$\eta^5 \longleftrightarrow \eta^3$ Hapticity Interconversion in Cycloheptadienyl Molybdenum Complexes†

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A series of reactions of the general type $[Mo(CO)_2L_2(\eta^5\text{-}C_7H_9)]^+ + L' \longrightarrow [Mo(CO)_2(L')L_2(\eta^3\text{-}C_7H_9)]^+$, involving $\eta^5 \longrightarrow \eta^3$ hapticity conversion at a molybdenum co-ordinated cycloheptadienyl ring, have been examined. The specific examples investigated comprise reactions of $[Mo(CO)_2L_2(\eta^5\text{-}C_7H_9)]^+$ [L_2 = 2,2′-bipyridyl (bipy) **1**, $Ph_2PCH_2PPh_2$ (dppm) **6**, $Ph_2PCH_2CH_2PPh_2$ (dppe) **7**; L = $CNBu^t$ **17** or PPh_3 **18**] with NCMe or $CNBu^t$. Complex **1** reacts reversibly with NCMe to give $[Mo(CO)_2(NCMe)(bipy)(\eta^3\text{-}C_7H_9)]^+$ **2** and, in NCMe, **7** exists as an equilibrium mixture with $[Mo(CO)_2(NCMe)(dppe)(\eta^3\text{-}C_7H_9)]^+$ **8**. The complexes **6**, **17** and **18** do not react with NCMe at ambient temperature. Treatment of **1**, **6** and **7** with $CNBu^t$ affords $[Mo(CO)_2(CNBu^t)L_2(\eta^3\text{-}C_7H_9)]^+$ (L_2 = bipy **4**, dppm **9** or dppe **11**) although **4** is better prepared by reaction of $[Mo(CO)_2(CNBu^t)(NCMe)_2(\eta^3\text{-}C_7H_9)]^+$ **5** with bipy. Complex **4** is resistant to carbonyl elimination but **9** and **11** undergo facile loss of CO to give $[Mo(CO)(CNBu^t)L_2(\eta^5\text{-}C_7H_9)]^+$ (L_2 = dppm **10** or dppe **12**) so establishing examples of associative ligand-substitution processes which proceed with $\eta^5 \longrightarrow \eta^3 \longrightarrow \eta^5$ hapticity interconversion at the C_7H_9 dienyl ligand. The reaction between **17** and $CNBu^t$ affords $[Mo(CO)(CNBu^t)_3(\eta^5\text{-}C_7H_9)]^+$ **19** with no observable $\eta^3\text{-}C_7H_9$ intermediate but **19** reacts with further $CNBu^t$ to yield $[Mo(CO)(CNBu^t)_4(\eta^3\text{-}C_7H_9)]^+$ **20**. The crystal structures of complexes **1** and **4** have been determined. Complex **1** adopts an asymmetric ligand arrangement similar to that previously described for **6**. Complex **4** has a pseudo-octahedral molecular geometry in which $CNBu^t$ is located *trans* to the η^3-bonded C_7H_9 ligand.

It is well established that the reactivity of complexes of dienyl ligands is enhanced by the potential for $\eta^5 \longleftrightarrow \eta^3$ hapticity interconversion/'ring slip' of the dienyl ligand. However, notwithstanding extensive investigations on complexes of cyclopentadienyl, indenyl,[1] and acyclic pentadienyl ligands,[2] very few studies have systematically addressed the design of complexes which undergo facile $\eta^5 \longleftrightarrow \eta^3$ interconversion or explored the factors which promote the stability of a specific hapticity type. Such studies are best carried out where *both* η^5 and η^3 hapticity types are isolable as part of a self-contained reaction sequence but the few reported examples of such reactions are mainly restricted to complexes of acyclic pentadienyl ligands.[3–5] An alternative and more faithful model for the ubiquitous cyclopentadienyl ligand may be provided by 'open' dienyl systems incorporated into cyclic hydrocarbon ligands such as cyclohexadienyl or cycloheptadienyl and, with this in mind, we have recently described some fundamental synthetic routes to a series of cycloheptadienyl molybdenum complexes and demonstrated the feasibility of $\eta^5 \longleftrightarrow \eta^3$ interconversion in these systems.[6,7] In this paper we report on $\eta^5 \longleftrightarrow \eta^3$ hapticity interconversions in complexes of general formula $[Mo(CO)_2L_2(\eta^5\text{-}C_7H_9)]^+$ [L_2 = 2,2′-bipyridyl (bipy), $Ph_2PCH_2CH_2PPh_2$ (dppe) or $Ph_2PCH_2PPh_2$ (dppm); L = $CNBu^t$ or PPh_3] induced by added ligands NCMe or $CNBu^t$. Previous studies on analogous acyclic pentadienyl complexes $[Mo(CO)_2L_2(\eta\text{-}C_5H_7)]^+$ [L_2 = bipy,[4] dppe or $Me_2PCH_2CH_2PMe_2$ (dmpe)[5]] have revealed that the identity of L_2 can affect the ease of $\eta^5 \longleftrightarrow \eta^3$ hapticity conversion and the current work sets out to extend these investigations to cyclic, 'open' dienyl complexes. Such studies permit direct comparison of systems differing only in the identity of the dienyl ligand (C_5H_7 *vs.* C_7H_9) and therefore the relative susceptibility of C_5H_7 and C_7H_9 towards $\eta^5 \longleftrightarrow \eta^3$ hapticity conversion can be assessed. This work will demonstrate a marked reactivity dependence upon the identity of L_2/L which controls, not only susceptibility to the initial $\eta^5 \longrightarrow \eta^3$ 'ring slip', but also appears to influence the stability of the η^3-dienyl complex towards reversion to the η^5-dienyl form.

Results and Discussion

The reactions examined are of the general type (1), where

$$[Mo(CO)_2L_2(\eta^5\text{-}C_7H_9)]^+ + L' \longrightarrow [Mo(CO)_2(L')L_2(\eta^3\text{-}C_7H_9)]^+ \quad (1)$$

L′ = NCMe or $CNBu^t$. The choice of L′ was guided by our previous studies on $\eta^7 \longleftrightarrow \eta^3$ hapticity interconversion in cycloheptatrienyl complexes of Mo and W[8,9] which have demonstrated that both NCMe and $CNBu^t$ are good ligands to promote 'ring slip' but, whereas NCMe bonds weakly and, in most cases, reversibly, $CNBu^t$ can promote an associative ligand-substitution process. The discussion is organised by the ligand type L_2/L in the complexes $[Mo(CO)_2L_2(\eta^5\text{-}C_7H_9)]^+$ since the identity of this ligand was found to be the principal factor in the disparate behaviour of the complexes studied towards $\eta^5 \longleftrightarrow \eta^3$ hapticity interconversion.

Reactions of $[Mo(CO)_2(bipy)(\eta^5\text{-}C_7H_9)]^+$ **1**.—Reaction of complex **1** with donor ligands L′ (L′ = NCMe, PMe_3 or $CNBu^t$) results in the formation of the 'ring slipped' adducts $[Mo(CO)_2L'(bipy)(\eta^3\text{-}C_7H_9)]^+$ [L′ = NCMe **2**, PMe_3 **3**, or $CNBu^t$ **4** (Scheme 1)]. Complex **2** was generated by dissolving **1** in NCMe whilst **3** was formed by reaction of **1** with PMe_3 in CH_2Cl_2. Treatment of complex **1** with $CNBu^t$ in CH_2Cl_2 also provides a route to **4** but samples obtained by this method were contaminated by a second reaction product, tentatively assigned as $[Mo(CNBu^t)_4(bipy)]$. Therefore an alternative synthesis of **4** was developed involving reaction of $[Mo(CO)_2(CNBu^t)(NCMe)_2(\eta^3\text{-}C_7H_9)]^+$ **5**[7] with bipy; effectively the

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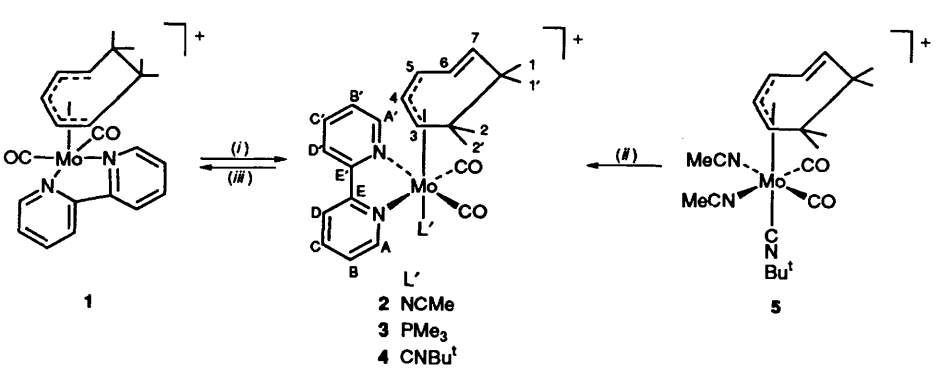
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



Scheme 1 Reagents and conditions: (*i*) L′ = NCMe, stir in NCMe; L′ = PMe$_3$, stir in CH$_2$Cl$_2$, 30 min; (*ii*) bipy, stir in CH$_2$Cl$_2$, 1 h; (*iii*) L′ = NCMe, stir in CH$_2$Cl$_2$

order of addition of CNBu^t and bipy is reversed. Spectroscopic data acquired for **4** were independent of the method of preparation. Complexes **3** and **4** were obtained as deep red solids but attempts to isolate an analytically pure sample of the NCMe adduct **2** were frustrated by facile loss of NCMe and reversion to the η^5-C$_7$H$_9$ complex **1**. The formation of complex **2** from **1** is a reversible process and when **2** was stirred in CH$_2$Cl$_2$, **1** was isolated as the exclusive product. The NMR spectroscopic data for complex **2** were conveniently obtained by dissolving samples of **1** in CD$_3$CN.

Details of the characterisation of complexes **2**–**4**, and of subsequently described compounds, are presented in Tables 1 (microanalytical, IR and mass spectroscopic data) and 2 (^{1}H, ^{13}C and ^{31}P NMR data). The formulation of complexes **2**–**4** as 'ring slipped' adducts of **1** with η^3-bonded C$_7$H$_9$ ligands is established by the spectroscopic data. We have previously identified the characteristic ^{13}C NMR resonances for an η^3-bonded C$_7$H$_9$ ring with chemical shifts for the unco-ordinated sp^2 carbons in the region δ 132–128 and for the three co-ordinated allyl carbons in an approximate range δ 95–70;[7] these groups of resonances are manifest in the ^{13}C NMR data for each of **2**, **3** and **4**. The 'ring slip' process is also accompanied by a shift to lower wavenumber in averaged carbonyl stretching frequency by *ca.* 30–50 cm^{-1} [*cf.* ν(CO) (CH$_2$Cl$_2$): 1988, 1922 cm^{-1} for **1** and 1955, 1881 cm^{-1} for **4**] and this observation is in accord with related studies on acyclic pentadienyl complexes involving the formation of [Mo(CO)$_2$(NCMe)L$_2$(η^3-C$_5$H$_7$)]$^+$ (L$_2$ = dppe or dmpe) from [Mo(CO)$_2$L$_2$(η^5-C$_5$H$_7$)]$^+$ and NCMe.[5]

Attempts were made to eliminate CO from complexes **3** and **4** to give the substituted products [Mo(CO)L′(bipy)(η^5-C$_7$H$_9$)]$^+$ (L′ = PMe$_3$ or CNBu^t) thus establishing **3** and **4** as intermediates in associative ligand-substitution processes. However no evidence was obtained for the formation of [Mo(CO)L′(bipy)(η^5-C$_7$H$_9$)]$^+$ from **3** and **4** either by photolysis in tetrahydrofuran (thf) or reaction with Me$_3$NO in CH$_2$Cl$_2$. The stability of **3** and **4** provided the opportunity to examine the structural consequences of η^5 ⟷ η^3 hapticity conversion by X-ray crystallographic studies on the 'ring slip' related pair **1** and **4**; the CNBu^t derivative **4** was selected for investigation because this provides the best comparison with subsequent work involving the reaction of [Mo(CO)$_2$L$_2$(η^5-C$_7$H$_9$)]$^+$ (L$_2$ = dppm or dppe) with CNBu^t (see later). The crystal structures of complexes **1** and **4** (and the crystallographic numbering schemes adopted) are illustrated in Figs 1 and 2 respectively. Important bond lengths and angles are summarised in Tables 3 (**1**) and 4 (**4**).

The molecular geometry of [Mo(CO)$_2$(bipy)(η^5-C$_7$H$_9$)][BF$_4$] **1** approximates to a square-based pyramid with the apical cycloheptadienyl ring η^5 bonded through C(19), C(13), C(14), C(15) and C(16) to the Mo(CO)$_2$(bipy) unit which, in accord with NMR data,[7] is orientated asymmetrically with respect to the C$_7$H$_9$ ring. The η^5 bonding of the C$_7$H$_9$ ring establishes a contrast with the analogous chemistry of the acyclic pentadienyl ligand C$_5$H$_7$ in which the bipyridyl derivative has been formulated as [Mo(σ-FBF$_3$)(CO)$_2$(bipy)(η^3-C$_5$H$_7$)] with preferred η^3 co-ordination of the pentadienyl ligand.[4] The structure of **1** is related to that of the diphosphine derivative [Mo(CO)$_2$(dppm)(η^5-C$_7$H$_9$)]$^+$ **6** which we have described previously[7] and some aspects warrant comparison. In both compounds **1** and **6** the Mo(CO)$_2$L$_2$ unit is significantly distorted from planarity. However, the non-bonded distances between the pentadienyl plane and the basal ligand donor atoms in **1** [C(1) 2.92, C(2) 2.61, N(1) 2.45, N(2) 3.17 Å] exhibit a smaller range of values than the corresponding distances in **6**. Although the Mo(CO)$_2$L$_2$ group is arranged asymmetrically with respect to the C$_7$H$_9$ ring in both **1** and **6**, the precise orientations are not identical. Thus in complex **1**, N(1) of the bipyridyl ligand is located directly below the bond connecting the sp^3 carbons [C(17), C(18)] of the C$_7$H$_9$ ring whereas the corresponding position in **6** is occupied by a carbonyl ligand.

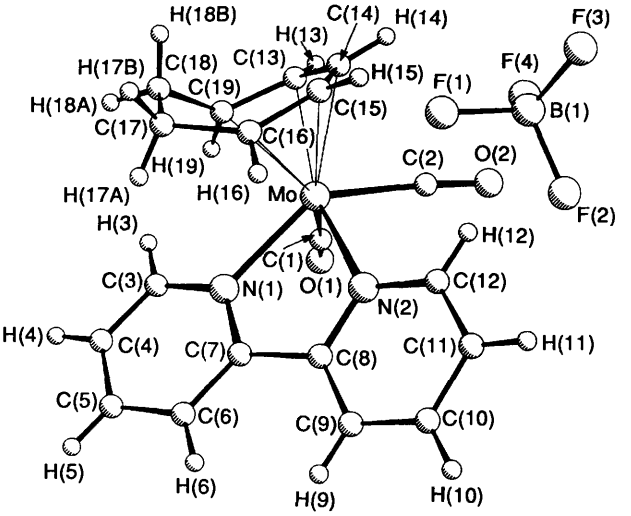


Fig. 1 The molecular structure of complex **1** showing the crystallographic numbering scheme

The structure of [Mo(CO)$_2$(CNBu^t)(bipy)(η^3-C$_7$H$_9$)][BF$_4$] **4** (Fig. 2) confirms that CNBu^t addition at the Mo centre is accompanied by η^5 ⟶ η^3 'ring slip' at the C$_7$H$_9$ ligand. A pseudo-octahedral geometry is adopted in which the CNBu^t is located *trans* to the η^3-C$_7$H$_9$ ligand [which is folded by 32.8° about the planes defined by C(13)–C(14)–C(15) and C(13)–C(15)–C(16)–C(19)] and the carbonyl and bipyridyl ligands are situated in an approximate equatorial plane. The geometric arrangement of ligands in **4** is consistent with that observed for the related allyl complex [Mo(CO)$_2$(py)(bipy)(η^3-C$_3$H$_5$)]$^+$ in which[10] pyridine (py) lies *trans* to the C$_3$H$_5$ ligand but contrasts with the molecular geometry of the pentadienyl complex [Mo(CO)$_2$(NCMe)(bipy)(η^3-C$_5$H$_7$)]$^+$, in which the

Table 1 Microanalytical, IR and mass spectroscopic data

Complex	Analysis^a (%) C	H	N	Infrared^b (cm^{-1}) ν(CO)	ν(CN)	Mass spectral data^c
2^d				1952, 1872^e		
3	46.2 (46.8)	4.9 (4.6)	5.0 (5.0)	1941, 1865		479 (M^+)
4	50.4 (50.4)	4.6 (4.6)	7.4 (7.4)	1955, 1881	2182	486 (M^+), 430 ($[M - 2CO]^+$)
7^f	53.3 (53.0)	4.5 (4.3)		2008, 1991 (sh), 1922		645 (M^+), 617 ($[M - CO]^+$), 587 ($[M - 2CO - 2H]^+$)
9	58.9 (58.6)	5.3 (5.0)	1.8 (1.7)	1974, 1914	2149	714 (M^+), 686 ($[M - CO]^+$), 587 ($[M - 2CO - 2H - CNBu^t]^+$)
10	59.4 (59.1)	5.3 (5.2)	1.8 (1.8)	1901	2155	686 (M^+), 656 ($[M - CO - 2H]^+$), 573 ($[M - CO - 2H - CNBu^t]^+$)
11	59.3 (59.0)	5.4 (5.2)	1.7 (1.7)	1963, 1904	2149	728 (M^+), 700 ($[M - CO]^+$), 645 ($[M - CNBu^t]^+$), 587 ($[M - 2CO - 2H - CNBu^t]^+$)
12	59.4 (59.6)	5.5 (5.4)	1.7 (1.8)	1903	2150	700 (M^+), 587 ($[M - 2CO - 2H - CNBu^t]^+$)
13	59.0 (59.2)	4.8 (4.9)	1.6 (1.7)	1963, 1913	2150	726 (M^+), 698 ($[M - CO]^+$), 643 ($[M - CNBu^t]^+$), 587 ($[M - 2CO - CNBu^t]^+$)
14	56.5 (56.7)	4.9 (4.9)	2.1 (2.1)	2007, 1939	2175	592 (M^+), 564 ($[M - CO]^+$), 534 ($[M - 2CO - 2H]^+$), 451 ($[M - 2CO - 2H - CNBu^t]^+$)
15	60.4 (60.4)	6.0 (5.7)	3.3 (3.3)	1886	2143, 2123	769 (M^+), 741 ($[M - CO]^+$), 686 ($[M - CNBu^t]^+$), 573 ($[M - 2CNBu^t - CO - 2H]^+$)
16	60.8 (60.8)	6.1 (5.9)	3.3 (3.2)	1880	2137, 2116	783 (M^+), 700 ($[M - CNBu^t]^+$)
19	49.3 (49.9)	6.5 (6.5)	7.5 (7.6)	1936	2178, 2152	468 (M^+), ($[M - CO - 2H]^+$), 385 ($M - CNBu^t$), 355 ($[M - CO - 2H - CNBu^t]^+$)
20	52.6 (52.8)	7.0 (7.1)	8.8 (8.8)	1899	2173, 2138	551 (M^+), 523 ($[M - CO]^+$), 468 ($[M - CNBu^t]^+$), 438 ($[M - CNBu^t - CO - 2H]^+$), 355 ($M - 2CNBu^t - CO - 2H]^+$)

^{a} Calculated values in parentheses. All complexes isolated as BF_4 salts. ^{b} Solution spectra in CH_2Cl_2 unless stated otherwise. ^{c} By FAB mass spectroscopy unless stated otherwise, *m*/*z* values based on ^{98}Mo. ^{d} Attempts to isolate **2** uncontaminated by **1** were unsuccessful. ^{e} In NCMe. ^{f} Analytical data for **7**·CH_2Cl_2: Cl found, 7.2; required, 8.7%.

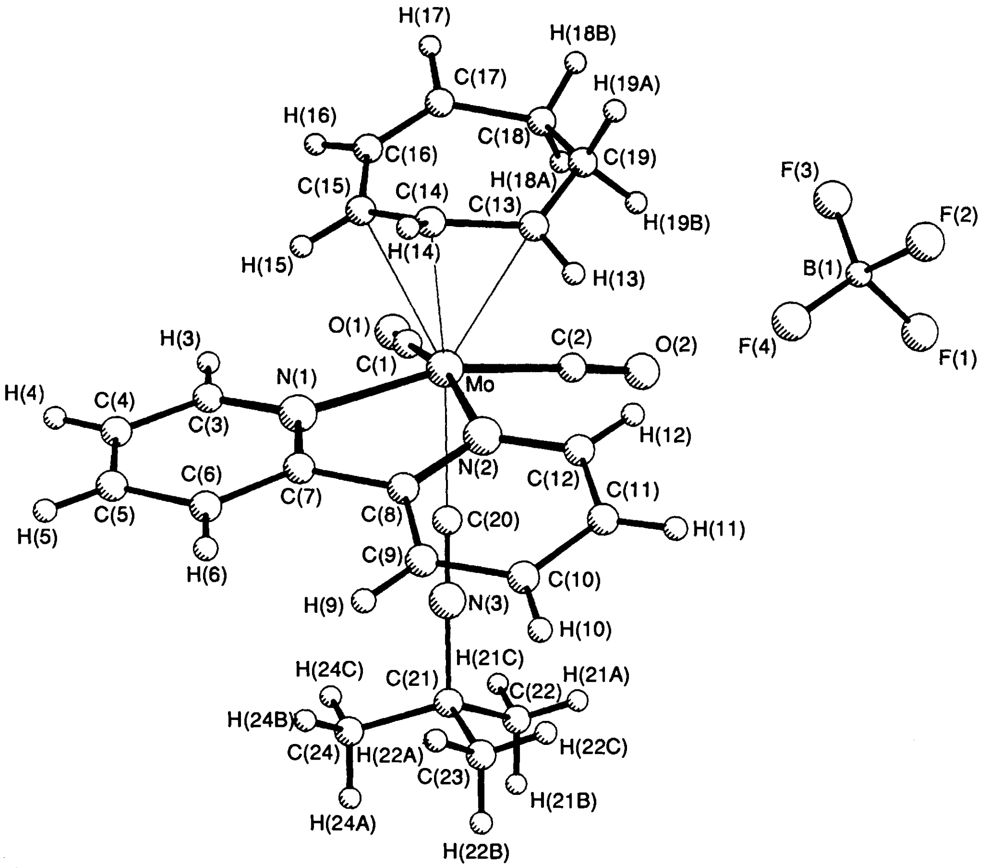


Fig. 2 The molecular structure of complex **4** showing the crystallographic numbering scheme

pentadienyl ligand is located *trans* to a bipyridyl nitrogen.[4] Other structural features of **4**, $[Mo(CO)_2(py)(bipy)(\eta^3\text{-}C_3H_5)]^+$ and $[Mo(CO)_2(NCMe)(bipy)(\eta^3\text{-}C_5H_7)]^+$, including bond lengths and angles defined at the molybdenum centre and the orientation of the 'open' face of the η^3-co-ordinated allyl unit towards the Mo–CO vectors, exhibit close similarity. The

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

Complex	^{1}H NMR (δ)[a]	^{13}C NMR (δ)[a]
2[b]	9.06 (m, 1 H), 8.87 (m, 1 H) (H$^{A,A'}$), 8.42 (m, 2 H, H$^{D,D'}$), 8.26 (m, 2 H, H$^{C,C'}$), 7.72 (m, 2 H, H$^{B,B'}$), 6.29 [m, 1 H, H^6, J(H^6–H^7) 11, J(H^5–H^6) 7], 5.43 (m, 1 H, H^7), 4.77 (m, 1 H, H^3), 4.64 (m, 1 H, H^5), 3.40 [t, 1 H, H^4, J(H^3–H^4) 7, J(H^4–H^5) 7], 2.60 (m, 1 H), 2.24 (m, 1 H), 2.11 (m, 1 H), 1.54 (m, 1 H, H$^{1,1',2,2'}$)	227.0, 225.9 (CO), 155.1, 155.0 (C$^{E,E'}$), 154.3, 153.4 (C$^{A,A'}$), 141.6, 141.2 (C$^{C,C'}$), 132.2, 129.4 (C^{6,7}), 128.1, 128.0 (C$^{B,B'}$), 124.6, 124.5 (C$^{D,D'}$), 81.1, 79.7, 77.9 (C$^{3-5}$), 31.1, 28.7 (C^{1,2})
3[b]	8.87 (m, 1 H), 8.66 (m, 1 H, H$^{A,A'}$), 8.52 (m, 2 H, H$^{D,D'}$), 8.29 (m, 2 H, H$^{C,C'}$), 7.70 (m, 2 H, H$^{B,B'}$), 6.24 [m, 1 H, H^6, J(H^6–H^7) 11, J(H^5–H^6) 7], 5.53 (m, 1 H, H^7), 4.69 (m, 2 H, H^{3,5}), 3.65 [t, 1 H, H^4, J(H^3–H^4) 8, J(H^4–H^5) 8], 2.54 (m, br, 1 H), 2.22 (m, 2 H), 1.55 (m, br, 1 H, H$^{1,1',2,2'}$), 1.03 [d, 9 H, PMe$_3$, J(P–H) 9]	227.9 [d, CO, J(C–P) 17], 226.3 [d, CO, J(C–P) 13], 154.7, 154.5, 153.7 (C$^{A,A',E,E'}$), 141.3, 140.7 (C$^{C,C'}$), 131.8, 129.8 (C^{6,7}), 128.2 (C$^{B,B'}$), 125.1, 125.0 (C$^{D,D'}$), 86.7, 84.1, 80.5 (C$^{3-5}$), 31.3, 29.0 (C^{1,2}), 13.6 [d, PMe$_3$, J(C–P) 26]
4[c]	9.15 (m, 1 H), 8.96 (m, 1 H, H$^{A,A'}$), 8.84 (m, 2 H, H$^{D,D'}$), 8.47 (m, 2 H, H$^{C,C'}$), 7.92 (m, 2 H, H$^{B,B'}$), 6.37 [m, 1 H, H^6, J(H^6–H^7) 11, J(H^5–H^6) 6], 5.57 (m, 1 H, H^7), 5.18 (m, 2 H, H^{3,5}), 4.06 [t, 1 H, H^4, J(H^3–H^4) 8, J(H^4–H^5) 8], 2,71 (m, 1 H), 2.30 (m, 1 H), 2.21 (m, 1 H), 1.65 (m, 1 H, H$^{1,1',2,2'}$), 1.28 (s, 9 H, CNCMe$_3$)	226.0, 224.0 (CO), 155.2, 154.9 (C$^{E,E'}$), 154.3, 153.3 (C$^{A,A'}$), 141.6, 141.0 (C$^{C,C'}$), 131.8, 129.8 (C^{6,7}), 128.1, (C$^{B,B'}$), 124.9, 124.8 (C$^{D,D'}$), 88.4, 85.6, 82.7 (C$^{3-5}$), 60.1 (CN*C*Me$_3$), 31.6, 29.5[d] (C^{1,2}, CNC*Me*$_3$)
7[e]	20 °C: 7.59–7.40 (m, 20 H, Ph), 5.34 (br, 1 H), 4.89 (t, 2 H), 4.05 (br, 2 H) (H$^{3-7}$), 3.13 (br, 2 H), 2.21 (br, 2 H) (CH$_2$, dppe), 1.83 (m, 4 H, H$^{1,1',2,2'}$)[f] −40 °C: 7.56–7.20 (m, 20 H, Ph), 5.43 (br, 1 H), 5.20 (br, 1 H), 4.62 (br, 1 H), 4.40 (br, 1 H), 3.78 (br, 1 H, H$^{3-7}$), 2.81 (br, 2 H, CH$_2$, dppe), 2.31, 1.95, 1.81, 1.71 (br, 6 H, CH$_2$, dppe, H$^{1,1',2,2'}$)[g]	20 °C: 228.1, br, (CO), 132.8, 131.4, 131.2, 131.0, 129.3, 128.9 (Ph), 101.3, 99.9 (C$^{3-7}$), 32.1 (C^{1,2}) 29.5[d] (CH$_2$, dppe)[c] −20 °C: 230.1, br, 226.7, br (CO), 133.1, 133.0, 131.6, 131.0, 129.3, 129.2, 129.1, 129.0 (Ph), 102.8 (br), 100.6 (br), 99.3 (br), 84.4 (br) (C$^{3-7}$), 32.7, 31.1 (C^{1,2}), 29.3[d] (CH$_2$, dppe)[c]
9	*h*	227.1, 215.0 (CO), 152.1 (*C*NCMe$_3$), 134.5–128.5 (Ph and C^{6,7}), 94.2, 86.2, 77.3 (C$^{3-5}$), 58.3 (CN*C*Me$_3$), 41.6 (CH$_2$, dppm), 36.1, 29.4 (C^{1,2}), 29.9 (CNC*Me*$_3$)[i]
10[j]	7.84, 7.77, 7.60, 7.41, 7.19, 6.62 (m, 20 H, Ph), 5.60 (m, 1 H), 4.95 (m, 1 H), 4.73 (br, 1 H), 4.36 (m, 1 H), 4.10 (m, 1 H), (H$^{3-7}$), 4.64 (m, 1 H), 3.94 (m, 1 H, CH$_2$, dppm), 2.35 (m, 1 H), 2.09 (m, 1 H), 1.90 (m, 2 H, H$^{1,1',2,2'}$), 1.12 (s, 9 H, CNCMe$_3$)	229.3 [dd, CO, J(C–P) 7, 17], 154.8 (*C*NCMe$_3$), 138.0–129.1 (Ph), 100.1, 99.8, 99.3, 97.8, 81.4 (C$^{3-7}$), 59.7 (CN*C*Me$_3$), 43.8 (CH$_2$, dppm), 34.4, 30.9 (C^{1,2}), 30.2 (CNC*Me*$_3$)
11[k]	7.70–6.95 (m, 20 H, Ph), 5.33 (br, 1 H), 5.13 (br, 1 H), 4.97 (br, 1 H), 4.80 (br, 1 H), 4.50 (br, 1 H, H$^{3-7}$), 2.99, 2.55, 2.14, 1.65 (br, 8 H, CH$_2$, dppe and H$^{1,1',2,2'}$), 0.74 (s, 9 H, CNCMe$_3$)[l]	229.1, 216.2 (CO), 151.2 (*C*NCMe$_3$), 137.1–128.0 (Ph and C^{6,7}), 89.3, 84.5, 74.3 (C$^{3-5}$), 58.6 (CN*C*Me$_3$), 33.8, 29.4 (C^{1,2}), 29.4 (CNC*Me*$_3$), 29.4, 27.9 (CH$_2$, dppe)[m]
12[n]	7.59–6.92 (m, 20 H, Ph), 4.90 (m, 2 H), 4.61 (m, 1 H), 4.26 (br, 1 H), 3.25 (br, 1 H, H$^{3-7}$), 2.69, 2.42, 2.09, 1.80 (br, 8 H, CH$_2$, dppe and H$^{1,1',2,2'}$), 1.18 (s, 9 H, CNCMe$_3$)[o]	234.8 [dd, CO, J(C–P) 4, 20], 160.4 (*C*NCMe$_3$), 137.0–128.0 (Ph), 101.7, 99.5, 97.8, 96.8, 81.7 (C$^{3-7}$), 60.1 (CN*C*Me$_3$), 34.0, 32.5 (C^{1,2}), 29.8 (CNC*Me*$_3$), 28.5 (CH$_2$, dppe)[p]
13[q]	8.07–7.52 (m, 20 H, Ph), 5.64 (s, 7 H, C$_7$H$_7$), 3.40 (br, 2 H, CH$_2$, dppe), 2.90 (br, 2 H, CH$_2$, dppe), 1.15 (s, 9 H, CNCMe$_3$)[c]	227.1, 215.9 (CO), 152.5 (br, *C*NCMe$_3$), 135.3–129.2 (Ph), 106.6 (C$_7$H$_7$), 59.1 (CN*C*Me$_3$), 29.7 (CNC*Me*$_3$), 28.9, 27.1 (CH$_2$, dppe)[b]
14	7.66–7.37 (m, 15 H, PPh$_3$), 5.80 (m, 1 H), 5.01 (m, 4 H, H$^{3-7}$), 2.40, 2.06 (m, 4 H, H$^{1,1',2,2'}$), 1.76 (s, 9 H, CNCMe$_3$)[r]	223.5 [d, CO, J(C–P) 23], 150.5 (*C*NCMe$_3$), 134.7–129.7 (PPh$_3$), 104.0, 101.6, 94.6 (C$^{3-7}$), 61.5 (CN*C*Me$_3$), 34.5 (C^{1,2}), 30.8 (CNC*Me*$_3$)[o]
19[f]	5.85 (m, 1 H, H^5), 5.06 (br, 2 H, H^{4,6}), 4.38 (br, 2 H, H^{3,7}), 1.94 (s, 4 H, H$^{1,1',2,2'}$), 1.54, 1.52 (27 H, CNCMe$_3$)	230.0 (CO), 157.4 (br, *C*NCMe$_3$), 102.3, 98.0 (C$^{3-7}$), 59.3, 58.5 (CN*C*Me$_3$), 33.0 (C^{1,2}), 30.6, 30.4 (CNC*Me*$_3$)
20	5.88 (m, 1 H, H^6), 5.28 (m, 1 H, H^7), 5.06 (m, 2 H, H^{3,4}), 4.94 (m, 1 H, H^5), 2.54 (m, 2 H), 2.23 (br, 1 H), 1.81 (br, 1 H, H$^{1,1',2,2'}$) 1.50, 1.37 (36 H, CNCMe$_3$)[s]	213.8 (CO), 160.7, 159.9, 157.8, 155.1 (*C*NCMe$_3$), 131.9 (C^6), 124.7 (C^7), 100.1, 83.7 (C^{3,4}), 81.7 (C^5), 59.3, 58.9, 57.0 (CN*C*Me$_3$), 37.5, 29.4 (C^{1,2}), 30.7 (CNC*Me*$_3$)[t]

[a] 300 MHz ^{1}H NMR spectra, 75 MHz ^{13}C NMR spectra; s = singlet, d = doublet, t = triplet, m = multiplet, br = broad; chemical shifts downfield from SiMe$_4$, coupling constants in Hz; numbering/lettering as in Schemes 1–3. [b] In CD$_3$CN. [c] In (CD$_3$)$_2$CO. [d] Signal obscured by (CD$_3$)$_2$CO solvent. [e] ^{31}P NMR spectrum in CD$_2$Cl$_2$: δ (−40 °C) 72.7 [d, J(P–P) 34], 70.1 [d, J(P–P) 35], δ (30 °C) 71.3 (s). [f] In CDCl$_3$. [g] In CD$_2$Cl$_2$. [h] Broad, ill defined resonances only. [i] In CD$_2$Cl$_2$ at 0 °C. [j] In CD$_2$Cl$_2$ at −20 °C. [k] ^{31}P NMR spectrum in (CD$_3$)$_2$CO at −20 °C: δ 59.2 [d, J(P–P) 27], 54.3 [d, J(P–P) 27]. [l] In CD$_2$Cl$_2$ at −90 °C. [m] In CD$_3$CN at 0 °C. [n] ^{31}P NMR spectrum in (CD$_3$)$_2$CO at −20 °C: δ 74.5 [d, J(P–P) 36], 72.9 [d, J(P–P) 35]. [o] In CD$_2$Cl$_2$ at −80 °C. [p] In CD$_3$CN at −20 °C. [q] ^{31}P NMR spectrum in CD$_2$Cl$_2$: δ 54.7 [d, J(P–P) 20], 52.5 [d, J(P–P) 20]. [r] In (CD$_3$)$_2$CO at −60 °C. [s] In CDCl$_3$–CNBu^t. [t] In CD$_2$Cl$_2$–CNBu^t; assignments made with the aid of a [^{1}H–^{13}C] heteronuclear correlation experiment.

principal structural consequences of the conversion of **1** to **4** are $\eta^5 \longrightarrow \eta^3$ 'ring slip' of the cycloheptadienyl ligand, a movement of the Mo(CO)$_2$(bipy) unit towards coplanarity and a significant reorientation of the C$_7$H$_9$ ligand with respect to the bipyridyl ligand. An increase in the molybdenum to pentadienyl/allyl plane distance (from 1.810 in **1**, to 2.084 Å in **4**) is also observed although the average molybdenum to cycloheptadienyl carbon bond distance is almost unaffected. The reorientation of the C$_7$H$_9$ ring with respect to the Mo(CO)$_2$(bipy) group on formation of **4** results in a structure with higher pseudo symmetry and may also serve to relieve interligand steric interaction between the dienyl and bipyridyl ligands.

Reactions of [Mo(CO)$_2$L$_2$(η^5-C$_7$H$_9$)]$^+$ (L$_2$ = dppm **6** *or* dppe **7**).—We have previously described the synthesis and characterisation of [Mo(CO)$_2$(dppm)(η^5-C$_7$H$_9$)]$^+$ **6**,[7] but to extend the scope of our current studies on hapticity interconversion it was necessary also to synthesise the dppe derivative [Mo(CO)$_2$(dppe)(η^5-C$_7$H$_9$)]$^+$ **7**. Complex **7**, as a CH$_2$Cl$_2$ solvate, was obtained in high yield as a pink-red solid by reaction of [Mo(CO)$_2$(NCMe)$_3$(η^3-C$_7$H$_9$)]$^+$ with dppe in

Table 3 Selected bond lengths (Å) and angles for complex **1**

Mo–N(1)	2.237(4)	C(4)–C(5)	1.376(8)
Mo–N(2)	2.222(4)	C(5)–C(6)	1.378(8)
Mo–C(1)	1.963(6)	C(6)–C(7)	1.376(7)
Mo–C(2)	1.975(6)	C(7)–C(8)	1.462(8)
Mo–C(13)	2.302(5)	C(8)–C(9)	1.388(7)
Mo–C(14)	2.300(5)	C(9)–C(10)	1.362(8)
Mo–C(15)	2.349(5)	C(10)–C(11)	1.377(9)
Mo–C(16)	2.448(5)	C(11)–C(12)	1.370(8)
Mo–C(19)	2.371(6)	C(13)–C(14)	1.405(8)
O(1)–C(1)	1.143(7)	C(13)–C(19)	1.415(8)
O(2)–C(2)	1.161(6)	C(14)–C(15)	1.423(8)
N(1)–C(3)	1.346(6)	C(15)–C(16)	1.377(8)
N(1)–C(7)	1.353(7)	C(16)–C(17)	1.520(8)
N(2)–C(8)	1.349(6)	C(17)–C(18)	1.499(9)
N(2)–C(12)	1.353(6)	C(18)–C(19)	1.501(8)
C(3)–C(4)	1.364(8)		

N(1)–Mo–N(2)	72.1(1)	C(8)–N(2)–C(12)	118.1(4)
N(1)–Mo–C(1)	80.2(2)	Mo–C(1)–O(1)	175.9(6)
N(1)–Mo–C(2)	139.7(2)	Mo–C(2)–O(2)	175.6(5)
N(2)–Mo–C(1)	107.0(2)	C(14)–C(13)–C(19)	121.1(5)
N(2)–Mo–C(2)	82.5(2)	C(13)–C(14)–C(15)	126.7(5)
C(1)–Mo–C(2)	77.9(2)	C(14)–C(15)–C(16)	128.3(5)
Mo–N(1)–C(3)	123.7(3)	C(15)–C(16)–C(17)	130.0(5)
Mo–N(1)–C(7)	118.1(3)	C(16)–C(17)–C(18)	113.8(5)
C(3)–N(1)–C(7)	118.1(4)	C(17)–C(18)–C(19)	116.1(5)
Mo–N(2)–C(8)	118.5(3)	C(13)–C(19)–C(18)	121.4(5)
Mo–N(2)–C(12)	123.5(3)		

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

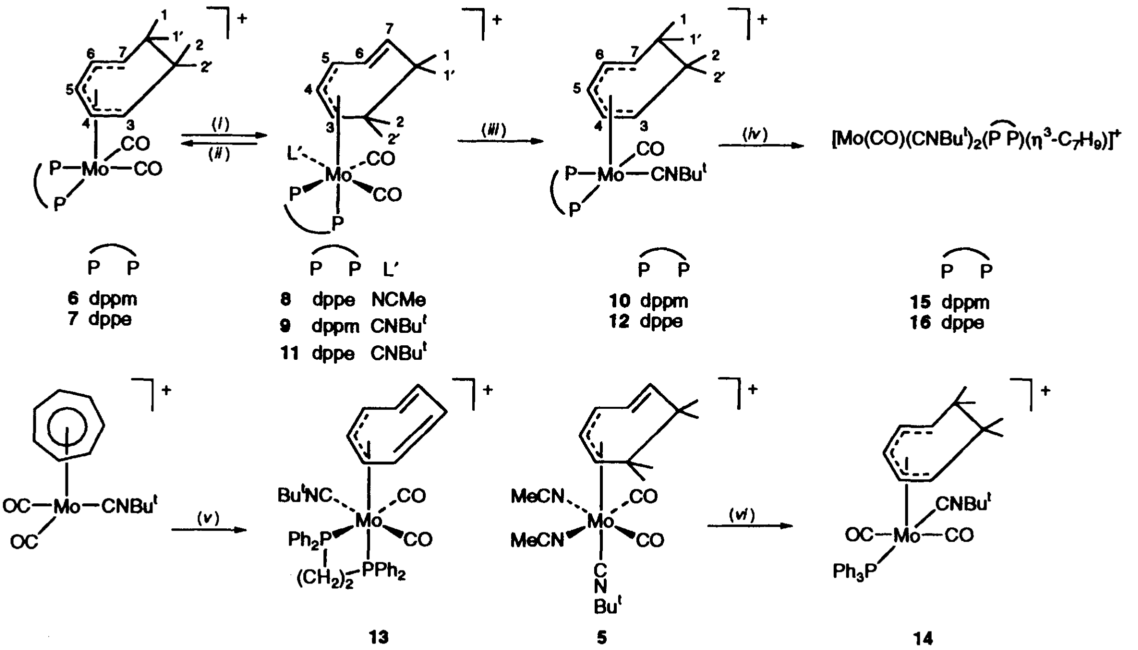
Mo–N(1)	2.228(6)	C(5)–C(6)	1.37(1)
Mo–N(2)	2.240(6)	C(6)–C(7)	1.38(1)
Mo–C(1)	1.936(9)	C(7)–C(8)	1.46(1)
Mo–C(2)	1.951(9)	C(8)–C(9)	1.38(1)
Mo–C(13)	2.393(9)	C(9)–C(10)	1.35(1)
Mo–C(14)	2.235(8)	C(10)–C(11)	1.36(1)
Mo–C(15)	2.442(9)	C(11)–C(12)	1.39(1)
Mo–C(20)	2.152(9)	C(13)–C(14)	1.40(1)
O(1)–C(1)	1.15(1)	C(13)–C(19)	1.48(1)
O(2)–C(2)	1.137(9)	C(14)–C(15)	1.36(1)
N(1)–C(3)	1.34(1)	C(15)–C(16)	1.47(1)
N(1)–C(7)	1.330(9)	C(16)–C(17)	1.25(2)
N(2)–C(8)	1.351(9)	C(17)–C(18)	1.46(2)
N(2)–C(12)	1.34(1)	C(18)–C(19)	1.36(2)
N(3)–C(20)	1.127(9)	C(21)–C(22)	1.46(1)
N(3)–C(21)	1.45(1)	C(21)–C(23)	1.45(2)
C(3)–C(4)	1.37(1)	C(21)–C(24)	1.47(2)
C(4)–C(5)	1.33(1)		

N(1)–Mo–N(2)	72.9(2)	C(3)–N(1)–C(7)	118.3(7)
N(1)–Mo–C(1)	102.2(3)	Mo–N(2)–C(8)	115.6(5)
N(1)–Mo–C(2)	164.2(3)	Mo–N(2)–C(12)	124.3(6)
N(1)–Mo–C(20)	80.2(3)	C(8)–N(2)–C(12)	118.4(7)
N(2)–Mo–C(1)	167.0(3)	C(20)–N(3)–C(21)	180(1)
N(2)–Mo–C(2)	100.9(3)	Mo–C(1)–O(1)	175.5(9)
N(2)–Mo–C(20)	78.4(3)	Mo–C(2)–O(2)	177(1)
C(1)–Mo–C(2)	80.5(4)	C(14)–C(13)–C(19)	123.8(9)
C(1)–Mo–C(20)	88.9(4)	C(13)–C(14)–C(15)	123.6(9)
C(2)–Mo–C(20)	84.3(4)	C(14)–C(15)–C(16)	127.9(9)
C(13)–Mo–C(14)	34.9(3)	C(15)–C(16)–C(17)	127(1)
C(13)–Mo–C(15)	60.3(3)	C(16)–C(17)–C(18)	128(1)
C(14)–Mo–C(15)	33.4(3)	C(17)–C(18)–C(19)	127(1)
Mo–N(1)–C(3)	124.4(6)	C(13)–C(19)–C(18)	127(1)
Mo–N(1)–C(7)	117.1(5)	Mo–C(20)–N(3)	174.6(8)

CH_2Cl_2. In common with **6**, the ^1H, ^{13}C and ^{31}P NMR data for **7** exhibit temperature-dependent behaviour which might be attributed to a high barrier to rotation of the co-ordinated $Mo(CO)_2L_2$ fragment with respect to the C_7H_9 ring and a preferred asymmetric orientation at low temperature akin to the crystallographically established arrangements in **1** and **6**. In Table 2, NMR data for **7** are presented at 20 °C (at which temperature some averaging of the ring environments is observed) and at low temperature where each individual ring hydrogen/carbon is distinct. In the ^{31}P NMR spectrum of complex **7**, a limiting low-temperature doublet of doublets spectrum was observed at −40 °C and the coalescence temperature was determined as −3 °C in CD_2Cl_2. A spectroscopic feature specific to **7** is a shoulder (at 1991 cm^{-1} in CH_2Cl_2) on the high wavenumber IR-active carbonyl stretching band; the relative absorption intensity of this shoulder increases in acetone and decreases in $CHCl_3$ suggesting that **7** might exist in solution as a mixture of conformers.

Our initial studies on $\eta^5 \longleftrightarrow \eta^3$ hapticity interconversion in **6** and **7** focused on reaction with NCMe. Complexes **6** and **7** were dissolved in NCMe and any reaction monitored by changes in the ν(CO) region of the IR spectrum. The dppm complex **6** was unreactive towards NCMe but the dppe complex **7** gave a four-band carbonyl spectrum in NCMe of which ν(CO)(NCMe) 1990, 1919 cm^{-1} were identified with **7** and ν(CO)(NCMe) 1946, 1868 cm^{-1} were subsequently assigned, on the basis of a collection of spectroscopic data, to the adduct $[Mo(CO)_2(NCMe)(dppe)(\eta^3\text{-}C_7H_9)]^+$ **8** (Scheme 2). When the reaction mixture of **7** and NCMe was evaporated to dryness and the residue redissolved in CH_2Cl_2, only the characteristic carbonyl stretching bands of **7** were observed in the IR spectrum. The assignment of [ν(CO)(NCMe) 1946, 1868 cm^{-1}] to **8** is supported by a comparison with data for the analogous pentadienyl complex $[Mo(CO)_2(NCMe)(dppe)(\eta^3\text{-}C_5H_7)]^+$ [ν(CO)(NCMe) 1956, 1873 cm^{-1}][5] but more definitive evidence for the formation of **8** from **7** and NCMe has been obtained from ^{31}P and ^{13}C NMR investigations on **7** in CD_3CN. The ambient-temperature ^{31}P NMR spectrum of a sample of **7** dissolved in CD_3CN exhibits a singlet at δ 73.0, assigned to **7** by comparison with data obtained in CD_2Cl_2 (see Table 2), and additionally two broad resonances centred around δ 64 and 57.5. Cooling the solution to −25 °C resulted in a significant change in the spectrum with the appearance of two incompletely resolved resonances at δ 74.2 and 72.3 (consistent with the variable-temperature behaviour of **7**) and two well defined doublet resonances [δ(CD_3CN) 64.8, d, *J*(P–P) 26.9; 57.3, d, *J*(P–P) 26.9 Hz] indicative of a second component in the reaction mixture. The low temperature (−25 °C) ^{13}C NMR spectrum of a sample of **7** dissolved in CD_3CN provides further confirmation of a two component reaction mixture. In the region δ 110–70, six ^{13}C resonances are observed. Three relatively broad resonances [δ(CD_3CN) 103.1, 99.1, 83.6] are attributable to **7** by examination of comparable data recorded in $(CD_3)_2CO$ at −20 °C (see Table 2) leaving three sharp resonances [δ(CD_3CN) 91.6, 87.1, 73.7], which have no equivalents in the $(CD_3)_2CO$ spectrum, to be accounted for by a reaction product. Taken as a whole the IR, ^{31}P and ^{13}C NMR spectroscopic data for the product formed from **7** and NCMe support the formulation $[Mo(CO)_2(NCMe)(dppe)(\eta^3\text{-}C_7H_9)]^+$ **8**. The shift of ν(CO) to lower wavenumber on formation of **8** from **7** is consistent with related $\eta^5 \longrightarrow \eta^3$ C_7H_9 'ring slip' processes, the chemical shifts of the ^{31}P NMR resonances are typical of complexes of formulation $[Mo(CO)_2L'(dppe)(\eta^3\text{-}R)]^+$ (L′ = NCMe[8] or $CNBu^t$, R = C_7H_9 or C_7H_7) (see later) and the ^{13}C NMR resonances in the range δ 92–70 are consistent with the three co-ordinated allyl carbons of an $\eta^3\text{-}C_7H_9$ ligand.

In summary the reactions of NCMe with $[Mo(CO)_2L_2(\eta^5\text{-}C_7H_9)]^+$ (L_2 = bipy **1**, dppe **7** or dppm **6**) reveal a gradation in susceptibility towards $\eta^5 \longrightarrow \eta^3$ 'ring slip' dependent upon the identity of L_2. Whilst all additions of NCMe to $[Mo(CO)_2L_2(\eta^5\text{-}C_7H_9)]^+$ are reversible, the adduct $[Mo(CO)_2(NCMe)(bipy)(\eta^3\text{-}C_7H_9)]^+$ **2** is fully formed in NCMe, but $[Mo(CO)_2(NCMe)(dppe)(\eta^3\text{-}C_7H_9)]^+$ **8** is in equilibrium with **7** and the solvent NCMe {we have previously described a related equilibrium between $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_7)]^+$ and $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)]^+$ in the chemistry of



Scheme 2 Reagents and conditions: (*i*) L′ = NCMe, P–P = dppe, stir in NCMe; L′ = CNBu^t, P–P = dppm, stir in CH$_2$Cl$_2$, 2 h, −40 °C; L′ = CNBu^t, P–P = dppe, stir in CH$_2$Cl$_2$, 4 h, 0 °C; (*ii*) L′ = NCMe, P–P = dppe, stir in CH$_2$Cl$_2$; (*iii*) L′ = CNBu^t only; P–P = dppm, stir in CH$_2$Cl$_2$; P–P = dppe, stir in CH$_2$Cl$_2$, 35 °C; (*iv*) P–P = dppm or dppe; CNBu^t, stir in CH$_2$Cl$_2$; (*v*) dppe, stir in CH$_2$Cl$_2$, 24 h; (*vi*) PPh$_3$, stir in CH$_2$Cl$_2$, 1 h

cycloheptatrienyl molybdenum complexes}.[8] Finally in the case of **6**, where L$_2$ = dppm, the complex appears to be resistant to NCMe induced 'ring slip'. By contrast each of the acyclic pentadienyl complexes [Mo(CO)$_2$(NCMe)L$_2$(η^5-C$_5$H$_7$)]$^+$ (L$_2$ = bipy,[4] dppe or dmpe[5]) are fully formed in NCMe and are isolable species. These comparisons, together with the contrasting structures of **1** and [Mo(σ-FBF$_3$)(CO)$_2$(bipy)(η^3-C$_5$H$_7$)], provide good evidence that the cyclic dienyl ligand C$_7$H$_9$ exhibits a reduced tendency to adopt an η^3-dienyl bonding mode by comparison with the pentadienyl ligand C$_5$H$_7$.

Several factors may contribute to the effect of L$_2$ on hapticity interconversion in [Mo(CO)$_2$L$_2$(η^5-C$_7$H$_9$)]$^+$. It has been suggested that the effect of bipy *vs.* dppe on the preferred hapticity of the pentadienyl ligand in [Mo(σ-FBF$_3$)(CO)$_2$(bipy)(η^3-C$_5$H$_7$)] and [Mo(CO)$_2$(dppe)(η^5-C$_5$H$_7$)][BF$_4$] might be correlated with interligand steric hindrance between the dienyl and bipy/dppe ligands.[4] However in the case of the cycloheptadienyl complexes **1** and **6**, it seems unlikely, on the basis of a comparison of non-bonded interligand interactions from the structural data, that a corresponding argument can, in itself, account for our results. Other important factors may include the details of Mo to L$_2$ bonding and the molecular geometry of the 'ring slipped' adduct. The crystal structure of complex **4** suggests that adducts of **1**, *i.e.* [Mo(CO)$_2$L′(bipy)(η^3-C$_7$H$_9$)]$^+$ adopt a structure in which L′ is located *trans* to C$_7$H$_9$ in common with the allyl complexes [Mo(CO)$_2$L′(bipy)(η^3-C$_3$H$_5$)]$^{z+}$ (z = 0, L′ = NCS;[11] z = 1, L′ = py[10]). Although no crystallographic data are available for cationic diphosphine complexes of general formulation [Mo(CO)$_2$(L′)L$_2$(η^3-R)]$^+$ (L$_2$ = dppe, dppm *etc.*; L′ = CO, PR$_3$ *etc.*; R = C$_3$H$_5$, C$_5$H$_7$ *etc.*), structural studies on the neutral derivatives [Mo(CO)$_2$L′(dppe)(η^3-R)] (L′ = halide, R = C$_3$H$_5$[12] or C$_5$H$_7$[13]) and the ring-substituted cycloheptatrienyl complex [MoCl(CO)$_2$(dppe)(η^3-C$_7$H$_6$R)] (R = C$_6$H$_4$F-4)[14] reveal a geometric arrangement of ligands, differing from that observed in bipy analogues, in which one phosphorus of the dppe ligand is situated *trans* to the η^3-bonded ligand. A corresponding asymmetric ligand arrangement for **8**, as illustrated in Scheme 2, is therefore suggested and is found to be most consistent with the ^{31}P NMR spectroscopic data. The geometric arrangement of ligands in the adducts [Mo(CO)$_2$(L′)L$_2$(η^3-C$_7$H$_9$)]$^+$ may therefore be an additional factor controlling the susceptibility of [Mo(CO)$_2$L$_2$(η^5-C$_7$H$_9$)] to η^5 ⟶ η^3 'ring slip'.

In the 'ring slip' chemistry of cycloheptatrienyl molybdenum complexes, we have observed that whereas NCMe adds reversibly at the molybdenum centre, corresponding reactions with CNBu^t lead to associative ligand-substitution processes involving η^7 ⟶ η^3 ⟶ η^7 hapticity conversions at the C$_7$H$_7$ ring.[9] In search of analogous associative ligand-substitution reactions proceeding with η^5 ⟶ η^3 ⟶ η^5 hapticity conversion at a cycloheptadienyl ring, we turned our attention to the reactions of complexes **6** and **7** with CNBu^t. Treatment of the dppm complex **6** with one equivalent of CNBu^t in CH$_2$Cl$_2$ at ambient temperature resulted in the isolation of the carbonyl substituted compound [Mo(CO)(CNBu^t)(dppm)(η^5-C$_7$H$_9$)]$^+$ **10**. Monitoring the reaction mixture by IR spectroscopy in the ν(CO) region revealed that the reaction proceeded *via* an observable intermediate species. The corresponding reaction of the dppe derivative **7** with CNBu^t also led to the formation of the carbonyl substituted [Mo(CO)(CNBu^t)(dppe)(η^5-C$_7$H$_9$)]$^+$ **12** but in this case the reaction intermediate was more persistent and complete conversion to **12** was assisted by warming the reaction mixture to 35 °C. Repetition of the above reactions at low temperature (−40 °C for **6**, 0 °C for **7**) resulted in the isolation of the intermediates [Mo(CO)$_2$(CNBu^t)L$_2$(η^3-C$_7$H$_9$)]$^+$ (L$_2$ = dppm **9** or dppe **11**). Characterisation data for complexes **9**–**12** are presented in Tables 1 and 2. The NMR spectroscopic data for [Mo(CO)(CNBu^t)L$_2$(η^5-C$_7$H$_9$)]$^+$ (L$_2$ = dppm **10** or dppe **12**) are similar to data obtained for the precursor dicarbonyl derivatives **6** and **7** except that in **10** and **12** further asymmetry is imposed by the substitution of CO by CNBu^t. The spectroscopic data for complexes **9** and **11**, formulated as the η^3-cycloheptadienyl species [Mo(CO)$_2$(CNBu^t)L$_2$(η^3-C$_7$H$_9$)]$^+$, warrant further detailed examination since an alternative, pendant phosphine formulation [Mo(CO)$_2$(CNBu^t)(σ-L–L)(η^5-C$_7$H$_9$)]$^+$ (Fig. 3) can be envisaged and it is important to exclude this in order to establish fully that the associative substitution processes **6** ⟶ **9** ⟶ **10** and **7** ⟶ **11** ⟶ **12** are accompanied by η^5 ⟶ η^3 ⟶ η^5 hapticity changes at the C$_7$H$_9$ ring.

To distinguish between the possible formulations [Mo(CO)$_2$-

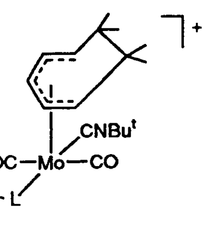


Fig. 3 An alternative structural formulation for complexes **9** and **11**

$(CNBu^t)L_2(\eta^3-C_7H_9)]^+$ and $[Mo(CO)_2(CNBu^t)(\sigma-L–L)(\eta^5-C_7H_9)]^+$, the spectroscopic data for **9** and **11** were compared with data for related complexes which serve as models for the two alternatives. Two model complexes were prepared. First the cycloheptatrienyl complex $[Mo(CO)_2(CNBu^t)(dppe)(\eta^3-C_7H_7)]^+$ **13** {representative of 'ring slipped' $[Mo(CO)_2(CNBu^t)(dppe)(\eta^3-C_7H_9)]^+$} was obtained by reaction of $[Mo(CO)_2(CNBu^t)(\eta^7-C_7H_7)]^+$ with dppe; we have also previously described the synthesis and spectroscopic properties of the acetonitrile derivative $[Mo(CO)_2(NCMe)(dppe)(\eta^3-C_7H_7)]^+$.[8] The η^5-cycloheptadienyl complex $[Mo(CO)_2(CNBu^t)(PPh_3)(\eta^5-C_7H_9)]^+$ **14** was prepared from the reaction of PPh_3 with $[Mo(CO)_2(CNBu^t)(NCMe)_2(\eta^3-C_7H_9)]^+$ **5** to serve as a model for the pendant phosphine formulation $[Mo(CO)_2(CNBu^t)(\sigma-L–L)(\eta^5-C_7H_9)]^+$. The main points of comparison rest with IR and ^{13}C and ^{31}P NMR data; the ^1H NMR spectra of **9** and **11** were broad and ill defined and did not provide a useful distinction between η^5 and η^3 hapticity of the cycloheptadienyl ring. Additionally the dppe derivative, **11**, provided the best source of data for comparison of NMR spectra; in solution, the dppm derivative **9** was susceptible to rapid conversion to the carbonyl substituted product **10** and moreover attempts to obtain a pure sample of the dppm derivative of the cycloheptatrienyl complex **13** were unsuccessful.

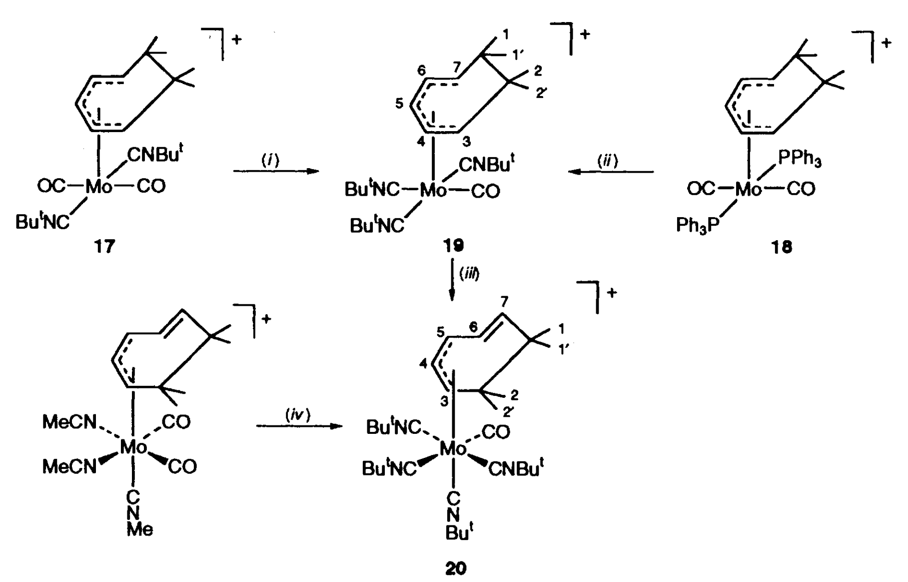
The weight of the spectroscopic evidence supports the 'ring slipped' formulation $[Mo(CO)_2(CNBu^t)L_2(\eta^3-C_7H_9)]^+$ for **9** and **11**. First, from a comparison of the IR data for **11** and the η^3-cycloheptatrienyl complex **13** (Table 1), the wavenumbers of ν(CN) and ν(CO) and the observed intensity patterns of the carbonyl bands (characteristic of *cis* carbonyl ligands) correspond very closely. The average ν(CO) for **13** is to marginally high wavenumber of that for **11** in accord with our previous findings on pairs of complexes differing only in the identity of the η^3 ligand (C_7H_7 *vs.* C_7H_9).[7] Moreover the conversion of **6** to **9** and of **7** to **11** results in a shift in averaged ν(CO) to lower wavenumber by 25 (**6** ⟶ **9**) and 32 cm^{-1} (**7** ⟶ **11**) consistent with trends established for $\eta^5 \longrightarrow \eta^3$ 'ring slip'. By contrast the IR data for **14** exhibit poor agreement with the data for **9** and **11**; not only are the ν(CN) and ν(CO) bands of **14** to significantly higher wavenumber of those of **9** and **11** but also the pattern of carbonyl stretching frequencies in **14** is indicative of a *trans*-carbonyl geometry. The ^{31}P NMR data for **11** {δ[$(CD_3)_2CO$, −20 °C] 59.2, d, *J*(P–P) 27; 54.3, d, *J*(P–P) 27 Hz} and **13** [δ(CD_2Cl_2, 25 °C) 54.7, d, *J*(P–P) 20; 52.5, d, *J*(P–P) 20 Hz] are also in good agreement and the relatively small chemical shift difference between the two phosphorus environments is inconsistent with a pendant diphosphine ligand. Finally the ^{13}C NMR spectra of **9** and **11** each exhibit three strong, sharp resonances in the region δ 95–70, not attributable to the carbonyl substitution product impurities **10** and **12**. Thus selected ^{13}C NMR resonances for **9** [δ(CD_2Cl_2, 0 °C) 94.2, 86.2, 77.3] and **11** [δ(CD_3CN, 0 °C) 89.3, 84.5, 74.3] are characteristic of the co-ordinated allyl fragment of the $\eta^3-C_7H_9$ ring. The range of chemical shifts of the resonances assigned to the co-ordinated allyl carbons in **9** and **11** is comparable to that observed for $[Mo(CO)_2(NCMe)(dppe)(\eta^3-C_7H_9)]^+$ **8**, but much larger than the corresponding range of shifts in the bipyridyl complexes **2**–**4**; this observation is consistent with an increased asymmetry in the diphosphine complexes **8**, **9** and **11**, imposed by the preferred ligand arrangement.

The reaction sequences **6** ⟶ **9** ⟶ **10** and **7** ⟶ **11** ⟶ **12** represent the first examples of associative ligand-substitution processes which proceed with $\eta^5 \longrightarrow \eta^3 \longrightarrow \eta^5$ hapticity conversion at a *cyclic* dienyl ligand in which the η^3-bonded dienyl intermediate is isolable. Despite the simplicity of the mechanism and its extensive application in the rationalisation of kinetics studies on cyclopentadienyl and indenyl complexes,[1] proven examples where the η^3-dienyl complex is an isolable intermediate in the ligand-substitution process are extremely elusive; to our knowledge the only precedent is provided by the acyclic pentadienyl complex $[Mn(CO)_3(\eta^5-C_5H_7)]$ which reacts with phosphines PR_3 to give $[Mn(CO)_2(PR_3)(\eta^5-C_5H_7)]$ *via* the intermediate $[Mn(CO)_3(PR_3)(\eta^3-C_5H_7)]$.[3] The contrasting behaviour of $[Mo(CO)_2(CNBu^t)(bipy)(\eta^3-C_7H_9)]^+$ **4**, and the diphosphine derivatives $[Mo(CO)_2(CNBu^t)L_2(\eta^3-C_7H_9)]^+$ (L_2 = dppm **9** or dppe **11**) towards elimination of CO and reversion to a $\eta^5-C_7H_9$ ring might be accounted for by the proposed, differing ligand arrangements of **4** in one case, and **9** and **11** in the other. We suggest that in complexes **9** and **11** the CO ligand situated *trans* to $CNBu^t$ must compete with $CNBu^t$ for metal electron density available for π back donation and this results in weakening of the molybdenum to carbonyl bond and a consequent lability of the complexes towards loss of CO. By contrast, in **4**, the carbonyl ligands are located *trans* to the bipyridyl nitrogens and experience less competition for metal electron density.

The 'ring slip' reactivity of the $CNBu^t$ substituted complexes $[Mo(CO)(CNBu^t)L_2(\eta^5-C_7H_9)]^+$ (L_2 = dppm **10** or dppe **12**) was also investigated. Consistent with our findings in the chemistry of cycloheptatrienyl molybdenum complexes, substitution of CO with $CNBu^t$ or phosphorus-donor ligands results in a decrease in reactivity towards 'ring slip' reactions and accordingly **12**, in contrast to the dicarbonyl derivative **7**, was unreactive towards NCMe. However, both **10** and **12** react further with $CNBu^t$. Treatment of CH_2Cl_2 solutions of **10** and **12** with $CNBu^t$ resulted in a shift in ν(CO) to lower wavenumber by *ca.* 20 cm^{-1} and the formation of yellow-orange products, formulated, on the basis of data in Table 1 only, as the $CNBu^t$ adducts $[Mo(CO)(CNBu^t)_2L_2(\eta^3-C_7H_9)]^+$ (L_2 = dppm **15** or dppe **16**). The dppe derivative **16** was also prepared by reaction of $[Mo(CO)_2(dppe)(\eta^5-C_7H_9)]^+$ **7** with an excess of $CNBu^t$ in CH_2Cl_2. Attempts to effect further carbonyl substitution by $CNBu^t$ in **15** and **16** to give $[Mo(CNBu^t)_2L_2(\eta^5-C_7H_9)]^+$ were unsuccessful; in common with $[Mo(CO)(CNBu^t)_4(\eta^3-R)]^+$ [R = C_7H_7 or C_7H_9 (see later)] the final carbonyl appears very difficult to displace and when **16** was warmed in acetone $[Mo(CO)(CNBu^t)(dppe)(\eta^5-C_7H_9)]^+$ **12** was regenerated. The relative lability of **15** and **16** towards loss of $CNBu^t$ hindered NMR spectroscopic characterisation and only broad and uninformative spectra were obtained. Therefore the NMR methods used to identify **9** and **11** as $\eta^3-C_7H_9$ complexes could not be extended to **15** and **16**.

Reactions of $[Mo(CO)_2L_2(\eta^5-C_7H_9)]^+$ (L = $CNBu^t$ **17** *or* PPh_3 **18**).—We have previously described the syntheses of complexes **17** and **18** from reaction of $[Mo(CO)_2(NCMe)_3(\eta^3-C_7H_9)]^+$ with two equivalents of L.[7] Complexes **17** and **18** differ from **1**, **6** and **7** in that the ligands L are monodentate and a *trans* carbonyl geometry is adopted, either as the major form (for **17**) or exclusively (for **18**). The 'ring slip' reactivity of **17** and **18** also differs significantly from that of **1**, **6** and **7**.

Neither **17** nor **18** react with NCMe but both complexes react with $CNBu^t$ although no evidence was obtained for the intermediacy of $\eta^3-C_7H_9$ complexes. Treatment of **17** with one equivalent of $CNBu^t$ in CH_2Cl_2 yielded $[Mo(CO)(CNBu^t)_3(\eta^5-C_7H_9)]^+$ **19** (Scheme 3). A possible intermediate for this substitution reaction is $[Mo(CO)_2(CNBu^t)_3(\eta^3-C_7H_9)]^+$ {analogous to the isolable cycloheptatrienyl complex



Scheme 3 Reagents and conditions: (*i*) CNBu^t, stir in CH$_2$Cl$_2$, 1 h; (*ii*) CNBu^t, stir in CH$_2$Cl$_2$, 7 d; (*iii*) CNBu^t in excess, stir in CH$_2$Cl$_2$, 1 h; (*iv*) CNBu^t in excess, stir in CH$_2$Cl$_2$, 15 min

[Mo(CO)$_2$(CNBu^t)$_3$(η^3-C$_7$H$_7$)]$^+$[9]} but, although the reaction mixture was carefully monitored by IR spectroscopy in the carbonyl stretching region, no evidence for an intermediate was obtained. Surprisingly, treatment of the PPh$_3$ complex **18** with CNBu^t also led to the formation of low yields of **19** after a prolonged reaction in which no intermediates were identified.

In common with complexes **10** and **12**, [Mo(CO)(CNBu^t)$_3$-(η^5-C$_7$H$_9$)]$^+$ **19**, reacts further with CNBu^t. Treatment of **19**, or alternatively [Mo(CO)$_2$(NCMe)$_3$(η^3-C$_7$H$_9$)]$^+$, with excess of CNBu^t in CH$_2$Cl$_2$ led to the formation of [Mo(CO)(CNBu^t)$_4$-(η^3-C$_7$H$_9$)]$^+$ **20** which was isolated as an orange solid. Complex **20** is an analogue of the cycloheptatrienyl complex [Mo(CO)(CNBu^t)$_4$(η^3-C$_7$H$_7$)]$^+$ which we have previously obtained by reaction of [Mo(CO)(CNBu^t)$_2$(η^7-C$_7$H$_7$)]$^+$ with CNBu^t.[9] However, unlike [Mo(CO)(CNBu^t)$_4$(η^3-C$_7$H$_7$)]$^+$, the cycloheptadienyl complex **20** readily dissociated CNBu^t leading to regeneration of **19**. Nevertheless, full characterisation data were obtained for **20** but solution spectra (NMR and IR) were carried out in the presence of added CNBu^t. Two alternative ligand arrangements can be proposed for **20**; that illustrated in Scheme 3 is preferred on the basis of the ^{13}C NMR data, which reveals four distinct isonitrile carbon resonances, and by comparison with [Mo(CO)(CNBu^t)$_4$(η^3-C$_7$H$_7$)]$^+$, which can be unequivocally identified as the asymmetric isomer from ^{13}C NMR data. In common with complexes **15** and **16**, no evidence was obtained for carbonyl elimination from **20**.

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)$_2$(bipy)(η^5-C$_7$H$_9$)][BF$_4$] **1**, [Mo(CO)$_2$(CNBu^t)(NCMe)$_2$(η^3-C$_7$H$_9$)][BF$_4$] **5**, [Mo(CO)$_2$-(NCMe)$_3$(η^3-C$_7$H$_9$)][BF$_4$], [Mo(CO)$_2$(dppm)(η^5-C$_7$H$_9$)]-[BF$_4$] **6**, [Mo(CO)$_2$(CNBu^t)(η^7-C$_7$H$_7$)][BF$_4$], [Mo(CO)$_2$-(CNBu^t)$_2$(η^5-C$_7$H$_9$)][BF$_4$] **17**, and [Mo(CO)$_2$(PPh$_3$)$_2$(η^5-C$_7$H$_9$)][BF$_4$] **18**, were prepared by published procedures.[7,9] The chemicals 2,2′-bipyridyl, PMe$_3$ (1.0 mol dm^{-3} solution in toluene), CNBu^t and dppe were supplied by Aldrich. The 300 MHz ^{1}H and 75 MHz ^{13}C NMR spectra were recorded on a Bruker AC 300 E or Varian Associates XL 300 spectrometer; 122 MHz ^{31}P NMR spectra were obtained on the Varian Associates XL 300 and positive chemical shifts are quoted downfield from H$_3$PO$_4$. 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.

Preparation.—[Mo(CO)$_2$(PMe$_3$)(bipy)(η^3-C$_7$H$_9$)][BF$_4$] **3**. A stirred solution of [Mo(CO)$_2$(bipy)(η^5-C$_7$H$_9$)][BF$_4$] **1** (0.299 g, 0.61 mmol) in CH$_2$Cl$_2$ (40 cm^3) was treated with PMe$_3$ (0.6 cm^3, 1.0 mol dm^{-3} solution in toluene). After 30 min, the solution was reduced in volume and diethyl ether added to precipitate the crude product. Recrystallisation from acetone–diethyl ether gave **3** as a maroon-red solid; yield 0.266 g (77%).

[Mo(CO)$_2$(CNBu^t)(bipy)(η^3-C$_7$H$_9$)][BF$_4$] **4**. A mixture of [Mo(CO)$_2$(CNBu^t)(NCMe)$_2$(η^3-C$_7$H$_9$)][BF$_4$] **5** (0.471 g, 0.95 mmol) and bipy (0.182 g, 1.17 mmol) was stirred in CH$_2$Cl$_2$ (50 cm^3). After 1 h, the solution was filtered, reduced in volume and treated with diethyl ether to precipitate the crude product. Recrystallisation from CH$_2$Cl$_2$–diethyl ether gave **4** as a red-brown solid; yield 0.436 g (81%).

[Mo(CO)$_2$(dppe)(η^5-C$_7$H$_9$)][BF$_4$]·CH$_2$Cl$_2$ **7**·CH$_2$Cl$_2$. A stirred solution of [Mo(CO)$_2$(NCMe)$_3$(η^3-C$_7$H$_9$)][BF$_4$] (2.013 g, 4.43 mmol) in CH$_2$Cl$_2$ (60 cm^3) was treated with dppe (1.764 g 4.43 mmol) which was added in small portions over a period of 15 min. After 40 min, the solution was filtered, reduced in volume and diethyl ether added to precipitate the crude product. Recrystallisation from CH$_2$Cl$_2$–diethyl ether gave **7** as a pink-red CH$_2$Cl$_2$ solvate; yield 3.103 g (87%).

[Mo(CO)$_2$(CNBu^t)(dppm)(η^3-C$_7$H$_9$)][BF$_4$] **9**. A stirred, cold (−40 °C) solution of [Mo(CO)$_2$(dppm)(η^5-C$_7$H$_9$)][BF$_4$] **6** (1.03 g, 1.44 mmol) in CH$_2$Cl$_2$ (40 cm^3) was treated with CNBu^t (0.120 g, 1.45 mmol). The reaction mixture was maintained at −40 °C for 2 h, after which time the solution was filtered and solvent removed. During this procedure and the subsequently described work-up, all solvents were maintained at temperatures below 0 °C. The residue was washed with diethyl ether then recrystallised from CH$_2$Cl$_2$–diethyl ether to give **9** as a red-brown solid; yield 0.877 g (76%). The complex [Mo(CO)$_2$-(CNBu^t)(dppe)(η^3-C$_7$H$_9$)][BF$_4$] **11** was obtained in 72% yield as a yellow-orange solid by a similar procedure to that described for **9**. A solution of **7**·CH$_2$Cl$_2$ (0.502 g, 0.62 mmol) in CH$_2$Cl$_2$ (40 cm^3) was treated with CNBu^t (0.073 g, 0.88 mmol) and stirred for 4 h at 0 °C before work-up as described for **9**.

[Mo(CO)(CNBu^t)(dppm)(η^5-C$_7$H$_9$)][BF$_4$] **10**. A stirred solution of **6** (0.291 g, 0.41 mmol) in CH$_2$Cl$_2$ (20 cm^3) was treated with CNBu^t (0.037 g, 0.45 mmol) and the reaction allowed to proceed for 1 h. Subsequently the reaction mixture was filtered and reduced in volume then diethyl ether was added to precipitate the crude product. Recrystallisation from $\mathrm{CH_2Cl_2}$–diethyl ether gave **10** as a yellow solid; yield 0.224 g (72%). The complex$[\mathrm{Mo(CO)(CNBu^t)(dppe)(\eta^5\text{-}C_7H_9)}][\mathrm{BF_4}]$ **12** was prepared as a yellow solid in 69% yield from $\mathbf{7}\cdot\mathrm{CH_2Cl_2}$ (0.745 g, 0.91 mmol) and $\mathrm{CNBu^t}$ (0.088 g, 1.06 mmol) stirred in $\mathrm{CH_2Cl_2}$ (50 $\mathrm{cm^3}$) for 3 h at 35 °C. The work-up procedure was identical to that described for **10**.

$[\mathrm{Mo(CO)_2(CNBu^t)(dppe)(\eta^3\text{-}C_7H_7)}][\mathrm{BF_4}]$ **13**. A solution of $[\mathrm{Mo(CO)_2(CNBu^t)(\eta^7\text{-}C_7H_7)}][\mathrm{BF_4}]$ (1.021 g, 2.47 mmol) in $\mathrm{CH_2Cl_2}$ (40 $\mathrm{cm^3}$) was treated with dppe (1.480 g, 3.72 mmol). The reaction mixture was stirred for 24 h then reduced in volume and diethyl ether added to precipitate the crude product. Recrystallisation from $\mathrm{CH_2Cl_2}$–diethyl ether gave **13** as an orange solid; yield 1.487 g (74%).

$[\mathrm{Mo(CO)_2(CNBu^t)(PPh_3)(\eta^3\text{-}C_7H_9)}][\mathrm{BF_4}]$ **14**. A mixture of $[\mathrm{Mo(CO)_2(CNBu^t)(NCMe)_2(\eta^3\text{-}C_7H_9)}][\mathrm{BF_4}]$ **5** (0.407 g, 0.82 mmol) and $\mathrm{PPh_3}$ (0.213 g, 0.81 mmol) was stirred for 1 h in $\mathrm{CH_2Cl_2}$ (40 $\mathrm{cm^3}$). Subsequent filtration of the reaction mixture, reduction in volume and addition of diethyl ether gave the crude product as an oily yellow solid. Recrystallisation from $\mathrm{CH_2Cl_2}$–diethyl ether gave **14** as a yellow solid; yield 0.328 g (59%).

$[\mathrm{Mo(CO)(CNBu^t)_2(dppm)(\eta^3\text{-}C_7H_9)}][\mathrm{BF_4}]$ **15**. Treatment of a stirred solution of **10** (0.246 g, 0.32 mmol) in $\mathrm{CH_2Cl_2}$ with $\mathrm{CNBu^t}$ (0.132 g, 1.59 mmol) resulted in a rapid colour change from yellow to orange-yellow. After 30 min the reaction mixture was reduced in volume and added to stirred diethyl ether to give the crude product as an orange-yellow solid; yield 0.11 g (40%). The analytical sample was obtained in very low yield by recrystallisation from thf–diethyl ether.

$[\mathrm{Mo(CO)(CNBu^t)_2(dppe)(\eta^3\text{-}C_7H_9)}][\mathrm{BF_4}]$ **16**. A solution of $\mathbf{7}\cdot\mathrm{CH_2Cl_2}$ (0.781 g, 0.96 mmol) in $\mathrm{CH_2Cl_2}$ (50 $\mathrm{cm^3}$) was treated with $\mathrm{CNBu^t}$ (0.178 g, 2.14 mmol). The reaction mixture was stirred for 3 h, then the solution was filtered, reduced in volume and diethyl ether added to precipitate the crude product. This was dissolved in $\mathrm{CH_2Cl_2}$ (5 $\mathrm{cm^3}$) and the $\mathrm{CH_2Cl_2}$ solution was added dropwise to stirred diethyl ether to give **16** as an orange-yellow solid; yield 0.356 g (43%).

$[\mathrm{Mo(CO)(CNBu^t)_3(\eta^5\text{-}C_7H_9)}][\mathrm{BF_4}]$ **19**. A stirred solution of $[\mathrm{Mo(CO)_2(CNBu^t)_2(\eta^5\text{-}C_7H_9)}][\mathrm{BF_4}]$ **17** (0.158 g, 0.32 mmol) in $\mathrm{CH_2Cl_2}$ (30 $\mathrm{cm^3}$) was treated with $\mathrm{CNBu^t}$ (0.03 g, 0.36 mmol) and the reaction allowed to proceed for 1 h. The solution was then filtered, reduced in volume and diethyl ether added to precipitate the crude product. Recrystallisation from $\mathrm{CH_2Cl_2}$–diethyl ether gave **19** as a yellow-orange solid; yield 0.122 g (70%).

$[\mathrm{Mo(CO)(CNBu^t)_4(\eta^3\text{-}C_7H_9)}][\mathrm{BF_4}]$ **20**. *Method* (*a*). The reaction of $[\mathrm{Mo(CO)(CNBu^t)_3(\eta^5\text{-}C_7H_9)}][\mathrm{BF_4}]$ **19** (0.217 g, 0.39 mmol) with an excess of $\mathrm{CNBu^t}$ (0.065 g, 0.78 mmol) in stirred $\mathrm{CH_2Cl_2}$ (20 $\mathrm{cm^3}$) resulted in a colour change from yellow to red-brown. After 1 h the reaction mixture was filtered and evaporated to dryness. The residue was washed with diethyl ether to afford **20** as an orange solid; yield 0.181 g (73%).

Method (*b*). A solution of $[\mathrm{Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_9)}][\mathrm{BF_4}]$ (0.320 g, 0.70 mmol) in $\mathrm{CH_2Cl_2}$ (20 $\mathrm{cm^3}$) was treated with $\mathrm{CNBu^t}$ (0.40 g, 4.82 mmol). After 15 min the reaction mixture was filtered and evaporated to dryness. The residue was thoroughly dried *in vacuo* and then washed with diethyl ether to give **20** as an orange solid; yield 0.247 g (55%).

Crystal-structure Analyses of **1** *and* **4**.—The majority of details of the structure analyses carried out on complexes **1** and **4** are given in Table 5; non-hydrogen atom positional parameters for **1** and **4** are listed in Tables 6 and 7 respectively. Red crystals of **1** and red-brown crystals of **4** were obtained by slow diffusion of diethyl ether into a $\mathrm{CH_2Cl_2}$ solution of the appropriate complex. Cell dimensions for **1** were determined from the setting angles of 19 carefully centred reflections in the range $77.57 < 2\theta < 79.87°$ and for **4** from 23 carefully centred reflections in the range $14.47 < 2\theta < 20.54°$. An empirical absorption correction was applied to the data for **1** (based on azimuthal scans) and **4** (using the program DIFABS);[15] in each case the data were also corrected for Lorentz and polarisation effects. Linear decay corrections were applied to the data for **1**

Table 5 Structure analyses of complexes **1** and **4**

	1	4
Formula	$\mathrm{C_{19}H_{17}BF_4N_2O_2Mo}$	$\mathrm{C_{24}H_{26}BF_4N_3O_2Mo}$
M	488.10	571.23
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	8.401 (1)	11.271 (8)
b/Å	10.840 (2)	13.318 (8)
c/Å	21.387 (3)	17.41 (1)
β/°	92.72 (1)	95.04 (6)
U/Å^3	1945.5 (9)	2604 (6)
T/K	296	296
Z	4	4
D_c/g cm^{-3}	1.666	1.457
F(000)	976	1160
μ/cm^{-1}	61.26 (Cu-Kα)	5.43 (Mo-Kα)
Diffractometer	Rigaku AFC5R	Rigaku AFC6S
Crystal dimensions/mm	0.07 × 0.35 × 0.45	0.22 × 0.22 × 0.32
λ/Å	1.541 78 (Cu-Kα)	0.710 69 (Mo-Kα)
θ range/°	4–60	1–25
Scan type	ω–2θ	ω–2θ
Scan width/°	$(1.26 + 0.30 \tan\theta)$	$(1.52 + 0.30 \tan\theta)$
Total data	3324	5073
Unique data	3089	4808
'Observed' data $[I > 3\sigma(I)]$, N_o	2589	2684
Least-squares variables, N_v	262	316
R	0.044	0.052
R'	0.058	0.065
S	2.23	2.28
Difference map features/e Å^{-3}	+0.63, −0.45	+0.95, −0.53

$R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$; $\Delta = F_o - F_c$.

and **4**, based in each case on the intensities of three representative reflections which were measured after every 150 reflections and declined by −0.10% for **1** and −3.70% for **4**. The structure of **1** was solved by direct methods whilst that of **4** was solved by a combination of automatic Patterson and Fourier methods; both structures were refined by full-matrix least squares. For both **1** and **4**, 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. For both **1** and **4**, $w = 4F_o{}^2/\sigma^2(F_o{}^2)$ with a p factor of 0.03 to weight down strong reflections. Complex neutral-atom scattering factors were taken from ref. 16; all calculations were performed using the TEXSAN crystallographic software packages of Molecular Structure Corporation.[17]

Table 6 Atomic coordinates for complex **1**

Atom	*x*	*y*	*z*
Mo	0.317 27(5)	0.157 14(4)	0.107 03(2)
O(1)	0.552 3(6)	−0.038 1(4)	0.164 1(2)
O(2)	0.296 1(6)	−0.053 5(4)	0.006 6(2)
N(1)	0.502 8(5)	0.282 0(4)	0.150 9(2)
N(2)	0.435 9(5)	0.254 7(4)	0.030 6(2)
C(1)	0.468 8(7)	0.033 7(5)	0.141 1(3)
C(2)	0.297 2(8)	0.024 5(5)	0.043 8(3)
C(3)	0.529 0(6)	0.294 8(5)	0.213 1(2)
C(4)	0.638 8(7)	0.374 8(6)	0.239 0(3)
C(5)	0.728 2(7)	0.446 2(6)	0.200 7(3)
C(6)	0.706 3(7)	0.429 9(5)	0.136 9(3)
C(7)	0.594 1(6)	0.348 3(4)	0.112 7(3)
C(8)	0.561 5(6)	0.328 0(4)	0.045 7(2)
C(9)	0.648 9(7)	0.383 9(6)	0.000 1(3)
C(10)	0.605 0(8)	0.368 2(6)	−0.061 5(3)
C(11)	0.472 1(7)	0.298 3(6)	−0.077 0(3)
C(12)	0.391 0(7)	0.242 3(5)	−0.030 7(2)
C(13)	0.112 6(7)	0.066 0(5)	0.158 0(3)
C(14)	0.048 8(6)	0.114 5(5)	0.101 2(3)
C(15)	0.064 0(6)	0.237 7(6)	0.079 5(3)
C(16)	0.139 4(7)	0.335 8(5)	0.109 2(3)
C(17)	0.149 5(7)	0.370 6(5)	0.178 2(3)
C(18)	0.120 7(7)	0.264 7(6)	0.221 3(3)
C(19)	0.190 1(7)	0.142 9(5)	0.203 4(3)

Table 7 Atomic coordinates for complex **4**

Atom	*x*	*y*	*z*
Mo	0.259 60(6)	0.215 86(5)	0.070 57(4)
O(1)	0.138 0(8)	0.312 2(6)	0.204 1(5)
O(2)	0.474 3(7)	0.306 5(7)	0.169 2(4)
N(1)	0.110 2(5)	0.191 6(4)	−0.020 0(3)
N(2)	0.341 0(6)	0.181 1(5)	−0.039 2(4)
N(3)	0.254 7(7)	0.432 5(6)	−0.018 6(4)
C(1)	0.179 0(8)	0.274 1(7)	0.153 6(5)
C(2)	0.396 8(8)	0.270 3(7)	0.133 1(5)
C(3)	−0.005 4(8)	0.193 8(7)	−0.007 3(5)
C(4)	−0.093 7(8)	0.183 5(8)	−0.065 7(7)
C(5)	−0.066(1)	0.171 8(9)	−0.138 0(7)
C(6)	0.051(1)	0.171 2(8)	−0.152 6(5)
C(7)	0.138 4(8)	0.181 3(6)	−0.092 2(4)
C(8)	0.265 3(8)	0.182 5(6)	−0.103 8(5)
C(9)	0.307(1)	0.188 2(9)	−0.175 9(5)
C(10)	0.425(1)	0.190(1)	−0.183 3(6)
C(11)	0.503(1)	0.185(1)	−0.118 7(7)
C(12)	0.458 5(8)	0.181 9(7)	−0.046 7(5)
C(13)	0.376(1)	0.077 6(7)	0.122 9(6)
C(14)	0.261(1)	0.050 7(6)	0.093 4(5)
C(15)	0.161 1(8)	0.074 7(8)	0.128 0(6)
C(16)	0.144(1)	0.074(1)	0.210 7(7)
C(17)	0.222(1)	0.059(1)	0.265 2(7)
C(18)	0.350(2)	0.079(1)	0.266 7(7)
C(19)	0.418(1)	0.073(1)	0.206 0(7)
C(20)	0.255 6(7)	0.360 6(7)	0.015 5(5)
C(21)	0.254(1)	0.525 1(8)	−0.062 7(7)
C(22)	0.319(1)	0.602(1)	−0.016 1(8)
C(23)	0.317(2)	0.505(1)	−0.130 7(9)
C(24)	0.130(2)	0.553(1)	−0.085(1)

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

Acknowledgements

We are grateful to the SERC for the award of a research studentship (to J. R. H.) and to CNPq (Consel e Nacionalde, Desenvoluimento Cientifico e Technologico), Brazil, for the award of a research studentship (to A.-L. A. B. de S.) and for generous financial support of this work.

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Received 22nd *April* 1994; *Paper* 4/02392G