ^{13}C NMR spectrum of **7** at −40 °C is sharp and well resolved with no evidence for the coexistence of two isomeric forms.

We are currently continuing our research on cycloheptadienyl complexes of the Group 6 transition metals with studies on $\eta^5 \longleftrightarrow \eta^3$ hapticity interconversions in complexes of the type **4b**, **5** and **6** and an investigation of the analogous chemistry of Cr and W.

Experimental

The preparation, purification and reactions of the complexes described were carried out under dry nitrogen. All solvents were dried by standard methods, distilled and deoxygenated before use. The complexes $[Mo(CO)_3(\eta^6-C_7H_8)]$[29] and $[Mo(CO)_2(PPh_3)(\eta^6-C_7H_8)]$[30] were prepared by published procedures and $[Mo(CO)_2(CNBu^t)(\eta^6-C_7H_8)]$ was prepared in 54% yield by reaction of $[Mo(CO)_2(CNBu^t)(\eta^7-C_7H_7)][BF_4]$[10] with $NaBH_4$. Aldrich Chemical Co. supplied $HBF_4 \cdot Et_2O$, PPh_3, $CNBu^t$, Na(cp) (1.0 mmol solution in tetrahydrofuran, thf), dppm, 2,2′-bipyridyl, cyclohexa-1,3-diene and norborna-2,5-diene; alumina (Brockman activity II) for column chromatography was purchased from Merck. Hydrogen-1 NMR spectra were recorded on a Bruker AC 300 E instrument and ^{13}C NMR spectra at 75 MHz on Bruker AC 300 E or Varian Associates XL 300 spectrometers. Infrared spectra were obtained on a Perkin Elmer FT 1710 spectrometer and mass spectra using a Kratos Concept 1S instrument. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

$[Mo(CO)_4(\eta^5-C_7H_9)][BF_4]$ **1a**.—A stirred CH_2Cl_2 solution (30 cm^3) of $[Mo(CO)_3(\eta^6-C_7H_8)]$ (2.09 g, 7.69 mmol) was cooled to −78 °C and purged with CO gas. The compound $HBF_4 \cdot Et_2O$ (1.49 g, 9.20 mmol) was added and the reaction mixture allowed to warm to room temperature, while at the same time maintaining a constant flow of CO through the solution. The reaction was deemed complete after 1 h upon the appearance of an orange precipitate, which was obtained in increased quantity after addition of diethyl ether (40 cm^3). The orange product $[Mo(CO)_4(\eta^5-C_7H_9)][BF_4]$ was filtered off on a G3 sinter and washed with diethyl ether (2 × 10 cm^3) then dried under vacuum; yield 2.52 g (84%).

$[Mo(CO)_3(CNBu^t)(\eta^5-C_7H_9)][BF_4]$ **1b**. A stirred CH_2Cl_2 solution (30 cm^3) of $[Mo(CO)_2(CNBu^t)(\eta^6-C_7H_8)]$ (0.403 g, 1.24 mmol) was cooled to −78 °C and purged with CO gas. The compound $HBF_4 \cdot Et_2O$ (0.2 cm^3) was added and the reaction mixture allowed to warm to room temperature while maintaining a constant flow of CO through the solution. After 1 h the solution was filtered, reduced in volume and treated with diethyl ether to precipitate the crude product which was obtained as a yellow solid following recrystallisation from thf–diethyl ether; yield 0.303 g (55%).

The complex $[Mo(CO)_3(PPh_3)(\eta^5-C_7H_9)][BF_4]$ **1c** was prepared by an identical method to that for **1b** except that $[Mo(CO)_2(PPh_3)(\eta^6-C_7H_8)]$ (0.285 g, 0.563 mmol) was treated with $HBF_4 \cdot Et_2O$ (0.2 cm^3) and the product was isolated as a salmon-pink solid after recrystallisation from acetone–diethyl ether; yield 0.153 g (44%).

$[Mo(CO)_2(NCMe)_3(\eta^3-C_7H_9)][BF_4]$ **2a**.—Acetonitrile (40 cm^3) was added to $[Mo(CO)_4(\eta^5-C_7H_9)][BF_4]$ **1a** (3.20 g, 8.25 mmol) and the solution was stirred for 20 min during which time CO gas was evolved and the colour of the solution became brown-red. After filtration the volume of the solution was reduced to 5 cm^3 and diethyl ether added which resulted in the precipitation of the product **2a** as a red-brown solid; yield 3.25 g (86%). Impure samples of **2a** may be further purified by recrystallisation from CH_2Cl_2–diethyl ether.

$[Mo(CO)_2(CNBu^t)(NCMe)_2(\eta^3-C_7H_9)][BF_4]$ **2b**.—An acetonitrile solution (40 cm^3) of $[Mo(CO)_3(CNBu^t)(\eta^5-C_7H_9)][BF_4]$ **1b** (0.280 g, 0.63 mmol) was stirred for 1.5 h during which time the colour changed from yellow to red-brown. After filtration the solution was reduced in volume to 2 cm^3 and then added dropwise to stirred diethyl ether which resulted in precipitation of the crude product. Subsequent washing with diethyl ether (2 × 10 cm^3) and recrystallisation from acetonitrile–diethyl ether gave pure complex **2b** as a red-brown solid; yield 0.162 g (52%).

$[Mo(CO)_2(\eta^3-C_7H_9)(cp)]$ **3**.—A stirred thf solution (40 cm^3) of complex **2a** (0.365 g, 0.80 mmol) was treated with Na(cp) (1 cm^3 of a 1.0 mmol solution in thf) and the reaction allowed to proceed at room temperature for 45 min. The solution was then filtered and the filtrate, reduced in volume to 5 cm^3, was transferred to an alumina–hexane chromatography column. Elution with hexane gave a yellow band which was collected, reduced in volume and cooled to −78 °C to give the crude product as a yellow precipitate. Pure complex **3** was obtained as a pale yellow solid by further recrystallisation from diethyl ether–hexane; yield 0.053 g (21%).

$[Mo(CO)_2(PPh_3)_2(\eta^5-C_7H_9)][BF_4]$ **4a**.—*Method* (*a*). A stirred solution of complex **2a** (0.254 g, 0.56 mmol) in CH_2Cl_2 (20 cm^3) was treated with PPh_3 (0.297 g, 1.13 mmol). After 1 h the solution was filtered, reduced in volume and diethyl ether added to precipitate the crude product as a yellow-brown solid. Subsequent washing with a small volume of thf and then diethyl ether gave complex **4a** as a bright yellow solid; yield 0.197 g (41%).

Method (*b*). A cold (−78 °C) stirred acetone solution of $[Mo(CO)_2(PPh_3)(\eta^6-C_7H_8)]$ (0.300 g, 0.59 mmol) was treated with $HBF_4 \cdot Et_2O$ (0.10 g, 0.62 mmol) and PPh_3 (0.311 g, 1.19 mmol). After 45 min the solvent was removed under vacuum and the residue washed with diethyl ether (2 x 10 cm^3). Recrystallisation of the crude product from CH_2Cl_2–diethyl ether and subsequent washing with a small volume of thf gave complex **4a** as a bright yellow solid; yield 0.188 g (37%).

[Mo(CO)$_2$(CNBu^t)$_2$(η^5-C_7H_9)][BF_4] **4b**.—A CH_2Cl_2 solution (20 cm^3) of complex **2a** (0.532 g, 1.17 mmol) was treated with CNBu^t (0.194 g, 2.34 mmol) and the mixture was stirred for 30 min. The solvent was then removed *in vacuo* and the residue thoroughly dried. Extraction of the residue with CH_2Cl_2, filtration, reduction in volume and addition of diethyl ether to the resulting solution gave the crude product as a yellow oil. Further recrystallisation from CH_2Cl_2–diethyl ether and subsequent washing with diethyl ether gave pure complex **4b** as a yellow oil; yield 0.217 g (37%).

[Mo(CO)$_2$(dppm)(η^5-C_7H_9)][BF_4] **5**.—A stirred CH_2Cl_2 solution (40 cm^3) of complex **2a** (0.221 g, 0.49 mmol) was treated with dppm (0.186 g, 0.48 mmol). After 1 h solvent was removed *in vacuo* and the residue recrystallised from CH_2Cl_2–diethyl ether to give complex **5** as an orange-pink solid; yield 0.185 g (53%).

[Mo(CO)$_2$(bipy)(η^5-C_7H_9)][BF_4] **6**.—A CH_2Cl_2 solution (40 cm^3) of complex **2a** (0.185 g, 0.41 mmol) was treated with 2,2′-bipyridyl (0.064 g, 0.41 mmol) and the reaction mixture was stirred for 1 h. The solution was then filtered, reduced in volume and diethyl ether added to precipitate the crude product which was recrystallised from CH_2Cl_2–diethyl ether to give complex **6** as a red solid; yield 0.084 g (42%).

[Mo(CO)$_2$(η^4-chd)(η^5-C_7H_9)][BF_4] **7**.—A CH_2Cl_2 solution (20 cm^3) of complex **2a** (0.333 g, 0.73 mmol) was treated with cyclohexa-1,3-diene (2 cm^3) and the mixture was stirred for 30 min. After filtration of the reaction solution and reduction in volume to 5 cm^3, diethyl ether was added to precipitate the crude product which was recrystallised from CH_2Cl_2–diethyl

Table 5 Structure analyses of complexes **3** and **5**

	3	**5**
Formula	$C_{14}H_{14}MoO_2$	$C_{34}H_{31}BF_4MoO_2P_2$
M	310.20	716.31
a/Å	13.892(1)	10.586(1)
b/Å	7.630(1)	16.6106(9)
c/Å	12.046(2)	19.767(1)
β/°	102.720(7)	113.660(4)
U/Å^3	1245.5(5)	3183.7(7)
T/K	294	293
D_c/g cm^{-3}	1.654	1.494
F(000)	624	1456
μ/cm^{-1}	10.14 (Mo-Kα)	48.60 (Cu-Kα)
Diffractometer	Enraf-Nonius CAD 4	Rigaku AFC5R
Crystal dimensions/mm	0.11 × 0.32 × 0.37	0.06 × 0.110 × 0.240
λ/Å	0.710 69 (Mo-Kα)	1.541 78 (Cu-Kα)
θ range (°)	1–25	2.5–60
Scan width (°)	(1.20 + 0.35 tanθ)	(1.10 + 0.30 tanθ)
Total data	2021	4014
Unique data	2018	3782
'Observed' data [$I > 3\sigma(I)$] N_o	1635	3026
Least-squares variables, N_v	154	490
R	0.027	0.040
R'	0.025	0.052
S	1.98	1.96
Difference map features (e Å^{-3})	+0.36, −0.38	+0.54, −0.44

* Details in common: monoclinic space group $P2_1/c$ (no. 14); $Z = 4$; ω–2θ scans; $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$; $\Delta = F_o - F_c$.

Table 6 Atomic coordinates for complex **3**

Atom	x	y	z
Mo	0.193 09(2)	0.194 05(4)	0.221 74(3)
O(8)	0.210 3(2)	−0.087 6(4)	0.408 8(3)
O(9)	0.116 6(2)	−0.122 0(4)	0.068 2(3)
C(1)	0.342 6(3)	0.254 4(6)	0.199 7(6)
C(2)	0.363 0(3)	0.191 9(1)	0.309 4(5)
C(3)	0.411 7(5)	0.030 2(17)	0.348 2(6)
C(4)	0.413 9(8)	−0.111 7(18)	0.293 5(11)
C(5)	0.371 4(5)	−0.154 6(9)	0.185 8(12)
C(6)	0.350 2(4)	−0.025 9(10)	0.088 9(5)
C(7)	0.310 0(3)	0.151 2(7)	0.106 9(4)
C(8)	0.206 0(3)	0.018 5(6)	0.339 6(4)
C(9)	0.147 7(3)	−0.003 9(6)	0.125 6(4)
C(10)	0.040 9(3)	0.298 3(7)	0.231 2(6)
C(11)	0.105 8(5)	0.378 2(7)	0.316 6(4)
C(12)	0.164 8(3)	0.485 9(6)	0.272 5(5)
C(13)	0.138 3(4)	0.475 9(6)	0.156 0(5)
C(14)	0.060 2(4)	0.358 6(7)	0.128 3(5)

Table 7 Atomic coordinates for complex **5**

Atom	x	y	z
Mo	0.409 17(5)	0.189 54(2)	0.254 70(3)
P(1)	0.656 5(2)	0.193 86(8)	0.259 81(8)
P(2)	0.429 8(2)	0.189 04(8)	0.125 16(8)
O(8)	0.105 2(5)	0.133 6(3)	0.147 6(3)
O(9)	0.474 1(5)	0.009 7(3)	0.287 3(3)
C(1)	0.491 4(8)	0.280 3(5)	0.343 4(4)
C(2)	0.422(1)	0.324 4(4)	0.276 3(5)
C(3)	0.286(1)	0.318 0(4)	0.228 2(5)
C(4)	0.166 8(8)	0.310 4(5)	0.251 6(5)
C(5)	0.173 1(9)	0.246 0(5)	0.304 3(5)
C(6)	0.296 8(8)	0.190 0(4)	0.326 5(4)
C(7)	0.433 8(9)	0.215 7(5)	0.365 1(4)
C(8)	0.214 2(8)	0.154 7(3)	0.182 6(4)
C(9)	0.451 5(7)	0.076 3(4)	0.269 3(4)
C(10)	0.617 3(7)	0.182 8(4)	0.161 2(4)
C(11)	0.763 9(7)	0.282 6(3)	0.293 3(4)
C(12)	0.862 9(9)	0.283 6(4)	0.365 3(5)
C(13)	0.943(1)	0.352 4(5)	0.392 5(5)
C(14)	0.924(1)	0.418 8(5)	0.350 2(6)
C(15)	0.824(1)	0.419 6(4)	0.280 0(6)
C(16)	0.744 7(8)	0.351 0(4)	0.251 7(4)
C(17)	0.774 6(6)	0.112 9(3)	0.304 1(3)
C(18)	0.777 2(8)	0.077 9(5)	0.368 7(4)
C(19)	0.867(1)	0.014 8(7)	0.399 6(7)
C(20)	0.954(1)	−0.011 3(6)	0.373(1)
C(21)	0.954(1)	0.022 0(7)	0.309 6(8)
C(22)	0.866 0(8)	0.085 2(5)	0.274 5(4)
C(23)	0.366 9(6)	0.107 1(3)	0.058 7(3)
C(24)	0.319 1(8)	0.036 2(4)	0.075 7(4)
C(25)	0.277 2(9)	−0.026 8(4)	0.026 0(5)
C(26)	0.281 5(8)	−0.019 9(5)	−0.041 6(4)
C(27)	0.329 6(9)	0.049 7(5)	−0.059 4(4)
C(28)	0.372 9(7)	0.113 6(4)	−0.010 4(3)
C(29)	0.375 9(6)	0.278 3(3)	0.067 2(3)
C(30)	0.468 6(8)	0.329 8(4)	0.056 7(4)
C(31)	0.420(1)	0.398 0(4)	0.013 8(5)
C(32)	0.282(1)	0.414 8(4)	−0.018 9(4)
C(33)	0.191 0(8)	0.361 7(4)	−0.010 8(4)
C(34)	0.237 5(8)	0.293 9(4)	0.032 9(4)

ether to give complex **7** as a yellow solid; yield 0.192 g (64%).

$[Mo(CO)_2(\eta^4\text{-nbd})(\eta^5\text{-}C_7H_9)][BF_4]$ **8**.—A CH_2Cl_2 solution (30 cm^3) of complex **2a** (0.300 g, 0.66 mmol) was treated with norborna-2,5-diene (0.251 g, 2.73 mmol) and the mixture stirred for 1 h during which time partial polymerisation of the norbornadiene occurred. The reaction solution was then filtered, reduced in volume and diethyl ether added to precipitate the crude product. Recrystallisation from CH_2Cl_2–diethyl ether and subsequent washing with a small volume of thf gave complex **8** as a yellow solid; yield 0.084 g (30%).

Crystal Structure Analyses of Complexes **3** *and* **5**.—The majority of the details of the structure analyses carried out on complexes **3** and **5** are given in Table 5; non-hydrogen atom positional parameters are listed in Tables 6 and 7 respectively. Yellow crystals of **3** were grown from a hexane solution of the complex cooled to −30 °C and red-brown crystals of **5** by slow diffusion of diethyl ether into an acetone solution of the complex. Cell dimensions were determined from the setting angles of 25 reflections in the ranges $18.6 < 2\theta < 24.4°$ for **3** and $77.98 < 2\theta < 79.58°$ for **5**. An empirical absorption correction, using the program DIFABS,[31] was applied; in each case the data were also corrected for Lorentz and polarisation effects. For **3** no decay correction was necessary but for **5** the intensities of three representative reflections, measured after every 150, declined by 1.04% and an appropriate linear correction factor was applied. The structures were solved by heavy-atom (direct or Patterson) methods, and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically; for **3** hydrogen atoms were located by Fourier difference maps and then maintained at idealised positions (C–H 0.95 Å) by recalculation at the beginning of each least-squares cycle as convergence was approached, whilst for **5** the hydrogens were located by Fourier difference maps and then their positional and isotropic thermal parameters allowed to refine. For both **3** and **5**, $w = 4F_o^2/\sigma^2(F_o^2)$ with a p factor of 0.03 to down weight strong reflections. Complex neutral atom scattering factors were taken from ref. 32; all calculations were performed using the TEXSAN crystallographic software packages.[33]

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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