# $\eta^5 \longleftrightarrow \eta^3$ Hapticity Interconversion in Cycloheptadienyl Molybdenum Complexes<sup>†</sup>

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A series of reactions of the general type  $[Mo(CO)_2L_2(\eta^5-C_7H_9)]^+ + L' \longrightarrow [Mo(CO)_2(L')L_2(\eta^3-C_7H_9)]^+$ , 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  $[Mo(CO)_2L_2(\eta^5-C_7H_9)]^+$  $[L_2 = 2.2'-bipyridyl (bipy) 1, Ph_2PCH_2Ph_2 (dppm) 6, Ph_2PCH_2CH_2Ph_2 (dppe) 7; L = CNBu' 17 or$  $PPh_3 18] with NCMe or CNBu'. Complex 1 reacts reversibly with NCMe to give <math>[Mo(CO)_2(NCMe)(bipy)(\eta^3-C_7H_9)]^+$  2 and, in NCMe, 7 exists as an equilibrium mixture with  $[Mo(CO)_2(NCMe)(dppe)(\eta^3-C_7H_9)]^+$  8. The complexes 6, 17 and 18 do not react with NCMe at ambient temperature. Treatment of 1, 6 and 7 with CNBu' affords  $[Mo(CO)_2(CNBu')L_2(\eta^3-C_7H_9)]^+$  $(L_2 = bipy 4, dppm 9 or dppe 11)$  although 4 is better prepared by reaction of  $[Mo(CO)_2(CNBu')L_2(\eta^3-C_7H_9)]^+$  $(CDBu')(NCMe)_2(\eta^3-C_7H_9)]^+ 5$  with bipy. Complex 4 is resistant to carbonyl elimination but 9 and 11 undergo facile loss of CO to give  $[Mo(CO)(CNBu')L_2(\eta^5-C_7H_9)]^+$   $(L_2 = dppm 10 or dppe$ 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' further CNBu' to yield  $[Mo(CO)(CNBu')_4(\eta^3-C_7H_9)]^+$  20. The crystal structures of complexes 1 and 4 have been determined. Complex 4 has a pseudo-octahedral molecular geometry in which CNBu' is located *trans* to the  $\eta^3$ -bonded  $C_7H_9$  ligand.

It is well established that the reactivity of complexes of dienyl ligands is enhanced by the potential for  $\eta^5 \leftrightarrow \eta^3$  hapticity interconversion/'ring slip' of the dienyl ligand. However, notwithstanding extensive investigations on complexes of cyclopentadienyl, indenyl,<sup>1</sup> and acyclic pentadienyl ligands,<sup>2</sup> very few studies have systematically addressed the design of complexes which undergo facile  $\eta^5 \leftrightarrow \eta^3$  interconversion or explored the factors which promote the stability of a specific hapticity type. Such studies are best carried out where both  $\eta^4$ and  $\eta^3$  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.<sup>3-5</sup> 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  $\eta^5 \leftrightarrow \eta^3$ interconversion in these systems.<sup>6,7</sup> In this paper we report on  $\eta^5 \leftrightarrow \eta^3$  hapticity interconversions in complexes of general formula  $[Mo(CO)_2L_2(\eta^5-C_7H_9)]^+[L_2 = 2,2'$ -bipyridyl (bipy), Ph\_2PCH\_2CH\_2PPh\_2 (dppe) or Ph\_2PCH\_2PPh\_2 (dppm); L = CNBu' or PPh<sub>3</sub>] induced by added ligands NCMe or CNBu'. Previous studies on analogous acyclic pentadienyl complexes  $[Mo(CO)_2L_2(\eta-C_5H_7)]^+$   $[L_2 = bipy,^4$  dppe or  $Me_2PCH_2CH_2PMe_2$  (dmpe)<sup>5</sup>] have revealed that the identity of  $L_2$  can affect the ease of  $\eta^5 \leftrightarrow \eta^3$  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  $\eta^5 \leftrightarrow \eta^3$  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  $\eta^3$ -dienyl complex towards reversion to the  $\eta^5$ -dienyl form.

### **Results and Discussion**

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

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

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

Reactions of  $[Mo(CO)_2(bipy)(\eta^5-C_7H_9)]^+ 1$ .—Reaction of complex 1 with donor ligands L' (L' = NCMe, PMe<sub>3</sub> or CNBu') results in the formation of the 'ring slipped' adducts  $[Mo(CO)_2L'(bipy)(\eta^3-C_7H_9)]^+ [L' = NCMe 2, PMe_3 3, or$ CNBu' 4 (Scheme 1)]. Complex 2 was generated by dissolving 1in NCMe whilst 3 was formed by reaction of 1 with PMe<sub>3</sub> inCH<sub>2</sub>Cl<sub>2</sub>. Treatment of complex 1 with CNBu' in CH<sub>2</sub>Cl<sub>2</sub> alsoprovides a route to 4 but samples obtained by this method werecontaminated by a second reaction product, tentatively $assigned as <math>[Mo(CNBu')_4(bipy)]$ . Therefore an alternative synthesis of 4 was developed involving reaction of  $[Mo(CO)_2-(CNBu')(NCMe)_2(\eta^3-C_7H_9)]^+ 5^7$  with bipy; effectively the

<sup>†</sup> 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  $CH_2Cl_2$ , 30 min; (ii) bipy, stir in  $CH_2Cl_2$ , 1 h; (iii) L' = NCMe, stir in  $CH_2Cl_2$ 

order of addition of CNBu<sup>4</sup> 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  $\eta^5$ -C<sub>7</sub>H<sub>9</sub> complex 1. The formation of complex 2 from 1 is a reversible process and when 2 was stirred in CH<sub>2</sub>Cl<sub>2</sub>, 1 was isolated as the exclusive product. The NMR spectroscopic data for complex 2 were conveniently obtained by dissolving samples of 1 in CD<sub>3</sub>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 (<sup>1</sup>H, <sup>3</sup>C and <sup>31</sup>P NMR data). The formulation of complexes 2–4 as 'ring slipped' adducts of 1 with  $\eta^3$ -bonded  $C_7H_9$  ligands is established by the spectroscopic data. We have previously identified the characteristic  ${}^{13}$ C NMR resonances for an  $\eta^3$ bonded C<sub>7</sub>H<sub>9</sub> ring with chemical shifts for the unco-ordinated sp<sup>2</sup> carbons in the region  $\delta$  132–128 and for the three coordinated allyl carbons in an approximate range  $\delta$  95–70;<sup>7</sup> these groups of resonances are manifest in the <sup>13</sup>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<sup>-1</sup> [cf. v(CO) (CH<sub>2</sub>Cl<sub>2</sub>): 1988, 1922 cm<sup>-1</sup> for 1 and 1955, 1881 cm<sup>-1</sup> for 4] and this observation is in accord with related studies on acyclic pentadienyl complexes involving the formation of  $[Mo(CO)_2(NCMe)L_2(\eta^3-C_5H_7)]^{-1}$  $(L_2 = dppe \text{ or } dmpe) \text{ from } [Mo(CO)_2 L_2(\eta^5 - C_5 H_7)]^+ \text{ and}$ NCMe.<sup>4</sup>

Attempts were made to eliminate CO from complexes 3 and 4 to give the substituted products  $[Mo(CO)L'(bipy)(\eta^5-C_7H_9)]^+$  $(L' = PMe_3 \text{ or } CNBu')$  thus establishing 3 and 4 as intermediates in associative ligand-substitution processes. However no evidence was obtained for the formation of  $[Mo(CO)L'(bipy)(\eta^5-C_7H_9)]^+$  from 3 and 4 either by photolysis in tetrahydrofuran (thf) or reaction with Me<sub>3</sub>NO in  $CH_2Cl_2$ . The stability of 3 and 4 provided the opportunity to examine the structural consequences of  $\eta^5 \leftrightarrow \eta^3$  hapticity conversion by X-ray crystallographic studies on the 'ring slip' related pair 1 and 4; the CNBut derivative 4 was selected for investigation because this provides the best comparison with subsequent work involving the reaction of  $[Mo(CO)_2L_2(\eta^5 (C_{7}H_{9})$ ]<sup>+</sup> (L<sub>2</sub> = dppm or dppe) with CNBu<sup>t</sup> (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  $[Mo(CO)_2(bipy)(\eta^5-C_7H_9)]$ -[BF<sub>4</sub>] 1 approximates to a square-based pyramid with the apical cycloheptadienyl ring  $\eta^5$  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,<sup>7</sup> is orientated asymmetrically with respect to the C<sub>7</sub>H<sub>9</sub> ring. The  $\eta^5$  bonding of the C<sub>7</sub>H<sub>9</sub> ring establishes a contrast with the analogous chemistry of the acyclic



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

pentadienyl ligand  $C_5H_7$  in which the bipyridyl derivative has been formulated as  $[Mo(\sigma -FBF_3)(CO)_2(bipy)(\eta^3 - C_5H_7)]$  with preferred  $\eta^3$  co-ordination of the pentadienyl ligand.<sup>4</sup> The structure of 1 is related to that of the diphosphine derivative  $[Mo(CO)_2(dppm)(\eta^5-C_7H_9)]^+$  6 which we have described previously<sup>7</sup> and some aspects warrant comparison. In both compounds 1 and 6 the  $Mo(CO)_2L_2$  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  $Mo(CO)_2L_2$  group is arranged asymmetrically with respect to the  $C_7H_9$  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<sup>3</sup> carbons [C(17), C(18)] of the  $C_7H_9$  ring whereas the corresponding position in 6 is occupied by a carbonyl ligand.

The structure of  $[Mo(CO)_2(CNBu')(bipy)(\eta^3-C_7H_9)][BF_4]$ 4 (Fig. 2) confirms that CNBu' addition at the Mo centre is accompanied by  $\eta^5 \longrightarrow \eta^3$  'ring slip' at the C<sub>7</sub>H<sub>9</sub> ligand. A pseudo-octahedral geometry is adopted in which the CNBu' is located *trans* to the  $\eta^3-C_7H_9$  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  $[Mo(CO)_2(py)(bipy)(\eta^3-C_3H_5)]^+$  in which <sup>10</sup> pyridine (py) lies *trans* to the C<sub>3</sub>H<sub>5</sub> ligand but contrasts with the molecular geometry of the pentadienyl complex  $[Mo(CO)_2(NCMe)(bipy)(\eta^3-C_5H_7)]^+$ , in which the

Table 1 Microanalytical, IR and mass spectroscopic data

	Analysis <sup>a</sup> (%)			Infrared <sup>b</sup> (cm <sup><math>-1</math></sup> )		
Complex	C	н	N	v(CO)	v(CN)	Mass spectral data <sup>c</sup>
2 <sup>d</sup>				1952, 1872 <i>°</i>		
3	46.2 (46.8)	4.9 (4.6)	5.0 (5.0)	1941, 1865		479 ( <i>M</i> <sup>+</sup> )
4	50.4 (50.4)	4.6 (4.6)	7.4 (7.4)	1955, 1881	2182	$486(M^+), 430([M - 2CO]^+)$
<b>7</b> <sup>f</sup>	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 $([M - 2CO - 2H - CNBu']^+)$
10	59.4 (59.1)	5.3 (5.2)	1.8 (1.8)	1901	2155	686 $(M^+)$ , 656 $([M - CO - 2H]^+)$ , 573 $([M - CO - 2H - CNBu']^+)$
11	59.3 (59.0)	5.4 (5.2)	1.7 (1.7)	1963, 1904	2149	$728 (M^+), 700 ([M - CO]^+), 645 ([M - CNBu']^+), 587 ([M - 2CO - 2H - CNBu']^+)$
12	59.4 (59.6)	5.5 (5.4)	1.7 (1.8)	1903	2150	$700 (M^+)$ , 587 ( $[M - 2CO - 2H - CNBu']^+$ )
13	59.0 (59.2)	4.8 (4.9)	1.6 (1.7)	1963, 1913	2150	726 $(M^+)$ , 698 $([M - CO]^+)$ , 643 $([M - CNBu']^+)$ , 587 $([M - 2CO - CNBu']^+)$
14	56.5 (56.7)	4.9 (4.9)	2.1 (2.1)	2007, 1939	2175	$(M^+)$ , 564 ( $[M - CO]^+$ ), 534 ( $[M - 2CO - 2H]^+$ ), 534 ( $[M - 2CO - 2H]^+$ ), 451 ( $[M - 2CO - 2H]^+$ )
15	60.4 (60.4)	6.0 (5.7)	3.3 (3.3)	1886	2143, 2123	$769(M^+), 741([M - CO]^+), 686([M - CNBu']^+), 573([M - 2CNBu' - CO - 2H]^+)$
16	60.8 (60.8)	6.1 (5.9)	3.3 (3.2)	1880	2137, 2116	$783 (M^+), 700 ([M - CNBu']^+)$
19	49.3 (49.9)	6.5 (6.5)	7.5 (7.6)	1936	2178, 2152	468 $(M^+)$ , $([M - CO - 2H]^+)$ , 385 $(M - CNBu^i)$ , 355 $([M - CO - 2H - CNBu^i]^+)$
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 $(M - 2CNBu^t - CO - 2H]^+)$

<sup>*a*</sup> Calculated values in parentheses. All complexes isolated as BF<sub>4</sub> salts. <sup>*b*</sup> Solution spectra in CH<sub>2</sub>Cl<sub>2</sub> unless stated otherwise. <sup>*c*</sup> By FAB mass spectroscopy unless stated otherwise, m/z values based on <sup>98</sup>Mo. <sup>*d*</sup> Attempts to isolate 2 uncontaminated by 1 were unsuccessful. <sup>*e*</sup> In NCMe. <sup>*f*</sup> Analytical data for 7·CH<sub>2</sub>Cl<sub>2</sub>: 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.<sup>4</sup> Other structural features of **4**,  $[Mo(CO)_2(py)(bipy)(\eta^3-C_3H_5)]^+$  and  $[Mo(CO)_2(NCMe)(bipy)(\eta^3-C_5H_7)]^+$ , including bond lengths and angles defined at the molybdenum centre and the orientation of the 'open' face of the  $\eta^3$ -co-ordinated allyl unit towards the Mo-CO vectors, exhibit close similarity. The

#### Table 2 Proton and <sup>13</sup>C NMR spectral data

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Complex	<sup>1</sup> Η NMR (δ) <i>"</i>	<sup>13</sup> C NMR ( $\delta$ ) <sup><i>a</i></sup>
2*	9.06 (m, 1 H), 8.87 (m, 1 H) (H <sup>A,A'</sup> ), 8.42 (m, 2 H, H <sup>D,D'</sup> ), 8.26 (m, 2 H, H <sup>C,C'</sup> ), 7.72 (m, 2 H, H <sup>B,B'</sup> ), 6.29 [m, 1 H, H <sup>6</sup> , $J$ (H <sup>6</sup> -H <sup>7</sup> ) 11, $J$ (H <sup>5</sup> -H <sup>6</sup> ) 7], 5.43 (m, 1 H, H <sup>7</sup> ), 4.77 (m, 1 H, H <sup>3</sup> ), 4.64 (m, 1 H, H <sup>5</sup> ), 3.40 [t, 1 H, H <sup>4</sup> , $J$ (H <sup>3</sup> -H <sup>4</sup> ) 7, $J$ (H <sup>4</sup> -H <sup>5</sup> ) 7], 2.60 (m, 1 H), 2.24 (m, 1 H), 2.11 (m, 1 H), 1.54 (m, 1 H, H <sup>1,1',2,2'</sup> )	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 <sup><i>b</i></sup>	8.87 (m, 1 H), 8.66 (m, 1 H, H <sup>A,A'</sup> ), 8.52 (m, 2 H, H <sup>D,D'</sup> ), 8.29 (m, 2 H, H <sup>C,C'</sup> ), 7.70 (m, 2 H, H <sup>B,B'</sup> ), 6.24 [m, 1 H, H <sup>6</sup> , $J$ (H <sup>6</sup> -H <sup>7</sup> ) 11, $J$ (H <sup>5</sup> -H <sup>6</sup> ) 7], 5.53 (m, 1 H, H <sup>7</sup> ), 4.69 (m, 2 H, H <sup>3.5</sup> ), 3.65 [t, 1 H, H <sup>4</sup> , $J$ (H <sup>3</sup> -H <sup>4</sup> ) 8, $J$ (H <sup>4</sup> -H <sup>5</sup> ) 8], 2.54 (m, br, 1 H), 2.22 (m, 2 H), 1.55 (m, br, 1 H, H <sup>1,1',2,2'</sup> ), 1.03 [d, 9 H, PMe <sub>3</sub> , $J$ (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 <sup>A,A',E,E'</sup> ), 141.3, 140.7 (C <sup>C,C'</sup> ), 131.8, 129.8 (C <sup>6,7</sup> ), 128.2 (C <sup>B,B'</sup> ), 125.1, 125.0 (C <sup>D,D'</sup> ), 86.7, 84.1, 80.5 (C <sup>3-5</sup> ), 31.3, 29.0 (C <sup>1,2</sup> ), 13.6 [d, PMe <sub>3</sub> , $J(C-P)$ 26]
4 <sup>.c</sup>	9.15 (m, 1 H), 8.96 (m, 1 H, H <sup>A,A'</sup> ), 8.84 (m, 2 H, H <sup>D,D'</sup> ), 8.47 (m, 2 H, H <sup>C,C'</sup> ), 7.92 (m, 2 H, H <sup>B,B'</sup> ), 6.37 [m, 1 H, H <sup>6</sup> , $J$ (H <sup>6</sup> -H <sup>7</sup> ) 11, $J$ (H <sup>5</sup> -H <sup>6</sup> ) 6], 5.57 (m, 1 H, H <sup>7</sup> ), 5.18 (m, 2 H, H <sup>3.5</sup> ), 4.06 [t, 1 H, H <sup>4</sup> , $J$ (H <sup>3</sup> -H <sup>4</sup> ) 8, $J$ (H <sup>4</sup> -H <sup>5</sup> ) 8], 2,71 (m, 1 H), 2.30 (m, 1 H), 2.21 (m, 1 H), 1.65 (m, 1 H, H <sup>1,1',2,2'</sup> ), 1.28 (s, 9 H, CNCMe <sub>3</sub> )	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 ( $CNCMe_3$ ), 31.6, 29.5 <sup>4</sup> ( $C^{1.2}$ , $CNCMe_3$ )
7*	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 <sup>3-7</sup> ), 3.13 (br, 2 H), 2.21 (br, 2 H) (CH <sub>2</sub> , dppe), 1.83 (m, 4 H, H <sup>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<sup>3-7</sup>), 2.81 (br, 2 H, CH<sub>2</sub>, dppe), 2.31, 1.95, 1.81, 1.71 (br, 6 H, CH<sub>2</sub>, dppe, H<sup>1,1',2,2') e</sup></sup>	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 <sup><i>d</i></sup> (CH <sub>2</sub> , dppe) <sup>c</sup> - 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 <sup><i>d</i></sup> (CH <sub>2</sub> , dppe) <sup>c</sup>
9	h	227.1, 215.0 (CO), 152.1 (CNCMe <sub>3</sub> ), 134.5–128.5 (Ph and $C^{6,7}$ ), 94.2, 86.2, 77.3 ( $C^{3-5}$ ), 58.3 (CNCMe <sub>3</sub> ), 41.6 (CH <sub>2</sub> , dppm), 36.1, 29.4 ( $C^{1,2}$ ), 29.9 (CNCMe <sub>3</sub> ) <sup><i>i</i></sup>
10 <sup>9</sup>	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 <sup>3-7</sup> ), 4.64 (m, 1 H), 3.94 (m, 1 H, CH <sub>2</sub> , dppm), 2.35 (m, 1 H), 2.09 (m, 1 H), 1.90 (m, 2 H, H <sup>1.1',2.2</sup> ), 1.12 (s, 9 H, CNCMe.)	229.3 [dd, CO, $J$ (C–P) 7, 17], 154.8 ( $C$ NCMe <sub>3</sub> ), 138.0–129.1 (Ph), 100.1, 99.8, 99.3, 97.8, 81.4 ( $C^{3-7}$ ), 59.7 (CNCMe <sub>3</sub> ), 43.8 (CH <sub>2</sub> , dppm), 34.4, 30.9 ( $C^{1.2}$ ), 30.2 (CNCMe <sub>3</sub> )
11*	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 <sup>3-7</sup> ), 2.99, 2.55, 2.14, 1.65 (br, 8 H, CH <sub>2</sub> , dppe and H <sup>1,1',2,2'</sup> ), 0.74 (s, 9 H, CNCMe <sub>3</sub> ) <sup>1</sup>	229.1, 216.2 (CO), 151.2 ( $CNCMe_3$ ), 137.1–128.0 (Ph and C <sup>6,7</sup> ), 89.3, 84.5, 74.3 (C <sup>3–5</sup> ), 58.6 ( $CNCMe_3$ ), 33.8, 29.4 ( $C^{1,2}$ ), 29.4 ( $CNCMe_3$ ), 29.4, 27.9 ( $CH_2$ , dppe) <sup>m</sup>
12"	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 <sup>3-7</sup> ), 2.69, 2.42, 2.09, 1.80 (br, 8 H, CH <sub>2</sub> , dppe and H <sup>1,1',2.2'</sup> ), 1.18 (s, 9 H, CNCMe <sub>3</sub> ) <sup><i>o</i></sup>	234.8 [dd, CO, $J(C-P)$ 4, 20], 160.4 ( $CNCMe_3$ ), 137.0–128.0 (Ph), 101.7, 99.5, 97.8, 96.8, 81.7 ( $C^{3-7}$ ), 60.1 ( $CNCMe_3$ ), 34.0, 32.5 ( $C^{1.2}$ ), 29.8 ( $CNCMe_3$ ), 28.5 ( $CH_2$ , dppe) <sup>P</sup>
134	8.07-7.52 (m, 20 H, Ph), 5.64 (s, 7 H, $C_7H_7$ ), 3.40 (br, 2 H, $CH_2$ , dppe), 2.90 (br, 2 H, $CH_2$ , dppe), 1.15 (s, 9 H, $CNCMe_3$ ) <sup>c</sup>	227.1, 215.9 (CO), 152.5 (br, $CNCMe_3$ ), 135.3–129.2 (Ph), 106.6 (C <sub>7</sub> H <sub>7</sub> ), 59.1 (CNCMe <sub>3</sub> ), 29.7 (CNCMe <sub>3</sub> ), 28.9, 27.1 (CH <sub>2</sub> , dppe) <sup>b</sup>
14	7.66–7.37 (m, 15 H, PPh <sub>3</sub> ), 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 <sub>3</sub> )'	223.5 [d, CO, $J(C-P)$ 23], 150.5 (CNCMe <sub>3</sub> ), 134.7-129.7 (PPh <sub>3</sub> ), 104.0, 101.6, 94.6 (C <sup>3-7</sup> ), 61.5 (CNCMe <sub>3</sub> ), 34.5 (C <sup>1.2</sup> ), 30.8 (CNCMe <sub>3</sub> ) <sup>o</sup>
19 <sup>f</sup>	5.85 (m, 1 H, H <sup>5</sup> ), 5.06 (br, 2 H, H <sup>4.6</sup> ), 4.38 (br, 2 H, H <sup>3.7</sup> ), 1.94 (s, 4 H, H <sup>1,1',2.2'</sup> ), 1.54, 1.52 (27 H, CNCMe <sub>3</sub> )	230.0 (CO), 157.4 (br, CNCMe <sub>3</sub> ), 102.3, 98.0 (C <sup>3-7</sup> ), 59.3, 58.5 (CNCMe <sub>3</sub> ), 33.0 (C <sup>1,2</sup> ), 30.6, 30.4 (CNCMe <sub>3</sub> )
20	5.88 (m, 1 H, H <sup>6</sup> ), 5.28 (m, 1 H, H <sup>7</sup> ), 5.06 (m, 2 H, H <sup>3.4</sup> ), 4.94 (m, 1 H, H <sup>5</sup> ), 2.54 (m, 2 H), 2.23 (br, 1 H), 1.81 (br, 1 H, H <sup>1,1',2,2'</sup> ) 1.50, 1.37 (36 H, CNCMe <sub>3</sub> ) <sup>3</sup>	213.8 (CO), 160.7, 159.9, 157.8, 155.1 ( $CNCMe_3$ ), 131.9 (C <sup>6</sup> ), 124.7 (C <sup>7</sup> ), 100.1, 83.7 (C <sup>3,4</sup> ), 81.7 (C <sup>5</sup> ), 59.3, 58.9, 57.0 ( $CNCMe_3$ ), 37.5, 29.4 ( $C^{1,2}$ ), 30.7 ( $CNCMe_3$ ) <sup>t</sup>
<sup>a</sup> 300 MHz	<sup>1</sup> H NMR spectra, 75 MHz <sup>13</sup> C NMR spectra; $s = singlet$ , $d = do om SiMe_{s}$ coupling constants in Hz; numbering dettering as in Sch	ublet, $t = triplet$ , $m = multiplet$ , $br = broad$ ; chemical shifts

Solv MHZ H NMR spectra, 75 MHZ C NMR spectra;  $s = singlet, d = doublet, t = triplet, m = multiplet, br = broad; chemical shifts downfield from SiMe<sub>4</sub>, coupling constants in Hz; numbering/lettering as in Schemes 1-3. <sup>b</sup> In CD<sub>3</sub>CN. <sup>c</sup> In (CD<sub>3</sub>)<sub>2</sub>CO. <sup>d</sup> Signal obscured by (CD<sub>3</sub>)<sub>2</sub>CO solvent. <sup>e 31</sup>P NMR spectrum in CD<sub>2</sub>Cl<sub>2</sub>: <math>\delta$  (-40 °C) 72.7 [d, J(P-P) 34], 70.1 [d, J(P-P) 35],  $\delta$  (30 °C) 71.3 (s). <sup>f</sup> In CDCl<sub>3</sub>. <sup>g</sup> In CD<sub>2</sub>Cl<sub>2</sub>. <sup>h</sup> Broad, ill defined resonances only. <sup>i</sup> In CD<sub>2</sub>Cl<sub>2</sub> at 0 °C. <sup>j</sup> In CD<sub>2</sub>Cl<sub>2</sub> at -20 °C. <sup>k 31</sup>P NMR spectrum in (CD<sub>3</sub>)<sub>2</sub>CO at -20 °C:  $\delta$  59.2 [d, J(P-P) 27], 54.3 [d, J(P-P) 27]. <sup>i</sup> In CD<sub>2</sub>Cl<sub>2</sub> at -90 °C. <sup>m</sup> In CD<sub>3</sub>CN at 0 °C. <sup>n 31</sup>P NMR spectrum in (CD<sub>3</sub>)<sub>2</sub>CO at -20 °C:  $\delta$  74.5 [d, J(P-P) 36], 72.9 [d, J(P-P) 35]. <sup>o</sup> In CD<sub>2</sub>Cl<sub>2</sub> at -80 °C. <sup>p</sup> In CD<sub>3</sub>CN at -20 °C. <sup>g 31</sup>P NMR spectrum in CD<sub>2</sub>Cl<sub>2</sub>:  $\delta$  54.7 [d, J(P-P) 20], 52.5 [d, J(P-P) 20]. <sup>r</sup> In (CD<sub>3</sub>)<sub>2</sub>CO at -60 °C. <sup>s</sup> In CDCl<sub>3</sub>-CNBu<sup>i</sup>. <sup>i</sup> In CD<sub>2</sub>Cl<sub>2</sub>-CNBu<sup>i</sup>; assignments made with the aid of a [<sup>i</sup>H-<sup>13</sup>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)<sub>2</sub>(bipy) unit towards coplanarity and a significant reorientation of the C<sub>7</sub>H<sub>9</sub> 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<sub>7</sub>H<sub>9</sub> ring with respect to the Mo(CO)<sub>2</sub>(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  $[Mo(CO)_2L_2(\eta^5-C_7H_9)]^+$  (L<sub>2</sub> = dppm 6 or dppe 7).—We have previously described the synthesis and characterisation of  $[Mo(CO)_2(dppm)(\eta^5-C_7H_9)]^+$  6,<sup>7</sup> but to extend the scope of our current studies on hapticity interconversion it was necessary also to synthesise the dppe derivative  $[Mo(CO)_2(dppe)(\eta^5-C_7H_9)]^+$  7. Complex 7, as a  $CH_2Cl_2$  solvate, was obtained in high yield as a pink-red solid by reaction of  $[Mo(CO)_2(NCMe)_3(\eta^3-C_7H_9)]^+$  with dppe in 
 Table 3
 Selected bond lengths (Å) and angles for complex 1

Mo-N(1) Mo-N(2) Mo-C(1) Mo-C(2) Mo-C(13) Mo-C(14) Mo-C(15) Mo-C(16) Mo-C(16) Mo-C(16) Mo-C(19) O(1)-C(1) O(2)-C(2) N(1)-C(3) N(1)-C(7) N(2)-C(8) N(2)-C(12) C(3)-C(4)	2.237(4) 2.222(4) 1.963(6) 1.975(6) 2.302(5) 2.300(5) 2.349(5) 2.348(5) 2.371(6) 1.143(7) 1.161(6) 1.346(6) 1.353(7) 1.349(6) 1.353(6) 1.353(6)	C(4)-C(5) $C(5)-C(6)$ $C(6)-C(7)$ $C(7)-C(8)$ $C(8)-C(9)$ $C(9)-C(10)$ $C(10)-C(11)$ $C(11)-C(12)$ $C(13)-C(14)$ $C(13)-C(14)$ $C(13)-C(19)$ $C(14)-C(15)$ $C(15)-C(16)$ $C(16)-C(17)$ $C(17)-C(18)$ $C(18)-C(19)$	1.376(8) 1.378(8) 1.376(7) 1.462(8) 1.388(7) 1.362(8) 1.377(9) 1.370(8) 1.405(8) 1.415(8) 1.423(8) 1.423(8) 1.520(8) 1.520(8) 1.501(8)
N(1)-Mo-N(2) N(1)-Mo-C(1) N(1)-Mo-C(2) N(2)-Mo-C(2) N(2)-Mo-C(2) C(1)-Mo-C(2) Mo-N(1)-C(2) Mo-N(1)-C(7) C(3)-N(1)-C(7) Mo-N(2)-C(8) Mo-N(2)-C(12)	72.1(1) 80.2(2) 139.7(2) 107.0(2) 82.5(2) 77.9(2) 123.7(3) 118.1(3) 118.1(4) 118.5(3) 123.5(3)	C(8)-N(2)-C(12) Mo-C(1)-O(1) Mo-C(2)-O(2) C(14)-C(13)-C(19) C(13)-C(14)-C(15) C(14)-C(15)-C(16) C(15)-C(16)-C(17) C(16)-C(17)-C(18) C(17)-C(18)-C(19) C(13)-C(19)-C(18)	118.1(4) 175.9(6) 175.6(5) 121.1(5) 126.7(5) 128.3(5) 130.0(5) 113.8(5) 116.1(5) 121.4(5)
Table 4 Selected b	oond lengths	(Å) and angles (°) for comple	ex 4
$\begin{array}{l} Mo-N(1)\\ Mo-N(2)\\ Mo-C(1)\\ Mo-C(2)\\ Mo-C(13)\\ Mo-C(13)\\ Mo-C(14)\\ Mo-C(15)\\ Mo-C(20)\\ O(1)-C(1)\\ O(2)-C(2)\\ N(1)-C(3)\\ N(1)-C(7)\\ N(2)-C(2)\\ N(3)-C(20)\\ N(3)-C(20)\\ N(3)-C(21)\\ C(3)-C(4)\\ C(4)-C(5) \end{array}$	2.228(6) 2.240(6) 1.936(9) 1.951(9) 2.393(9) 2.235(8) 2.442(9) 2.152(9) 1.15(1) 1.137(9) 1.34(1) 1.330(9) 1.34(1) 1.127(9) 1.45(1) 1.37(1) 1.33(1)	C(5)-C(6) $C(6)-C(7)$ $C(7)-C(8)$ $C(8)-C(9)$ $C(9)-C(10)$ $C(10)-C(11)$ $C(11)-C(12)$ $C(13)-C(14)$ $C(13)-C(19)$ $C(14)-C(15)$ $C(15)-C(16)$ $C(16)-C(17)$ $C(17)-C(18)$ $C(18)-C(19)$ $C(21)-C(22)$ $C(21)-C(23)$ $C(21)-C(24)$	$\begin{array}{c} 1.37(1)\\ 1.38(1)\\ 1.46(1)\\ 1.38(1)\\ 1.35(1)\\ 1.36(1)\\ 1.39(1)\\ 1.40(1)\\ 1.48(1)\\ 1.36(1)\\ 1.47(1)\\ 1.25(2)\\ 1.46(2)\\ 1.36(2)\\ 1.46(1)\\ 1.45(2)\\ 1.47(2)\\ \end{array}$
N(1)-Mo-N(2) N(1)-Mo-C(1) N(1)-Mo-C(2) N(2)-Mo-C(2) N(2)-Mo-C(2) N(2)-Mo-C(2) C(1)-Mo-C(2) C(1)-Mo-C(2) C(1)-Mo-C(2) C(2)-Mo-C(20) C(13)-Mo-C(14) C(13)-Mo-C(15) C(14)-Mo-C(15) Mo-N(1)-C(3) Mo-N(1)-C(7)	$\begin{array}{c} 72.9(2)\\ 102.2(3)\\ 164.2(3)\\ 80.2(3)\\ 167.0(3)\\ 100.9(3)\\ 78.4(3)\\ 80.5(4)\\ 88.9(4)\\ 84.3(4)\\ 34.9(3)\\ 60.3(3)\\ 33.4(3)\\ 124.4(6)\\ 117.1(5) \end{array}$	$\begin{array}{c} C(3)-N(1)-C(7)\\ Mo-N(2)-C(8)\\ Mo-N(2)-C(12)\\ C(8)-N(2)-C(12)\\ C(20)-N(3)-C(21)\\ Mo-C(1)-O(1)\\ Mo-C(2)-O(2)\\ C(14)-C(13)-C(19)\\ C(13)-C(14)-C(15)\\ C(14)-C(15)-C(16)\\ C(15)-C(16)-C(17)\\ C(16)-C(17)-C(18)\\ C(17)-C(18)-C(19)\\ C(13)-C(19)-C(18)\\ Mo-C(20)-N(3)\\ \end{array}$	118.3(7) 115.6(5) 124.3(6) 118.4(7) 180(1) 175.5(9) 177(1) 123.8(9) 127.9(9) 127.9(9) 127(1) 128(1) 127(1) 127(1) 174.6(8)

 $CH_2Cl_2$ . In common with 6, the <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>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<sub>7</sub>H<sub>9</sub> 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 <sup>31</sup>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<sub>2</sub>Cl<sub>2</sub>. A spectroscopic feature specific to 7 is a shoulder (at 1991 cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>) on the high wavenumber IR-active carbonyl stretching band; the relative absorption intensity of this shoulder increases in acetone and decreases in CHCl<sub>3</sub> suggesting that 7 might exist in solution as a mixture of conformers.

Our initial studies on  $\eta^5 \leftrightarrow \eta^3$  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 v(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 v(CO)(NCMe) 1990, 1919 cm<sup>-1</sup> were identified with 7 and v(CO)(NCMe) 1946, 1868 cm<sup>-1</sup> were subsequently assigned, on the basis of a collection of spectroscopic data, to the adduct  $[Mo(CO)_2(NCMe)(dppe)(\eta^3 - C_7H_9)]^+$  8 (Scheme 2). When the reaction mixture of 7 and NCMe was evaporated to dryness and the residue redissolved in CH<sub>2</sub>Cl<sub>2</sub>, only the characteristic carbonyl stretching bands of 7 were observed in the IR spectrum. The assignment of [v(CO)(NCMe) 1946, 1868 cm<sup>-1</sup>] to 8 is supported by a comparison with data for the analogous pentadienyl complex  $[Mo(CO)_2(NCMe)(dppe)(\eta^3-C_5H_7)]^+$ [v(CO)(NCMe) 1956, 1873 cm<sup>-1</sup>]<sup>5</sup> but more definitive evidence for the formation of 8 from 7 and NCMe has been obtained from <sup>31</sup>P and <sup>13</sup>C NMR investigations on 7 in CD<sub>3</sub>CN. The ambienttemperature <sup>31</sup>P NMR spectrum of a sample of 7 dissolved in CD<sub>3</sub>CN exhibits a singlet at  $\delta$  73.0, assigned to 7 by comparison with data obtained in  $CD_2Cl_2$  (see Table 2), and additionally two broad resonances centred around  $\delta$  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  $\delta$  74.2 and 72.3 (consistent with the variabletemperature behaviour of 7) and two well defined doublet resonances [ $\delta$ (CD<sub>3</sub>CN) 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  $(-25 \text{ °C})^{13}$ C NMR spectrum of a sample of 7 dissolved in CD<sub>3</sub>CN provides further confirmation of a two component reaction mixture. In the region  $\delta$  110–70, six <sup>13</sup>C resonances are observed. Three relatively broad resonances [ $\delta(CD_3CN)$  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 [ $\delta(CD_3CN)$  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, <sup>31</sup>P and <sup>13</sup>C NMR spectroscopic data for the product formed from 7 and NCMe support the formulation  $[Mo(CO)_2(NCMe)(dppe)(\eta^3 (C_7H_9)$ ]<sup>+</sup> 8. The shift of v(CO) to lower wavenumber on formation of 8 from 7 is consistent with related  $\eta^5 \longrightarrow \eta^3 C_7 H_9$ 'ring slip' processes, the chemical shifts of the <sup>31</sup>P NMR resonances are typical of complexes of formulation  $[Mo(CO)_2L'(dppe)(\eta^3-R)]^+$  (L' = NCMe<sup>8</sup> or CNBu', R =  $C_7H_9$  or  $C_7H_7$ ) (see later) and the <sup>13</sup>C NMR resonances in the range  $\delta$  92-70 are consistent with the three co-ordinated allyl carbons of an  $\eta^3$ -C<sub>7</sub>H<sub>9</sub> ligand.

In summary the reactions of NCMe with  $[Mo(CO)_2L_2(\eta^5 - C_7H_9)]^+$  (L<sub>2</sub> = 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<sub>2</sub>. Whilst all additions of NCMe to  $[Mo(CO)_2L_2 - (\eta^5 - C_7H_9)]^+$  are reversible, the adduct  $[Mo(CO)_2(NCMe) - (bipy)(\eta^3 - C_7H_9)]^+$  2 is fully formed in NCMe, but  $[Mo(CO)_2(NCMe)(dppe)(\eta^3 - C_7H_9)]^+$  8 is in equilibrium with 7 and the solvent NCMe {we have previously described a related equilibrium between  $[Mo(CO)_2(NCMe)(\eta^7 - C_7H_7)]^+$ and  $[Mo(CO)_2(NCMe)_3(\eta^3 - C_7H_7)]^+$  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  $CH_2Cl_2$ , 2 h,  $-40 \,^{\circ}C$ ;  $L' = CNBu^{t}$ , P-P = dppe, stir in  $CH_2Cl_2$ , 4 h, 0  $^{\circ}C$ ; (ii) L' = NCMe, P-P = dppe, stir in  $CH_2Cl_2$ ; (iii)  $L' = CNBu^{t}$  only; P-P = dppm, stir in  $CH_2Cl_2$ ; P-P = dppe, stir in  $CH_2Cl_2$ , 35  $^{\circ}C$ ; (iv) P-P = dppm or dppe;  $CNBu^{t}$ , stir in  $CH_2Cl_2$ ; (v) dppe, stir in  $CH_2Cl_2$ , 24 h; (vi) PPh<sub>3</sub>, stir in  $CH_2Cl_2$ , 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  $[Mo(CO)_2(NCMe)L_2(\eta^5-C_5H_7)]^+$ (L<sub>2</sub> = bipy,<sup>4</sup> dppe or dmpe<sup>5</sup>) are fully formed in NCMe and are isolable species. These comparisons, together with the contrasting structures of 1 and  $[Mo(\sigma-FBF_3)(CO)_2(bipy)(\eta^3 C_5H_7$ ], provide good evidence that the cyclic dienyl ligand  $C_7H_9$  exhibits a reduced tendency to adopt an  $\eta^3$ -dienyl bonding mode by comparison with the pentadienyl ligand  $C_5H_7$ . Several factors may contribute to the effect of L<sub>2</sub> on hapticity interconversion in  $[Mo(CO)_2L_2(\eta^5-C_7H_9)]^+$ . It has been suggested that the effect of bipy vs. dppe on the preferred hapticity of the pentadienyl ligand in  $[Mo(\sigma-FBF_3)(CO)_2 (bipy)(\eta^3-C_5H_7)$  and  $[Mo(CO)_2(dppe)(\eta^5-C_5H_7)][BF_4]$ might be correlated with interligand steric hindrance between the dienyl and bipy/dppe ligands.<sup>4</sup> 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<sub>2</sub> 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)<sub>2</sub>L'(bipy)- $(\eta^3 - C_7 H_9)$ <sup>+</sup> adopt a structure in which L' is located *trans* to  $C_7H_9$  in common with the allyl complexes [Mo(CO)<sub>2</sub>L'(bipy)- $(\eta^{3}-C_{3}H_{5})^{z^{+}}$  (z = 0, L' = NCS;<sup>11</sup> z = 1, L' = py<sup>1</sup> Although no crystallographic data are available for cationic diphosphine complexes of general formulation [Mo(CO)2- $(L')L_2(\eta^3-R)]^+$  (L<sub>2</sub> = dppe, dppm etc.; L' = CO, PR<sub>3</sub> etc.; (L)  $H_2(\eta^{-1}R)_1$  (L<sub>2</sub> = dppc), dppni tto,  $\Sigma = 0.6$ ,  $H_3$  etc.),  $R = C_3H_5$ ,  $C_5H_7$  etc.), structural studies on the neutral derivatives [Mo(CO)<sub>2</sub>L'(dppe)( $\eta^3$ -R)] (L' = halide,  $R = C_3H_5^{12}$  or  $C_5H_7^{13}$ ) and the ring-substituted cycloheptatrienyl complex [MoCl(CO)<sub>2</sub>(dppe)( $\eta^3$ -C<sub>7</sub>H<sub>6</sub>R)] ( $R = C_6H_4F$ -4)<sup>14</sup> 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  $\eta^3$ -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 <sup>31</sup>P NMR spectroscopic data. The geometric arrangement of ligands in the adducts  $[Mo(CO)_2$ -

 $(L')L_2(\eta^3-C_7H_9)]^+$  may therefore be an additional factor controlling the susceptibility of  $[Mo(CO)_2L_2(\eta^5-C_7H_9)]$  to  $\eta^5 \longrightarrow \eta^3$  (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<sup>t</sup> lead to associative ligand-substitution processes involving  $\eta^7 \longrightarrow \eta^3 \longrightarrow \eta^7$  hapticity conversions at the  $C_7 H_7$ ring.<sup>9</sup> In search of analogous associative ligand-substitution reactions proceeding with  $\eta^5 \longrightarrow \eta^3 \longrightarrow \eta^5$  hapticity conversion at a cycloheptadienyl ring, we turned our attention to the reactions of complexes 6 and 7 with CNBu<sup>t</sup>. 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<sup>t</sup>)(dppm)( $\eta^{5}$ -C<sub>7</sub>H<sub>9</sub>)] 10. Monitoring the reaction mixture by IR spectroscopy in the v(CO) region revealed that the reaction proceeded via an observable intermediate species. The corresponding reaction of the dppe derivative 7 with CNBu<sup>t</sup> also led to the formation of the carbonyl substituted  $[Mo(CO)(CNBu^{t})(dppe)(\eta^{5}-C_{7}H_{9})]^{+}$ 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  $[Mo(CO)_2(CNBu^t)L_2(\eta^3 (C_7H_9)$ ]<sup>+</sup> (L<sub>2</sub> = dppm 9 or dppe 11). Characterisation data for complexes 9-12 are presented in Tables 1 and 2. The NMR spectroscopic data for  $[Mo(CO)(CNBu^{t})L_{2}(\eta^{5}-C_{7}H_{9})]$  $(L_2 = dppm 10 \text{ or } dppe 12)$  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<sup>t</sup>. The spectroscopic data for complexes 9 and 11, formulated as the  $\eta^3$ -cycloheptadienyl species  $[Mo(CO)_2$ -(CNBu')L<sub>2</sub>( $\eta^3$ -C<sub>7</sub>H<sub>9</sub>)]<sup>+</sup>, warrant further detailed examination since an alternative, pendant phosphine formulation [Mo- $(CO)_2(CNBu')(\sigma-L-L)(\eta^5-C_7H_9)]^+$  (Fig. 3) can be envisaged and it is important to exclude this in order to establish fully that the associative substitution processes  $6 \longrightarrow 9$  — and  $7 \longrightarrow 11 \longrightarrow 12$  are accompanied by  $\eta^5 \longrightarrow \eta^3$  — **→ 10** hapticity changes at the C7H9 ring.

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



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

 $(CNBu^{t})L_{2}(\eta^{3}-C_{7}H_{9})]^{+}$  and  $[Mo(CO)_{2}(CNBu^{t})(\sigma-L-L)(\eta^{5}-L)$  $(C_7H_9)$ <sup>+</sup>, 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  $[Mo(CO)_2(CNBu^t)(dppe)(\eta^3 (C_7H_7)$ ]<sup>+</sup> 13 {representative of 'ring slipped' [Mo(CO)<sub>2</sub>- $(CNBu')(dppe)(\eta^3-C_7H_9)]^+$  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  $[Mo(CO)_2(NCMe)(dppe)(\eta^3 (C_{7}H_{7})$ <sup>+</sup>.<sup>8</sup> The  $\eta^{5}$ -cycloheptadienyl complex [Mo(CO)<sub>2</sub>-(CNBu')(PPh<sub>3</sub>)( $\eta^{5}$ -C<sub>7</sub>H<sub>9</sub>)]<sup>+</sup> 14 was prepared from the reaction of PPh<sub>3</sub> 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 <sup>13</sup>C and <sup>31</sup>P NMR data; the <sup>1</sup>H NMR spectra of 9 and 11 were broad and ill defined and did not provide a useful distinction between  $\eta^5$  and  $\eta^3$  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  $\eta^3$ -cycloheptatrienyl complex 13 (Table 1), the wavenumbers of v(CN) and v(CO) and the observed intensity patterns of the carbonyl bands (characteristic of cis carbonyl ligands) correspond very closely. The average v(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  $\eta^3$  ligand  $(C_7H_7 vs. C_7H_9)$ .<sup>7</sup> Moreover the conversion of 6 to 9 and of 7 to 11 results in a shift in averaged v(CO) to lower wavenumber by 25 ( $6 \rightarrow 9$ ) and 32 cm<sup>-1</sup> (7  $\longrightarrow$  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 v(CN)and v(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 <sup>31</sup>P NMR data for 11 { $\delta$ [(CD<sub>3</sub>)<sub>2</sub>CO, -20 °C] 59.2, d, J(P-P) 27; 54.3, d, J(P-P) 27 Hz} and 13 [δ(CD<sub>2</sub>Cl<sub>2</sub>, 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 <sup>13</sup>C NMR spectra of 9 and 11 each exhibit three strong, sharp resonances in the region  $\delta$  95-70, not attributable to the carbonyl substitution product impurities 10 and 12. Thus selected <sup>13</sup>C NMR resonances for 9  $[\delta(CD_2Cl_2, 0 \circ C) 94.2, 86.2, 77.3]$  and 11  $[\delta(CD_3CN, 0 \circ C)]$ 89.3, 84.5, 74.3] are characteristic of the co-ordinated allyl fragment of the  $\eta^3$ -C<sub>7</sub>H<sub>9</sub> 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)<sub>2</sub>- $(NCMe)(dppe)(\eta^3-C_7H_9)$ ]<sup>+</sup> 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  $6 \longrightarrow 9 \longrightarrow 10$  and  $7 \longrightarrow 10$  $11 \longrightarrow 12$  represent the first examples of associative ligandsubstitution processes which proceed with  $\eta^5 \longrightarrow \eta^3 \longrightarrow \eta^5$  hapticity conversion at a *cyclic* dienyl ligand in which the  $\eta^3$ substitution processes which proceed with  $\eta^5 \longrightarrow \eta^3 \longrightarrow$ 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,  $^{1}\ proven \ examples \ where \ the \ \eta^{3}\text{-dienyl}$ 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<sub>3</sub> to  $[Mn(CO)_2(PR_3)(\eta^5-C_5H_7)]$  via the intermediate give [Mn(CO)<sub>3</sub>(PR<sub>3</sub>)( $\eta^3$ -C<sub>5</sub>H<sub>7</sub>)].<sup>3</sup> The contrasting behaviour of [Mo(CO)<sub>2</sub>(CNBu<sup>1</sup>)(bipy)( $\eta^3$ -C<sub>7</sub>H<sub>9</sub>)]<sup>+</sup> 4, and the diphosphine derivatives [Mo(CO)<sub>2</sub>(CNBu<sup>1</sup>)L<sub>2</sub>( $\eta^3$ -C<sub>7</sub>H<sub>9</sub>)]<sup>+</sup> (L<sub>2</sub> = 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<sup>t</sup> must compete with CNBu<sup>t</sup> for metal electron density available for  $\pi$  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' substituted complexes  $[Mo(CO)(CNBu')L_2(\eta^5-C_7H_9)]^+$  (L<sub>2</sub> = dppm 10 or dppe 12) was also investigated. Consistent with our findings in the chemistry of cycloheptatrienyl molybdenum complexes, substitution of CO with CNBu<sup>t</sup> 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<sup>1</sup>. Treatment of CH<sub>2</sub>Cl<sub>2</sub> solutions of 10 and 12 with CNBu<sup>t</sup> resulted in a shift in v(CO) to lower wavenumber by ca. 20 cm<sup>-1</sup> and the formation of yellow-orange products, formulated, on the basis of data in Table 1 only, as the CNBu<sup>t</sup> adducts  $[Mo(CO)(CNBu<sup>t</sup>)_2L_2(\eta^3-C_7H_9)]^+$   $(L_2 =$ 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' in CH<sub>2</sub>Cl<sub>2</sub>. Attempts to effect further carbonyl substitution by CNBu' in 15 and 16 to give  $[Mo(CNBu')_2 L_2(\eta^5 - C_7 H_9)]^+$  were unsuccessful; in common with [Mo(CO)- $(CNBu^{t})_{4}(\eta^{3}-R)]^{+}$  [R = C<sub>7</sub>H<sub>7</sub> or C<sub>7</sub>H<sub>9</sub> (see later)] the final carbonyl appears very difficult to displace and when 16 was warmed in acetone  $[Mo(CO)(CNBu<sup>t</sup>)(dppe)(\eta^5-C_7H_9)]^+$  12 was regenerated. The relative lability of 15 and 16 towards loss of CNBu<sup>t</sup> 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<sup>1</sup> 17 or PPh<sub>3</sub> 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.<sup>7</sup> 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<sup>t</sup> although no evidence was obtained for the intermediacy of  $\eta^3$ -C<sub>7</sub>H<sub>9</sub> complexes. Treatment of 17 with one equivalent of CNBu<sup>t</sup> in CH<sub>2</sub>Cl<sub>2</sub> yielded [Mo(CO)-(CNBu<sup>t</sup>)<sub>3</sub>( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)]<sup>+</sup> 19 (Scheme 3). A possible intermediate for this substitution reaction is [Mo(CO)<sub>2</sub>(CNBu<sup>t</sup>)<sub>3</sub>( $\eta^3$ -C<sub>7</sub>H<sub>9</sub>)]<sup>+</sup> {analogous to the isolable cycloheptatrienyl complex



Scheme 3 Reagents and conditions: (i) CNBu<sup>t</sup>, stir in CH<sub>2</sub>Cl<sub>2</sub>, 1 h; (ii) CNBu<sup>t</sup>, stir in CH<sub>2</sub>Cl<sub>2</sub>, 7 d; (iii) CNBu<sup>t</sup> in excess, stir in CH<sub>2</sub>Cl<sub>2</sub>, 1 h; (iv) CNBu<sup>t</sup> in excess, stir in CH<sub>2</sub>Cl<sub>2</sub>, 15 min

 $[Mo(CO)_2(CNBu^{t})_3(\eta^3-C_7H_7)]^{+9}$  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<sub>3</sub> complex 18 with CNBu<sup>t</sup> 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<sup>t</sup>)<sub>3</sub>,  $(\eta^5 - C_7 H_9)$ ]<sup>+</sup> 19, reacts further with CNBu<sup>t</sup>. Treatment of 19, or alternatively  $[Mo(CO)_2(NCMe)_3(\eta^3-C_7H_9)]^+$ , with excess of CNBu<sup>t</sup> in CH<sub>2</sub>Cl<sub>2</sub> led to the formation of  $[Mo(CO)(CNBu^t)_4$ - $(\eta^3 - C_7 H_0)$ <sup>+</sup> 20 which was isolated as an orange solid. Complex 20 is an analogue of the cycloheptatrienyl complex [Mo(CO)(CNBu')<sub>4</sub>( $\eta^3$ -C<sub>7</sub>H<sub>7</sub>)]<sup>+</sup> which we have previously obtained by reaction of [Mo(CO)(CNBu')<sub>2</sub>( $\eta^7$ -C<sub>7</sub>H<sub>7</sub>)]<sup>+</sup> with CNBu'.<sup>9</sup> However, unlike [Mo(CO)(CNBu')<sub>4</sub>( $\eta^3$ -C<sub>7</sub>H<sub>7</sub>)]<sup>+</sup>, the cycloheptadienyl complex 20 readily dissociated CNBut 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 CNBut. Two alternative ligand arrangements can be proposed for 20; that illustrated in Scheme 3 is preferred on the basis of the <sup>13</sup>C NMR data, which reveals four distinct isonitrile carbon resonances, and by comparison with  $[Mo(CO)(CNBu^{t})_{4}(\eta^{3}-C_{7}H_{7})]^{+}$ , which can be unequivocally identified as the asymmetric isomer from <sup>13</sup>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  $[Mo(CO)_2(bipy)(\eta^5-C_7H_9)][BF_4]$  1,  $[Mo(CO)_2(CNBu^1)(NCMe)_2(\eta^3-C_7H_9)][BF_4]$  5,  $[Mo(CO)_2(NCMe)_3(\eta^3-C_7H_9)][BF_4]$ ,  $[Mo(CO)_2(dppm)(\eta^5-C_7H_9)][BF_4]$  6,  $[Mo(CO)_2(CNBu^1)(\eta^7-C_7H_7)][BF_4]$ ,  $[Mo(CO)_2(PPh_3)_2(\eta^5-C_7H_9)][BF_4]$  17, and  $[Mo(CO)_2(PPh_3)_2(\eta^5-C_7H_9)][BF_4]$  18, were prepared by published procedures.<sup>7,9</sup> The chemicals 2,2'-bipyridyl, PMe<sub>3</sub> (1.0 mol dm<sup>-3</sup> solution in toluene), CNBu<sup>1</sup> and dppe were supplied by Aldrich. The 300 MHz <sup>1</sup>H and 75 MHz <sup>13</sup>C NMR spectra were recorded on a Bruker AC 300 E or Varian Associates XL 300 spectrometer; 122 MHz <sup>31</sup>P NMR spectra were obtained on the Varian Associates XL 300 and positive chemical shifts are quoted downfield from H<sub>3</sub>PO<sub>4</sub>. 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)<sub>2</sub>(PMe<sub>3</sub>)(bipy)( $\eta^3$ -C<sub>7</sub>H<sub>9</sub>)][BF<sub>4</sub>] 3. A stirred solution of [Mo(CO)<sub>2</sub>(bipy)( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)][BF<sub>4</sub>] 1 (0.299 g, 0.61 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 cm<sup>3</sup>) was treated with PMe<sub>3</sub> (0.6 cm<sup>3</sup>, 1.0 mol dm<sup>-3</sup> 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%).

 $[Mo(CO)_2(CNBu^1)(bipy)(\eta^3-C_7H_9)][BF_4]$  4. A mixture of  $[Mo(CO)_2(CNBu^1)(NCMe)_2(\eta^3-C_7H_9)][BF_4]$  5 (0.471 g, 0.95 mmol) and bipy (0.182 g, 1.17 mmol) was stirred in CH<sub>2</sub>Cl<sub>2</sub> (50 cm<sup>3</sup>). After 1 h, the solution was filtered, reduced in volume and treated with diethyl ether to precipitate the crude product. Recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>-diethyl ether gave 4 as a redbrown solid; yield 0.436 g (81%).

 $[Mo(CO)_2(dppe)(\eta^5-C_7H_9)][BF_4]\cdot CH_2Cl_2$  7·CH\_2Cl<sub>2</sub>. A stirred solution of  $[Mo(CO)_2(NCMe)_3(\eta^3-C_7H_9)][BF_4]$  (2.013 g, 4.43 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (60 cm<sup>3</sup>) 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<sub>2</sub>Cl<sub>2</sub>-diethyl ether gave 7 as a pink-red CH<sub>2</sub>Cl<sub>2</sub> solvate; yield 3.103 g (87%).

[Mo(CO)<sub>2</sub>(CNBu')(dppm)( $\eta^3$ -C<sub>7</sub>H<sub>9</sub>)][BF<sub>4</sub>]9. A stirred, cold (-40 °C) solution of [Mo(CO)<sub>2</sub>(dppm)( $\eta^3$ -C<sub>7</sub>H<sub>9</sub>)][BF<sub>4</sub>] 6 (1.03 g, 1.44 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 cm<sup>3</sup>) was treated with CNBu<sup>t</sup> (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<sub>2</sub>Cl<sub>2</sub>-diethyl ether to give 9 as a redbrown solid; yield 0.877 g (76%). The complex [Mo(CO)<sub>2</sub>-(CNBu<sup>t</sup>)(dppe)( $\eta^3$ -C<sub>7</sub>H<sub>9</sub>)][BF<sub>4</sub>] 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<sub>2</sub>Cl<sub>2</sub> (0.502 g, 0.62 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 cm<sup>3</sup>) was treated with CNBu<sup>t</sup> (0.073 g, 0.88 mmol) and stirred for 4 h at 0 °C before work-up as described for 9.

 $[Mo(CO)(CNBu^{t})(dppm)(\eta^{5}-C_{7}H_{9})][BF_{4}]$  10. A stirred solution of 6 (0.291 g, 0.41 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) was treated with CNBu<sup>t</sup> (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 CH<sub>2</sub>Cl<sub>2</sub>-diethyl ether gave **10** as a yellow solid; yield 0.224 g (72%). The complex[Mo(CO)(CNBu<sup>1</sup>)(dppe)( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)][BF<sub>4</sub>] **12** was prepared as a yellow solid in 69% yield from 7·CH<sub>2</sub>Cl<sub>2</sub> (0.745 g, 0.91 mmol) and CNBu<sup>1</sup> (0.088 g, 1.06 mmol) stirred in CH<sub>2</sub>Cl<sub>2</sub> (50 cm<sup>3</sup>) for 3 h at 35 °C. The work-up procedure was identical to that described for **10**.

 $[Mo(CO)_2(CNBu')(dppe)(\eta^3-C_7H_7)][BF_4]$  13. A solution of  $[Mo(CO)_2(CNBu')(\eta^7-C_7H_7)][BF_4]$  (1.021 g, 2.47 mmol) in  $CH_2Cl_2$  (40 cm<sup>3</sup>) 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  $CH_2Cl_2$ -diethyl ether gave 13 as an orange solid; yield 1.487 g (74%).

[Mo(CO)<sub>2</sub>(CNBu<sup>1</sup>)(PPh<sub>3</sub>)( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)][BF<sub>4</sub>] 14. A mixture of [Mo(CO)<sub>2</sub>(CNBu<sup>1</sup>)(PPh<sub>3</sub>)( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)][BF<sub>4</sub>] 5 (0.407 g, 0.82 mmol) and PPh<sub>3</sub> (0.213 g, 0.81 mmol) was stirred for 1 h in CH<sub>2</sub>Cl<sub>2</sub> (40 cm<sup>3</sup>). 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 CH<sub>2</sub>Cl<sub>2</sub>-diethyl ether gave 14 as a yellow solid; yield 0.328 g (59%).

[Mo(CO)(CNBu<sup>1</sup>)<sub>2</sub>(dppm)( $\eta^3$ -C<sub>7</sub>H<sub>9</sub>)][BF<sub>4</sub>] **15**. Treatment of a stirred solution of **10** (0.246 g, 0.32 mmol) in CH<sub>2</sub>Cl<sub>2</sub> with CNBu<sup>1</sup> (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.

 $[Mo(CO)(CNBu^{1})_{2}(dppe)(\eta^{3}-C_{7}H_{9})][BF_{4}]$  16. A solution of 7-CH<sub>2</sub>Cl<sub>2</sub> (0.781 g, 0.96 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 cm<sup>3</sup>) was treated with CNBu<sup>4</sup> (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 CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) and the CH<sub>2</sub>Cl<sub>2</sub> solution was

added dropwise to stirred diethyl ether to give 16 as an orangeyellow solid; yield 0.356 g (43%).

[Mo(CO)(CNBu<sup>1</sup>)<sub>3</sub>( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)][BF<sub>4</sub>] **19**. A stirred solution of [Mo(CO)<sub>2</sub>(CNBu<sup>1</sup>)<sub>2</sub>( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)][BF<sub>4</sub>] **17** (0.158 g, 0.32 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 cm<sup>3</sup>) was treated with CNBu<sup>1</sup> (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 CH<sub>2</sub>Cl<sub>2</sub>diethyl ether gave **19** as a yellow-orange solid; yield 0.122 g (70%).

[Mo(CO)(CNBu')<sub>4</sub>( $\eta^3$ -C<sub>7</sub>H<sub>9</sub>)][BF<sub>4</sub>] **20**. Method (a). The reaction of [Mo(CO)(CNBu')<sub>3</sub>( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)][BF<sub>4</sub>] **19** (0.217 g, 0.39 mmol) with an excess of CNBu' (0.065 g, 0.78 mmol) in stirred CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) 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  $[Mo(CO)_2(NCMe)_3(\eta^3-C_7H_9)]$ -[BF<sub>4</sub>] (0.320 g, 0.70 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) was treated with CNBu<sup>t</sup> (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 CH<sub>2</sub>Cl<sub>2</sub> 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);<sup>15</sup> in each case the data were also corrections were applied to the data for 1

Table 5 Structure analyses of complexes 1 and 4

		1	4
F	ormula	C10H17BF4N2O2MO	C <sub>24</sub> H <sub>26</sub> BF <sub>4</sub> N <sub>2</sub> O <sub>2</sub> Mo
M	1	488.10	571.23
С	rystal system	Monoclinic	Monoclinic
S	pace group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/	Å	8.401 (1)	11.271 (8)
<b>b</b> /	/Å	10.840 (2)	13.318 (8)
c/	'Å	21.387 (3)	17.41 (1)
β	/o	92.72 (1)	95.04 (6)
Ū	∕/ų	1945.5 (9)	2604 (6)
T	/K	296	296
Z		4	4
D	$c/g \text{ cm}^{-3}$	1.666	1.457
F	(000)	976	1160
μ/	/cm <sup>-1</sup>	61.26 (Cu-Ka)	5.43 (Mo-Ka)
D	iffractometer	Rigaku AFC5R	Rigaku AFC6S
C	rystal dimensions/mm	$0.07 \times 0.35 \times 0.45$	$0.22 \times 0.22 \times 0.32$
λ/	/Å	1.541 78 (Cu-Kα)	0.710 69 (Mo-Kα)
θ	range/°	4-60	1–25
Science	can type	ω–2θ	ω-2θ
Sc	can width/°	$(1.26 + 0.30 \tan \theta)$	$(1.52 + 0.30 \tan \theta)$
T	otal data	3324	5073
U	nique data	3089	4808
ʻC	Observed' data $[I > 3\sigma(I)], N_o$	2589	2684
Le	east-squares variables, $N_{\rm v}$	262	316
R		0.044	0.052
R	,	0.058	0.065
S		2.23	2.28
D	ifference map features/e Å <sup>-3</sup>	+0.63, -0.45	+0.95, -0.53
$R = \Sigma  \Delta  / \Sigma  F_{o} ; R' = (\Sigma w \Delta)$	$^{2}/\Sigma w F_{o}^{2})^{\frac{1}{2}}; S = [\Sigma w \Delta^{2}/(N_{o} - N_{v})]^{\frac{1}{2}}$	$\Delta = F_{\rm o} - F_{\rm c}.$	

#### Table 6 Atomic coordinates for complex 1

Atom	x	У	Z
Мо	0.317 27(5)	0.157 14(4)	0.107 03(2)
<b>O(1)</b>	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	у	Ζ
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)

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

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

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### References

- 1 J. M. O'Connor and C. P. Casey, Chem. Rev., 1987, 87, 307.
- 2 R. D. Ernst, Chem. Rev., 1988, 88, 1255
- 3 M. de los Angeles Paz-Sandoval, P. Powell, M. G. B. Drew and R. N. Perutz, *Organometallics*, 1984, 3, 1026.
- 4 S.-F. Lush, S.-H. Wang, G.-H. Lee, S.-M. Peng, S.-L. Wang and R.-S. Liu, Organometallics, 1990, 9, 1862.
- 5 G.-H. Lee, S.-M. Peng, I.-C. Tsung, D. Mu and R.-S. Liu, Organometallics, 1989, 8, 2248.
- 6 J. R. Hinchliffe and M. W. Whiteley, J. Organomet. Chem., 1991, 402, C50.
- 7 R. L. Beddoes, J. R. Hinchliffe and M. W. Whiteley, J. Chem. Soc., Dalton Trans., 1993, 501.
- 8 R. Breeze, M. S. Plant, A. Ricalton, D. J. Sutton and M. W. Whiteley, J. Organomet. Chem., 1988, 356, 343.
- 9 J. R. Hinchliffe, A. Ricalton and M. W. Whiteley, *Polyhedron*, 1991, 10, 267.
- 10 R. H. Fenn and A. J. Graham, J. Organomet. Chem., 1972, 37, 137.
- 11 A. J. Graham and R. H. Fenn, J. Organomet. Chem., 1969, 17, 405.
- 12 J. W. Faller, D. A. Haitko, R. D. Adams and D. F. Chodosh, J. Am. Chem. Soc., 1979, 101, 865.
- 13 G.-H. Lee, S.-M. Peng, F.-C. Liu, D. Mu and R.-S. Liu, Organometallics, 1989, 8, 402.
- 14 R. L. Beddoes, A. Roberts and M. W. Whiteley, unpublished work.
- 15 N. Walker and D. Stuart, Acta Crystallogr., Sect. A, 1983, **39**, 158. 16 D. T. Cromer and J. T. Waber, International Tables for X-Ray
- *Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
- 17 TEXSAN-TEXRAY, Structure analysis package, Molecular Structure Corporation, The Woodlands, TX, 1985.

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