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Synthesis, structure and hapticity interconversion reactions of pentahapto-bonded cyclooctadienyl complexes of molybdenum†

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The pentahapto-bonded cyclooctadienylmolybdenum complexes $[Mo(CO)_2(L_2)(1\text{–}3{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$ ($L_2 = Ph_2P(CH_2)_nPPh_2$, $n = 1$, (dppm), **1a**; $n = 2$, (dppe), **2a**) are synthesised by reaction of $[MoBr(CO)_2(L_2)(1\text{–}3\text{-}\eta{:}5,6\text{-}C_8H_{11})]$ with $Ag[BF_4]$ in CH_2Cl_2; $[Mo(CO)_2(dppm)(1\text{–}5\text{-}\eta\text{-}C_8H_{11})][BF_4]$, **1b**, is obtained from $[MoBr(CO)_2(dppm)(1\text{–}3\text{-}\eta{:}4,5\text{-}C_8H_{11})]$ by an identical procedure. Related syntheses afford $[Mo(CO)_2\{P(OMe)_3\}_2(1\text{–}5\text{-}\eta\text{-}C_8H_{11})][BF_4]$, **4b**, and $[Mo(CO)_2(CNBu^t)_2(1\text{–}3{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$, **5a**. The complexes $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_8H_{11})]^+$ ($\eta^3\text{-}C_8H_{11}$ = $1\text{–}3\text{-}\eta{:}5,6\text{-}C_8H_{11}$, $1\text{–}3\text{-}\eta{:}4,5\text{-}C_8H_{11}$) are precursors to $[Mo(CO)(CNBu^t)_3(1\text{–}3{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$, **6a**, $[Mo(CO)(CNBu^t)_3(1\text{–}5\text{-}\eta\text{-}C_8H_{11})][BF_4]$, **6b** and $[Mo(CO)_2(norborna\text{-}2,5\text{-}diene)(1\text{–}3{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$, **7a**. The X-ray crystal structures of complexes **1a** and **6b** have been determined. NMR spectroscopic investigations on the $1\text{–}5\text{-}\eta\text{-}C_8H_{11}$ complexes **1b**, **4b** and **6b**, indicate a high barrier to rotation of the metal group with respect to the cyclooctadienyl ring. Complexes **1a**, **1b** and **2a** undergo ligand addition reactions with accompanying $\eta^5 \longrightarrow \eta^3$ hapticity conversion at the cyclooctadienyl ligand to yield adducts $[Mo(CO)_2(L')(L_2)(\eta^3\text{-}C_8H_{11})]^+$ (L' = NCMe or CO, L_2 = dppm or dppe, $\eta^3\text{-}C_8H_{11} = 1\text{–}3\text{-}\eta{:}5,6\text{-}C_8H_{11}$ or $1\text{–}3\text{-}\eta{:}4,5\text{-}C_8H_{11}$, not all combinations). The facility of these processes is strongly dependent upon the identity of the variables L_2 and C_8H_{11}.

Introduction

Edge-bridged dienyl ligands such as 6,6-dimethylcyclohexadienyl, cycloheptadienyl ($1\text{–}5\text{-}\eta\text{-}C_7H_9$) and cyclooctadienyl ($1\text{–}5\text{-}\eta\text{-}C_8H_{11}$), present a special interest in the chemistry of metal-dienyl complexes.[1] In general, such ligands possess properties intermediate between "closed", cyclic systems such as cyclopentadienyl and "open", acyclic ligands such as pentadienyl and 2,4-dimethylpentadienyl. However, even within the sequence of six-, seven- and eight-membered, edge-bridged systems, there are some significant differences in structure and reactivity as demonstrated by a series of investigations on edge-bridged metallocenes and their ligand adducts.[2–5] Clearly, it is important to understand the role of the edge-bridge and the impact of its size in terms of effects on structure and reactivity and our contribution to this objective centres upon our work with half-sandwich complexes of Mo and W containing the edge-bridged dienyls C_7H_9[6–8] and C_8H_{11}.[9,10] The merits of these systems are first, the direct comparability of C_7H_9 and C_8H_{11} ligands with, in each case, only H substituents attached to the edge-bridge methylene carbons and secondly the ready availability of data for analogous cyclopentadienyl, indenyl[11] and pentadienyl[12–15] complexes for purposes of comparison. The criteria that we have examined to elucidate the effect of the additional methylene group in the edge-bridge of the $1\text{–}5\text{-}\eta\text{-}C_8H_{11}$ ligand, include structural and spectroscopic data and, most definitively, ligand addition reactions of complexes of the type $[Mo(CO)_2(L_2)(\eta^5\text{-dienyl})]^+$ to give adducts in which the dienyl ligand is bonded trihapto. The cyclooctadienyl ligand is commonly encountered in two isomeric forms and, for the purpose of additional comparisons, both types are described in this paper. The $1\text{–}5\text{-}\eta\text{-}C_8H_{11}$ ligand incorporates an authentic, fully conjugated, η^5-dienyl system, edge-bridged by three adjacent methylene groups and it is this ligand which permits a direct comparison with our previous studies on cycloheptadienyl chemistry. The $1\text{–}3{:}5,6\text{-}\eta\text{-}C_8H_{11}$ ligand may also be considered as pentahapto-bonded but it incorporates isolated allyl and "ene"units separated by a methylene group (C^4) and edge-bridged by methylenes C^7 and C^8. Further to our preliminary communication,[9] we now present a full report on the synthesis, structure and reactivity of the first examples of complexes of both $1\text{–}3{:}5,6\text{-}\eta\text{-}C_8H_{11}$ and $1\text{–}5\text{-}\eta\text{-}C_8H_{11}$ ligands coordinated to molybdenum.

Results and discussion

Synthesis of pentahapto-bonded cyclooctadienylmolybdenum complexes

We have previously described[10] the synthesis of a series of molybdenum complexes containing the trihapto-bonded cyclooctadienyl ligands, $1\text{–}3\text{-}\eta{:}5,6\text{-}C_8H_{11}$ and $1\text{–}3\text{-}\eta{:}4,5\text{-}C_8H_{11}$ and these complexes, $[MoBr(CO)_2(L_2)(\eta^3\text{-}C_8H_{11})]$ (L_2 = dppm, dppe, 2,2′-bipy, $2CNBu^t$) and $[Mo(CO)_2(L)_3(\eta^3\text{-}C_8H_{11})]^+$ (L = NCMe or $CNBu^t$), now serve as the precursors to pentahapto-bonded cyclooctadienyl systems. Two synthetic strategies have been explored. First, by analogy with the acyclic pentadienyl chemistry developed by Liu and co-workers,[13] halide abstraction from $[MoBr(CO)_2(L_2)(\eta^3\text{-}C_8H_{11})]$ would be expected to afford cationic products of formulation $[Mo(CO)_2(L_2)(\eta^5\text{-}C_8H_{11})]^+$. The alternative approach, developed mainly in the chemistry of the cycloheptadienylmolybdenum system, involves reaction of the tris-nitrile complex $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_8H_{11})]^+$ with ligand(s) L_2, resulting in displacement of all three nitrile ligands and formation of $[Mo(CO)_2(L_2)(\eta^5\text{-}C_8H_{11})]^+$. Both synthetic routes were successfully employed in the current work but the application of $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_8H_{11})]^+$ as a precursor was limited by the formation of stable mono-nitrile complexes $[Mo(CO)_2(NCMe)(L_2)(\eta^3\text{-}C_8H_{11})]^+$ for some identities of L_2. Our synthetic studies (Scheme 1(a) and (b)) resulted in the isolation of four categories of pentahapto-bonded cyclooctadienyl system as classified by the supporting ligands (chelate P-donor ligands, monodentate P-donor ligands, isocyanide ligands and diene ligands). Microanalytical, IR and mass spectroscopic data for the new pentahapto-bonded cyclooctadienyl complexes are given in Table 1 whilst NMR spectroscopic data (^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) are presented in Table 2.

Treatment of red, CH_2Cl_2 solutions of $[MoBr(CO)_2(dppm)(\eta^3\text{-}C_8H_{11})]$ ($\eta^3\text{-}C_8H_{11} = 1\text{–}3\text{-}\eta{:}5,6\text{-}C_8H_{11}$ or $1\text{–}3\text{-}\eta{:}4,5\text{-}C_8H_{11}$) with $Ag[BF_4]$ in CH_2Cl_2 resulted in precipitation of AgBr and

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† Electronic supplementary information (ESI) available: ^1H and ^{13}C NMR data for $[Mo(CO)_2(L')(L_2)(\eta^3\text{-}C_8H_{11})]$ **8a**, **9a** **11a**, **12a**, **3b**, **8b**, **9b**, **10b**, **11b**, **12b**. See http://www.rsc.org/suppdata/dt/b2/b209975f/

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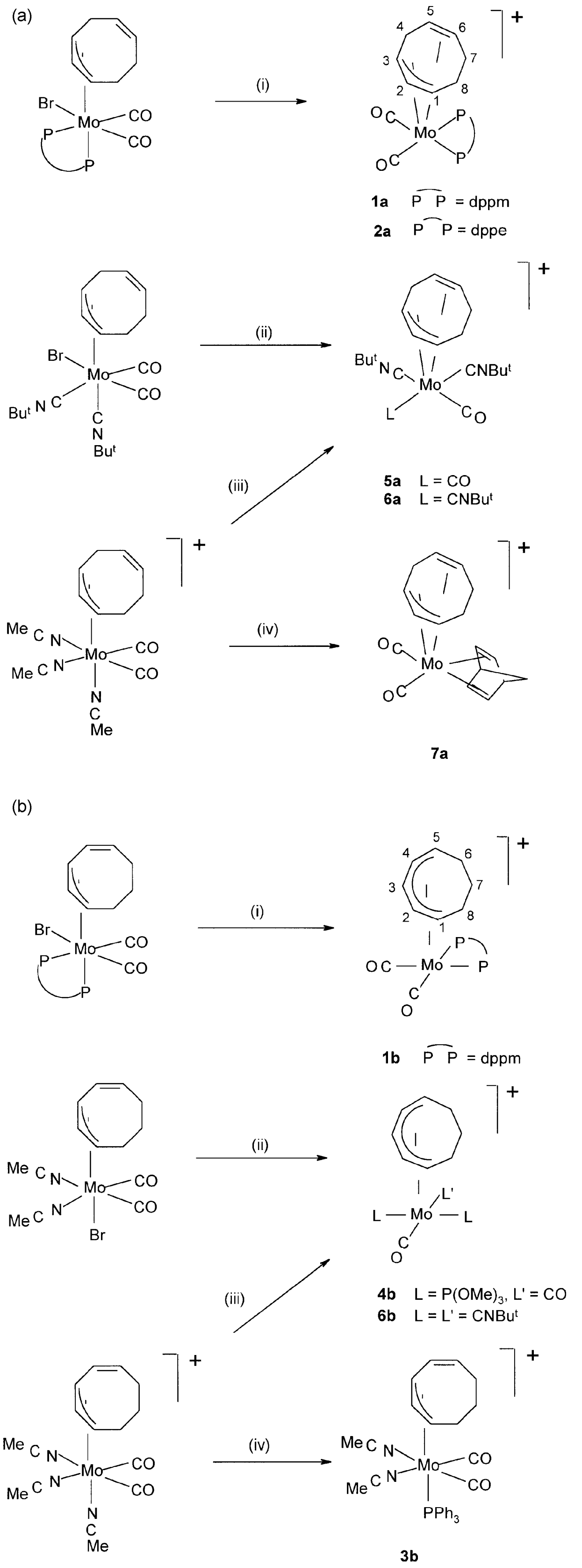


Scheme 1 Reagents and conditions: **(a)**: (i) Ag[BF$_4$] in CH$_2$Cl$_2$, 1 h stirring; (ii) L = CO, Ag[BF$_4$] in CH$_2$Cl$_2$, 20 min stirring; (iii) L = CNBu^t, (a) 3 equivalents of CNBu^t in CH$_2$Cl$_2$, 15 min stirring, remove solvent and dry *in vacuo* for 1 h; (b) reflux in CH$_2$Cl$_2$, 1 h; (iv) 5+ equivalents of nbd in CH$_2$Cl$_2$, 24 h stirring. **(b)**: (i) Ag[BF$_4$] in CH$_2$Cl$_2$, 1 h stirring; (ii) L = P(OMe)$_3$, L′ = CO, (a) 2 equivalents of P(OMe)$_3$ in CH$_2$Cl$_2$ (−70 °C warmed to 0 °C over 30 min stirring), remove solvent and dry *in vacuo* for 1 h; (b) Ag[BF$_4$] in CH$_2$Cl$_2$, 30 min; (iii) L = L′ = CNBu^t, (a) 3 equivalents of CNBu^t in CH$_2$Cl$_2$, 15 min stirring, remove solvent and dry *in vacuo* 1 h; (b) reflux in CH$_2$Cl$_2$, 1 h; (iv) 1 equivalent of PPh$_3$ in CH$_2$Cl$_2$, 30 min stirring at 0 °C.

the respective formation of [Mo(CO)$_2$(dppm)(η^5-C$_8$H$_{11}$)][BF$_4$] (η^5-C$_8$H$_{11}$ = 1–3:5,6-η-C$_8$H$_{11}$, **1a**; 1–5-η-C$_8$H$_{11}$, **1b**) which were isolated as orange–pink solids. An identical synthetic procedure starting from [MoBr(CO)$_2$(dppe)(1–3-η:5,6-C$_8$H$_{11}$)] afforded [Mo(CO)$_2$(dppe)(1–3:5,6-η-C$_8$H$_{11}$)][BF$_4$], **2a** which was isolated as a CH$_2$Cl$_2$ solvate. However, attempts to prepare [Mo(CO)$_2$(dppe)(1–5-η-C$_8$H$_{11}$)][BF$_4$] starting from [MoBr(CO)$_2$(dppe)(1–3-η:4,5-C$_8$H$_{11}$)] were unsuccessful. IR monitoring of the reaction solution suggested the intermediacy of the required product (ν(CO)(CH$_2$Cl$_2$): 1988, 1919 cm^{-1}) but isolation attempts resulted in the formation of low yields of [Mo(CO)$_3$(dppe)(1–3-η:4,5-C$_8$H$_{11}$)][BF$_4$] which was identified by comparison of spectroscopic data with those of an authentic sample prepared by an independent route (see later). The reactions of [Mo(CO)$_2$(NCMe)$_3$(η^3-C$_8$H$_{11}$)][BF$_4$] (η^3-C$_8$H$_{11}$ = 1–3-η:5,6-C$_8$H$_{11}$ or 1–3-η:4,5-C$_8$H$_{11}$) with dppm or dppe in CH$_2$Cl$_2$ were also investigated as an alternative route to **1a**, **1b** and **2a**. The procedure was successful in the case of [Mo(CO)$_2$(dppm)(1–3:5,6-η-C$_8$H$_{11}$)][BF$_4$], **1a**, but in all other examples, the required product was formed as an inseparable mixture with the corresponding acetonitrile adduct [Mo(CO)$_2$(NCMe)(L$_2$)(η^3-C$_8$H$_{11}$)][BF$_4$] (L$_2$ = dppm or dppe) (see later).

In contrast with the chelate phosphine complexes, our attempts to form pentahapto-bonded cyclooctadienyl complexes starting from the 2,2′-bipyridine precursors [MoBr(CO)$_2$(bipy)(η^3-C$_8$H$_{11}$)] (η^3-C$_8$H$_{11}$ = 1–3-η:5,6-C$_8$H$_{11}$ or 1–3-η:4,5-C$_8$H$_{11}$) were unsuccessful. We were unable to characterise satisfactorily the products resulting from reaction of [MoBr(CO)$_2$(bipy)(η^3-C$_8$H$_{11}$)] with Ag[BF$_4$] but IR monitoring of the reaction mixtures revealed ν(CO) data more consistent with the retention of a trihapto bonding mode for the cyclooctadienyl ligand. A possible explanation for this is that the cyclooctadienylmolybdenum system behaves analogously to the acyclic pentadienyl complex [MoBr(CO)$_2$(bipy)(η^3-C$_5$H$_7$)] which affords anion-coordinated [Mo(σ-FBF$_3$)(CO)$_2$(bipy)(η^3-C$_5$H$_7$)] on reaction with Ag[BF$_4$].[14] In this respect, the chemistry of the cyclooctadienyl and cycloheptadienyl molybdenum systems shows a clear distinction, with the structure of the corresponding pentahapto-bonded cycloheptadienyl complex [Mo(CO)$_2$(bipy)(η^5-C$_7$H$_9$)][BF$_4$] established crystallographically.[7]

The existence of the cycloheptadienyl complexes [Mo(CO)$_2$(L$_2$)(η^5-C$_7$H$_9$)][BF$_4$] with monodentate P-donor ligands (L$_2$ = 2PPh$_3$ or 2P(OMe)$_3$) prompted an investigation of the synthesis of analogous cyclooctadienyl complexes. Our initial approach involved reaction of [Mo(CO)$_2$(NCMe)$_3$(η^3-C$_8$H$_{11}$)][BF$_4$] (η^3-C$_8$H$_{11}$ = 1–3-η:5,6-C$_8$H$_{11}$ or 1–3-η:4,5-C$_8$H$_{11}$) with two equivalents of PPh$_3$ or P(OMe)$_3$ in CH$_2$Cl$_2$, a strategy successfully applied in the analogous cycloheptadienylmolybdenum system. However, with the ligand PPh$_3$, this reaction led to the formation of mono-substituted products [Mo(CO)$_2$(NCMe)$_2$(PPh$_3$)(η^3-C$_8$H$_{11}$)][BF$_4$]; an analytical sample of [Mo(CO)$_2$(NCMe)$_2$(PPh$_3$)(1–3-η:4,5-C$_8$H$_{11}$)][BF$_4$], **3b**, was prepared by reaction of [Mo(CO)$_2$(NCMe)$_3$(1–3-η:4,5-C$_8$H$_{11}$)][BF$_4$] with one equivalent of PPh$_3$ in CH$_2$Cl$_2$ at 0 °C. Spectroscopic data (see ESI data, Tables S1 and S2†), particularly the magnitude of *J*(P–C) couplings to carbonyl carbons, suggest that **3b** adopts a structure in which PPh$_3$ is located *trans* to the cyclooctadienyl ring. Attempts to displace further NCMe ligands with PPh$_3$ were unsuccessful and, when **3b** was dissolved in NCMe, the tris nitrile complex [Mo(CO)$_2$(NCMe)$_3$(1–3-η:4,5-C$_8$H$_{11}$)][BF$_4$] was reformed, indicating a relatively weak attachment of the PPh$_3$ ligand. The reaction of the complexes [Mo(CO)$_2$(NCMe)$_3$(η^3-C$_8$H$_{11}$)][BF$_4$] with two equivalents of P(OMe)$_3$ also gave trihapto-bonded cyclooctadienyl products but in this case we were unable to establish the extent of substitution of NCMe by P(OMe)$_3$. An alternative strategy for the synthesis of [Mo(CO)$_2$(L$_2$)(η^5-C$_8$H$_{11}$)][BF$_4$] (η^5-C$_8$H$_{11}$ = 1–3:5,6-η-C$_8$H$_{11}$ or 1–5-η-C$_8$H$_{11}$; L$_2$ = 2PPh$_3$ or 2 P(OMe)$_3$) involves initial formation of [MoBr(CO)$_2$(L$_2$)(η^3-C$_8$H$_{11}$)] followed by halide

Table 1 Microanalytical, IR and mass spectroscopic data

Complex	Analysis[a] (%)			IR[b] ν(CO)/cm^{-1}	Mass spectral data
	C	H	N		
1a $[Mo(CO)_2(dppm)(1\text{–}3{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$	57.9 (57.6)	4.6 (4.6)		1998, 1897	645 (M^+), 615 ($[M - CO - 2H]^+$), 585 ($[M - 2CO - 4H]^+$)
1b $[Mo(CO)_2(dppm)(1\text{–}5\text{-}\eta\text{-}C_8H_{11})][BF_4]$	57.7 (57.6)	4.6 (4.6)		1996, 1930	645 (M^+), 615 ($[M - CO - 2H]^+$), 585 ($[M - 2CO - 4H]^+$)
2a $[Mo(CO)_2(dppe)(1\text{–}3{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]CH_2Cl_2$	53.7 (53.6)	4.3[d] (4.5)		1986, 1886	659 (M^+), 629 ($[M - CO - 2H]^+$), 599 ($[M - 2CO - 4H]^+$)
3b $[Mo(CO)_2(NCMe)_2(PPh_3)(1\text{–}3\text{-}\eta{:}4,5\text{-}C_8H_{11})][BF_4]$	55.6 (55.7)	4.3 (4.7)	3.9[e] (4.1)	1947, 1868	523 ($[M - 2NCMe]^+$), 465 ($[M - 2NCMe - 2CO - 2H]^+$)
4b $[Mo(CO)_2\{P(OMe)_3\}_2(1\text{–}5\text{-}\eta\text{-}C_8H_{11})][BF_4]$	32.1 (32.3)	4.8 (4.9)		2001, 1929	509 (M^+), 479 ($[M - CO - 2H]^+$), 451 ($[M - 2CO - 2H]^+$), 385 ($[M - P(OMe)_3]^+$), 355 ($[M - P(OMe)_3 - CO - 2H]^+$), 325 ($[M - P(OMe)_3 - 2CO - 4H]^+$)
5a $[Mo(CO)_2(CNBu^t)_2(1\text{–}3{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$	46.9 (46.9)	5.8 (5.7)	5.7 (5.5)	2013, 1919[f]	427 (M^+), 399 ($[M - CO]^+$), 369 ($[M - 2CO - 2H]^+$), 343 ($[M - CNBu^t]^+$), 313 ($[M - CNBu^t - CO - 2H]^+$), 286 ($[M - CNBu^t - 2CO - 2H]^+$)
6a $[Mo(CO)(CNBu^t)_3(1\text{–}3{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$	50.5 (50.8)	6.7 (6.8)	7.4 (7.4)	1888[f]	482 (M^+), 452 ($[M - CO - 2H]^+$), 369 ($[M - CO - CNBu^t - 2H]^+$)
6b $[Mo(CO)(CNBu^t)_3(1\text{–}5\text{-}\eta\text{-}C_8H_{11})][BF_4]$	50.1 (50.8)	6.4 (6.8)	7.6 (7.4)	1937[f]	482 (M^+), 454 ($[M - CO]^+$), 399 ($[M - CNBu^t]^+$), 369 ($[M - CO - CNBu^t - 2H]^+$)
7a $[Mo(CO)_2(\eta^4\text{-}C_7H_8)(1\text{–}3{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$	46.3 (46.6)	4.4 (4.4)		2033, 1967	353 (M^+), 325 ($[M - CO]^+$), 295 ($[M - 2CO - 2H]^+$)
8a $[Mo(CO)_2(NCMe)(dppm)(1\text{–}3\text{-}\eta{:}5,6\text{-}C_8H_{11})][BF_4]$	56.7 (57.6)	4.7 (4.7)	1.4 (1.8)	1958, 1871[g]	645 ($[M - NCMe]^+$), 615 ($[M - NCMe - CO - 2H]^+$), 585 ($[M - NCMe - 2CO - 4H]^+$), 482 ($[M - NCMe - 2CO - C_8H_{11}]^+$)
8b $[Mo(CO)_2(NCMe)(dppm)(1\text{–}3\text{-}\eta{:}4,5\text{-}C_8H_{11})][BF_4]$	57.4 (57.6)	4.9 (4.7)	1.9 (1.8)	1962, 1870[g]	645 ($[M - NCMe]^+$), 615 ($[M - NCMe - CO - 2H]^+$), 585 ($[M - NCMe - 2CO - 4H]^+$), 482 ($[M - NCMe - 2CO - C_8H_{11}]^+$)
9a $[Mo(CO)_2(NCMe)(dppe)(1\text{–}3\text{-}\eta{:}5,6\text{-}C_8H_{11})][BF_4]$	58.3 (58.1)	5.2 (4.9)	1.8 (1.8)	1947, 1864[g]	659 ($[M - NCMe]^+$), 629 ($[M - NCMe - CO - 2H]^+$), 599 ($[M - NCMe - 2CO - 4H]^+$), 496 ($[M - NCMe - 2CO - C_8H_{11}]^+$)
9b $[Mo(CO)_2(NCMe)(dppe)(1\text{–}3\text{-}\eta{:}4,5\text{-}C_8H_{11})][BF_4]$	57.6 (58.1)	5.4 (4.9)	2.0 (1.8)	1949, 1865[g]	659 ($[M - NCMe]^+$), 629 ($[M - NCMe - CO - 2H]^+$), 599 ($[M - NCMe - 2CO - 4H]^+$), 496 ($[M - NCMe - 2CO - C_8H_{11}]^+$)
10b $[Mo(CO)_3(dppm)(1\text{–}3\text{-}\eta{:}4,5\text{-}C_8H_{11})][BF_4]$	56.7 (57.0)	4.5 (4.4)		2044m, 1983m, 1948s	673 (M^+), 645 ($[M - CO]^+$), 615 ($[M - 2CO - 2H]^+$), 585 ($[M - 3CO - 4H]^+$), 482 ($[M - 3CO - C_8H_{11}]^+$)
11a $[Mo(CO)_3(dppe)(1\text{–}3\text{-}\eta{:}5,6\text{-}C_8H_{11})][BF_4]$	57.5 (57.5)	4.6 (4.6)		2039m, 1968m, 1939s	687 (M^+), 659 ($[M - CO]^+$), 629 ($[M - 2CO - 2H]^+$), 599 ($[M - 3CO - 4H]^+$), 496 ($[M - 3CO - C_8H_{11}]^+$)
11b $[Mo(CO)_3(dppe)(1\text{–}3\text{-}\eta{:}4,5\text{-}C_8H_{11})][BF_4]$	57.3 (57.5)	4.8 (4.6)		2039m, 1970 (sh), 1943s	687 (M^+), 659 ($[M - CO]^+$), 629 ($[M - 2CO - 2H]^+$), 599 ($[M - 3CO - 4H]^+$), 496 ($[M - 3CO - C_8H_{11}]^+$)
12a $[Mo(CO)(CNBu^t)_4(1\text{–}3\text{-}\eta{:}5,6\text{-}C_8H_{11})][BF_4]$	53.5 (53.5)	7.3 (7.3)	8.6 (8.6)	1890[f]	565 (M^+), 537 ($[M - CO]^+$), 482 ($[M - CNBu^t]^+$), 452 ($[M - CNBu^t - CO - 2H]^+$), 369 ($[M - 2CNBu^t - CO - 2H]^+$)
12b $[Mo(CO)(CNBu^t)_4(1\text{–}3\text{-}\eta{:}4,5\text{-}C_8H_{11})][BF_4]$	53.7 (53.5)	6.9 (7.3)	8.6 (8.6)	1896[f]	482 ($[M - CNBu^t]^+$), 452 ($[M - CNBu^t - CO - 2H]^+$), 369 ($[M - 2CNBu^t - CO - 2H]^+$)

[a] Calculated values in parentheses. [b] Solution spectra in CH_2Cl_2 unless stated otherwise, s = strong, m = medium, sh = shoulder. [c] FAB mass spectra, m/z values based on ^{98}Mo. [d] Cl 8.2 (8.6%). [e] P 4.8 (4.5%) [f] $\nu(CNBu^t)$ data (cm^{-1}): **5a** 2181, 2162; **6a** 2171, 2140; **6b** 2175, 215; **12a** 2175, 213; **12b** 2173, 2131. [g] In NCMe.

Table 2 ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR data for [Mo(CO)$_2$(L$_2$)(η^5-C$_8$H$_{11}$)]$^+$ and [Mo(CO)(L)$_3$(η^5-C$_8$H$_{11}$)]$^{+a}$

	^{1}H NMR			^{13}C{^{1}H} NMR			
	H$_{\text{dienyl}}$	H$_{\text{methylene}}$	L	CO	C$_{\text{dienyl}}$	C$_{\text{methylene}}$	L
1a^{b,e}	5.35, 1H, m, H^1; 5.08, 1H, at, H^2, *J*(H^2–H^1/H^3) 8; 4.95, 2H, m, H^3, H^6; 2.97, 1H, m, H^5	3.13, 1H, m, H$^{4,4'}$; 2.62, 2H, m, H$^{7,7'}$, H$^{8,8'}$; 2.32, 3H, m, H$^{4,4'}$, H$^{7,7'}$, H$^{8,8'}$	7.76–7.09, Ph; 5.14, 1H, m; 4.44, 1H, m, CH$_2$	227.2, dd, *J*(C–P) 27, 8; 218.1, dd	115.6, C^6; 103.6, C^2; 78.9, C^1; 70.8 C^3; 64.6, C^5	31.1, C^7; 27.8, C^8; 21.5, C^4	133.3–128.3, Ph; 41.7, t, *J*(P–C) 29, CH$_2$
2a^{b,c,d,e}	5.41, 1H, m, H^1; 5.03, 1H, at, H^2, *J*(H^2–H^1/H^3) 8; 4.93, 1H, m, H^3; 4.14, 1H, t, H^6, *J*(H^5–H^6) 8; 2.94, 1H, m, H^5	2.80, 1H, m, H$^{4,4'}$; 2.75, 1H, m, H$^{8,8'}$; 2.50, 1H, m, H$^{7,7'}$; 2.32, 1H, m, H$^{8,8'}$; 2.09, 1H, m, H$^{7,7'}$; 1.68, 1H, m, H$^{4,4'}$	7.65–7.34, Ph; 3.27, 1H, m, 3.13, 1H, m, 2.84, 1H, m, 2.70, 1H, m, CH$_2$	229.7, dd, 220.0, dd	118.9, C^6; 103.7, C^2; 77.4 C^1; 72.5 C^3; 63.9, C^5	31.0, C^7; 28.4, C^8; 21.6, C^4	135.3–128.7, Ph; 31.0, 27.4, m, CH$_2$
5a	5.47, 1H, m, H^1; 5.05 2H, m, H^3, H^6; 4.82, 1H, at, H^2, *J*(H^2–H^1/H^3) 8; 4.02, 1H, m, H^5	3.51, 1H, m, 3.42 1H, m, 2.60, 2H, m, 2.45, 2H, m, H$^{4,4'}$, H$^{7,7'}$, H$^{8,8'}$	1.70, 1.66, CNC*Me*$_3$	223.0, 217.7	113.3, C^6; 105.6, C^2; 83.1, 73.8, br, 66.0, C^{1,3,5}	32.2, C^7; 28.0, C^8; 23.8, C^4	151.6, 149.3, *C*NBu^t; 60.2, 60.0, CN*C*Me$_3$; 30.3, 30.1, CNC*Me*$_3$
6a^{d,e}	5.11, 1H, m, H^1; 4.64, 1H, at, H^2, *J*(H^2–H^1/H^3) 8; 4.46, 1H, m, H^6; 4.28, 1H, m, H^3; 3.36, 2H, m, H^5 and H$^{4,4'}$	3.36, 2H, m, H^5 and H$^{4,4'}$; 3.23, 1H, m, H$^{4,4'}$; 2.39, 3H, m, H$^{7,7'}$, H$^{8,8'}$; 2.28, 1H, m, H$^{8,8'}$	1.60, 1.59, 1.51, CNC*Me*$_3$	218.8	108.6, C^6; 104.7, C^2; 83.4, C^1; 65.1 C^3; 62.1, C^5	32.9, C^7; 28.2, C^8; 24.0, C^4	161.6, 159.9, 158.3, *C*NBu^t; 59.8, 59.6, 59.4, CN*C*Me$_3$; 30.8 CNC*Me*$_3$
7a^{d,e}	5.92, 1H, m, H^6; 5.04, 1H, at, H^2, *J*(H^2–H^1/H^3) 8; 4.99, 2H, m, H^1 and C$_7$H$_8$; 4.86, 1H, m, H^5; 4.25, 1H, m, H^3	3.76, 1H, m, H$^{4,4'}$; 3.60, 1H, m, H$^{4,4'}$; 2.63, 3H, m, H$^{7,7'}$, H$^{8,8'}$; 2.45, 1H, m, H$^{8,8'}$	5.41, 1H, m; 4.99, 2H, m, H$_5$ and C$_7$H$_8$; 4.08, 1H, m; 3.94, 1H, br,; 3.91, 1H, m; 3.87, 1H, br; 1.54, 1H, d; 1.43, 1H, d	218.6, 217.6	118.6, C^6; 106.5, C^2; 92.3, C^3; 78.7, 77.7, C^1 and C$_7$H$_8$; 65.4, C^5	31.6, C^7; 28.3, C^8; 22.2, C^4	78.7 and 77.7, C^1 and C$_7$H$_8$, 72.3, 62.1, 61.9, 50.6, 49.4
1b^{b,c,e}	5.97, 1H, m, H^3; 5.81, 1H, br, H^{2,4}; 4.61, 1H, br, H^{1,5}; 4.57, 1H, br, H^{1,5}; 3.96, 1H, m, H^{2,4}	2.56, 1H, br, 2.51, 1H, br, 2.13, 1H, br, 1.74, 1H, br, H$^{6,6'}$, H$^{8,8'}$; 1.26, 1H, br, 0.52, 1H, br, H$^{7,7'}$	7.97–6.90, Ph; 4.94, 1H, m, 4.28, 1H, m, CH$_2$	223.7, dd, *J*(C–P) 15, 7; 221.9, dd, *J*(C–P) 27, 7	106.9, C^3; 94.2, C^{2,4}; 93.6, C^{1,5}; 93.4, C^{2,4}; 69.8, C^{1,5}	28.8, 27.0, C^{6,8}; 18.7, C^7	134.0–129.3, Ph; 40.5, t, *J*(C–P) 27, CH$_2$
4b	6.54, 1H, t, H^3, *J*(H^3–H^{2,4}) 7; 4.79, 2H, br, H^{2,4}; 4.28, 2H, br, H^{1,5}	2.43, 2H, m, 1.84, 2H, m, H$^{6,6'}$, H$^{8,8'}$; 1.31, 1H, m, 0.65, 1H, m, H$^{7,7'}$	3.88 [d, *J*(H–P) 11)], P(OC*H*$_3$)$_3$	223.7, t, *J*(C–P) 33	110.6, C^3; 94.9, C^{2,4}; 81.7, C^{1,5}	28.3, C^{6,8}; 19.3, C^7	55.2, d, *J*(C–P) 8, P(O*C*H$_3$)$_3$
6b^{d,e}	6.15, 1H, t, H^3, *J*(H^3–H^{2,4}) 8; 4.76, 1H, at, H^{2,4}, *J*(H^{2,4}–H^3/H^{1,5}) 8; 4.56, 1H, at, H^{2,4}, *J*(H^{2,4}–H^3/H^{1,5}) 8; 4.10, 1H, m, H^{1,5}; 4.05, 1H, m, H^{1,5}	2.38, 2H, m, 1.62, 1H, m, 1.42, 1H, m, H$^{6,6'}$, H$^{8,8'}$; 1.12, 1H, m, 0.41, 1H, m, H$^{7,7'}$	1.61, 1.48, 1.41, CNC*Me*$_3$	229.7	111.2, C^3; 91.3, 91.2, C^{2,4}; 81.7, 71.7, C^{1,5}	30.4, 29.6, C^{6,8}; 19.8, C^7	157.6, br, *C*NBu^t; 59.6, 59.3, 58.9, CN*C*Me$_3$; 31.1, 30.9, 30.6, CNC*Me*$_3$

[a] 300 MHz ^{1}H, 75 MHz ^{13}C{^{1}H} NMR spectra unless stated otherwise; d = doublet, t = triplet, at = apparent triplet, m = multiplet, br = broad; chemical shifts downfield from SiMe$_4$, coupling constants in Hz; in CD$_2$Cl$_2$ solution unless stated otherwise, numbering as in Scheme 1(a) and (b). All spectra recorded at room temperature. [b] ^{31}P{^{1}H} NMR data: **1a**: δ −7.7, d, *J*(P–P) 58; −9.9, d, *J*(P–P) 58; **2a** (−20 °C): 68.1, d, *J*(P–P) 32; 62.2, d, *J*(P–P) 32; **1b**: −6.1, d, *J*(P–P) 60; −8.7, d, *J*(P–P) 60. [c] In CDCl$_3$ (^{13}C{^{1}H} only for **2a**). [d] 500 MHz ^{1}H NMR spectrum. [e] Assignments made with the aid of standard 2D techniques.

abstraction. Reaction of $[MoBr(CO)_2(NCMe)_2(\eta^3\text{-}C_8H_{11})]$ ($\eta^3\text{-}C_8H_{11}$ = 1–3-η:5,6-C_8H_{11} or 1–3-η:4,5-C_8H_{11}) with two equivalents of $P(OMe)_3$ in CH_2Cl_2 at −60 °C followed by slow warming to ambient temperature resulted in the formation of orange product solutions (IR: *ν*(CO)(CH_2Cl_2): $\eta^3\text{-}C_8H_{11}$ = 1–3-η:5,6-C_8H_{11}, 1956, 1869 cm^{-1}; 1–3-η:4,5-C_8H_{11}, 1977, 1940, 1854 cm^{-1}). These data may suggest the formation of $[MoBr(CO)_2\{P(OMe)_3\}_2(\eta^3\text{-}C_8H_{11})]$ but attempts to isolate these products as solids suitable for characterisation were unsuccessful resulting only in partially decomposed materials. However, in the case of the 1–3-η:4,5-C_8H_{11} derivative, further *in situ* reaction with $Ag[BF_4]$ in CH_2Cl_2 resulted in the formation of $[Mo(CO)_2\{P(OMe)_3\}_2(1\text{–}5\text{-}\eta\text{-}C_8H_{11})][BF_4]$, **4b**, which was isolated as a yellow solid following extensive purification. Attempts to employ an analogous synthesis of the PPh_3 derivatives $[Mo(CO)_2(PPh_3)_2(\eta^5\text{-}C_8H_{11})][BF_4]$ were unsuccessful.

We have previously described isocyanide derivatives of the cycloheptadienylmolybdenum system $[Mo(CO)_{3-n}(CNBu^t)_n(\eta^5\text{-}C_7H_9)]^+$ (*n* = 2 or 3)[7] and this suggested that analogous cyclooctadienylmolybdenum complexes might be accessible, albeit *via* different synthetic routes. In principle, the bis(isocyanide) complexes $[Mo(CO)_2(CNBu^t)_2(\eta^5\text{-}C_8H_{11})][BF_4]$ ($\eta^5\text{-}C_8H_{11}$ = 1–3:5,6-η-C_8H_{11}, **5a**, or 1–5-η-C_8H_{11}, **5b**) can be obtained *via* reaction of the appropriate $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_8H_{11})][BF_4]$ derivative with two equivalents of $CNBu^t$. However, the degree of substitution in $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_8H_{11})][BF_4]$ is difficult to control, with tris(isocyanide) products $[Mo(CO)_2(CNBu^t)_3(\eta^3\text{-}C_8H_{11})][BF_4]$ very readily formed. Therefore **5a** and **5b** were more conveniently prepared by treatment of the halide precursors $[MoBr(CO)_2(CNBu^t)_2(\eta^3\text{-}C_8H_{11})]$ with $Ag[BF_4]$ in CH_2Cl_2. Complex **5a** was isolated as an orange–red solid and fully characterised but the 1–5-η-C_8H_{11} derivative **5b** (IR, (CH_2Cl_2): *ν*(CN) 2182, 2163 cm^{-1}; *ν*(CO) 2029, 1964 cm^{-1}) could not obtained in a pure form. The tris(isocyanide) complexes $[Mo(CO)(CNBu^t)_3(\eta^5\text{-}C_8H_{11})][BF_4]$ ($\eta^5\text{-}C_8H_{11}$ = 1–3:5,6-η-C_8H_{11}, **6a**, or 1–5-η-C_8H_{11}, **6b**) were obtained by carbonyl elimination from the appropriate precursor derivative of $[Mo(CO)_2(CNBu^t)_3(\eta^3\text{-}C_8H_{11})][BF_4]$.[10] In practice, $[Mo(CO)_2(CNBu^t)_3(\eta^3\text{-}C_8H_{11})][BF_4]$ were generated *in situ* from the reaction of $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_8H_{11})][BF_4]$ with three equivalents of $CNBu^t$ and then converted directly to **6a**, **6b**. Both carbonyl eliminations are effected by gentle warming (30–40 °C) of $[Mo(CO)_2(CNBu^t)_3(\eta^3\text{-}C_8H_{11})][BF_4]$ in CH_2Cl_2 but, as we have noted previously,[10] the formation of **6a** will proceed slowly even at ambient temperature. Finally, we examined the synthesis of the diene complexes $[Mo(CO)_2(\eta^4\text{-nbd})(\eta^5\text{-}C_8H_{11})][BF_4]$ (nbd = norborna-2,5-diene) *via* reaction of $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_8H_{11})][BF_4]$ ($\eta^3\text{-}C_8H_{11}$ = 1–3-η:5,6-C_8H_{11} or 1–3-η:4,5-C_8H_{11}) with nbd in CH_2Cl_2; this method parallels that employed in the synthesis of the cycloheptadienyl analogue $[Mo(CO)_2(\eta^4\text{-nbd})(\eta^5\text{-}C_7H_9)][BF_4]$.[6] However, in the current work, the reactions were accompanied by extensive polymerisation of norbornadiene and only one example, $[Mo(CO)_2(\eta^4\text{-nbd})(1\text{–}3{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$, **7a**, was isolated successfully.

Structural and spectroscopic characterisation of pentahapto-bonded cyclooctadienylmolybdenum complexes

The complexes described above are the first examples both of 1–3:5,6-η-C_8H_{11} and 1–5-η-C_8H_{11} ligands coordinated to molybdenum and therefore merit a full structural investigation. Moreover, structurally characterised examples of complexes containing the 1–3:5,6-η-C_8H_{11} ligand are very scarce, irrespective of the identity of the metal. Therefore X-ray structural characterisations were carried out on two representative complexes, $[Mo(CO)_2(dppm)(1\text{–}3{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$, **1a**, and $[Mo(CO)(CNBu^t)_3(1\text{–}5\text{-}\eta\text{-}C_8H_{11})][BF_4]$, **6b**. The key features of interest are the ring conformation, the metal to cyclooctadienyl ligand bond distances and the orientation of the MoL_4 unit with respect to the cyclooctadienyl ring. The molecular configurations, annotated with crystallographic numbering schemes, and tables of important bond lengths and angles are given in: Fig. 1, Table 3, **1a**; Fig. 2, Table 4, **6b**.

Table 3 Important bond lengths (Å) and angles (°) for complex **1a**

Mo–P(1)	2.484(2)	C(10)–O(10)	1.138(10)
Mo–P(2)	2.519(2)	C(1)–C(2)	1.52(1)
Mo–C(2)	2.495(7)	C(2)–C(3)	1.32(1)
Mo–C(3)	2.576(7)	C(3)–C(4)	1.50(1)
Mo–C(6)	2.350(7)	C(4)–C(5)	1.44(1)
Mo–C(7)	2.329(8)	C(5)–C(6)	1.49(1)
Mo–C(8)	2.482(8)	C(6)–C(7)	1.42(1)
Mo–C(9)	1.935(8)	C(7)–C(8)	1.37(1)
Mo–C(10)	2.010(8)	C(8)–C(1)	1.49(1)
C(9)–O(9)	1.157(10)		
P(1)–Mo–P(2)	67.95(6)	C(1)–C(2)–C(3)	122.5(7)
C(9)–Mo–C(10)	86.2(3)	C(2)–C(3)–C(4)	125.2(8)
P(1)–Mo–C(9)	92.3(2)	C(3)–C(4)–C(5)	120.6(8)
P(1)–Mo–C(10)	82.5(2)	C(4)–C(5)–C(6)	120.6(8)
P(2)–Mo–C(9)	84.1(2)	C(5)–C(6)–C(7)	126.4(7)
P(2)–Mo–C(10)	148.3(2)	C(6)–C(7)–C(8)	128.1(8)
Mo–C(9)–O(9)	177.1(6)	C(7)–C(8)–C(1)	131.3(7)
Mo–C(10)–O(10)	175.7(7)	C(8)–C(1)–C(2)	109.5(7)

In the complex $[Mo(CO)_2(dppm)(1\text{–}3{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$, **1a**, the 1–3:5,6-η-$C_8H_{11}$ ligand is attached to molybdenum through an η^3-allyl system [C(6)–C(8)] (crystallographic numbering

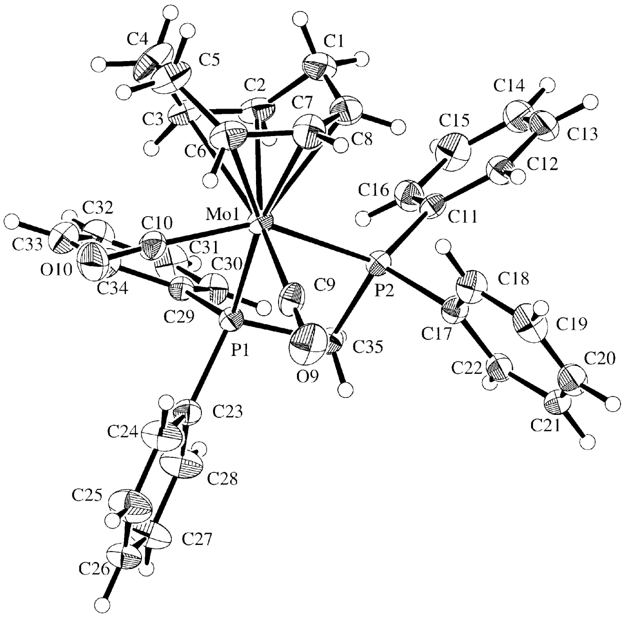


Fig. 1 Molecular structure of complex **1a**; BF_4 counter anion omitted.

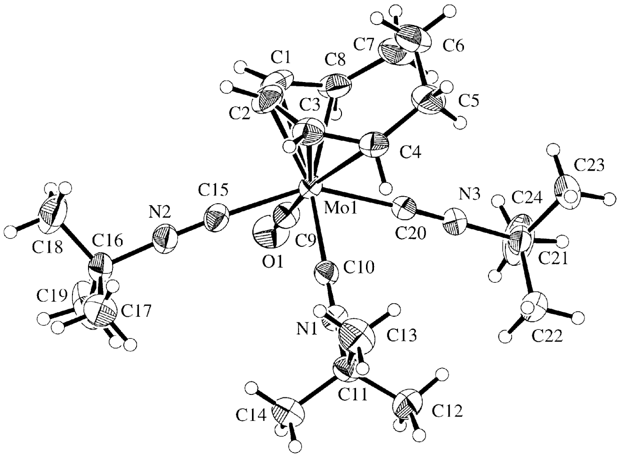


Fig. 2 Molecular structure of complex **6b**; BF_4 counter anion omitted.

Table 4 Important bond lengths (Å) and angles (°) for complex **6b**

Mo–C(1)	2.300(6)	C(15)–N(2)	1.133(8)
Mo–C(2)	2.307(5)	C(20)–N(3)	1.142(6)
Mo–C(3)	2.300(5)	C(1)–C(2)	1.391(9)
Mo–C(4)	2.422(6)	C(2)–C(3)	1.413(9)
Mo–C(8)	2.359(6)	C(3)–C(4)	1.404(8)
Mo–C(9)	1.974(6)	C(4)–C(5)	1.494(9)
Mo–C(10)	2.095(5)	C(5)–C(6)	1.494(10)
Mo–C(15)	2.108(7)	C(6)–C(7)	1.496(10)
Mo–C(20)	2.113(5)	C(7)–C(8)	1.490(9)
C(9)–O(1)	1.140(7)	C(8)–C(1)	1.412(9)
C(10)–N(1)	1.145(6)		
C(9)–Mo–C(10)	102.5(2)	Mo–C(20)–N(3)	178.0(5)
C(9)–Mo–C(15)	78.5(2)	C(1)–C(2)–C(3)	129.2(6)
C(9)–Mo–C(20)	82.7(2)	C(2)–C(3)–C(4)	128.2(6)
C(10)–Mo–C(15)	78.4(2)	C(3)–C(4)–C(5)	128.6(5)
C(10)–Mo–C(20)	80.6(2)	C(4)–C(5)–C(6)	117.0(6)
C(15)–Mo–C(20)	147.9(2)	C(5)–C(6)–C(7)	112.9(6)
Mo–C(9)–O(1)	179.1(5)	C(6)–C(7)–C(8)	118.4(6)
Mo–C(10)–N(1)	174.0(4)	C(7)–C(8)–C(1)	125.5(6)
Mo–C(15)–N(2)	174.5(5)	C(8)–C(1)–C(2)	127.6(6)

scheme), and an isolated alkene unit [C(2)–C(3)] and these five coordinated atoms are approximately coplanar (mean deviation 0.056 Å). The non-bonded methylene carbons [C(1), C(4) and C(5)] are folded away from the metal centre giving a boat conformation of the C_8H_{11} ligand with interplanar angles [C(3)–C(4)–C(5)–C(6)]–[C(2)–C(3)/C(6)–C(7)–C(8)] 55°; [C(2)–C(1)–C(8)]–[C(2)–C(3)/C(6)–C(7)–C(8)] 54°. Similar boat conformations of the 1–3:5,6-η-C_8H_{11} ligand are observed in each of the reported examples [Ru(1–3:5,6-η-C_8H_{11})(η^6-C_8H_{10})][PF_6],[16] [Ru(1–3:5,6-η-C_8H_{11})(η^6-$C_6H_5BX_3$)] (X = Ph or F),[17] [Ru(1,4,7-trithiacyclononane)(1–3:5,6-η-C_8H_{11})][PF_6][18] and [{Ir(μ-Cl)-(σ-$CCF_3C(H)CF_3$)(1–3:5,6-η-C_8H_{11})}$_2$].[19] Carbon–carbon bond lengths within the cyclooctadienyl ring compare reasonably well with other examples, with the C(2)–C(3) carbon–carbon double bond shortest as expected. A comparison of metal to ring carbon distances for complexes of the 1–3:5,6-η-C_8H_{11} ligand is presented in Table 5 (ring numbering system adjusted to that employed in this work). Two features of interest emerge. First, in common with some other reported structures, there is an elongation of the Mo–C(8) distance leading to an asymmetric Mo–(η^3-allyl) interaction. Secondly, the average Mo to alkene distance [Mo–C(2), Mo–C(3)] is *ca.* 0.15 Å longer than the average Mo to allyl carbon distance and also *ca.* 0.12 Å longer than the average molybdenum to alkene carbon distance in [Mo(CO)$_4$(η^4-nbd)] (Mo to alkene carbon distances (Å) 2.401(2), 2.407(2), 2.422(3), 2.434(2)).[20] Only for [{Ir(μ-Cl)-(σ-$CCF_3C(H)CF_3$)(1–3:5,6-η-C_8H_{11})}$_2$] is a similar elongation of the metal to alkene carbon bond distances observed. It has been suggested that the 1–3:5,6-η-C_8H_{11} ligand is a sterically demanding group with an estimated ligand cone angle of 196° (*cf.* 1–5-η-C_8H_{11}, 159°) and in complexes of the type [RuL$_3$-(η^5-C_8H_{11})]$^+$, sterically demanding ligands L appear to promote adoption of the 1–5-η-C_8H_{11} form.[16] In half-sandwich molybdenum complexes of the type [MoL$_4$(η^5-C_8H_{11})]$^+$, we have not observed interchange of 1–3:5,6-η-C_8H_{11} and 1–5-η-C_8H_{11} forms, but suggest that the elongation of metal to alkene carbon distances is an alternative response to the steric requirements of the 1–3:5,6-η-C_8H_{11} ligand, especially in cases where the MoL$_4$ unit incorporates a sterically demanding ligand such as dppm.

The Mo(CO)$_2$(dppm) unit of **1a** adopts a distorted square-based pyramidal arrangement, very similar to that observed in the related cycloheptadienyl complex [Mo(CO)$_2$(dppm)-(η^5-C_7H_9)][BF_4].[6] Thus the two complexes exhibit P–Mo–CO bond angles comparable to within ±5° and non-bonded ligand-to-dienyl plane distances are also very similar (P-ligand donor atom to dienyl plane distances (Å), **1a**: 2.82, 3.66; [Mo(CO)$_2$-(dppm)(η^5-C_7H_9)][BF_4]: 3.04, 3.64; carbonyl ligand donor atom to dienyl plane distances (Å), **1a**: 1.94, 2.96; [Mo(CO)$_2$-(dppm)(η^5-C_7H_9)][BF_4]: 1.92, 2.93). The preferred orientation of the ML$_4$ unit with respect to the dienyl ligand is a subject of considerable interest. There are no previous examples of complexes of the type [ML$_4$(1–3:5,6-η-C_8H_{11})]$^{n+}$ for comparison but, in **1a**, the P(2)–Mo–C(10) axis roughly bisects the 1–3:5,6-η-C_8H_{11} ligand along C(1) and the mid-point of C(4)–C(5) whilst the carbonyl carbon C(9) is located under the allyl unit, C(6)–C(8). Significantly, P(1) lies under the alkene unit C(2)–C(3) consistent with sterically induced elongation of the Mo–C(2) and Mo–C(3) bond lengths.

In the complex [Mo(CO)(CNBu^t)$_3$(1–5-η-C_8H_{11})][BF_4], **6b**, the cyclooctadienyl ligand is attached to Mo through the dienyl carbons C(8)–C(1)–C(2)–C(3)–C(4) (crystallographic numbering scheme) which are roughly coplanar. In common with the majority of structurally characterised examples of this ligand,[16,21,22] the 1–5-η-C_8H_{11} ring may be considered as folded into three planes defined by C(8)–C(1)–C(2)–C(3)–C(4), C(4)–C(5)–C(7)–C(8) and C(5)–C(6)–C(7) (respective interplanar angles as defined in ref. 23: α = 133°, β = 58° measured on the face of the ligand remote from the Mo centre). The metal to ring-carbon bonding distances also comply with a general pattern in which the molybdenum to terminal dienyl carbon distances Mo–C(4) and Mo–C(8) are elongated by comparison with the bonds to C(1)–C(3). The average elongation of approximately 0.1 Å is very similar to that observed for [Mo(CO)$_2$L$_2$(η^5-C_7H_9)]$^+$ (L$_2$ = dppm,[6] bipy[7]) and [Ru(PMe$_2$-Ph)$_3$(1–5-η-C_8H_{11})]$^+$.[16] However, a more detailed comparison of the structural parameters of the dienyl ligand in [Mo(CO)$_2$-(bipy)(η^5-C_7H_9)][BF_4] and **6b** reveals some significant differences. An obvious impact of the additional methylene group in the edge-bridge of the cyclooctadienyl ligand is to increase the separation between the terminal dienyl carbons. Thus in **6b**, the non-bonded, transannular separations are C(1)–C(3): 2.54(1) Å, C(4)–C(8): 3.15(1) Å. The corresponding distances for the dienyl unit of the cycloheptadienyl ring in [Mo(CO)$_2$-(bipy)(η^5-C_7H_9)][BF_4][7] are 2.53(1) and 2.92(1) Å, respectively. A second effect is evident in a folding of the plane of the η^5-dienyl unit. In **6b**, the dienyl unit is folded about C(1) and C(3) with an interplanar angle [C(1)–C(2)–C(3) to C(1)–C(3)–C(4)–C(8)] of 9.6° (towards the high end of previously reported values[4]) but, by contrast, the corresponding fold in the cycloheptadienyl ring of [Mo(CO)$_2$(bipy)(η^5-C_7H_9)][BF_4] is just 3.5°.

In common with other complexes of formulation [ML′$_3$L″-(η^5-dienyl)]$^{n+}$, ([ReH(PMe$_2$Ph)$_3$(η^5-2,4-Me$_2$-pentadienyl)]$^+$,[24] [Nb(CO)$_3$(PMe$_2$Ph)(η^5-2,4-Me$_2$-pentadienyl)][25] and [V(CO)$_3$-

Table 5 Comparison of metal–ligand bonding distances (Å) in complexes of the 1–3:5,6-η-C_8H_{11} (L) ligand[a]

M–C distance	**1a**	[Ru(L)(η^6-C_8H_{10})]$^+$	[Ru(L)(η^6-$C_6H_5BPh_3$)]	[Ru(L)(9-S-3)]$^+$	[{Ir(μ-Cl)(σ-$CCF_3C(H)CF_3$)(L)}$_2$]
M–C(2)	2.49	2.31	2.16	2.21	2.35
M–C(3)	2.58	2.26	2.18	2.19	2.37
M–C(6)	2.35	2.21	2.23	2.23	2.18
M–C(7)	2.33	2.20	2.23	2.19	2.13
M–C(8)	2.48	2.46	2.69	2.42	2.19

[a] Data from refs. 16–19; atom numbering scheme for the 1–3:5,6-η-C_8H_{11} ligand adjusted to that employed in the current work. 9-S-3 = 1,4,7-trithiacyclononane.

Table 6 IR data (ν(CO)/cm^{-1}), for $[Mo(CO)_2(L_2)(\eta^5\text{-dienyl})]^+$[a]

	η^5-Dienyl		
L_2	C_7H_9	1–5-η-C_8H_{11}	1–3:5,6-η-C_8H_{11}
dppe[b]	2008, 1991 (sh), 1922	1988, 1919[c]	1986, 1886
dppm	2014, 1924	1996, 1930	1998, 1897
2 $P(OMe)_3$	2002, 1931	2001, 1929	—
2 $CNBu^t$	2030, 1963	2029, 1964[c]	2013, 1919
nbd	2037, 1990	—	2033, 1967

[a] Solution spectra in CH_2Cl_2. [b] Comparative data for analogous dienyl systems, ν(CO)/cm^{-1}, CH_2Cl_2: closed, cyclic, $[Mo(CO)_2(dppe)(\eta\text{-}C_5H_5)]^+$, 1995, 1928;[27] open, acyclic, $[Mo(CO)_2(dppe)(\eta\text{-}C_5H_7)]^+$, 1980, 1930.[13] [c] Complex not isolated.

Table 7 Comparison of ^{1}H and $^{13}C\{^1H\}$ NMR data for Mo and Ru complexes of 1–3:5,6-η-C_8H_{11} and 1–5-η-C_8H_{11} ligands[a]

	^{1}H NMR								$^{13}C\{^1H\}$ NMR							
Complex	H^1	H^2	H^3	H^4	H^5	H^6	H^7	H^8	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8
6a	5.11	4.64	4.28	3.36, 3.23	3.36	4.46	2.39	2.39, 2.28	83.4	104.7	65.1	24.0	62.1	108.6	32.9	28.2
A	3.95	3.93	3.55	2.96, 2.93	3.16	4.55	2.33, 2.27	2.05, 1.80	68.1	99.5	37.1	20.7	62.0	104.9	35.0	27.0
4b	4.28	4.79	6.54			2.43, 1.84	1.31, 0.65		81.7	94.9	110.6			28.3	19.3	
B	3.48	4.77	6.27			2.03, 1.72	1.16, 0.34		53.2	94.4	99.0			26.1	19.4	

[a] Complex **A** = $[Ru(CNBu^t)_3(1\text{–}3\text{:}5,6\text{-}\eta\text{-}C_8H_{11})]^+$ in $CDCl_3$, complex **B** = $[Ru\{P(OMe)_3\}_3(1\text{–}5\text{-}\eta\text{-}C_8H_{11})]^+$ in $(CD_3)_2CO$, data from ref. 16; complexes **6a** and **4b** in CD_2Cl_2; numbering as in Scheme 1(a) and (b); in the 1–5-η-C_8H_{11} ligand, pairs of carbons or protons [(2 with 4), (1 with 5) and (6 with 8)] are equivalent.

$(PMe_2Ph)(\eta^5\text{-}C_5H_7)]$),[26] the 1–5-$\eta$-$C_8H_{11}$ ring of **6b**, orientates itself above the ML'_3L'' fragment such that two of the metal–ligand bonds lie in the vertical mirror plane bisecting the dienyl ligand. In **6b**, $CNBu^t$ ligands are placed beneath the central dienyl carbon C(2) and the centre of the edge bridge C(6). This locates a $CNBu^t$ and carbonyl ligand beneath the bonds C(3)–C(4) and C(1)–C(8), respectively, and thereby imposes an asymmetry upon the molecular structure in contrast to other reported examples of the type $[ML'_3L''(\eta^5\text{-dienyl})]^{n+}$.

IR spectroscopic data for $[Mo(CO)_2(L_2)(\eta^5\text{-}C_8H_{11})]^+$ (Table 1) are generally consistent with a *cis* arrangement of carbonyl ligands with the exception of the $P(OMe)_3$ derivative **4b** and possible exceptions of $[Mo(CO)_2(CNBu^t)_2(\eta^5\text{-}C_8H_{11})][BF_4]$, ($\eta^5$-$C_8H_{11}$ = 1–3:5,6-η-C_8H_{11} **5a**, or 1–5-η-C_8H_{11}, **5b**). In the case of **4b**, the relative intensities of the two ν(CO) bands are clearly indicative of a *trans* arrangement of CO ligands. A similar pattern is observed for **5b** (for both ν(CO) and ν(CN)) but we were unable to isolate this complex in a pure form to permit further investigations. By contrast, the 1–3:5,6-η-C_8H_{11} derivative **5a**, exhibited relative intensity patterns for ν(CO) and ν(CN) bands more typical of a *cis* ligand arrangement although, as with $[Mo(CO)_2(CNBu^t)_2(\eta^5\text{-}C_7H_9)]^+$,[6] there was some evidence in the $^{13}C\{^1H\}$ NMR spectrum of **5a** for the presence of two species, albeit with one in very low relative abundance.

Table 6 presents a comparison of ν(CO) data for the series of complexes $[Mo(CO)_2(L_2)(\eta^5\text{-dienyl})]^+$ (dienyl = 1–5-η-C_7H_9, 1–5-η-C_8H_{11} or 1–3:5,6-η-C_8H_{11}) classified by the dienyl ligand and the supporting ligand(s) L_2. Two conclusions can be drawn concerning the influence of the dienyl ligand. First, comparison of the authentic η^5-dienyl ligands 1–5-η-C_7H_9 and 1–5-η-C_8H_{11} reveals little difference in ν(CO) data with the relatively small exception of L_2 = dppm, dppe. This suggests that exchange of 1–5-η-C_7H_9 for 1–5-η-C_8H_{11} does not have a major electronic influence upon the Mo centre despite the additional methylene group in the edge bridge of the cyclooctadienyl ligand. By contrast, exchange of 1–5-η-C_8H_{11} for 1–3:5,6-η-C_8H_{11} results in a shift in $\nu(CO)_{average}$ to lower wavenumber by *ca.* 15–30 cm^{-1} and an increase in the separation of the carbonyl bands by *ca.* 30 cm^{-1}. It seems therefore that the 1–3:5,6-η-C_8H_{11} ligand, with isolated η^3-allyl and η^2-alkene groups, acts as a better net electron donor to the Mo centre than the isomeric 1–5-C_8H_{11} system. For comparison, IR data for $[Mo(CO)_2(dppe)(\eta^5\text{-pentadienyl})]^+$[13] and $[Mo(CO)_2(dppe)(\eta\text{-}C_5H_5)]^+$,[27] are also included in Table 6 but the differences in ν(CO) are relatively small and, in contrast to $[V(CO)(\eta^5\text{-dienyl})_2]$,[4] no significant trend emerges.

The NMR data in Table 2 are arranged to facilitate comparison between complexes of each specific ligand type; thus complexes of the 1–3:5,6-η-C_8H_{11} ligand (**1a**, **2a**, **5a**–**7a**) are presented first followed by those of the 1–5-η-C_8H_{11} ligand (**1b**, **4b**, **6b**). The spectroscopic numbering scheme is shown in Scheme 1(a) and (b). In the majority of cases the spectral assignments were fully elucidated with the aid of [^{1}H–^{1}H] COSY and [^{1}H–^{13}C] HETCOR experiments. Table 7 presents a comparison of ^{1}H and $^{13}C\{^1H\}$ NMR data for $[Mo(CO)(CNBu^t)_3(1\text{–}3\text{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$ **6a**, and $[Mo(CO)_2\{P(OMe)_3\}_2(1\text{–}5\text{-}\eta\text{-}C_8H_{11})][BF_4]$, **4b**, with the related cyclooctadienylruthenium half-sandwich complexes $[Ru(CNBu^t)_3(1\text{–}3\text{:}5,6\text{-}\eta\text{-}C_8H_{11})][PF_6]$ and $[Ru\{P(OMe)_3\}_3(1\text{–}5\text{-}\eta\text{-}C_8H_{11})][PF_6]$.[16] First, it is clear that the NMR data for a specific cyclooctadienyl ring type correlate well, independent of the identity of the attached metal centre. The exceptions to this are most apparent in the $^{13}C\{^1H\}$ NMR spectra. For the 1–3:5,6-η-C_8H_{11} ligand, the terminal allyl carbon C^3 is significantly more shielded in the Ru system and again for the 1–5-η-C_8H_{11} ligand, the terminal dienyl carbons $C^{1,5}$ are shielded in the Ru complex by comparison with **4b**. However comparison of $^{13}C\{^1H\}$ NMR data for **4b** with that of its cycloheptadienyl analogue $[Mo(CO)_2\{P(OMe)_3\}_2(\eta^5\text{-}C_7H_9)][BF_4]$ (see Experimental section) reveals that the terminal dienyl carbons of the latter complex have an additional low field shift of *ca.* 10 ppm.

The remainder of the discussion will focus on the complexes **1b**, **4b** and **6b** which contain the 1–5-η-C_8H_{11} ligand. In principle, the ligand is bisected by a plane of symmetry and therefore, assuming either free rotation of the MoL_4 unit or alternatively a symmetrical orientation of a static MoL_4 unit with respect to the ring, it might be expected that only five ring carbon environments would be observed in the $^{13}C\{^1H\}$ NMR spectrum. However, this is the case only for **4b**. For **1b** and **6b**, it is clear that the two sides of the cyclooctadienyl ring are distinct and eight discrete ring carbon resonances are detected. This observation can be rationalised by a combination of two factors: first a high activation barrier to rotation of the MoL_4 group and secondly a preferred asymmetric orientation of the MoL_4 unit with respect to the 1–5-η-C_8H_{11} ring. It is well established that the 1–5-η-C_8H_{11} ligand presents a relatively high activation barrier with respect to rotation of an attached ML_n group[23] and moreover, in **6b**, we have demonstrated crystallographically that the $Mo(CO)(CNBu^t)_3$ unit is located to exclude a symmetry plane through the molecule. Therefore, for **6b**, retention of the solid state structure in solution could rationalise the observed NMR data. Furthermore, we suggest that the same constraints operate for $[Mo(CO)_2\{P(OMe)_3\}_2$-(1–5-η-C_8H_{11})][BF_4], **4b**. The distinction here is that the two $P(OMe)_3$ ligands are mutually *trans* and therefore, assuming that the MoL_4 unit is orientated with respect to the 1–5-η-C_8H_{11} ligand as in **6b**, a symmetry plane through the cyclooctadienyl ligand will be retained without the need for averaging by rotation of the MoL_4 unit. Finally, in **1b**, a static, asymmetric $Mo(CO)_2$(dppm) unit would exclude a symmetry plane through the molecule. In fact $^{31}P\{^1H\}$ NMR investigations on **1b** confirm two discrete phosphorus environments at 25 °C in contrast to the cycloheptadienyl analogue $[Mo(CO)_2(dppm)(\eta^5\text{-}C_7H_9)][BF_4]$ which exhibits a singlet resonance in the $^{31}P\{^1H\}$ NMR spectrum at 25 °C; only on cooling to −20 °C are two separate phosphorus environments observed. Moreover, the ^1H and $^{13}C\{^1H\}$ NMR spectra of $[Mo(CO)_2(dppm)(\eta^5\text{-}C_7H_9)][BF_4]$ are broad at ambient temperature but low-temperature spectra are consistent with an asymmetric structure in which all C_7H_9 ring resonances are inequivalent.[6] We suggest that the contrast in the ambient temperature NMR spectra of $[Mo(CO)_2(dppm)(\eta^5\text{-dienyl})][BF_4]$ (dienyl = C_7H_9 or 1–5-η-C_8H_{11}) is a clear example of the effect of increasing the size of the edge-bridge of the dienyl ligand upon the activation energy to rotation of the attached ML_n unit and that our results are in accord with theoretical predictions.[23]

$\eta^5 \longrightarrow \eta^3$ Hapticity interconversion reactions of $[Mo(CO)_2(L_2)(\eta^5\text{-}C_8H_{11})]^+$ ($\eta^5\text{-}C_8H_{11}$ = 1–3:5,6-η-C_8H_{11} or 1–5-η-C_8H_{11})

It is well established that the identity of the dienyl ligand has a marked effect on the facility of $\eta^5 \longrightarrow \eta^3$ hapticity changes promoted by ligand addition at the metal centre. Thus "open" acyclic pentadienyl ligands undergo hapticity interconversions much more readily than "closed", cyclic dienyls such as the cyclopentadienyl ligand. Edge-bridged dienyls appear to have properties intermediate between those of the "open" acyclic and "closed" cyclic systems and the purpose of the current work was to fit the cyclooctadienyl ligand into this pattern.

The reactions examined are of the general type:

$$[Mo(CO)_2(L_2)(\eta^5\text{-}C_8H_{11})]^+ + L' \longrightarrow [Mo(CO)_2(L')(L_2)(\eta^3\text{-}C_8H_{11})]^+ \quad (1)$$

where L′ (NCMe, CO or $CNBu^t$) promotes hapticity conversion between the η^5 and η^3 bonding modes of the cyclooctadienyl ligand. The principal objectives of our investigations were:

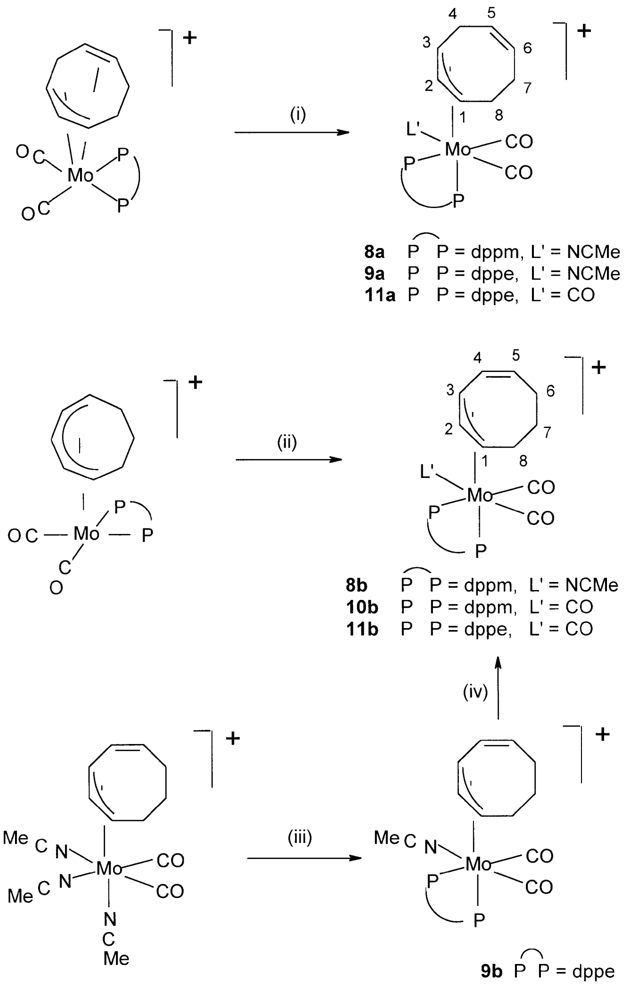
(i) to compare the facility with which directly analogous $\eta^5\text{-}C_7H_9$ and 1–5-η-C_8H_{11} complexes undergo $\eta^5 \longrightarrow \eta^3$ hapticity conversions, thus allowing an assessment of the effect of an additional methylene group in the edge bridge,

(ii) to determine the effect of different conjugation patterns in the cyclooctadienyl ring (1–3:5,6-η-C_8H_{11} *vs.* 1–5-η-C_8H_{11}) on $\eta^5 \longrightarrow \eta^3$ conversions processes and

(iii) to examine the effect of the supporting ligand(s) L_2.

The majority of the useful results in addressing these objectives was obtained with the chelate phosphine derivatives $[Mo(CO)_2(L_2)(\eta^5\text{-}C_8H_{11})]^+$ ($\eta^5\text{-}C_8H_{11}$ = 1–3:5,6-η-C_8H_{11}, L_2 = dppm, **1a**, L_2 = dppe, **2a**; $\eta^5\text{-}C_8H_{11}$ = 1–5-η-C_8H_{11}, L_2 = dppm, **1b**) and therefore these reactions, as summarised in Scheme 2, are discussed first.

When **1a**, **2a** and **1b** were dissolved in NCMe, the respective mono-acetonitrile adducts $[Mo(CO)_2(NCMe)(L_2)(\eta^3\text{-}C_8H_{11})][BF_4]$ ($\eta^3\text{-}C_8H_{11}$ = 1–3-η:5,6-C_8H_{11}, L_2 = dppm, **8a**, L_2 = dppe, **9a**; $\eta^3\text{-}C_8H_{11}$ = 1–3-η:4,5-C_8H_{11}, L_2 = dppm, **8b**) were fully formed (as monitored by IR spectroscopy). The complexes were isolable as stable yellow to orange solids with the exception of **8a** which very readily dissociates NCMe. The formal acetonitrile adduct of $[Mo(CO)_2(dppe)(1\text{–}5\text{-}\eta\text{-}C_8H_{11})]^+$, i.e. $[Mo(CO)_2(NCMe)(dppe)(1\text{–}3\text{-}\eta\text{:}4,5\text{-}C_8H_{11})][BF_4]$, **9b**, was also synthesised by reaction of $[Mo(CO)_2(NCMe)_3(1\text{–}3\text{-}\eta\text{:}4,5\text{-}C_8H_{11})][BF_4]$ with dppe in acetonitrile. These isolable products present a contrast with the analogous cycloheptadienyl system; $[Mo(CO)_2(dppe)(\eta^5\text{-}C_7H_9)]^+$ dissolves in NCMe to form an equilibrium mixture with $[Mo(CO)_2(NCMe)(dppe)(\eta^5\text{-}C_7H_9)]^+$ and $[Mo(CO)_2(dppm)(\eta^5\text{-}C_7H_9)]^+$ does not react with NCMe.[6,7]



Scheme 2 Reagents and conditions: (i)/(ii) L′ = NCMe, stir in NCMe, 1 h; L′ = CO, stir in CH_2Cl_2 with passage of CO gas, **11a**, 3 h, 0 °C; **10b**, 25 min, ambient temperature; (iii) dppe in NCMe, 1.5 h stirring; (iv) L′ = CO, stir in CH_2Cl_2 with passage of CO gas, 45 min.

The relative ease of formation of the acetonitrile adducts, **8a**, **8b** and **9a** suggested that other ligands, not employed for the cycloheptadienyl analogues, might drive $\eta^5 \longrightarrow \eta^3$ conversions in the cyclooctadienyl system. Accordingly, passage of CO gas through CH_2Cl_2 solutions of **1b** and **2a** led to the respective isolation of the tricarbonyl complexes $[Mo(CO)_3(dppm)(1\text{–}3\text{-}\eta\text{:}4,5\text{-}C_8H_{11})][BF_4]$ **10b** and $[Mo(CO)_3(dppe)(1\text{–}3\text{-}\eta\text{:}5,6\text{-}C_8H_{11})][BF_4]$ **11a**. The complex $[Mo(CO)_3(dppe)(1\text{–}3\text{-}\eta\text{:}4,5\text{-}C_8H_{11})][BF_4]$, **11b** (the formal CO adduct of $[Mo(CO)_2(dppe)(1\text{–}5\text{-}\eta\text{-}C_8H_{11})][BF_4]$) was also prepared by reaction of **9b** with CO in CH_2Cl_2 and identified as the product of the attempted preparation of $[Mo(CO)_2(dppe)(1\text{–}5\text{-}\eta\text{-}C_8H_{11})][BF_4]$ from $[MoBr(CO)_2(dppe)(1\text{–}3\text{-}\eta\text{:}4,5\text{-}C_8H_{11})]$ and $Ag[BF_4]$. By contrast, complex **1a** was unreactive towards CO, a result consistent with the relatively poor stability of **8a** (the NCMe adduct of **1a**).

Characterisation details for the new complexes [Mo(CO)$_2$(L′)(L$_2$)(η^3-C$_8$H$_{11}$)]$^+$ are given in Table 1 (microanalytical, IR and mass spectroscopic data) and Tables S1 (^{1}H, ^{31}P{^{1}H} NMR data) and S2 (^{13}C{^{1}H} NMR data).† We have previously discussed the important features of the NMR spectra of trihapto-bonded cyclooctadienylmolybdenum systems[10] and therefore limit this discussion to issues specific to the complexes [Mo(CO)$_2$(L′)(L$_2$)(η^3-C$_8$H$_{11}$)]$^+$ described here. In common with other systems of the type [Mo(CO)$_2$(L′)(L$_2$)(η^3-R)]$^+$, (L$_2$ = chelate P-donor ligand, R = η^3-allyl[28,29] or η^3-dienyl[7,13]), spectroscopic data for complexes **8**–**11** are consistent with a structure in which one P-donor atom is located *trans* to the cyclooctadienyl ligand; ^{31}P{^{1}H} NMR data for **9b** and **10b** reveal, in each case, two discrete phosphorus environments. Moreover, in each group of complexes (L′ = NCMe or CO) the pattern of *J*(P–C) values for the separate carbonyl resonances is consistent with only one carbonyl (that at low field) arranged *trans* to a P-donor atom. This imposes a meridional arrangement of carbonyl ligands in the tricarbonyl complexes **11a**, **10b** and **11b**. The ambient temperature ^{1}H and ^{13}C NMR spectra of the acetonitrile adducts **8a**,**b**, **9a**,**b** exhibited some broadened features which resolved on cooling to −30 °C and in the case of complexes of the 1–3-η:5,6-C$_8$H$_{11}$ ligand (**8a**, **9a**), resolved spectra indicated the presence of two isomeric components similar to our previous observations for [MoBr(CO)$_2$(L$_2$)(η^3-C$_8$H$_{11}$)] (L$_2$ = dppm, dppe).[10] The NCMe adducts **8b**, **9b** incorporating the 1–3-η:4,5-C$_8$H$_{11}$ ligand did not exhibit this phenomenon.

Although our investigations on the reactions of the pentahapto-dienyl complexes **1a**, **1b** and **2a** with ligands L′ led to the successful isolation of adducts [Mo(CO)$_2$(L′)(L$_2$)(η^3-C$_8$H$_{11}$)]$^+$-(L′ = NCMe or CO), they failed to provide a clear distinction between the effect of the identity of ligands L$_2$ and C$_8$H$_{11}$ upon the relative stability of trihapto- and pentahapto- bonding modes of the dienyl ligand. Further to address this issue, we examined the ease of reversion of [Mo(CO)$_2$(L′)(L$_2$)(η^3-C$_8$H$_{11}$)]$^+$ to the precursor η^5-dienyls. When the acetonitrile adducts **8a**, **8b**, **9a**, and **9b**, were dissolved in CH$_2$Cl$_2$ (*ca.* 0.05 g in 5 cm^3) and the reaction monitored by IR spectroscopy, differences in reactivity dependent upon the identity of L$_2$ and the cyclooctadienyl ligand became clear. Both complexes of the 1–3-η:5,6-C$_8$H$_{11}$ ligand (**8a**, L$_2$ = dppm and **9a**, L$_2$ = dppe) rapidly lost NCMe with reversion to the pentahapto-bonded dienyls **1a** and **2a**, respectively. However, whilst conversion of **8a** to **1a** was complete, the dppe complex **2a** was formed as an inseparable mixture with small quantities of unchanged **9a**. The acetonitrile adducts of complexes of the 1–3-η:4,5-C$_8$H$_{11}$ ligand (**8b**, L$_2$ = dppm and **9b**, L$_2$ = dppe) exhibited much greater stability in CH$_2$Cl$_2$. Monitoring by IR spectroscopy revealed only slow conversion to the respective pentahapto-bonded dienyls and moreover, in each case, a substantial proportion of **8b** or **9b** was retained even after heating the reaction solution. Further distinction between 1–3-η:5,6-C$_8$H$_{11}$ and 1–3-η:4,5-C$_8$H$_{11}$ ligands is apparent from the carbonyl elimination reactions of the tricarbonyl complexes [Mo(CO)$_3$(dppe)(η^3-C$_8$H$_{11}$)][BF$_4$]. The 1–3-η:5,6-C$_8$H$_{11}$ complex **11a**, rapidly undergoes CO elimination in CH$_2$Cl$_2$ leading to complete conversion to **2a**, after 30 min at 30 °C. By contrast, CH$_2$Cl$_2$ solutions of the 1–3-η:4,5-C$_8$H$_{11}$ complex **11b**, are unchanged under these conditions although reflux in CH$_2$Cl$_2$ for 2 h resulted in conversion to unidentified products.

To complete our investigations on the effect of supporting ligand L$_2$ on hapticity conversion processes, we examined the reactions of the remaining three classes of complex, [Mo(CO)$_2${P(OMe)$_3$}$_2$(1–5-η-C$_8$H$_{11}$)][BF$_4$], **4b**; the isocyanide complexes **5a**, **6a** and **6b**, and the diene complex [Mo(CO)$_2$(η^4-nbd)(1–3:5,6-η-C$_8$H$_{11}$)][BF$_4$] **7a** with NCMe and (in selected cases) CNBu^t. Complexes **5a**, **6a**, **6b** and **7a** (in common with their cycloheptadienyl analogues) were unreactive towards NCMe, an observation consistent with the successful syntheses of these materials from the tris(nitrile) precursors [Mo(CO)$_2$(NCMe)$_3$(η^3-C$_8$H$_{11}$)][BF$_4$]. The bis(phosphite) complex **4b** did react when dissolved in NCMe but a product mixture was formed, probably by partial ligand substitution of P(OMe)$_3$ by NCMe. Each of the isocyanide complexes **5a**, **6a** and **6b** reacted with a further equivalent of CNBu^t. The bis(isocyanide) complex **5a** yielded the adduct [Mo(CO)$_2$(CNBu^t)$_3$(1–3-η:5,6-C$_8$H$_{11}$)][BF$_4$], previously obtained by direct reaction of [Mo(CO)$_2$(NCMe)$_3$(1–3-η:5,6-C$_8$H$_{11}$)][BF$_4$] with three equivalents of CNBu^t.[10] This observation contrasts with the cycloheptadienyl analogue [Mo(CO)$_2$(CNBu^t)$_2$(η^5-C$_7$H$_9$)]$^+$ which reacts with CNBu^t to yield carbonyl-substituted [Mo(CO)(CNBu^t)$_3$(η^5-C$_7$H$_9$)]$^+$ directly[7] with no explicit evidence for the intermediacy of [Mo(CO)$_2$(CNBu^t)$_3$(η^3-C$_7$H$_9$)][BF$_4$]. The tris(isocyanide) complexes **6a** and **6b** react with a further equivalent of CNBu^t to yield the adducts [Mo(CO)(CNBu^t)$_4$(η^3-C$_8$H$_{11}$)][BF$_4$] (η^3-C$_8$H$_{11}$ = 1–3-η:5,6-C$_8$H$_{11}$, **12a**; 1–3-η:4,5-C$_8$H$_{11}$, **12b**) which could also be prepared *via* direct reaction of the appropriate derivative of [Mo(CO)$_2$(NCMe)$_3$(η^3-C$_8$H$_{11}$)][BF$_4$] with four equivalents of CNBu^t. We have previously reported on the related complexes [Mo(CO)(CNBu^t)$_4$(η^3-R)]$^+$ (R = C$_7$H$_7$[30] or C$_7$H$_9$[7]) and, on the basis of the four spectroscopically distinct CNBu^t ligands, it is probable that **12a** and **12b** share their asymmetric structure with a CNBu^t ligand located *trans* to the η^3-C$_8$H$_{11}$ ring.

To conclude, we now address the objectives outlined at the beginning of this section. First, a comparison is made of analogous complexes of the fully conjugated dienyl ligands, η^5-C$_7$H$_9$ and 1–5-η-C$_8$H$_{11}$. Based on the reactions of [Mo(CO)$_2$(dppm)(η^5-dienyl)]$^+$ with L′ (dienyl = η^5-C$_7$H$_9$ or 1–5-η-C$_8$H$_{11}$; L′ = NCMe and CO), it is clear that the 1–5-η-C$_8$H$_{11}$ ligand preferentially enhances reactivity to addition of L′ with accompanying change in dienyl ligand hapticity from η^5 to η^3. Thus [Mo(CO)$_2$(dppm)(1–5-η-C$_8$H$_{11}$)]$^+$ reacts with both NCMe and CO to give stable adducts of formulation [Mo(CO)$_2$(L′)(dppm)(1–3-η:4,5-C$_8$H$_{11}$)]$^+$ but the cycloheptadienyl analogue [Mo(CO)$_2$(dppm)(η^5-C$_7$H$_9$)]$^+$ does not react with either NCMe or CO under similar conditions. Other observations further support the conclusion that the 1–5-η-C$_8$H$_{11}$ ligand exhibits a reduced preference for the pentahapto bonding mode by comparison with the corresponding cycloheptadienyl system. For example, we have demonstrated that [Mo(CO)$_2$(bipy)(η^5-C$_7$H$_9$)]$^+$ is an isolable complex with a structure established by X-ray crystallography but attempts to synthesise [Mo(CO)$_2$(bipy)(1–5-η-C$_8$H$_{11}$)]$^+$ were unsuccessful, probably due to formation of a BF$_4$ coordinated system analogous to the corresponding acyclic pentadienyl system. Secondly, reaction of [Mo(CO)$_2$(CNBu^t)$_2$(η^5-dienyl)]$^+$ (dienyl = η^5-C$_7$H$_9$ or 1–5-η-C$_8$H$_{11}$) with one equivalent of CNBu^t affords carbonyl-substituted [Mo(CO)(CNBu^t)$_3$(η^5-dienyl)]$^+$ but only in the cyclooctadienyl system can the intermediate [Mo(CO)$_2$(CNBu^t)$_3$(η^3-dienyl)]$^+$ be observed prior to CO elimination. Finally, reaction of [Mo(CO)$_2$(NCMe)$_3$(η^3-dienyl)]$^+$ with two equivalents of PPh$_3$ proceeds very differently dependent on the identity of the dienyl ligand; the cycloheptadienyl complex [Mo(CO)$_2$(PPh$_3$)$_2$(η^5-C$_7$H$_9$)]$^+$ is formed with elimination of all three NCMe ligands whereas the cyclooctadienyl system undergoes more limited substitution to yield [Mo(CO)$_2$(NCMe)$_2$(PPh$_3$)(1–3-η-4,5-C$_8$H$_{11}$)]$^+$ in which the trihapto-bonding mode is retained. The origin of the contrasting behaviour of η^5-C$_7$H$_9$ or 1–5-η-C$_8$H$_{11}$ systems is difficult to rationalise simply in terms of differences in electronic effects and metal–ligand bonding parameters; as discussed in the previous section, structural and spectroscopic data are generally comparable except for the increased barrier to rotation of the MoL$_4$ group in the cyclooctadienyl system. However, the differences in reactivity might be accounted for by the relative stabilities of η^5 and η^3 bonded forms. For both dienyl ligands, the conversion from a pentahapto- to trihapto-bonded dienyl ligand with accompanying folding of the edge-bridge away from the metal centre should relieve steric interactions with co-ligands at the molybdenum centre. However, we believe that the relative stabilities of pentahapto-bonded 1–5-η-C_8H_{11} and η^5-C_7H_9 ligands differ as follows. First, folding of the dienyl unit in the 1–5-η-C_8H_{11} system together with an increase in the separation of the terminal dienyl carbons may result in destabilisation by comparison with analogous η^5-C_7H_9 complexes. Secondly, it is probable that the enlarged edge-bridge of the 1–5-η-C_8H_{11} will increase steric interactions with co-ligands, an effect which may be augmented by the high barrier to rotation of the MoL_4 unit with respect to the 1–5-η-C_8H_{11} ligand.

The second comparison is between analogous complexes of the two distinct types of cyclooctadienyl ligand, 1–5-η-C_8H_{11} and 1–3:5,6-η-C_8H_{11}. We note that reaction of $[Mo(CO)_2(dppm)(\eta\text{-}C_8H_{11})]^+$ (**1a** and **1b**) with CO to give $[Mo(CO)_3(dppm)(\eta^3\text{-}C_8H_{11})]^+$ proceeds only for the 1–5-η-C_8H_{11} derivative **1b**. Conversely ligand adducts of the type $[Mo(CO)_2(L')(L_2)(\eta^3\text{-}C_8H_{11})]^+$ revert to pentahapto-bonded forms much less readily where the product contains the 1–5-η-C_8H_{11} ligand (compare, for example, the NCMe adducts **8a**, **8b** and the CO adducts **11a** and **11b**). Finally, carbonyl elimination from $[Mo(CO)_2(CNBu^t)_3(\eta^3\text{-}C_8H_{11})]^+$ to give $[Mo(CO)(CNBu^t)_3(\eta^5\text{-dienyl})]^+$ (dienyl = 1–3:5,6-η-C_8H_{11}, **6a**; 1–5-η-C_8H_{11}, **6b**) proceeds much more readily in the formation of **6a**. The observation that complexes of the pentahapto-bonded 1–3:5,6-η-C_8H_{11} ligand are relatively more stable with respect to conversion to η^3-bonded adducts is difficult to explain simply on the basis of steric requirements (estimated ligand cone angles: 1–5-η-C_8H_{11}, 159°; 1–3:5,6-η-C_8H_{11}, 196°)[16] although the separation of the coordinated carbons into separate allyl and ene units eliminates the need for folding of the dienyl plane and any resultant effect on stability. Alternatively, ν(CO) data (Table 6) suggest that the 1–3:5,6-η-C_8H_{11} ligand is a better electron donor than its 1–5-η-C_8H_{11} counterpart so allowing 1–3:5,6-η-C_8H_{11} to compete more effectively with ligands L′ for a coordination site at the Mo centre.

Finally, as in the analogous cycloheptadienyl complexes, the supporting ligands of the MoL_4 unit significantly affect reactivity. Based on the reactions of $[Mo(CO)_2(L_2)(1\text{–}3\text{:}5,6\text{-}\eta\text{-}C_8H_{11})]^+$ (L_2 = dppe, dppm, 2CNBu^t, nbd) with NCMe, the pattern of reactivity is very similar to that observed for analogous cycloheptadienyl systems, although in the current work the comparison is limited to a smaller range of ligands L_2. The activating effect towards $\eta^5 \longrightarrow \eta^3$ hapticity conversion in the cyclooctadienyl complexes lies in the order dppe > dppm > CNBu^t, nbd and it is probable that the large steric requirements of dppe and dppm ligands contribute to their effectiveness in promoting $\eta^5 \longrightarrow \eta^3$ hapticity conversions. Pertinently, our synthetic studies demonstrate that the combination of dppe and 1–5-η-C_8H_{11} ligands affords an unstable system in the complex $[Mo(CO)_2(dppe)(1\text{–}5\text{-}\eta\text{-}C_8H_{11})]^+$.

Conclusions

This paper continues our investigations on the synthesis, structure and reactivity of edge-bridged dienyl ligands coordinated to molybdenum and tungsten. The first examples of complexes of the cyclooctadienyl ligands 1–3:5,6-η-C_8H_{11} and 1–5-η-C_8H_{11}, bonded pentahapto to molybdenum are reported. Two synthetic routes to these complexes were developed involving either halide abstraction from $[MoBr(CO)_2(L_2)(\eta^3\text{-}C_8H_{11})]$ or displacement of NCMe from $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_8H_{11})]^+$ (η^3-C_8H_{11} = 1–3-η:5,6-C_8H_{11} or 1–3-η:4,5-C_8H_{11}). The latter method is similar to that employed for the synthesis of analogous complexes of the C_7H_9 (cycloheptadienyl) ligand but is less generally applicable to the cyclooctadienyl system. X-Ray structural studies on the representative complexes $[Mo(CO)_2(dppm)(1\text{–}3\text{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$, **1a**, and $[Mo(CO)(CNBu^t)_3(1\text{–}5\text{-}\eta\text{-}C_8H_{11})]^+$, **6b**, reveal asymmetric structures and, in **1a**, elongation of some metal to cyclooctadienyl ligand bonds. Selected complexes of the type $[Mo(CO)_2(L_2)(\eta^5\text{-}C_8H_{11})]^+$ (η^5-C_8H_{11} = 1–3:5,6-η-C_8H_{11} or 1–5-η-C_8H_{11}) react with ligands L′ (L′ = NCMe or CO) to give adducts $[Mo(CO)_2(L')(L_2)(\eta^3\text{-}C_8H_{11})]^+$ (η^3-C_8H_{11} = 1–3-η:5,6-C_8H_{11} or 1–3-η:4,5-C_8H_{11}) with accompanying $\eta^5 \longrightarrow \eta^3$ hapticity conversion at the cyclooctadienyl ligand. Complexes of the 1–5-η-C_8H_{11} ligand are activated to $\eta^5 \longrightarrow \eta^3$ hapticity conversions by comparison with exactly analogous complexes of the cycloheptadienyl system; steric interactions imposed by the additional methylene group in the edge-bridge of the 1–5-η-C_8H_{11} ligand and differences in dienyl unit configuration are probably responsible for this effect. The 1–3:5,6-η-C_8H_{11} ligand is less effective than 1–5-η-C_8H_{11} in promoting $\eta^5 \longrightarrow \eta^3$ hapticity conversions; this may be connected with the enhanced donor capacity of the 1–3:5,6-η-C_8H_{11} ligand and/or the configuration of the coordinated carbons into two separate groups.

In many respects, the chemistry of the cyclooctadienylmolybdenum system most closely resembles that of analogous acyclic pentadienyl complexes. The dominant hapticity type of both cyclooctadienyl ligand types is trihapto. This is in contrast to the cycloheptadienyl ligand which exhibits a comparative preference for pentahapto-bonding and is more similar to related indenyl complexes. Directly analogous complexes of the η^5-C_7H_9 and 1–5-η-C_8H_{11} differ only by the additional methylene group in the edge-bridge, yet the contrast in reactivity is considerable. There is no clear evidence for a major difference in electronic factors between η^5-C_7H_9 and 1–5-η-C_8H_{11} and therefore the impact of the enlarged edge-bridge most probably originates from increased steric interactions between the edge-bridge and supporting co-ligands and from differences in the dienyl unit configuration.

Experimental

General procedures

The preparation, purification and reactions of the complexes described were carried out under dry nitrogen. All solvents were dried by standard methods, distilled and deoxygenated before use. The complexes $[MoBr(CO)_2(L_2)(\eta^3\text{-}C_8H_{11})]$, ($L_2$ = dppm, dppe, bipy, 2 NCMe or 2 CNBu^t) and $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_8H_{11})]^+$ (η^3-C_8H_{11} = 1–3-η:5,6-C_8H_{11}, 1–3-η:4,5-C_8H_{11}) were prepared by published procedures.[10] The chemicals dppe, dppm, $P(OMe)_3$, CNBu^t, and norborna-2,5-diene were supplied by Aldrich Chemical Co.; $Ag[BF_4]$ was purchased from Lancaster Synthesis. 300 MHz ^{1}H, 121.5 MHz $^{31}P\{^1H\}$ and 75 MHz $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AC 300 E, Varian Associates XL 300 or Varian Unity Inova 300 spectrometers; 500 MHz ^{1}H and 125 MHz $^{13}C\{^1H\}$ NMR spectra were obtained on a Varian Unity 500 instrument. IR spectra were acquired on a Perkin Elmer FT 1710 spectrometer and mass spectra using a Kratos Concept 1S instrument. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

Preparations

$[Mo(CO)_2(dppm)(1\text{–}3\text{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$ 1a. *Method (a).* $[MoBr(CO)_2(dppm)(1\text{–}3\text{-}\eta\text{:}5,6\text{-}C_8H_{11})]$ (0.185 g, 0.26 mmol) was dissolved in CH_2Cl_2 (20 cm^3) followed by addition of $Ag[BF_4]$ (0.055 g, 0.28 mmol). After stirring for 1 h, the solution was filtered to remove AgBr and the resulting orange solution reduced in volume and treated with diethyl ether to precipitate **1a** as an orange–pink solid. The product was recrystallised from CH_2Cl_2–diethyl ether; yield 0.135 g (71%). The pale orange complex $[Mo(CO)_2(dppe)(1\text{–}3\text{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4].CH_2Cl_2$, **2a**, was prepared similarly in 73% yield starting from $[MoBr(CO)_2(dppe)(1\text{–}3\text{-}\eta\text{:}5,6\text{-}C_8H_{11})]$ (0.500 g, 0.68 mmol) and $Ag[BF_4]$ (0.149g, 0.76 mmol). *Method (b).* $[Mo(CO)_2(NCMe)_3(1\text{–}3\text{-}\eta\text{:}5,6\text{-}C_8H_{11})][BF_4]$ (0.250 g, 0.53 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and dppm (0.205 g, 0.53 mmol) added to give an orange solution. After 1 h stirring, the solution was filtered and work up carried out as described in method (a); yield 0.270 g (69%).

[Mo(CO)$_2$(dppm)(1–5-η-C$_8$H$_{11}$)][BF$_4$] 1b. [MoBr(CO)$_2$(dppm)(1–3-η:4,5-C$_8$H$_{11}$)] (0.142 g, 0.20 mmol) was dissolved in CH$_2$Cl$_2$ (20 cm^3) followed by addition of Ag[BF$_4$] (0.042 g, 0.22 mmol). After stirring for 1 h, the solution was filtered to remove AgBr and the resulting orange solution reduced in volume and treated with diethyl ether to precipitate **1b** as an orange–pink solid. The product was recrystallised from CH$_2$Cl$_2$–diethyl ether; yield 0.112 g (79%).

[Mo(CO)$_2$(NCMe)$_2$(PPh$_3$)(1–3-η:4,5-C$_8$H$_{11}$)][BF$_4$] 3b. A stirred solution of [Mo(CO)$_2$(NCMe)$_3$(1–3-η:4,5-C$_8$H$_{11}$)][BF$_4$] (0.214 g, 0.456 mmol) in CH$_2$Cl$_2$ (20 cm^3) at 0 °C was treated with PPh$_3$ (0.120 g, 0.456 mmol). After 30 min the solution was filtered and the volume reduced to *ca.* 5 cm^3 followed by addition of NCMe (3 cm^3). Subsequent addition of diethyl ether yielded the product **3b** as an orange solid; yield 0.202 g (64%).

[Mo(CO)$_2${P(OMe)$_3$}$_2$(1–5-η-C$_8$H$_{11}$)][BF$_4$] 4b. [MoBr(CO)$_2$(NCMe)$_2$(1–3-η:4–5-C$_8$H$_{11}$)] (0.500 g, 1.19 mmol) was dissolved in CH$_2$Cl$_2$ (30 cm^3) and the reaction solution cooled to −70 °C. The solution was treated with P(OMe)$_3$ (0.32 g, 2.58 mmol) then stirred for 30 min as the temperature was increased to 0 °C. The resulting orange solution was evaporated to dryness whilst retaining the temperature at 0 °C and the residue dried *in vacuo* for 1 h. Subsequently the residue was redissolved in CH$_2$Cl$_2$ (20 cm^3) and immediately treated with Ag[BF$_4$] (0.232 g, 1.19 mmol). After 30 min stirring the resulting green solution was filtered to remove AgBr, the volume of the solution reduced and diethyl ether added to precipitate the crude product as an orange oil. Fractional crystallisation of the crude product from CH$_2$Cl$_2$–diethyl ether afforded [Mo(CO)$_2${P(OMe)$_3$}$_2$(1–5-η-C$_8$H$_{11}$)][BF$_4$] **4b** as a bright yellow solid; yield 0.135 g (19%).

[Mo(CO)$_2$(CNBu^t)$_2$(1–3:5,6-η-C$_8$H$_{11}$)][BF$_4$] 5a. Reaction of [MoBr(CO)$_2$(CNBu^t)$_2$(1–3-η:5,6-C$_8$H$_{11}$)] (0.169 g, 0.335 mmol) with Ag[BF$_4$] (0.072 g, 0.369 mmol) in CH$_2$Cl$_2$ (20 cm^3) gave an orange solution. After 15 min the reaction mixture was filtered, reduced in volume and diethyl ether added to precipitate an orange oil. Removal of the mother liquors and subsequent stirring in neat diethyl ether for 30 min gave the product **5a** as a red–orange solid, yield 0.05 g (30%).

[Mo(CO)(CNBu^t)$_3$(1–3:5,6-η-C$_8$H$_{11}$)][BF$_4$] 6a. [Mo(CO)$_2$(NCMe)$_3$(1–3-η:5,6-C$_8$H$_{11}$)][BF$_4$] (0.265 g, 0.565 mmol) was dissolved in CH$_2$Cl$_2$ (20 cm^3) and three equivalents of CNBu^t (0.141 g, 1.70 mmol) added resulting in a colour change from yellow to orange. The reaction mixture was stirred at room temperature for 15 min then solvent was removed *in vacuo* and the residue dried under vacuum for 1 h. The residue was redissolved in CH$_2$Cl$_2$ (20 cm^3) and the solution was refluxed gently for 1 h then filtered, reduced in volume and diethyl ether added to precipitate the crude product as an orange oil. Subsequent stirring in neat diethyl ether for 1 h. gave **6a** as an orange–yellow solid, yield 0.179 g (56%). The complex [Mo(CO)(CNBu^t)$_3$(1–5-η-C$_8$H$_{11}$)][BF$_4$], **6b** was similarly prepared as an orange–red solid in 71% yield starting from [Mo(CO)$_2$(NCMe)$_3$(1–3-η:4–5-C$_8$H$_{11}$)][BF$_4$] (0.440 g, 0.94 mmol) and CNBu^t (0.234 g, 2.82 mmol) in CH$_2$Cl$_2$ (20 cm^3).

[Mo(CO)$_2$(η^4-nbd)(1–3:5,6-η-C$_8$H$_{11}$)][BF$_4$] 7a. [Mo(CO)$_2$(NCMe)$_3$(1–3-η:5,6-C$_8$H$_{11}$)][BF$_4$] (0.115 g, 0.245 mmol) was dissolved in CH$_2$Cl$_2$ (20 cm^3) and a five molar excess of norbornadiene (0.113 g, 1.23 mmol) was added. Strands of black oily material (assumed to be associated with polymerisation of norbornadiene) rapidly formed in a yellow solution. Additional norbornadiene was added dropwise and the solution stirred for 24 h. The reaction mixture was then filtered and reduced in volume resulting in further precipitation of polymeric material. The remaining yellow solution was transferred to a separate flask and diethyl ether added to precipitate **7a** as a bright yellow solid; yield 0.057 g (53%).

[Mo(CO)$_2$(NCMe)(dppm)(1–3-η:5,6-C$_8$H$_{11}$)][BF$_4$] 8a. The complex [Mo(CO)$_2$(dppm)(1–3:5,6-η-C$_8$H$_{11}$)][BF$_4$], **1a** (0.233 g, 0.319 mmol) was stirred in NCMe (30 cm^3) for 1 h. The resulting solution was filtered, reduced in volume and diethyl ether added to precipitate the crude product. Subsequent recrystallisation from NCMe–diethyl ether gave **8a** as an orange–yellow solid; yield 0.158 g (64%). The complexes [Mo(CO)$_2$(NCMe)(dppm)(1–3-η:4–5-C$_8$H$_{11}$)][BF$_4$] **8b** and [Mo(CO)$_2$(NCMe)(dppe)(1–3-η:5,6-C$_8$H$_{11}$)][BF$_4$] **9a** were prepared similarly and isolated as orange and yellow solids, respectively. Complex **8b** was prepared in 57% yield from [Mo(CO)$_2$(dppm)(1–5-η-C$_8$H$_{11}$)][BF$_4$] (0.206 g, 0.282 mmol); complex **9a** was obtained in 48% yield starting from [Mo(CO)$_2$(dppe)(1–3:5,6-η-C$_8$H$_{11}$)][BF$_4$].CH$_2$Cl$_2$ (0.201 g, 0.24 mmol).

[Mo(CO)$_2$(NCMe)(dppe)(1–3-η:4,5-C$_8$H$_{11}$)][BF$_4$] 9b. The complex [Mo(CO)$_2$(NCMe)$_3$(1–3-η:4,5-C$_8$H$_{11}$)][BF$_4$] (0.800 g, 1.71 mmol) was dissolved in NCMe (20 cm^3) and dppe (0.679 g, 1.71 mmol) added. The resulting orange solution was stirred for 1.5 h then filtered, reduced in volume and the product precipitated as a red oil by addition of diethyl ether. Subsequent removal of the mother-liquor and stirring the crude product in neat diethyl ether gave **9b** as an orange solid; yield 1.225 g (92%).

[Mo(CO)$_3$(dppm)(1–3-η:4,5-C$_8$H$_{11}$)][BF$_4$] 10b. [Mo(CO)$_2$(dppm)(1–5-η-C$_8$H$_{11}$)][BF$_4$] (0.206 g, 0.282 mmol) was dissolved in CH$_2$Cl$_2$ (20 cm^3) at room temperature and CO gas bubbled through the resulting orange solution. After 25 min, monitoring by IR spectroscopy suggested that the reaction was complete. The reaction mixture was filtered to give a yellow solution which was reduced in volume and treated with diethyl ether to precipitate the crude product. Subsequent recrystallisation from CH$_2$Cl$_2$–diethyl ether gave **10b** as a bright yellow solid, yield 0.142 g (66%).

[Mo(CO)$_3$(dppe)(1–3-η:5,6-C$_8$H$_{11}$)][BF$_4$] 11a. [Mo(CO)$_2$(dppe)(1–3:5,6-η-C$_8$H$_{11}$)][BF$_4$]·CH$_2$Cl$_2$ (0.222 g, 0.27 mmol) was dissolved in CH$_2$Cl$_2$ (20 cm^3) at 0 °C and CO gas bubbled through the resulting orange solution. The solution was maintained at 0 °C over a period of 3 h during which time the colour slowly changed to yellow. After 3 h the solution was filtered cold, reduced in volume and cold (0 °C) diethyl ether added to precipitate **11a** as a yellow solid; yield 0.142 g (68%).

[Mo(CO)$_3$(dppe)(1–3-η:4,5-C$_8$H$_{11}$)][BF$_4$] 11b. The complex [Mo(CO)$_2$(NCMe)(dppe)(1–3-η:4,5-C$_8$H$_{11}$)][BF$_4$] (0.158 g, 0.201 mmol) was dissolved in CH$_2$Cl$_2$ at ambient temperature and CO gas bubbled through the solution. The progress of the reaction was monitored by IR spectroscopy and after 45 min the resulting yellow reaction mixture was filtered, reduced in volume and diethyl ether added to precipitate the crude product. Subsequent removal of the mother-liquor and stirring the crude product in neat diethyl ether gave **11b** as a yellow solid; yield 0.102 g (66%).

[Mo(CO)(CNBu^t)$_4$(1–3-η:5,6-C$_8$H$_{11}$)][BF$_4$] 12a. The complex [Mo(CO)(CNBu^t)$_3$(1–3:5,6-η-C$_8$H$_{11}$)][BF$_4$] (0.096 g, 0.169 mmol) was dissolved in CH$_2$Cl$_2$ (20 cm^3) and treated with a small excess of CNBu^t (0.017 g, 0.205 mmol). The reaction mixture was stirred for 2 h, then filtered, reduced in volume and diethyl ether added to precipitate **12a** as an orange oil. The mother-liquor was removed, and the product washed with diethyl ether then dried *in vacuo* to give **12a** as an orange solid; yield 0.038 g (35%). The complex [Mo(CO)(CNBu^t)$_4$(1–3-η:4,5-

Table 8 Crystal and data collection parameters for complexes **1a** and **6b**

	1a	**6b**
Formula	$C_{35}H_{33}MoO_2P_2BF_4$	$C_{24}H_{38}MoON_3BF_4$
Mass	730.34	567.32
Crystal system	Monoclinic	Monoclinic
Temperature, T/°C	22	22
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	10.182(4)	13.396(2)
b/Å	16.698(4)	13.653(19)
c/Å	19.141(6)	15.810(2)
β/°	94.86(3)	94.126(12)
Volume, V/Å^3	3243(2)	2884(4)
No. of molecules in unit cell, Z	4	4
μ/cm^{-1}	47.83	5.00
Total data	5005	5111
'Observed' data, N_o	3808[a]	3774[b]
R	0.056	0.057
R_w	0.069	0.150

[a] $[I > 3\sigma(I)]$, [b] $[I > 2\sigma(I)]$.

$C_8H_{11})][BF_4]$ **12b** was prepared similarly in 18% yield starting from $[Mo(CO)(CNBu^t)_3(1–5\text{-}\eta\text{-}C_8H_{11})][BF_4]$ (0.172 g, 0.303 mmol) and $CNBu^t$ (0.030 g, 0.361 mmol) except that the reaction was complete after 30 min.

$[Mo(CO)_2\{P(OMe)_3\}_2(\eta^5\text{-}C_7H_9)][BF_4]$. A stirred solution of $[Mo(CO)_2(NCMe)_3(\eta^5\text{-}C_7H_9)][BF_4]$[6] (0.272 g, 0.598 mmol) in CH_2Cl_2 (20 cm^3) was treated with $P(OMe)_3$ (0.160 g, 1.29 mmol) resulting in an immediate colour change from red–brown to yellow. The volume of the solution was reduced to *ca.* 2 cm^3 *in vacuo* and then the reaction mixture was treated with diethyl ether. The product, $[Mo(CO)_2\{P(OMe)_3\}_2(1–5\text{-}\eta\text{-}C_7H_9)][BF_4]$ precipitated as a yellow solid; yield 0.159 g (46%). IR ν(CO)-(CH_2Cl_2)/cm^{-1}: 2002m, 1931s; microanalysis: found (calc.): C, 30.9 (31.0); H, 4.7 (4.7); mass spectrum (FAB): 495 (M^+), 467 ([M − CO]), 371 ($[M - P(OMe)_3]^+$), 341 ($[M - P(OMe)_3 - CO - 2H]^+$), 311 ($[M - P(OMe)_3 - 2CO - 4H]^+$); ^{1}H NMR ($CDCl_3$, 300 MHz), numbering scheme as in ref. 6: 6.25, m, 1H, H^5; 5.21, m, $J(H^4–H^3) = J(H^6–H^7) = 10$, 2H, $H^{4,6}$; 4.73, m, 2H, $H^{3,7}$; 3.88, d, J(P–H) 11, 18H, $P(OCH_3)_3$; 2.24, m, 2H, 2.06, m, 2H, $H^{1,1',2,2'}$; ^{13}C NMR ($CDCl_3$, 75 MHz): 222.8, t, J(P–C) 34, CO; 101.5, 96.2, 95.2, $C^{3–7}$; 54.9, m, $P(OCH_3)_3$; 34.4, $C^{1,2}$.

Crystallography

The majority of details of the structure analyses carried out on **1a** and **6b** are given in Table 8. A Rigaku AFC5R diffractometer was employed for both structures utilising either a Mo-Kα source (λ = 0.71069 Å) (**6b**) or a Cu-Kα source (λ = 1.54178 Å) (**1a**). Neutral atom scattering factors were taken from ref. 31 and all calculations were performed using the TEXSAN crystallographic software package,[32] with the exception of the computing structure solution which was carried out with SIR92[33] for **1a** and DIRDIF92 PATTY[34] for **6b** and the computing structure refinement for **6b** (SHELXL-97).[35]

$[Mo(CO)_2(dppm)(1–3{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$ **1a**–Orange, prismatic crystals of **1a** were grown by vapour diffusion of diethyl ether into a CH_2Cl_2 solution of the complex. The unit cell dimensions were derived from the setting angles of 25 reflections in the range 29.18 < 2θ < 32.98°. The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection the standards decreased by 1.60% and a linear correction factor was applied to the data to account for this phenomenon. An empirical absorption correction based on azimuthal scans was applied which resulted in transmission factors ranging from 0.87 to 1.00 and the data were corrected for Lorentz and polarisation effects. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the structure factor calculation in idealised positions (C–H = 0.95 Å).

$[Mo(CO)(CNBu^t)_3(1–5\text{-}\eta\text{-}C_8H_{11})]$ **6b**–Orange, prismatic crystals of **6b** were grown by vapour diffusion of diethyl ether into a CH_2Cl_2 solution of the complex. The unit cell dimensions were derived from the setting angles of 15 reflections in the range 20.45 < 2θ < 24.50°. The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection the standards decreased by 3.0% and a linear correction factor was applied to the data to account for this phenomenon. An empirical absorption correction based on azimuthal scans was applied which resulted in transmission factors ranging from 0.95 to 1.00 and the data were corrected for Lorentz and polarisation effects. The structure was solved by Patterson methods. All non-hydrogen atoms except for B(1) were refined anisotropically, B(1) was refined isotropically. Hydrogen atoms were included in calculated positions.

CCDC reference numbers 195204 and 195205.

See http://www.rsc.org/suppdata/dt/b2/b209975f/ for crystallographic data in CIF or other electronic format.

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