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$\eta^7 \longrightarrow \eta^3$ Hapticity interconversion in cycloheptatrienyl complexes of molybdenum and tungsten. Crystal structures of $[Mo(NCS)(CO)_2(C_{10}H_8N_2)(\eta^3\text{-}C_7H_7)]$ and $[MoCl(CO)_2(Ph_2PCH_2CH_2PPh_2)(\eta^3\text{-}C_7H_6C_6H_4F\text{-}4)]$

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A series of reactions of the general type $[MX(CO)_2(\eta^7\text{-}C_7H_6R)]^{n+} + 2L' \longrightarrow [MX(CO)_2L'_2(\eta^3\text{-}C_7H_6R)]^{n+}$ involving $\eta^7 \rightarrow \eta^3$ hapticity conversion at a molybdenum or tungsten co-ordinated cycloheptatrienyl ring have been examined with the objective of determining the effects of variation of X, M and R on the reactivity of $[MX(CO)_2(\eta^7\text{-}C_7H_6R)]^{n+}$ towards adduct formation with ligands $L' = NCMe$, $L'_2 = Ph_2PCH_2CH_2PPh_2$ (dppe) or 2,2′-bipyridyl (bipy). The complexes $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]$ exhibit a markedly X-dependent reactivity. The derivatives with X = NCO or NCS form adducts $[MoX(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$ **1** and **2**, $[MoX(CO)_2(bipy)(\eta^3\text{-}C_7H_7)]$ **3** and **4** and $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_7H_7)]$ {as an equilibrium mixture with $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]$ in NCMe}. By contrast $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]$ (X = C≡CPh, C_6F_5 or $SnPh_3$) do not react with dppe, bipy or NCMe at room temperature. Tungsten complexes $[WX(CO)_2(\eta^7\text{-}C_7H_7)]^{n+}$ are activated towards adduct formation with L′ = NCMe by comparison with the molybdenum analogues. Thus $[WX(CO)_2(\eta^7\text{-}C_7H_7)]$ (X = NCO or Br) react with NCMe to form $[WX(CO)_2(NCMe)_2(\eta^3\text{-}C_7H_7)]$ (X = NCO **5** or Br **6**). The composition of equilibrium mixtures of $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_6R)]^+$ and $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_6R)]^+$ in NCMe is dependent upon R and temperature; the % composition of the $\eta^7\text{-}C_7H_6R$ component is enhanced by electron-donating ring substituents (R = Me) and by an increase in temperature. The crystal structures of **4** and $[MoCl(CO)_2(dppe)(\eta^3\text{-}C_7H_6C_6H_4F\text{-}4)]$ have been determined. Both exhibit a pseudo-octahedral ligand arrangement at the Mo but, whilst 4 possesses a symmetrical structure with NCS located *trans* to the $\eta^3\text{-}C_7H_7$ ring, the latter complex adopts an asymmetric ligand arrangement with one phosphorus of the dppe ligand positioned *trans* to the cycloheptatrienyl ring.

The organometallic chemistry of cycloheptatrienyl,[1] C_7H_7, has been slow to develop by comparison with the chemistry of cyclopentadienyl and its derivatives. However, several specific properties of C_7H_7, including its steric requirements[2] and its versatility to act as an η^7-, η^5-, η^3- or η^1-bonded ligand,[3] or as a bridging ligand in bimetallics,[4] have encouraged recent interest. Our work in this area has centred on the chemistry of C_7H_7 complexes of Mo and W and this paper is focused upon $\eta^7 \longrightarrow \eta^3$ hapticity conversion (or ring slippage) of the cycloheptatrienyl ring.[5–7] Hapticity conversions ($\eta^5 \longrightarrow \eta^3$) in cyclic dienyl complexes (dienyl = C_5H_5, indenyl, *etc.*) have been implicated in mechanisms of ligand substitution[8] and migration,[9] yet few systematic studies have been made to elucidate the factors which promote ring slippage, probably because of difficulty in the observation and isolation of $\eta^3\text{-}C_5H_5$ complexes. One approach to this problem which we have initiated is to investigate analogous systems incorporating 'open' cyclic dienyl ligands such as cycloheptadienyl (C_7H_9)[10,11] or cyclooctadienyl (C_8H_{11})[12] in which the delocalisation of the dienyl system is broken and the relative stability of the η^3-bonded form is increased. Our second line of inquiry has been to study $\eta^7 \longrightarrow \eta^3$ conversions in cycloheptatrienyl complexes of Mo and W.[5–7] Such conversions, which involve a four-electron change at the metal centre, although not directly comparable with the two-electron $\eta^5 \longrightarrow \eta^3$ conversions of dienyl ligands, offer the advantage of stable, isolable $\eta^3\text{-}C_7H_7$ products for a wide range of co-ordinating metal centres. The objective of this paper is to combine new results, described herein, with previous work in this area in order to delineate those factors which promote $\eta^7 \longrightarrow \eta^3$ hapticity conversion in cycloheptatrienyl molybdenum and tungsten complexes of general formulation $[MX(L)_2(\eta^7\text{-}C_7H_6R)]^{n+}$.

Results and Discussion

Synthetic studies

This section describes a series of synthetic studies which examine the effect of changes in the variables L, X, M and R on the general reaction shown in equation (1). In equation (1),

$$[MX(L)_2(\eta^7\text{-}C_7H_6R)]^{n+} + 2L' \longrightarrow [MX(L)_2L'_2(\eta^3\text{-}C_7H_6R)]^{n+} \quad (1)$$

M = Mo or W, and L′ = ligand added to promote $\eta^7 \longrightarrow \eta^3$ conversion. Two distinct series of complexes undergo this general reaction: a neutral series (*n* = 0, X = one-electron ligand) and a cationic series (*n* = 1, X = two-electron ligand). Ligands L′, which are known to promote $\eta^7 \longrightarrow \eta^3$ ring slippage by addition to the metal centre of $[MX(L)_2(\eta^7\text{-}C_7H_7)]^{n+}$, are restricted to monodentate NCMe[6] and $CNBu^t$,[7] and the chelates $(L')_2 = R''_2P(CH_2)_nPR''_2$ (R″ = Ph, *n* = 1 or 2;[5,6,13,14] R″ = Me, *n* = 2[14,15]) and $H_2NCH_2CH_2NH_2$;[5] additionally, in this work we describe the first confirmed examples involving the 2,2′-bipyridyl (bipy) ligand. Anionic ligands such as $C_5H_5^-$[16] and pyrazolyl-derived species[17–20] also induce $\eta^7 \longrightarrow \eta^3\text{-}C_7H_7$ conversion in $[MX(CO)_2(\eta^7\text{-}C_7H_7)]$ (X = halide) but the reactions proceed with halide displacement to yield products best classified as $[M(CO)_2L'_3(\eta^3\text{-}C_7H_7)]$ in which the ligands $C_5H_5^-$, *etc.*, represented as L'_3, occupy three co-ordination sites. The current work has concentrated on L′ = NCMe and L'_2 = dppe ($Ph_2PCH_2CH_2PPh_2$) or bipy; these exhibit differing abilities to promote $\eta^7 \longrightarrow \eta^3$ hapticity conversion and so provide a range of reactivity against which the effect of other variables in equation (1) can be probed. Not all possible combinations of reactions with $[MX(L)_2(\eta^7\text{-}C_7H_7)]$ are described but rather we have selected those examples which best illustrate the effects of variation of L, X, M and R.

Effect of L

With one known exception only,[7] all complexes $[MX(L)_2(\eta^7\text{-}C_7H_6R)]^{n+}$ which undergo $\eta^7 \longrightarrow \eta^3$ ring slippage have L = CO. This suggests that $\eta^7 \longrightarrow \eta^3$ conversions are promoted by good π-acceptor ligands and a relatively electron-poor metal centre. The exception to this general observation, $[Mo(CO)(CNBu^t)_2(\eta^7\text{-}C_7H_7)]^+$, also has a metal centre co-ordinated to good acceptor ligands and in fact the observed reaction with $CNBu^t$ to give $[Mo(CO)(CNBu^t)_4(\eta^3\text{-}C_7H_7)]^+$ proceeds to completion only in the presence of an excess of $CNBu^t$.

Effect of X

A wide range of molybdenum complexes $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]^{n+}$, differing only in the identity of X, is readily accessible. In the current work the complexes selected for investigation were: $n = 0$, X = NCS,[21] NCO,[21] Cl, Br, I, C≡CPh,[22] C_6F_5[23] or $SnPh_3$;[24] $n = 1$, X = NCMe,[6] $CNBu^t$[7] or PPh_3.[25] The typical spectroscopic changes, diagnostic of $\eta^7 \longrightarrow \eta^3$ ring slippage in these dicarbonyl complexes, are: (*i*) in the infrared spectrum, a shift to lower wavenumber in the average carbonyl stretching frequency by approximately 80–90 cm^{-1}; (*ii*) in the ^{13}C NMR spectrum, a shift to low field for both the CO and C_7H_7 resonances; and (*iii*) in the ^1H NMR spectrum, a shift to high field of the C_7H_7 resonance. Details of the characterisation of the new complexes **1**–**10** described in this paper are presented in Tables 1 (microanalytical, infrared and mass spectroscopic data) and 2 (^1H and ^{13}C NMR data) and only spectroscopic data of special significance will be discussed further.

First examined were the reactions of the neutral species $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]$ with L'_2 = dppe which, of the three L′-type ligands employed in this work, is the most effective in promoting $\eta^7 \longrightarrow \eta^3$ ring slippage. We have previously reported that $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]$ (X = I or Cl) react with dppe in CH_2Cl_2 at room temperature to yield[5] $[MoX(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$ and an analogous product is obtained for X = Br. Similarly, treatment of green, CH_2Cl_2 solutions of $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]$ (X = NCO or NCS) with dppe also proceeded to give the new, red, ring-slipped adducts $[MoX(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$ (X = NCO **1** or NCS **2**). However the complexes $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]$ (X = C≡CPh, C_6F_5 or $SnPh_3$) did not form $\eta^3\text{-}C_7H_7$ adducts with dppe.

Further classification of the X-dependent reactivity of $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]$ was realised by an investigation of reactions with acetonitrile. The ligand L′ = NCMe is generally less effective than dppe at inducing $\eta^7 \longrightarrow \eta^3$ ring slippage and therefore only those complexes which form $\eta^3\text{-}C_7H_7$ adducts with dppe (X = NCO, NCS or halide) would be expected to undergo reaction. When $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]$ (X = NCO or NCS) were dissolved in acetonitrile, monitoring of the reaction mixture by infrared, ^1H and ^{13}C NMR spectroscopy revealed the formation of an equilibrium mixture of $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]$ and ring-slipped $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_7H_7)]$ analogous to the $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_7)]^+ \rightleftharpoons [Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)]^+$ equilibrium, which we have described previously.[6] Full details of the spectroscopic data and assignments for the equilibrium mixtures observed in NCMe are presented in Table 3. The experiments were carried out under standard conditions of concentration and temperature and the percentage equilibrium concentrations, which were calculated from ^1H NMR integrals of the C_7H_7 resonances at 20 °C, are based on three independent and closely consistent results. By contrast, corresponding spectroscopic investigations on the halide complexes $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]$ (X = Br or I), dissolved in NCMe, suggest that $\eta^3\text{-}C_7H_7$ adducts are not formed with NCMe. The case of the chloride derivative $[MoCl(CO)_2(\eta^7\text{-}C_7H_7)]$ dissolved in NCMe was less straightforward; although there was some spectroscopic evidence consistent with the formation of an $\eta^3\text{-}C_7H_7$ adduct, NMR data indicated a complex reaction mixture.

The results of these investigations with L′ = NCMe, L'_2 = dppe lead to the classification of complexes $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]$ into three reactivity types: type (*i*), X = NCS or NCO, which form $\eta^3\text{-}C_7H_7$ adducts with both dppe and NCMe (X = Cl may be borderline); type (*ii*), X = Br or I, which form adducts with dppe only and type (*iii*), X = C≡CPh, C_6F_5 or $SnPh_3$, which are unreactive towards ring-slippage reactions. The lack of reactivity of type (*iii*) complexes may be partially attributable to steric effects but the results obtained also

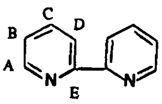
Table 1 Microanalytical, infrared and mass spectroscopic data

	Analysis (%)[a]			Infrared[b] (cm^{-1})		
Complex	C	H	N	ν(CO)	ν(CN)	Mass spectral data[c]
1 $[Mo(NCO)(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$	63.3 (63.3)	4.7 (4.5)	2.0 (2.0)	1933, 1855	2220	629 ($[M - 2CO]^+$), 587 ($[M - 2CO - NCO]^+$)
2 $[Mo(NCS)(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$	61.7 (61.8)	4.4 (4.4)	2.1 (2.0)[d]	1940, 1865	2081	643 ($[M - 2CO]^+$), 587 ($[M - 2CO - NCS]^+$)
3 $[Mo(NCO)(CO)_2(bipy)(\eta^3\text{-}C_7H_7)]$	54.3 (54.4)	3.7 (3.4)	9.3 (9.5)	1952, 1876	2219	401 ($[M - NCO]^+$), 387 ($[M - 2CO]^+$), 345 ($[M - 2CO - NCO]^+$)
4 $[Mo(NCS)(CO)_2(bipy)(\eta^3\text{-}C_7H_7)]$	52.1 (52.5)	3.3 (3.3)	9.1 (9.2)[e]	1955, 1882	2081	*f*
5 $[W(NCO)(CO)_2(NCMe)_2(\eta^3\text{-}C_7H_7)]$	36.6 (37.0)	3.2 (2.9)	8.6 (9.2)	1943, 1863[g,h]		457 (M^+), 429 ($[M - CO]^+$)
6 $[WBr(CO)_2(NCMe)_2(\eta^3\text{-}C_7H_7)]$	31.5 (31.7)	2.7 (2.6)	5.7 (5.7)	1946, 1868[g]		*f*
7 $[WCl(CO)_2(dmbipy)(\eta^3\text{-}C_7H_7)]$	45.3 (45.9)	3.3 (3.5)	5.1 (5.1)	1943, 1864		550 (M^+), 494 ($[M - 2CO]^+$), 459 ($[M - 2CO - Cl]^+$)
8 $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_6C_6H_4Me\text{-}4][BF_4]$	46.9 (46.9)	3.6 (3.5)	3.0 (3.0)	2032, 1990		376 (M^+), 348 ($[M - CO]^+$), 320 ($[M - 2CO]^+$)
9 $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_6Me][BF_4]$	37.0 (37.4)	3.2 (3.1)	3.4 (3.6)	2031, 1987		300 (M^+)
10 $[MoCl(CO)_2(dppe)(\eta^3\text{-}C_7H_6C_6H_4F\text{-}4)]$	63.5 (63.9)	4.9 (4.4)		1935, 1853		736 ($[M - Cl]^+$), 708 ($[M - Cl - CO]^+$), 680 ($[M - Cl - 2CO]^+$)

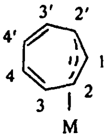
[a] Calculated values in parentheses. [b] Solution spectra in CH_2Cl_2 unless stated otherwise. [c] By FAB; *m*/*z* values based on ^{98}Mo and ^{184}W. [d] S, 4.6 (4.6)%. [e] S, 7.2 (7.0)%. [f] Attempts to obtain satisfactory mass spectrum unsuccessful. [g] In NCMe. [h] ν(C≡N) of NCO obscured by solvent.

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

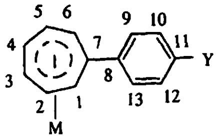
Bipyridyl ligands



Complex **3**



Ring-substituted complexes



Y = Me or F

Complex	^{1}H NMR (δ)[a]	^{13}C NMR (δ)[a]
1	7.65, 7.50 (m, 20 H, Ph, dppe); 5.27 (s, 7 H, C_7H_7); 2.82 (m, 2 H), 2.32 (m, 2 H) (CH_2, dppe)	227.0 [dd, *J*(P–C) 17, 26], 224.0 (at) (CO); 134.5–128.0 (Ph, dppe); 105.6 (C_7H_7); 26.7 (m), 24.7 (m) (CH_2, dppe)[b]
2	7.52 (br, 20 H, Ph, dppe); 5.28 (s, 7 H, C_7H_7); 2.80 (br, 2 H), 2.40 (br, 2 H) (CH_2, dppe)	226.8 [dd, *J*(P–C) 20, 26], 223.3 (at) (CO); 140.9 (NCS); 134.3–128.9 (Ph, dppe); 105.9 (C_7H_7); 26.9 (m), 25.2 (m) (CH_2, dppe)[c]
3	20 °C: 9.43 (m, 2 H, H^A); 8.67 (m, 2 H, H^D); 8.37 (m, 2 H, H^C); 7.90 (m, 2 H, H^B); 5.18 (s, C_7H_7).[d] −90 °C: 9.39 (m, 2 H, H^A); 8.71 (m, 2 H, H^D); 8.35 (m, 2 H, H^C); 7.85 (m, 2 H, H^B); 6.89 (br, 2 H, $H^{3,3'}$), 5.53 (br, 2 H, $H^{4,4'}$); 4.85 (br, 2 H, $H^{2,2'}$); 1.57 (br, 1 H, H^1)[d]	
5	4.92 (br, 7 H, C_7H_7)[e]	
6	5.03 (br, 7 H, C_7H_7)[e]	
7	9.06 (d, 2 H, H^A); 8.01 (s, 2 H, H^D); 7.43 (d, 2 H, H^B); 4.77 (br, 7 H, C_7H_7); 2.58 (s, 6 H, Me)[f]	221.5 (CO); 154.8 (C^E); 152.5 (C^A); 151.8 (C^C); 128.2 (C^B); 123.8 (C^D); 21.9 (Me)[f]
8	7.48 [d, 2 H, $H^{9,13}$, *J*($H^{9/13}$–$H^{10/12}$) 8]; 7.27 (d, 2 H, $H^{10,12}$); 5.94 (m, 6 H, H^{1-6}); 2.39 (s, 3 H); 2.34 (s, 3 H) ($C_6H_4CH_3$ and $NCCH_3$)	215.5 (CO); 140.4, 135.1 (C^8, C^{11}); 131.4 (N*C*Me); 129.9, 128.4 ($C^{9,10,12,13}$); 116.0 (C^7); 96.9, 96.4, 95.8 (C^{1-6}); 21.2 ($C_6H_4CH_3$); 4.2 ($NCCH_3$)
9	5.79 (m, 4 H, H^{2-5}); 5.50 [d, 2 H, $H^{1,6}$, *J*(H–$H^{2/5}$) 7]; 2.60 (s, 3 H); 2.45 (s, 3 H) ($C_7H_6CH_3$ and $NCCH_3$)	215.8 (CO); 131.1 (N*C*Me); 112.8 (C^7); 96.9, 96.4 (C^{1-6}); 25.4 ($C_7H_6CH_3$); 4.3 ($NCCH_3$)
10	7.75–6.92 (m, 24 H, Ph of dppe and C_6H_4F-4); 5.94 (br, 2 H), 5.50 (br, 2 H), 4.51 (br, 1 H), 3.86 (br, 1 H) (H^{1-6}); 3.00 (br, 2 H), 2.56 (br, 1 H), 2.04 (br, 1 H), (CH_2, dppe)[c]	227.6 (br), 224.3 (br) (CO); 161.8 [d, C^{11}, *J*(C^{11}–F) 245]; 141.5–128.0 (C^{7-9}, C^{13} and Ph, dppe); 121.0, 113.2, 104.6, 85.4, 81.4 (br, C^{1-6}); 114.9 [d, $C^{10,12}$, *J*($C^{10/12}$–F) 21]; 26.0 (m), 24.4 (m) (CH_2, dppe)[c]

[a] 300 MHz ^{1}H NMR spectra, 75 MHz ^{13}C NMR spectra; s = singlet, d = doublet, t = triplet, at = apparent triplet, m = multiplet, br = broad. Chemical shifts downfield from $SiMe_4$, coupling constants in Hz. In $CDCl_3$ solution unless stated otherwise. Numbering/lettering shown above. Satisfactory ^{13}C NMR data for complexes **3**–**6** and ^{1}H NMR data for **4** not obtained due to very low solubility. [b] In $CDCl_3$ at −20 °C. [c] In CD_2Cl_2 at −30 °C. [d] In $(CD_3)_2CO$. [e] In CD_3CN, NCMe ligands exchange with solvent. [f] In CD_2Cl_2, ^{13}C NMR resonance of C_7H_7 not observed.

Table 3 Infrared, ^{1}H and ^{13}C NMR data for the equilibrium systems $[MX(CO)_2(\eta^7\text{-}C_7H_6R)]^{n+} \rightleftharpoons [MX(CO)_2(NCMe)_2(\eta^3\text{-}C_7H_6R)]^{n+}$

Complex			$[MX(CO)_2(\eta^7\text{-}C_7H_6R)]^{n+}$		$[MX(CO)_2(NCMe)_2(\eta^3\text{-}C_7H_6R)]^{n+}$		% $\eta^7:\eta^3$[a]		
M	X	R	Infrared ν(CO)[b]	^{1}H and ^{13}C NMR[c]	Infrared ν(CO)[b]	^{1}H and ^{13}C NMR[c]	20 °C	40 °C	Other
Mo	NCO	H	2015 1960	^{1}H: 5.51 (s, C_7H_7) ^{13}C: 219.4 (CO), 96.9 (C_7H_7)	1950 1872	^{1}H: 5.21 (br, C_7H_7) ^{13}C: 226.7 (CO), 103.5 (br, C_7H_7)	58:42	79:21	
Mo	NCS	H	2021 1972	^{1}H: 5.60 (s, C_7H_7) ^{13}C: 218.8 (CO), 97.6 (C_7H_7)	1953 1876	^{1}H: 5.28 (br, C_7H_7) ^{13}C: 226.5 (CO), 105.1 (br, C_7H_7)	66:34	80:20	
Mo	NCMe	H	2034 1989	^{1}H: 5.82 (s, C_7H_7) ^{13}C: 216.9 (CO), 98.0 (C_7H_7)	1960 1887	^{1}H: 5.51 (s, C_7H_7) ^{13}C: 224.9 (CO), 106.3 (br, C_7H_7)	64:36	82:18	
Mo	NCMe	C_6H_4Me-4	2031 1986	^{1}H: 7.61 (d, 2 H, $H^{9,13}$); 7.42 (d, 2 H, $H^{10,12}$); 6.11 (d, 2 H, $H^{1,6}$); 6.03 (m, 2 H), 5.81 (m, 2 H), (H^{2-5}); 2.48 (s, 3 H, $C_6H_4CH_3$)	1959 1887	^{1}H: 7.45 (d, 2 H, $H^{9,13}$); 7.27 (d, 2 H, $H^{10,12}$); 6.26 (d, 2 H, $H^{1,6}$); 5.23 (m, 2 H), 5.09 (m, 2 H) (H^{2-5}); 2.42 (s, 3 H, $C_6H_4CH_3$)	38:62	61:39	24:76 (−20 °C)
Mo	NCMe	Me	2029 1984	^{1}H: 5.87 (m, 2 H), 5.67 (m, 2 H) (H^{2-5}); 5.60 (d, 2 H, $H^{1,6}$); 2.55 (s, 3 H, $C_7H_6CH_3$)	1959 1884	^{1}H: 5.92–5.59, 4.52 (br, 6 H, H^{1-6}); 2.22 (s, $C_7H_6CH_3$)	82:18		61:39 (−20 °C)
W	NCMe	H		^{1}H: 5.74 (s, C_7H_7)	1956 1880	^{1}H: 5.20 (s, C_7H_7)	0:100	2:98	9:91 (70 °C)

[a] For 0.1 mol dm^{-3} solutions, based on ^{1}H NMR integrals; ratios at 20 °C determined as average of three independent results. Variation in % η^7 does not exceed ± 5% of averaged value. [b] In MeCN, in cm^{-1}. [c] In CD_3CN, key as in Table 2 footnote.

support the operation of an electronic effect. Thus the most activated complexes exhibit carbonyl stretching frequencies to high wavenumber of those in the unreactive type (*iii*) complexes {[MoX(CO)$_2$(η^7-C$_7$H$_7$)], ṽ(CO)(CH$_2$Cl$_2$)/cm^{-1}: X = NCS, 2028, 1983; X = I, 2018, 1972; X = C$_6$F$_5$, 2011, 1962} suggesting that, as for L, an important requirement for X to promote η^7 ⟶ η^3 hapticity conversion is to maintain an electron-poor metal centre.

The identification of type (*i*) complexes, most activated to η^7 ⟶ η^3 ring slippage, can be applied in the synthesis of previously unobtainable η^3-C$_7$H$_7$ adducts [MoX(CO)$_2$L'$_2$(η^3-C$_7$H$_7$)]. For example, hitherto 2,2'-bipyridyl derivatives [MX(CO)$_2$(bipy)(η^3-C$_7$H$_7$)] were unknown, yet analogous complexes [MX(CO)$_2$(bipy)(η^3-R')] (X = halide, NCS, *etc.*) with a wide range of η^3-bonded ligands (R' = allyl, C$_3$H$_5$;[26] pentadienyl, C$_5$H$_7$;[27] cyclopentenoyl, C$_5$H$_5$O,[28] *etc.*) are well established species. However, when [MoX(CO)$_2$(η^7-C$_7$H$_7$)] (X = NCO or NCS) were treated with bipy in CH$_2$Cl$_2$ at room temperature a reaction did indeed proceed to afford moderate yields of red [MoX(CO)$_2$(bipy)(η^3-C$_7$H$_7$)] (X = NCO **3** or NCS **4**). Complexes **3** and **4** are the first examples of bipy derivatives of η^3-C$_7$H$_7$ complexes and are of further interest for their structure (see below). The chloride derivative [MoCl(CO)$_2$(η^7-C$_7$H$_7$)] also reacts slowly with bipy in CH$_2$Cl$_2$ at room temperature but in this case only carbonyl-substituted [MoCl(bipy)(η^7-C$_7$H$_7$)] {an analogue of previously reported[14] [MoI(bipy)(η^7-C$_7$H$_7$)]} was isolated. This observation highlights a complication in that some complexes of general formulation [MX(CO)$_2$L'$_2$(η^3-C$_7$H$_7$)]$^{n+}$, whilst possible intermediates in a reaction, may not be observed because of their instability with respect to a substituted η^7-C$_7$H$_7$ product.

In the cationic series [MoX(CO)$_2$(η^7-C$_7$H$_7$)]$^+$ we have examined the ring-slippage reactivity of the derivatives with X = NCMe, CNBu^t or PPh$_3$. As described previously [MoX(CO)$_2$(η^7-C$_7$H$_7$)]$^+$ (X = NCMe or CNBu^t) react with dppe[6,11] to give [MoX(CO)$_2$(dppe)(η^3-C$_7$H$_7$)]$^+$. By contrast [Mo(CO)$_2$(PPh$_3$)(η^7-C$_7$H$_7$)]$^+$ is unreactive towards dppe at room temperature. The precise reactivity ordering of NCMe *vs.* CNBu^t is difficult to investigate due to the substitution lability of NCMe in [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_7$)]$^+$. However, whilst [Mo(CO)$_2$(CNBu^t)(η^7-C$_7$H$_7$)]$^+$ does not react with NCMe solvent, [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_7$)]$^+$, dissolved in NCMe, forms an equilibrium mixture[6] with [Mo(CO)$_2$(NCMe)$_3$(η^3-C$_7$H$_7$)]$^+$.

Effect of M

From our investigations to date, results which establish an effect of M (Mo *vs.* W) are restricted to the reactions of [MX(CO)$_2$(η^7-C$_7$H$_7$)]$^{n+}$ with L' = NCMe. In these examples the tungsten derivatives are activated to η^7 ⟶ η^3-C$_7$H$_7$ conversion by comparison with the molybdenum analogues, a result which may be attributable to stronger W–NCMe bonds.[29]

The observation that the behaviour of the neutral molybdenum complexes [MoX(CO)$_2$(η^7-C$_7$H$_7$)] (X = NCO or NCS), dissolved in NCMe, parallels that of cationic [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_7$)]$^+$, suggested that the tungsten analogues [WX(CO)$_2$(η^7-C$_7$H$_7$)] (X = NCO or NCS) might form stable η^3-C$_7$H$_7$ adducts with NCMe. Accordingly, when [W(NCO)(CO)$_2$(η^7-C$_7$H$_7$)] was dissolved in NCMe a change from green to brown-yellow accompanied the formation of [W(NCO)(CO)$_2$(NCMe)$_2$(η^3-C$_7$H$_7$)] **5**, which, in common with [W(CO)$_2$(NCMe)$_3$(η^3-C$_7$H$_7$)]$^+$, is a stable, isolable acetonitrile adduct. Moreover, the halide derivatives [WX(CO)$_2$(η^7-C$_7$H$_7$)] (X = I, Br or Cl) are also activated towards NCMe addition by the tungsten centre. For example, whilst [MoBr(CO)$_2$(η^7-C$_7$H$_7$)] does not form an η^3-C$_7$H$_7$ adduct with NCMe, dissolution of [WBr(CO)$_2$(η^7-C$_7$H$_7$)] in NCMe resulted in the rapid formation of an orange precipitate, which was identified as [WBr(CO)$_2$(NCMe)$_2$(η^3-C$_7$H$_7$)] **6**; analogous reactions were also observed for the iodo and chloro derivatives. Complex **6**, which is the first C$_7$H$_7$ analogue of the well established allyl complexes, [MX(CO)$_2$(NCMe)$_2$(η^3-C$_3$H$_5$)],[30] is only very sparingly soluble in NCMe and, when dissolved in CH$_2$Cl$_2$, rapidly loses NCMe to reform [WBr(CO)$_2$(η^7-C$_7$H$_7$)].

An additional effect of the tungsten metal centre is to stabilise complexes of the type [MX(CO)$_2$L'$_2$(η^3-C$_7$H$_7$)] with respect to loss of CO[13] and the resultant formation of carbonyl-substituted [MX(L')$_2$(η^7-C$_7$H$_7$)]. For example, reaction of [MoX(CO)$_2$(η^7-C$_7$H$_7$)] with bipy proceeds in refluxing benzene (X = I)[14] or at room temperature in CH$_2$Cl$_2$ (X = Cl) to give carbonyl-substituted [MoX(bipy)(η^7-C$_7$H$_7$)]. By contrast, treatment of [WCl(CO)$_2$(η^7-C$_7$H$_7$)] with 4,4'-dimethyl-2,2'-bipyridyl (dmbipy) in CH$_2$Cl$_2$ at room temperature led to the formation and isolation of [WCl(CO)$_2$(dmbipy)(η^3-C$_7$H$_7$)] **7** (the corresponding reaction with bipy appeared to proceed analogously but satisfactory characterisation of the resulting, highly insoluble product was not achieved). The activating effect of X = Cl *vs.* I is also clear from these investigations; neither of the iodo derivatives [MI(CO)$_2$(η^7-C$_7$H$_7$)] (M = Mo or W) reacts with bipy at room temperature.

Effect of R

Previous investigations on the effect of ring substituents R on ring slippage have focused on carbonyl-substitution reactions of the cyclopentadienylrhodium complexes [Rh(CO)$_2$(η^5-C$_5$H$_4$R)].[31,32] Kinetics studies are consistent with the intermediacy of [Rh(CO)$_2$L'(η^3-C$_5$H$_4$R)] in the formation of [Rh(CO)L'(η^5-C$_5$H$_4$R)] from [Rh(CO)$_2$(η^5-C$_5$H$_4$R)] and L'. By comparison with R = H, the rate of carbonyl substitution is enhanced by electron-withdrawing substituents (R = NO$_2$, CF$_3$, *etc.*) and decreased by electron-donating R = Me; these observations have been rationalised by the ability of the ring substituent to stabilise the η^3-C$_5$H$_4$R intermediate by charge delocalisation. Thus electron-withdrawing or delocalising substituents promote η^5 ⟶ η^3 ring slippage whilst electron-donating substituents impede the process. Despite their elegance, these previous studies do not, and cannot, approach the problem by direct observation of the ring-slipped intermediate. However, the cycloheptatrienylmolybdenum system provides such an opportunity; not only are η^3-cycloheptatrienyl complexes readily observable but also equilibria of the type [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_6$R)]$^+$ $\rightleftharpoons$ [Mo(CO)$_2$(NCMe)$_3$(η^3-C$_7$H$_6$R)]$^+$ furnish systems sensitive to small changes in the relative stabilities of η^7- and η^3-C$_7$H$_6$R forms. With this objective, we explored syntheses of the ring-substituted complexes [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_6$R)]$^+$.

We have recently described a convenient route to ring-substituted cycloheptatrienylmolybdenum complexes[33] involving reaction of [Mo(CO)$_3$(NCMe)$_3$] with C$_7$H$_6$R$^+$ to give [Mo(CO)$_3$(η^7-C$_7$H$_6$R)]$^+$. The tricarbonyl complexes [Mo(CO)$_3$(η^7-C$_7$H$_6$R)]$^+$ are precursors to [MoI(CO)$_2$(η^7-C$_7$H$_6$R)] as we have previously reported for R = Me.[33] For the current investigation the ring substituents (R = C$_6$H$_4$Me-4 or Me) were selected to provide respective examples of electron-delocalising and electron-donating substituents, both of which possess good spectroscopic handles for distinction between η^7- and η^3-bonded forms. Subsequent reaction of [MoI(CO)$_2$(η^7-C$_7$H$_6$R)] with Ag[BF$_4$] in NCMe followed by recrystallisation from CH$_2$Cl$_2$–diethyl ether afforded [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_6$R)]$^+$ (R = C$_6$H$_4$Me-4 **8** or Me **9**).

The effect of R on the relative stabilities of [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_6$R)]$^+$ and [Mo(CO)$_2$(NCMe)$_3$(η^3-C$_7$H$_6$R)]$^+$ was investigated by recording the ^{1}H NMR spectra of isolated samples of $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_6R)]^+$ (R = C_6H_4Me-4, H or Me), redissolved in CD_3CN. Full details of the spectroscopic data (the assignment of ^1H NMR data was facilitated by variable-temperature studies, see below) are presented in Table 3. The composition of each equilibrium mixture $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_6R)]^+ \rightleftharpoons [Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_6R)]^+$ was determined using integrals for ^1H NMR resonances characteristic of $\eta^7\text{-}C_7H_6R$ and $\eta^3\text{-}C_7H_6R$ forms. In the case R = H the singlet resonances of the C_7H_7 rings were employed, for R = C_6H_4Me-4 three separate pairs of integrals were available for comparison [δ 7.61 (η^7), 7.27 (η^3), C_6H_4Me; 6.11 (η^7), 6.26 (η^3), $H^{1,6}$; 2.48 (η^7), 2.42 (η^3), C_6H_4Me] and for R = Me the relative integrals of the Me substituent resonances [δ 2.55 (η^7), 2.22 (η^3)] were used (resonances associated with the six ring protons of the $\eta^3\text{-}C_7H_6Me$ ligand were either overlapping or too broad to provide accurate integration data). The experiments were carried out under standard conditions of concentration and temperature and the percentage equilibrium concentrations at 20 °C are based on replicate determinations. Examination of the % $\eta^7:\eta^3$ ratios in Table 3 for $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_6R)]^+$ dissolved in NCMe at 20 °C reveals a significant R dependence with the ratio increasing in the order R = C_6H_4Me-4 < H < Me. The operation of a steric effect, associated with the ring substituent, in the promotion of a specific hapticity type cannot be totally excluded but, in these monosubstituted systems at least, any such effect is likely to be small. Furthermore, only an electronic effect can account for the opposing trend (by comparison with R = H) exhibited by the two ring substituents Me and C_6H_4Me-4. Therefore, consistent with the studies on $[Rh(CO)_2(\eta^5\text{-}C_5H_4R)]$, in the cycloheptatrienylmolybdenum system, ring slippage induced by addition of NCMe is promoted by the electron-delocalising substituent C_6H_4Me-4 but is impeded by the electron-donating Me substituent.

Temperature effects

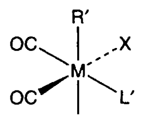
There are several reports in the literature which describe the conversion of $[MX(CO)_2L'_2(\eta^3\text{-}C_7H_7)]^{n+}$ into $[MX(L')_2(\eta^7\text{-}C_7H_7)]^{n+}$ at elevated temperature[7,14] so implying that η^7-bonded cycloheptatrienyl complexes are the more stable at high temperature. In the current work a new approach to investigate temperature effects was developed using the equilibrium systems $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_6R)]^+ \rightleftharpoons [Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_6R)]^+$ and $[MoX(CO)_2(\eta^7\text{-}C_7H_7)] \rightleftharpoons [MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_7H_7)]$ (X = NCO or NCS).

Variable-temperature ^1H NMR studies were carried out on samples of $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_6R)]^+$ (R = C_6H_4Me-4, H or Me) and $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]$ (X = NCO or NCS) dissolved in CD_3CN and the % $\eta^7:\eta^3$ ratios at −20 and 40 °C (as summarised in Table 3) were calculated on the basis of the relative integrals described in the previous section. The interpretation of low-temperature studies on all C_7H_7 complexes (R = H) was impeded by broadening of the resonance for the η^3-bonded form (as coalescence of a 1,2 shift process is approached) so precluding accurate determination of ^1H NMR integrals. However, where R = C_6H_4Me-4 or Me, the spectroscopic markers associated with the R substituent were independent of this effect and therefore low-temperature investigations focused on these two complexes. Examination of % $\eta^7:\eta^3$ ratios at 20 and −20 °C establishes that the proportion of η^7-bonded complex in the equilibrium mixture decreases with decrease in temperature suggesting that the η^3-bonded form is relatively stabilised at low temperature. Conversely, as shown by inspection of % $\eta^7:\eta^3$ ratios at 20 and 40 °C, an increase in temperature results in an increase in the proportion of the η^7-bonded complex present in the equilibrium mixture. The enhanced relative stability of the η^7-bonded form with increase in temperature is also manifest in the analogous tungsten system. Thus, ^1H NMR investigations demonstrate that whilst $[W(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)]^+$ is the single component present in solution in CD_3CN at 20 °C, increase in temperature leads to the reversible growth of a new singlet resonance at $\delta(CD_3CN)$ 5.74 attributable to $[W(CO)_2(NCMe)(\eta^7\text{-}C_7H_7)]^+$. Essentially, the enhanced stability of the $\eta^7\text{-}C_7H_7$ complex at high temperature partially offsets the stabilising effect of tungsten on the $\eta^3\text{-}C_7H_7$ form although, even at 70 °C, $[W(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)]^+$ is still the major equilibrium component (see Table 3).

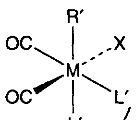
Structural studies

In addition to the effects of L, X, M and R, which we have sought to control and systematically vary, $\eta^7 \longrightarrow \eta^3$ hapticity conversions and the stability of the resulting $\eta^3\text{-}C_7H_7$ adducts might also be influenced by steric effects and by the geometric arrangement of ligands in the η^3-bonded adduct $[MX(CO)_2L'_2(\eta^3\text{-}C_7H_6R)]^{n+}$. We have not made a systematic investigation of the importance of these effects but the structural studies, described below, demonstrate the potential for different molecular configurations in complexes of the type $[MX(CO)_2L'_2(\eta^3\text{-}C_7H_6R)]^{n+}$.

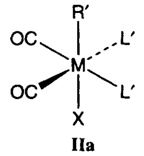
Complexes of general formulation $[MX(CO)_2L'_2(\eta^3\text{-}R')]^{n+}$ (R′ = allyl,[30] pentadienyl,[27,34] hexadienyl,[35] cyclopentenoyl,[28] cycloheptadienyl,[10,11] cyclooctadienyl,[12] cycloheptatrienyl, *etc.*) are an important class of compounds in the organometallic chemistry of molybdenum and tungsten. Almost without exception,[36] structural studies reveal six-coordinate, pseudo-octahedral ligand arrangements with the η^3-R′ ligand occupying one co-ordination site. Several geometric isomers, differing in the arrangement of ligands X, CO, L′ and R′ around M, can be proposed but in practice two basic structural types are observed: the asymmetric ligand arrangement of **Ia** with its bidentate ligand equivalent **Ib** and the corresponding symmetric arrangements **IIa** and **IIb**; examples in which a CO ligand is located *trans* to R′ are unknown. Without exception, complexes of the bidentate chelate ligand dppe $[MoX(CO)_2(dppe)(\eta^3\text{-}R')]$ (X = Cl, R′ = C_3H_5;[37] X = Br or Cl, R′ = C_5H_7,[34] *etc.*) adopt structure **Ib**. Examples of the monodentate equivalent **Ia** are very scarce but are represented by $[MoBr(CO)_2(C_3H_4N_2)_2(\eta^3\text{-}1\text{-}PhC_3H_4)]$ ($C_3H_4N_2$ = pyrazole).[38] Examples of structure types **IIa** and **IIb** are mainly restricted to L′ = N-donor ligand. Thus $[MoBr(CO)_2(NCMe)_2(\eta^3\text{-}C_5H_6Me)]$ (C_5H_6Me = hexadienyl)[35] is an instance of **IIa** and there are numerous cases of **IIb** including $[Mo(NCS)(CO)_2(bipy)(\eta^3\text{-}C_3H_5)]$,[39] $[Mo(CO)_2(C_5H_5N)(bipy)(\eta^3\text{-}C_3H_5)][BF_4]$ (C_5H_5N = pyridine),[40] $[MoBr(CO)_2(C_6H_{11}N{=}CHCH{=}NC_6H_{11})(\eta^3\text{-}C_3H_5)]$ (C_6H_{11} = cyclohexyl)[41] and $[Mo(CO)_2(CNBu^t)(bipy)(\eta^3\text{-}C_7H_9)][BF_4]$ (C_7H_9 = cycloheptadienyl).[11] However, adoption of structure type **IIb** is not a necessary requirement for derivatives of N-donor chelates; recently, $[Mo(CO)_2(NCMe)(bipy)(\eta^3\text{-}C_5H_7)][BF_4]$ (C_5H_7 = pentadienyl)[27] and $[Mo(O_2CCF_3)(CO)_2(phen)(\eta^3\text{-}C_3H_5)]$ (phen = 1,10-phenanthroline)[42] have been shown to possess structure type **Ib**.



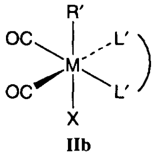
Ia



Ib



IIa



IIb

X-Ray structural studies on monometallic, trihapto-bonded cycloheptatrienyl complexes of Mo or W are restricted to just four reports[17,18,20,43] and none of these can be strictly classified as of the type $[MX(CO)_2L'_2(\eta^3\text{-}C_7H_7)]$. The crystal structures of two representative $\eta^3\text{-}C_7H_7$ complexes were therefore obtained: $[Mo(NCS)(CO)_2(bipy)(\eta^3\text{-}C_7H_7)]$ **4** and $[MoCl(CO)_2(dppe)(\eta^3\text{-}C_7H_6C_6H_4F\text{-}4)]$ **10**. Repeated attempts to obtain suitable crystals of $[MX(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$ (X = halide) were unproductive, but the ring-substituted derivative **10**, prepared from the reaction of $[MoCl(CO)_2(\eta^7\text{-}C_7H_6C_6H_4F\text{-}4)]$ with dppe, proved to be more successful. The molecular configurations, annotated with the crystallographic numbering schemes, and tables of important bond lengths and angles for **4** and **10** are presented respectively in Fig. 1, Table 4, and Fig. 2, Table 5. The gross structures lead to their assignment to the basic pseudo-octahedral types **4**, **IIb** and **10**, **Ib**, respectively. Structural features in common to **4** and **10** are the location of the two carbonyl ligands directly beneath the terminal carbons of the η^3-allyl fragment, a shortening of the M–C (central allyl) distance by comparison with M–C (terminal allyl) bond and a folding of the cycloheptatrienyl ligand about the best planes defined by [{C(15)–C(14)–C(20)}–{C(15)–C(16)–C(17)–C(18)–C(19)–C(20)}] 32° for **4** and [{C(29)–C(30)–C(31)}–{C(31)–C(32)–C(33)–C(34)–C(35)–C(29)}] 33° for **10**. An additional feature of interest in **10** is the location of the C_6H_4F-4 ring substituent on the terminal diene carbon C(35) and adjacent to the equatorial PPh_2 group of the dppe ligand. The shortest, non-bonded intramolecular contacts between the fluorophenyl substituent and the phenyls attached to P(2) are 2.88 [H(16)···H(41)] and 2.91 Å [H(26)···C(41)]. The structures of **4** and **10** may be compared directly with those of the analogous allyl complexes $[Mo(NCS)(CO)_2(bipy)(\eta^3\text{-}C_3H_5)]$[39] and $[MoCl(CO)_2(dppe)(\eta^3\text{-}C_3H_5)]$[37] respectively; no significant differences in bond lengths or angles around the Mo are apparent.

The solid-state structures of complexes **4** and **10** are consistent with solution structures deduced from spectroscopic studies. For all complexes $[MX(CO)_2L'_2(\eta^3\text{-}C_7H_7)]$ reported in this paper the pattern of the infrared-active carbonyl stretching bands is indicative of a *cis* arrangement of CO ligands. Poor solubility impeded NMR investigations on the bipyridyl derivatives $[MoX(CO)_2(bipy)(\eta^3\text{-}C_7H_7)]$ (X = NCO **3** or NCS **4**), but a variable-temperature ^1H NMR study on **3** was accomplished. Complexes of Mo and W in which C_7H_7 is bonded trihapto, generally show a singlet resonance for the C_7H_7 ring due to the operation of a 1,2-shift process which renders the ring environments equivalent.[44] However, in appropriate cases, low-temperature studies allow freezing out of the fluxional process[5,19,44] and observation of all separate environments of the $\eta^3\text{-}C_7H_7$ ring. Complexes with an approximate mirror plane exhibit four separate carbon or hydrogen ring environments,[44] whereas with an asymmetric

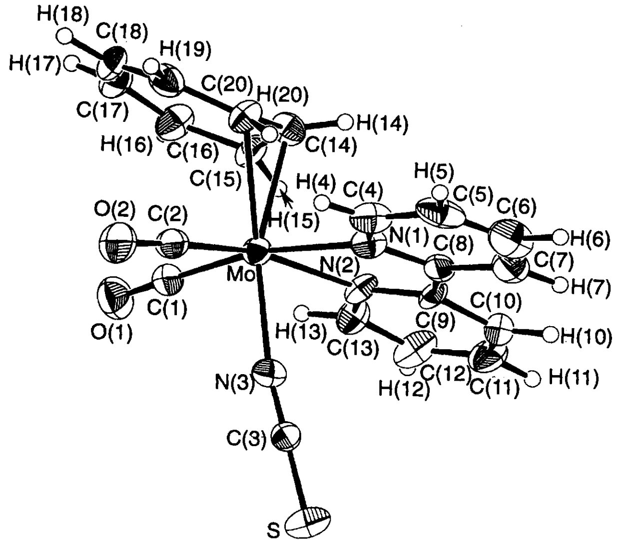


Fig. 1 Molecular structure of complex **4** showing the crystallographic numbering scheme

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

Mo–N(1)	2.251(9)	N(1)–C(8)	1.36(1)
Mo–N(2)	2.228(8)	N(2)–C(9)	1.33(1)
Mo–N(3)	2.131(10)	N(3)–C(3)	1.16(1)
Mo–C(1)	1.95(1)	C(8)–C(9)	1.46(1)
Mo–C(2)	1.94(1)	C(14)–C(15)	1.40(1)
Mo–C(14)	2.19(1)	C(14)–C(20)	1.38(1)
Mo–C(15)	2.42(1)	C(15)–C(16)	1.45(2)
Mo–C(20)	2.36(1)	C(16)–C(17)	1.36(2)
S–C(3)	1.60(1)	C(17)–C(18)	1.43(2)
O(1)–C(1)	1.15(1)	C(18)–C(19)	1.32(2)
O(2)–C(2)	1.17(1)	C(19)–C(20)	1.45(2)
N(1)–Mo–N(2)	72.2(3)	C(14)–Mo–C(20)	35.0(4)
N(1)–Mo–N(3)	79.6(3)	C(15)–Mo–C(20)	61.2(4)
N(1)–Mo–C(1)	168.6(4)	Mo–N(1)–C(4)	125.2(9)
N(1)–Mo–C(2)	102.4(4)	Mo–N(1)–C(8)	117.5(8)
N(1)–Mo–C(14)	83.0(4)	C(4)–N(1)–C(8)	117(1)
N(2)–Mo–N(3)	79.7(3)	Mo–N(2)–C(9)	118.2(7)
N(2)–Mo–C(1)	100.5(4)	Mo–N(2)–C(13)	123.3(7)
N(2)–Mo–C(2)	165.7(4)	Mo–N(3)–C(3)	171.4(10)
N(2)–Mo–C(14)	86.9(4)	Mo–C(1)–O(1)	178(1)
N(3)–Mo–C(1)	90.5(4)	Mo–C(2)–O(2)	175(1)
N(3)–Mo–C(2)	86.4(4)	S–C(3)–N(3)	176(1)
N(3)–Mo–C(14)	160.6(4)	C(15)–C(14)–C(20)	121(1)
N(3)–Mo–C(15)	151.1(4)	C(14)–C(15)–C(16)	126(1)
N(3)–Mo–C(20)	147.6(4)	C(15)–C(16)–C(17)	128(1)
C(1)–Mo–C(2)	82.6(5)	C(16)–C(17)–C(18)	127(1)
C(1)–Mo–C(14)	105.7(5)	C(17)–C(18)–C(19)	127(1)
C(2)–Mo–C(14)	105.8(5)	C(18)–C(19)–C(20)	131(1)
C(14)–Mo–C(15)	35.1(4)	C(14)–C(20)–C(19)	126(1)

Table 5 Important bond lengths (Å) and angles (°) for complex **10**

Mo–P(1)	2.546(2)	P(2)–C(2)	1.836(6)
Mo–P(2)	2.598(2)	P(2)–C(15)	1.827(6)
Mo–Cl	2.561(2)	P(2)–C(21)	1.834(6)
Mo–C(27)	1.965(6)	C(29)–C(30)	1.406(8)
Mo–C(28)	1.966(6)	C(29)–C(35)	1.467(8)
Mo–C(29)	2.422(5)	C(30)–C(31)	1.387(8)
Mo–C(30)	2.241(5)	C(31)–C(32)	1.452(9)
Mo–C(31)	2.435(6)	C(32)–C(33)	1.33(1)
O(1)–C(27)	1.137(7)	C(33)–C(34)	1.419(9)
O(2)–C(28)	1.149(7)	C(34)–C(35)	1.364(8)
P(1)–C(1)	1.854(6)	C(35)–C(36)	1.491(8)
P(1)–C(3)	1.845(6)	F–C(39)	1.35(1)
P(1)–C(9)	1.836(6)		
P(1)–Mo–P(2)	76.01(5)	C(28)–Mo–C(30)	104.6(2)
P(1)–Mo–Cl	77.86(5)	C(29)–Mo–C(30)	34.8(2)
P(1)–Mo–C(27)	90.0(2)	C(30)–Mo–C(31)	34.2(2)
P(1)–Mo–C(28)	92.2(2)	C(29)–Mo–C(31)	60.5(2)
P(1)–Mo–C(29)	148.2(1)	Mo–C(27)–O(1)	174.5(5)
P(1)–Mo–C(30)	158.1(1)	Mo–C(28)–O(2)	174.2(6)
P(1)–Mo–C(31)	150.7(1)	C(29)–C(30)–C(31)	122.5(5)
P(2)–Mo–Cl	82.00(5)	C(30)–C(31)–C(32)	126.7(6)
P(2)–Mo–C(27)	102.6(2)	C(31)–C(32)–C(33)	128.2(6)
P(2)–Mo–C(28)	168.2(2)	C(32)–C(33)–C(34)	129.3(6)
P(2)–Mo–C(30)	86.5(1)	C(33)–C(34)–C(35)	130.0(6)
Cl–Mo–C(27)	165.7(2)	C(34)–C(35)–C(29)	124.7(6)
Cl–Mo–C(28)	94.2(2)	C(35)–C(29)–C(30)	128.3(5)
Cl–Mo–C(30)	86.9(1)	C(29)–C(35)–C(36)	116.8(5)
C(27)–Mo–C(28)	78.6(2)	C(34)–C(35)–C(36)	118.4(6)
C(27)–Mo–C(30)	106.8(2)		

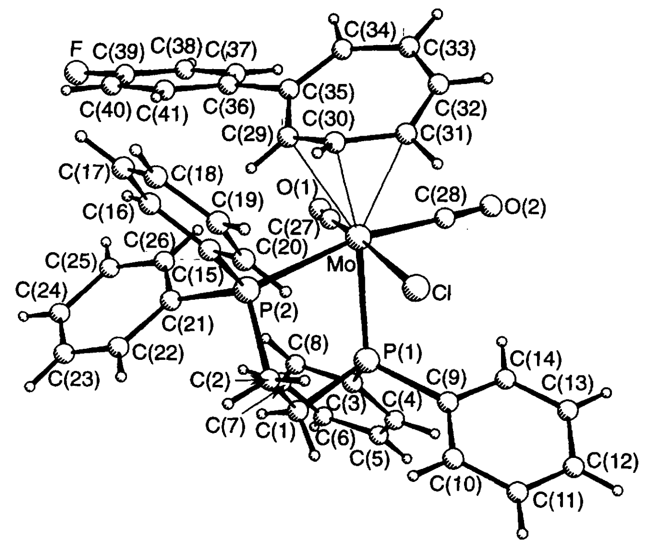


Fig. 2 Molecular structure of complex **10** showing the crystallographic numbering scheme

metal centre seven discrete positions may be observed.[5] We, and others,[5,19] have found that η^3-C_7H_7 complexes of Mo and W containing N-bonded ligands provide easily accessible, limiting low-temperature spectra and therefore the variable-temperature behaviour of the ^1H NMR spectrum of **3** was investigated. At room temperature, in $(CD_3)_2CO$, a singlet resonance was observed for the C_7H_7 ring but cooling to −90 °C revealed four discrete resonances attributable to the C_7H_7 ring (Table 2) consistent with a symmetric ligand arrangement at Mo as demonstrated crystallographically for **4**. This conclusion is further supported by the bipyridyl region of the spectrum; only four signals attributable to bipyridyl protons, each with a relative integral of two, were observed. The variable-temperature behaviour of NMR spectra of the dppe complex **10** is complicated by effects arising from a combination of the cycloheptatrienyl ring substituent with an asymmetric ligand arrangement at Mo, but we have previously described[5] a series of variable-temperature ^1H, ^{13}C and ^{31}P NMR studies on $[MX(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$ (M = Mo or W, X = I or Cl) which specifically address the structure. The structural conclusions drawn from these spectroscopic studies are now corroborated by the crystal structure of **10**.

Experimental

General procedures

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 $[M(NCO)(CO)_2(\eta^7\text{-}C_7H_7)]$ (M = Mo or W),[21] $[M(CO)_2(NCMe)(\eta^7\text{-}C_7H_7)][BF_4]$ (M = Mo or W),[6] $[Mo(CO)_3(\eta^7\text{-}C_7H_6C_6H_4F\text{-}4)][PF_6]$[33] and $[MoI(CO)_2(\eta^7\text{-}C_7H_6Me)]$[33] were prepared by published procedures but the literature preparation[21] of $[Mo(NCS)(CO)_2(\eta^7\text{-}C_7H_7)]$ was modified as described below. The chemicals dppe, $CNBu^t$ and 2,2′-bipyridyl were supplied by Aldrich Chemical Co. and $Ag[BF_4]$ was obtained from Lancaster Synthesis. The 300 MHz ^1H and 75 MHz ^{13}C NMR spectra were recorded on Bruker AC 300 E or Varian Associates XL 300 spectrometers, infrared spectra 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.

Preparations

$[Mo(NCS)(CO)_2(\eta^7\text{-}C_7H_7)]$. A stirred solution of $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_7)][BF_4]$ (1.70 g, 4.58 mmol) in acetone (30 cm^3) was cooled to −78 °C and treated with K[NCS] (0.49 g, 5.04 mmol). The solution was allowed to warm to room temperature over a period of 15 min and then solvent removed *in vacuo*. Recrystallisation of the residue from CH_2Cl_2–hexane gave $[Mo(NCS)(CO)_2(\eta^7\text{-}C_7H_7)]$ as an analytically pure green solid without the need for chromatographic separation[21] from $K_3[Mo(NCS)_6]$; yield 1.20 g (87%).

$[Mo(NCO)(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$ 1. Treatment of a green solution of $[Mo(NCO)(CO)_2(\eta^7\text{-}C_7H_7)]$ (0.85 g, 2.98 mmol) in CH_2Cl_2 (30 cm^3) with dppe (1.19 g, 2.99 mmol) produced an immediate change to red. After 30 min the reaction mixture was evaporated to dryness and the residue was recrystallised, first from CH_2Cl_2–hexane, then toluene–hexane to give complex **1** as a red solid; yield 0.60 g (29%). Complex **2**, red $[Mo(NCS)(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$, was obtained in 57% yield by an analogous procedure starting from $[Mo(NCS)(CO)_2(\eta^7\text{-}C_7H_7)]$ (0.65 g, 2.16 mmol) and dppe (0.91 g, 2.29 mmol).

$[Mo(NCS)(CO)_2(bipy)(\eta^3\text{-}C_7H_7)]$ 4. A green, stirred solution of $[Mo(NCS)(CO)_2(\eta^7\text{-}C_7H_7)]$ (0.37 g, 1.23 mmol) in CH_2Cl_2 (30 cm^3) was treated with 2,2′-bipyridyl (0.19 g, 1.22 mmol). The reaction mixture turned red-brown and a red precipitate of complex **4** formed over a period of 2 h. After separation from the mother-liquors, the product was washed with CH_2Cl_2 (2 × 5 cm^3) and then dried *in vacuo*; yield 0.17 g (30%). Complex **3**, red $[Mo(NCO)(CO)_2(bipy)(\eta^3\text{-}C_7H_7)]$, was obtained in 11% yield by an analogous procedure from $[Mo(NCO)(CO)_2(\eta^7\text{-}C_7H_7)]$ (0.497 g, 1.74 mmol) and bipy (0.271 g, 1.74 mmol).

$[W(NCO)(CO)_2(NCMe)_2(\eta^3\text{-}C_7H_7)]$ 5. A solution of $[W(NCO)(CO)_2(\eta^7\text{-}C_7H_7)]$ (0.20 g, 0.53 mmol) in NCMe (20 cm^3) was stirred for 3 h resulting in a change from green to brown-yellow. The solution was filtered, reduced in volume, and treated with diethyl ether to give complex **5** as a brown solid; yield 0.15 g (62%).

$[WBr(CO)_2(NCMe)_2(\eta^3\text{-}C_7H_7)]$ 6. A green solution of $[WBr(CO)_2(\eta^7\text{-}C_7H_7)]$ (1.57 g, 3.83 mmol) was stirred in acetonitrile (30 cm^3) at room temperature and after 5 min an orange precipitate of the product began to form. After 30 min the acetonitrile mother-liquors were separated from the orange product which was then washed with diethyl ether (2 × 5 cm^3) and dried *in vacuo*; yield 1.54 g (82%).

$[WCl(CO)_2(dmbipy)(\eta^3\text{-}C_7H_7)]$ 7. A green solution of $[WCl(CO)_2(\eta^7\text{-}C_7H_7)]$ (0.172 g, 0.47 mmol) was treated with 4,4′-dimethyl-2,2′-bipyridyl (0.086 g, 0.47 mmol) in CH_2Cl_2 (20 cm^3). The reaction mixture was stirred for 6 h to give a red solution. The crude product was then precipitated by addition of hexane and subsequently recrystallised from CH_2Cl_2–hexane to give **7** as a purple-red solid; yield 0.124 g (48%).

$[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_6C_6H_4Me\text{-}4)][BF_4]$ 8. The complex $[Mo(CO)_3(\eta^7\text{-}C_7H_6C_6H_4Me\text{-}4)][PF_6]$ was prepared in 57% yield by an identical procedure to that previously described[33] for $[Mo(CO)_3(\eta^7\text{-}C_7H_6R)]^+$, starting from $Mo(CO)_6$ (1.69 g, 6.40 mmol) and $[C_7H_6C_6H_4Me\text{-}4][PF_6]$ (1.41 g, 4.33 mmol) and was subsequently converted into $[MoI(CO)_2(\eta^7\text{-}C_7H_6C_6H_4Me\text{-}4)]$ in 49% yield by reaction with NaI stirred in acetone for 1.5 h. A stirred solution of $[MoI(CO)_2(\eta^7\text{-}C_7H_6C_6H_4Me\text{-}4)]$ (0.29 g, 0.62 mmol) in acetonitrile (40 cm^3) was treated with $Ag[BF_4]$ (0.12 g, 0.62 mmol) and, after 20 min, the reaction mixture was filtered,

Table 6 Crystal and data-collection parameters for complexes **4** and **10***

	4	**10**
Formula	$C_{20}H_{15}MoN_3O_2S$	$C_{41}H_{34}ClFMoO_2P_2$
M	457.36	771.06
Crystal system	Monoclinic	Triclinic
Crystal colour, habit	Red, prismatic	Red, tabular
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	9.821(6)	11.717(1)
b/Å	16.845(9)	16.192(2)
c/Å	11.807(6)	10.202(1)
α/°		96.66(1)
β/°	106.49(4)	113.475(7)
γ/°		77.922(9)
U/Å^3	1873(1)	1734.9(3)
T/°C	19	22
Z	4	2
D_c/g cm^{-3}	1.622	1.476
F(000)	920	788
μ/cm^{-1}	8.09 (Mo-Kα)	50.90 (Cu-Kα)
Crystal dimensions/mm	0.03 × 0.05 × 0.15	0.01 × 0.22 × 0.25
Radiation (λ/Å)	Mo-Kα (0.710 69)	Cu-Kα (1.541 78)
2θ range/°	2–50.1	5–120.1
Scan type	ω	ω–2θ
Scan width/°	$0.84 + 0.30\tan\theta$	$1.21 + 0.30\tan\theta$
Total data	3659	7074
Unique data	3449	5175
'Observed' data $[I > 3\sigma(I)]$, N_o	1666	4248
Least-squares variables, N_v	244	433
R	0.057	0.047
R'	0.054	0.064
Goodness of fit, S	1.55	2.12
Difference-map features/e Å^{-3}	+0.60, −0.63	+0.49, −0.42

* Details in common: Rigaku AFC5R diffractometer; $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$; $\Delta = F_o - F_c$.

evaporated to dryness and the residue dissolved in CH_2Cl_2 (30 cm^3). After 30 min of stirring in CH_2Cl_2, the solution was filtered, reduced in volume and the crude product precipitated with diethyl ether. The analytical sample of complex **8** was obtained as a green solid by recrystallisation from CH_2Cl_2–diethyl ether; yield 0.14 g (49%). Complex **9**, green $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_6Me)][BF_4]$, was obtained in 35% yield by an analogous procedure from $[MoI(CO)_2(\eta^7\text{-}C_7H_6Me)]$ (0.32 g, 0.83 mmol) and $Ag[BF_4]$ (0.17 g, 0.87 mmol).

$[MoCl(CO)_2(dppe)(\eta^3\text{-}C_7H_6C_6H_4F\text{-}4)]$ 10. The complex $[MoCl(CO)_2(\eta^7\text{-}C_7H_6C_6H_4F\text{-}4)]$ was prepared in 51% yield from a mixture of $[Mo(CO)_3(\eta^7\text{-}C_7H_6C_6H_4F\text{-}4)][PF_6]$ (2.20 g, 4.31 mmol) and LiCl (0.30 g, 7.08 mmol) stirred in acetone for 10 min. A mixture of $[MoCl(CO)_2(\eta^7\text{-}C_7H_6C_6H_4F\text{-}4)]$ (0.75 g, 2.01 mmol) and dppe (0.80 g, 2.01 mmol) was stirred in CH_2Cl_2 (50 cm^3) to give a red-brown solution. After 5 h the solution was filtered and the crude product precipitated with hexane. Recrystallisation from CH_2Cl_2–hexane gave complex **10** as a red solid; yield 0.36 g (23%).

Crystallography

The majority of the details of the structure analyses carried out on complexes **4** and **10** are given in Table 6. Neutral atom scattering factors were taken from ref. 45 and all calculations were performed using the TEXSAN crystallographic software package.[46]

$[Mo(NCS)(CO)_2(bipy)(\eta^3\text{-}C_7H_7)]$ 4. Red, prismatic crystals of complex **4** were grown by vapour diffusion of diethyl ether into a CH_2Cl_2 solution of it. The unit-cell dimensions were derived from the setting angles of 10 reflections in the range $9.69 < 2\theta < 13.67°$ (the small number of reflections, all low θ, used for unit-cell determination is attributed to the weak diffracting power of the crystal such that the automatic search procedure reduced the θ limit until satisfactory cell-determining reflections were found). The intensities of three representative reflections were measured after every 150. Over the course of data collection the standards increased by 0.1% and a linear correction factor was applied. An empirical absorption correction based on azimuthal scans was applied which resulted in transmission factors ranging from 0.94 to 1.00 and the data were corrected for Lorentz-polarisation effects. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included but not refined. The weighting scheme was $w = 1/[\sigma_c^2(F_o) + \frac{p^2}{4}(F_o^2)]$ with a p factor of 0.005 to downweight intense reflections.

$[MoCl(CO)_2(dppe)(\eta^3\text{-}C_7H_6C_6H_4F\text{-}4)]$ 10. Red, tabular crystals of complex **10** were grown by slow diffusion of a hexane layer into a CH_2Cl_2 solution of it. The unit-cell dimensions were derived from the setting angles of 23 reflections in the range $75.12 < 2\theta < 79.85°$. The intensities of three representative reflections, measured after every 150, declined by 0.7% and a linear correction factor was applied. An empirical absorption correction based on azimuthal scans was applied which resulted in transmission factors ranging from 0.50 to 1.00 and the data were corrected for Lorentz-polarisation effects. The structure was solved by direct methods and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in the structure-factor calculation in idealised positions (C–H 0.95 Å) and were assigned isotropic thermal parameters which were 20% greater than the equivalent B value of the atom to which they were bonded. The weighting scheme was $w = 4F_o^2/\sigma^2(F_o^2)$ with a p factor of 0.03 to downweight intense reflections.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/190.

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