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FULL PAPER

Synthesis and reactions of the cyclooctadienylmolybdenum complexes [MoBr(CO)$_2$(NCMe)$_2$(η^3-C$_8$H$_{11}$)] (η^3-C$_8$H$_{11}$ = 1–3-η:4,5-C$_8$H$_{11}$ or 1–3-η:5,6-C$_8$H$_{11}$)

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Received 21st August 2001, Accepted 17th December 2001
First published as an Advance Article on the web 13th February 2002

The first examples of cyclooctadienylmolybdenum complexes, [MoBr(CO)$_2$(NCMe)$_2$(1–3-η:5,6-C$_8$H$_{11}$)] and [MoBr(CO)$_2$(NCMe)$_2$(1–3-η:4,5-C$_8$H$_{11}$)], accessible by reaction of [Mo(CO)$_3$(NCMe)$_3$] with bromocyclooctadienes, are precursors to [MoBr(CO)$_2$(L$_2$)(η^3-C$_8$H$_{11}$)] [L$_2$ = 2,2′-bipyridine; Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1 or 2); 2CNBu^t]; [Mo(CO)$_2$(η^3-C$_8$H$_{11}$)Cp], and [Mo(CO)$_2$(L$_3$)(η^3-C$_8$H$_{11}$)]$^+$ (L$_3$ = NCMe or CNBu^t). The X-ray crystal structures of [MoBr(CO)$_2$(L$_2$)(1–3-η:5,6-C$_8$H$_{11}$)] (L$_2$ = 2,2′-bipyridine or Ph$_2$PCH$_2$CH$_2$PPh$_2$) and [Mo(CO)$_2$(CNBu^t)$_3$(1–3-η:4,5-C$_8$H$_{11}$)][BF$_4$] have been determined and the solid state conformations of the two types of trihapto-bonded cyclooctadienyl ring investigated. The characteristic ^{1}H and ^{13}C{^{1}H} NMR spectral features of the 1–3-η:5,6-C$_8$H$_{11}$ and 1–3-η:4,5-C$_8$H$_{11}$ ligands are defined.

The variable hapticity of dienyl ligands and the interconversion of η^5, η^3, and σ bonding modes represent an area of continued interest in organometallic chemistry.[1,2] Dienyl complexes of Mo and W appear to be particularly productive for such investigations, as evidenced by recent reports on indenyl,[3] cycloheptadienyl,[4–6] and pentadienyl systems.[7,8] Our contribution to progress in this field has focused on $\eta^5 \leftrightarrow \eta^3$ hapticity interconversions in edge-bridged "open" dienyl systems in which the two terminal dienyl carbon atoms are linked *via* a bridging unit. Following our development of the chemistry of cycloheptadienylmolybdenum complexes, we have endeavoured to extend our investigations to the related "open" edge-bridged dienyl systems cyclohexadienyl and cyclooctadienyl with the objective of establishing the effect of ring size and conjugation pattern upon hapticity interconversion processes and the relative stabilities of η^3 and η^5 bonding modes. This paper reports our route for entry into the chemistry of the cyclooctadienylmolybdenum system, together with details of the synthesis and structure of a series of η^3-cyclooctadienylmolybdenum complexes. Subsequent to our preliminary account,[9] others[10] have found application for the basic syntheses that we reported.

Results and discussion

Synthetic studies

Although the organometallic chemistry of the cyclooctadienyl ligand is well developed, the majority of reports concern the chemistry of the Fe[11–14] and Co[15–18] triads, together with a few accounts of complexes of Ti,[14] Zr,[19] V,[14] Re,[20] and Ni.[21] Prior to our work in this area, there were no examples of the cyclooctadienyl ligand coordinated to molybdenum or tungsten. However the "pseudo-metallocene" [Cr(η^5-C$_8$H$_{11}$)$_2$] was known,[22] together with [CrH(PF$_3$)$_3$(C$_8$H$_{11}$)], although the latter may be formulated alternatively as a cyclooctadiene system with an agostic hydrogen.[23] Two distinct types of cyclooctadienyl ligand are observed, depending upon the relative positions of the allyl and olefin groups. Considering η^3-bound forms of the ligand, the 1–3-η:4,5-C$_8$H$_{11}$ configuration places the allyl and olefin groups adjacent to each other, whereas in the 1–3-η:5,6-C$_8$H$_{11}$ configuration, these groups are separated by a methylene ring carbon, C(4). The vast majority of syntheses of cyclooctadienyl complexes involve cycloocta-1,3-diene (1,3-cod) or cycloocta-1,5-diene (1,5-cod) as precursors and, in general, 1–3-η:4,5-C$_8$H$_{11}$ ligands are derived from 1,3-cod, whereas 1,5-cod gives rise to the 1–3-η:5,6-C$_8$H$_{11}$ ligand type (or their pentahapto-bonded equivalents). The principal synthetic methods to cyclooctadienyl complexes involve either direct reaction of 1,3-cod or 1,5-cod with a suitable metal precursor system[12,18,19] or, alternatively, modification of a pre-coordinated cyclooctadiene[11,15] ligand. The synthetic route that we have developed to cyclooctadienylmolybdenum complexes represents a departure from these tried and trusted methods in that it involves the reaction of bromocyclooctadienes with [Mo(CO)$_3$(NCMe)$_3$]. Our method parallels that reported by Liu *et al.*[24] as a route to the acyclic pentadienyl complexes [MoX(CO)$_2$(NCMe)$_2$(η^3-C$_5$H$_7$)]$^+$ (X = Br or Cl), but the current work is the first example of the addition of a *cyclic* halodiene to [Mo(CO)$_3$(NCMe)$_3$].

Bromocyclooctadienes were prepared by the literature procedures,[25,26] from 1,5-cod (as a mixture of 3-Br-1,5-cod and 6-Br-1,4-cod) and 1,3-cod (as a mixture of 5-Br-1,3-cod and 3-Br-1,4-cod). However, on reaction with [Mo(CO)$_3$(NCMe)$_3$] in acetonitrile, each separate mixture of bromocyclooctadienes simplified to one product type, [MoBr(CO)$_2$(NCMe)$_2$(1–3-η:5,6-C$_8$H$_{11}$)] **1a**, derived from 1,5-cod, and [MoBr(CO)$_2$(NCMe)$_2$(1–3-η:4,5-C$_8$H$_{11}$)] **1b**, derived from 1,3-cod. Complexes **1a** and **1b** precipitated from the reaction mixtures after stirring at room temperature for 1 h and were isolated as orange–yellow solids.

Complexes of the type [MoX(CO)$_2$(NCMe)$_2$(η^3-R)] (R = allyl,[27] pentadienyl,[24] cyclopentenoyl,[28] *etc.*) represent an important class of compounds in the organometallic chemistry of molybdenum. In particular, they act as precursors to a wide range of related complexes [MoX(CO)$_2$(L$_2$)(η^3-R)] through substitution of the labile acetonitrile ligands with L$_2$, as exemplified by the reaction chemistry of **1a** and **1b**, described below. However, in addition to the provision of defining examples for the characteristic spectroscopic and structural parameters of the 1–3-η:4,5-C$_8$H$_{11}$ and 1–3-η:5,6-C$_8$H$_{11}$ ligands bound to molybdenum, the principal objective of the synthetic

DOI: 10.1039/b107581k

studies was to develop a varied series of η^3-C_8H_{11} systems, suitable for investigations on conversion to pentahapto-bonded ligands. We therefore set out to synthesise cyclooctadienyl complexes analogous to the pentadienyl or cycloheptadienyl derivatives known to be precursors to pentahapto dienyl systems.

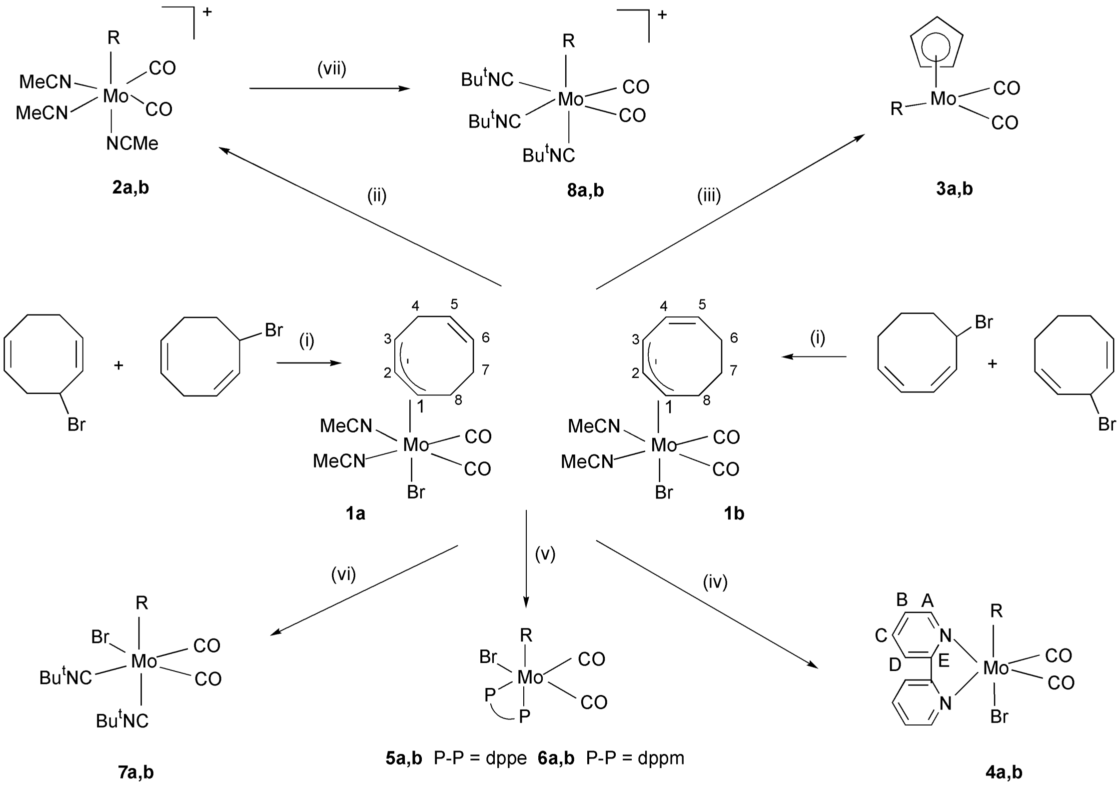
The ligand substitution chemistry of **1a** and **1b** is summarised in Scheme 1. Reaction of **1a** or **1b** with $Ag[BF_4]$ in NCMe results in halide abstraction and formation of $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}R)][BF_4]$ (R = 1–3-η:5,6-C_8H_{11}, **2a**; 1–3-η:4,5-C_8H_{11}, **2b**), which were isolated as yellow solids following filtration to remove AgBr. The yellow cyclopentadienyl complexes $[Mo(CO)_2(\eta^3\text{-}R)Cp]$ (R = 1–3-η:5,6-C_8H_{11}, **3a**; 1–3-η:4,5-C_8H_{11}, **3b**) were obtained by reaction of **1a** or **1b** with sodium cyclopentadienide in thf and purified by column chromatography. Formation of the complexes $[MoBr(CO)_2(L_2)(\eta^3\text{-}R)]$ [R = 1–3-η:5,6-C_8H_{11}, L_2 = 2,2′-bipyridine (bipy) **4a**, $Ph_2PCH_2CH_2PPh_2$ (dppe) **5a**, $Ph_2PCH_2PPh_2$ (dppm) **6a**, $2CNBu^t$ **7a**; R = 1–3-η:4,5-C_8H_{11}, L_2 = bipy **4b**, dppe **5b**, dppm **6b** or $2CNBu^t$ **7b**] proceeded by direct reaction of **1a** or **1b** with the appropriate stoichiometric amount of L_2 in CH_2Cl_2 or thf. Finally, $[Mo(CO)_2(CNBu^t)_3(\eta^3\text{-}R)][BF_4]$ (R = 1–3-η:5,6-C_8H_{11}, **8a**; 1–3-η:4,5-C_8H_{11}, **8b**) were synthesised from the respective precursors **2a** and **2b** by reaction with three equivalents of $CNBu^t$ in CH_2Cl_2 at 0 °C.

Structural studies

The series of references (ref. 10–23) might be taken to suggest that the structural and spectroscopic parameters of metal coordinated cyclooctadienyl systems are well defined. In fact, reports concerning fully established trihapto-bonded cyclooctadienyl ligands are very scarce and are essentially restricted to complexes of Rh or those of Mo developed from our work in this area. Consequently a detailed examination of the structural and spectroscopic properties of the complexes prepared in the current work seemed appropriate. A discussion of the structural work is presented first since the results of these investigations impact upon the spectroscopic studies.

To our knowledge, there are four previous examples of the structural characterisation of complexes containing the trihapto-bonded cyclooctadienyl ligand. These include one example of the 1–3-η:5,6-C_8H_{11} ligand[18] in $[Rh(PPh_3)_2(1\text{–}3\text{-}\eta\text{:}5,6\text{-}C_8H_{11})]$, whilst structural characterisations of the 1–3-η:4,5-C_8H_{11} ligand comprise $[Rh(\eta^4\text{-}C_8H_{12})(1\text{–}3\text{-}\eta\text{:}4,5\text{-}C_8H_{11})]$,[17] $[Mo(CO)_2(BH_2pz_2)(1\text{–}3\text{-}\eta\text{:}4,5\text{-}C_8H_{11})]$, and $[Mo(CO)_2\{BH(OPh)pz_2\}(1\text{–}3\text{-}\eta\text{:}4,5\text{-}C_8H_{11})]$ (pz = 3,5-dimethyl-1-pyrazolyl).[10] In the current work, three complexes were selected for X-ray structural characterisation: $[MoBr(CO)_2(bipy)(1\text{–}3\text{-}\eta\text{:}5,6\text{-}C_8H_{11})]$ **4a**, $[MoBr(CO)_2(dppe)(1\text{–}3\text{-}\eta\text{:}5,6\text{-}C_8H_{11})]$ **5a**, and $[Mo(CO)_2(CNBu^t)_3(1\text{–}3\text{-}\eta\text{:}4,5\text{-}C_8H_{11})][BF_4]$ **8b**. Taken as a group, these complexes serve the dual purpose of investigating conformations of the two ring types and of defining the preferred geometric arrangement of ligands L in complexes of the type $[MoBr(CO)_2(L_2)(\eta^3\text{-}C_8H_{11})]$ and $[Mo(CO)_2(L_3)(\eta^3\text{-}C_8H_{11})]^+$.

The molecular configurations, annotated with the crystallographic numbering schemes, and a table of important bond lengths and angles (excluding bond lengths and angles of the cylooctadienyl ligand) for **4a**, **5a**, and **8b** are presented in Fig. 1–3, respectively, and Table 1). Each of **4a**, **5a**, and **8b** exhibit the structural features characteristic of an η^3-allyl-type ligand coordinated to a $MoX(CO)_2(L_2)$ (X = halide or pseudohalide) or $Mo(CO)_2(L_3)$ metal group. Thus, the two carbonyl ligands are positioned directly beneath the terminal carbons of the η^3-allyl fragment and the Mo–C(central allyl) distance is shorter than the Mo–C(terminal allyl) bond lengths. The geometric arrangement of the $MoX(CO)_2(L_2)$ fragment in **4a** and **5a** follows a well established pattern which we have discussed previously in some detail with respect to analogous η^3-cycloheptatrienyl systems.[29] Accordingly, in the bipyridine complex **4a**, the $MoBr(CO)_2(bipy)$ group adopts a symmetric arrangement with Br located *trans* to the cyclooctadienyl ligand, whereas in **5a** an asymmetric ligand set is observed, in



Scheme 1 *Reagents and conditions*: (i) $[Mo(CO)_3(NCMe)_3]$ in NCMe, 1 h stirring; (ii) $Ag[BF_4]$ in NCMe, 30 min stirring; (iii) NaCp in thf, 24 h stirring; (iv) 2,2′-bipyridine in thf, 2 h stirring; (v) dppe or dppm in CH_2Cl_2, 1–2 h stirring; (vi) 2 equivalents of $CNBu^t$ in CH_2Cl_2, cooled to −78 °C then allowed to warm to room temperature over a period of 1 h; (vii) 3 equivalents of $CNBu^t$ in CH_2Cl_2, 0 °C for 30 min. R ≡ C_8H_{11}, **a** indicates 1–3-η:5,6-C_8H_{11} and **b** 1–3-η:4,5-C_8H_{11}.

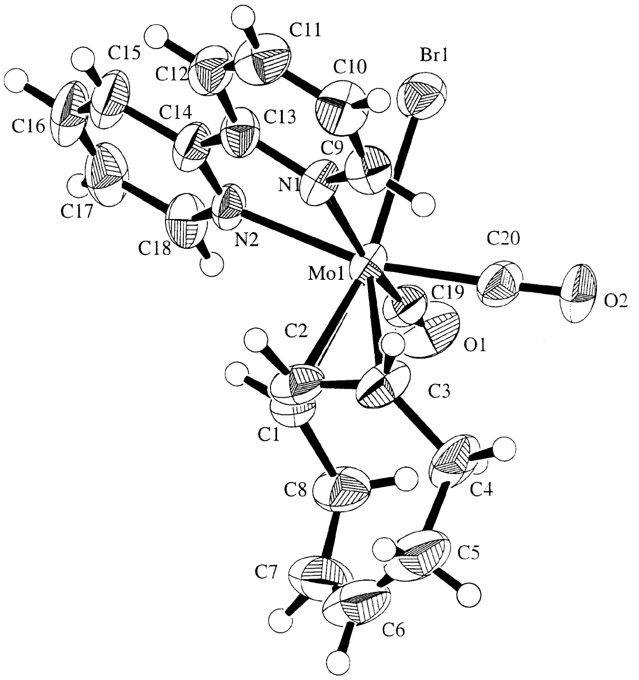


Fig. 1 Molecular structure of complex **4a**.

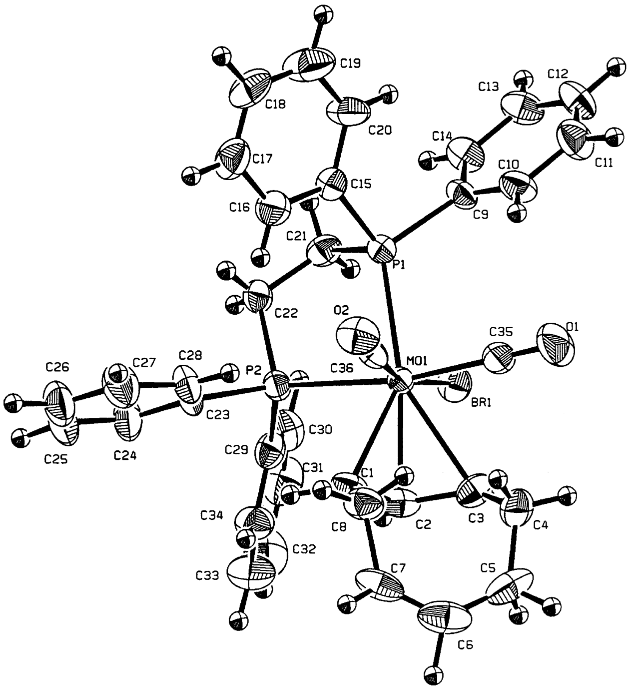


Fig. 2 Molecular structure of complex **5a**.

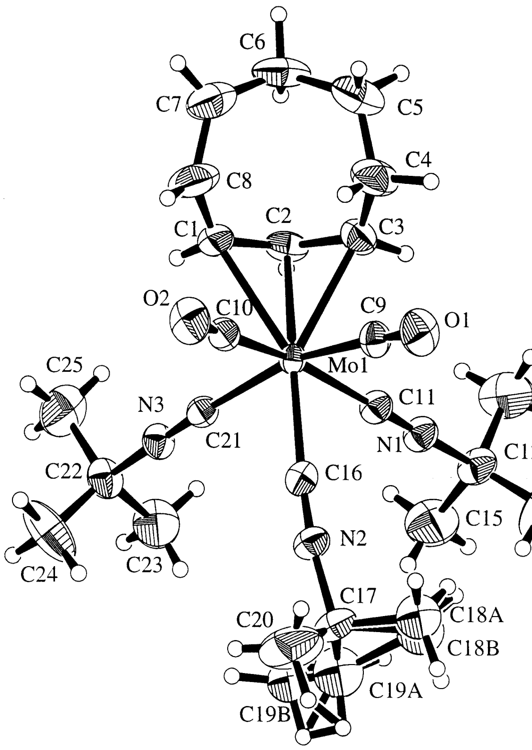


Fig. 3 Molecular structure of complex **8b**; BF$_4$ counter anion omitted.

which a PPh$_2$ group of the dppe ligand is positioned *trans* to the ring. The structure of **8b** reveals that the three (CNBu^t ligands assume a facial disposition with the remaining two carbonyl ligands mutually *cis*. This structure concurs with others of the type [Mo(CO)$_2$(L$_3$)(η^3-R)]$^+$,[30] although spectroscopic studies on **8b** indicated the presence of a second isomeric form in solution (see later). Our structural investigations have not defined the ligand geometry in complexes of the type [MoBr(CO)$_2$(CNBu^t)$_2$(η^3-C$_8$H$_{11}$)] (**7a** and **7b**), but the results of X-ray structural investigations on the related cycloheptatrienyl complex [WI(CO)$_2$(CNBu^t)$_2$(η^3-C$_7$H$_7$)][31] and spectroscopic studies on **7a** and **7b** intimate an asymmetric ligand arrangement in these complexes, with one CNBu^t ligand located *trans* to the cyclooctadienyl ring.

The parameters associated with the η^3-cyclooctadienyl ring in **4a**, **5a**, **8b**, and the other reported crystallographically characterised examples are surveyed in Table 2. For the structures determined in the current work (**4a**, **5a**, and **8b**) a common crystallographic numbering system has been adopted for the cyclooctadienyl ring and the data in Table 2 for previously reported examples have been adjusted to this system. Thus in both ring types the η^3-allyl carbons are C(1), C(2), and C(3) whilst the double bond is positioned between C(7)–C(8) in the 1–3-η:4,5-C$_8$H$_{11}$ ligand and between C(6)–C(7) in the 1–3-η:5,6-C$_8$H$_{11}$ ligand. The principal objective of the structural comparisons was to explore the preferred conformations of the 1–3-η:4,5-C$_8$H$_{11}$ and 1–3-η:5,6-C$_8$H$_{11}$ ligands and to assess the generality of these conformations.

Considering first the 1–3-η:4,5-C$_8$H$_{11}$ ligand of **8b**, [Mo(CO)$_2$(BH$_2$pz$_2$)(1–3-η:4,5-C$_8$H$_{11}$)], and [Rh(η^4-C$_8$H$_{12}$)(1–3-η:4,5-C$_8$H$_{11}$)],[17] the short bond lengths in the allyl group C(1)–C(2), C(2)–C(3) and the double bond C(7)–C(8) are evident from Table 2. Furthermore, the angle C(5)–C(6)–C(7) associated with the sp^3 carbon C(6) is consistently small (*ca.* 112°) whilst the angle C(8)–C(1)–C(2) associated with the terminal allyl carbon C(1) on the same side of the ring as the double bond is always larger than average (*ca.* 127°). Calculations on the data for **8b** suggest that the coordinated 1–3-η:4,5-C$_8$H$_{11}$ ligand is folded about C(1)–C(3), C(4)–C(8), and C(5)–C(7) into four planes: C(1)–C(2)–C(3), C(1)–C(3)–C(4)–C(8), C(4)–C(5)–C(7)–C(8), and C(5)–C(6)–C(7). Deviations from the plane C(1)–C(3)–C(4)–C(8) are very small, but the plane C(4)–C(5)–C(7)–C(8), which incorporates the double bond C(7)–C(8), is less well defined. As a result of this configuration, the sp^3 carbon C(6) is tilted back towards the allyl group. Comparison of the torsion angles presented in Table 2 suggests that this configuration of the 1–3-η:4,5-C$_8$H$_{11}$ ligand in the solid state is common at least to the two molybdenum complexes **8b** and [Mo(CO)$_2$(BH$_2$pz$_2$)(1–3-η:4,5-C$_8$H$_{11}$)].

The 1–3-η:5,6-C$_8$H$_{11}$ ligand of **4a**, **5a**, and [Rh(PPh$_3$)$_2$(1–3-η:5,6-C$_8$H$_{11}$)] also exhibits short bond lengths associated with the allyl group C(1)–C(2), C(2)–C(3) and the double bond C(6)–C(7). Bond angles at the sp^3 carbons C(4) and C(8) adjacent to the terminal allyl carbons are smaller than average (*ca.* 112°) whilst the angle C(5)–C(6)–C(7) at the sp^2 carbon C(6) is consistently large (*ca.* 131°). Inspection of the torsion angles for the 1–3-η:5,6-C$_8$H$_{11}$ ligand of **4a** and **5a** reveal an

Table 1 Important bond lengths and angles for complexes **4a**, **5a**, and **8b**

4a		**5a**		**8b**	
Bond lengths/Å					
Mo(1)–C(1)	2.366(9)	Mo(1)–C(1)	2.385(9)	Mo(1)–C(1)	2.445(5)
Mo(1)–C(2)	2.222(9)	Mo(1)–C(2)	2.243(7)	Mo(1)–C(2)	2.277(5)
Mo(1)–C(3)	2.37(1)	Mo(1)–C(3)	2.437(7)	Mo(1)–C(3)	2.412(5)
Mo(1)–C(19)	1.94(1)	Mo(1)–C(35)	1.972(8)	Mo(1)–C(9)	1.974(5)
Mo(1)–C(20)	1.97(1)	Mo(1)–C(36)	1.925(8)	Mo(1)–C(10)	1.974(5)
Mo(1)–Br(1)	2.640(1)	Mo(1)–Br(1)	2.689(1)	Mo(1)–C(16)	2.115(5)
Mo(1)–N(1)	2.251(8)	Mo(1)–P(1)	2.554(2)	Mo(1)–C(11)	2.191(5)
Mo(1)–N(2)	2.245(9)	Mo(1)–P(2)	2.601(2)	Mo(1)–C(21)	2.189(5)
Bond angles/°					
C(19)–Mo(1)–C(20)	81.9(5)	C(35)–Mo(1)–C(36)	81.8(3)	C(9)–Mo(1)–C(10)	80.94(19)
C(20)–Mo(1)–N(1)	103.3(4)	C(36)–Mo(1)–P(2)	102.5(2)	C(10)–Mo(1)–C(21)	97.97(17)
N(1)–Mo(1)–N(2)	72.9(3)	P(1)–Mo(1)–P(2)	76.85(6)	C(21)–Mo(1)–C(11)	84.34(16)
N(2)–Mo(1)–C(19)	99.0(4)	C(35)–Mo(1)–Br(1)	90.4(3)	C(11)–Mo(1)–C(9)	94.06(18)
C(20)–Mo(1)–N(2)	166.7(3)	C(35)–Mo(1)–P(2)	167.9(3)	C(10)–Mo(1)–C(11)	168.77(18)
C(19)–Mo(1)–N(1)	166.1(4)	C(36)–Mo(1)–Br(1)	165.3(2)	C(9)–Mo(1)–C(21)	165.51(18)
Br(1)–Mo(1)–C(2)	164.8(3)	P(1)–Mo(1)–C(2)	161.3(2)	C(16)–Mo(1)–C(2)	164.97(18)
Br(1)–Mo(1)–C(19)	87.9(3)	P(1)–Mo(1)–C(35)	92.0(2)	C(16)–Mo(1)–C(9)	83.41(18)
Br(1)–Mo(1)–C(20)	84.0(3)	P(1)–Mo(1)–C(36)	89.7(2)	C(16)–Mo(1)–C(10)	89.06(18)

Table 2 Comparison of structural parameters for trihapto-bonded cyclooctadienyl ligands[a]

	8b	**A**	**B**	**4a**	**5a**	**C**
Bond lengths/Å						
C(1)–C(2)	1.369(8)	1.379(8)	1.46	1.39(2)	1.41(1)	1.39(2)
C(2)–C(3)	1.397(7)	1.411(8)	1.52	1.42(2)	1.39(1)	1.40(2)
C(3)–C(4)	1.473(8)	1.492(8)	1.50	1.52(2)	1.51(1)	1.51(2)
C(4)–C(5)	1.403(8)	1.427(10)	1.46	1.50(2)	1.50(1)	1.48(2)
C(5)–C(6)	1.503(9)	1.473(10)	1.53	1.44(2)	1.42(2)	1.49(3)
C(6)–C(7)	1.469(10)	1.503(10)	1.49	1.37(2)	1.36(1)	1.42(3)
C(7)–C(8)	1.361(9)	1.390(9)	1.40	1.51(2)	1.53(1)	1.48(2)
C(8)–C(1)	1.488(9)	1.477(9)	1.40	1.53(2)	1.53(1)	1.49(2)
Bond angles/°						
C(1)–C(2)–C(3)	122.1(5)	122.5(5)	122	120(1)	121.9(6)	
C(2)–C(3)–C(4)	124.9(6)	123.8(5)	121	123(1)	124.1(8)	
C(3)–C(4)–C(5)	120.1(6)	121.1(6)	119	112(1)	112.1(6)	
C(4)–C(5)–C(6)	119.3(5)	119.5(6)	115	121(1)	124.0(8)	
C(5)–C(6)–C(7)	112.4(5)	114.6(7)	112	131(1)	130.2(9)	
C(6)–C(7)–C(8)	122.7(7)	120.8(5)	122	124(1)	123.8(10)	
C(7)–C(8)–C(1)	121.4(7)	120.8(6)	129	112(1)	112.2(6)	
C(8)–C(1)–C(2)	127.1(6)	125.6(5)	127	123(1)	122.2(6)	
Torsion angles/°						
C(1)–C(2)–C(3)–C(4)	−39(1)	45	−37	−45(1)	43(1)	
C(2)–C(3)–C(4)–C(5)	−53(1)	47	−61	−55(1)	56(1)	
C(3)–C(4)–C(5)–C(6)	43(1)	−40	56	74(1)	−73(1)	
C(4)–C(5)–C(6)–C(7)	60(1)	−61	53	−1(3)	−1(1)	
C(5)–C(6)–C(7)–C(8)	−67(1)	64	−85	1(3)	0(1)	50
C(6)–C(7)–C(8)–C(1)	−31(1)	37	−6	−74(1)	75(1)	
C(7)–C(8)–C(1)–C(2)	44(1)	−48	27	52(1)	−55(1)	
C(8)–C(1)–C(2)–C(3)	41(1)	−43	45	46(1)	−43(1)	

[a] **A** = [Mo(CO)$_2$(BH$_2$pz$_2$)(1–3-η:4,5-C$_8$H$_{11}$)], **B** = [Rh(η^4-C$_8$H$_{12}$)(1–3-η:4,5-C$_8$H$_{11}$)], **C** = [Rh(PPh$_3$)$_2$(1–3-η:5,6-C$_8$H$_{11}$)], numbering scheme for the cyclooctadienyl ligand standardised to the crystallographic numbering scheme employed in this paper. Data for **A**, **B**, and **C** from ref. 10, 17, and 18, respectively. Torsion angles for **A** and **B** calculated from atomic coordinates supplied in ref. 10 and 17.

almost identical ring conformation; very little data are available for [Rh(PPh$_3$)$_2$(1–3-η:5,6-C$_8$H$_{11}$)], the only other example available for comparison, but the reported torsion angle C(5)–C(6)–C(7)–C(8) suggests a very different conformation for the ligand in this complex. In **4a** and **5a** the 1–3-η:5,6-C$_8$H$_{11}$ ligand is folded about C(1)–C(3) and C(4)–C(8) into three planes: C(1)–C(2)–C(3), C(1)–C(3)–C(4)–C(8), and C(4)–C(5)–C(6)–C(7)–C(8). The co-planarity of C(4)–C(5)–C(6)–C(7)–C(8) is clear from inspection of the torsion angles C(4)–C(5)–C(6)–C(7) and C(5)–C(6)–C(7)–C(8), and is presumably imposed by the location of the double bond between C(6) and C(7). Therefore, in contrast with the 1–3-η:4,5-C$_8$H$_{11}$ ligand, the 1–3-η:5,6-C$_8$H$_{11}$ ring is not folded about C(5)–C(7) and consequently, in this ligand, C(6) is not significantly tilted back towards the allyl group.

Spectroscopic studies

Microanalytical, infrared, and mass spectroscopic data for the new complexes are summarised in Table 3. All of the complexes are dicarbonyl derivatives and, with the exception of **8b**, (see later), each exhibits carbonyl stretching bands with relative intensities indicative of *cis* carbonyls. The identity of the cyclooctadienyl ligand (1–3-η:5,6-C$_8$H$_{11}$ *vs.* 1–3-η:4,5-C$_8$H$_{11}$) has only a very small effect upon the observed carbonyl stretching frequencies but, in the majority of cases, complexes of the 1–3-

Table 3 Microanalytical, infrared, and mass spectroscopic data for $[\mathrm{MoBr(CO)_2(L_2)(\eta^3\text{-}C_8H_{11})}]$ and $[\mathrm{Mo(CO)_2(L_3)(\eta^3\text{-}C_8H_{11})}]^+$

Complex	Analysis[a] (%) C	H	N	IR[b]/cm^{-1} $\nu(\mathrm{CNBu^t})$	$\nu(\mathrm{CO})$	FAB-MS[c], *m*/*z*
1a	40.1 (39.9)	4.2 (4.1)	6.9 (6.7)		1944, 1857[d]	384 ($[\mathrm{M-NCMe}]^+$), 340 ($[\mathrm{M-2NCMe-2H}]^+$), 302 ($[\mathrm{M-NCMe-Br}]^+$)
1b	39.8 (39.9)	4.0 (4.1)	6.4 (6.7)		1945, 1858[d]	383 ($[\mathrm{M-NCMe}]^+$), 340 ($[\mathrm{M-2NCMe-2H}]^+$), 302 ($[\mathrm{M-NCMe-Br}]^+$)
2a	41.7 (41.0)	4.2 (4.3)	8.8 (9.0)		1958, 1875[d]	384 (M^+), 343 ($[\mathrm{M-NCMe}]^+$), 302 ($[\mathrm{M-2NCMe}]^+$), 274 ($[\mathrm{M-2NCMe-CO}]^+$), 246 ($[\mathrm{M-2NCMe-2CO}]^+$)
2b	41.1 (41.0)	4.5 (4.3)	8.6 (9.0)		1958, 1875[d]	384 (M^+), 343 ($[\mathrm{M-NCMe}]^+$), 302 ($[\mathrm{M-2NCMe}]^+$), 274 ($[\mathrm{M-2NCMe-CO}]^+$), 246 ($[\mathrm{M-2NCMe-2CO}]^+$)
3a	55.7 (55.7)	4.8 (5.0)			1935, 1850	326 (M^+), 298 ($[\mathrm{M-CO}]^+$)
3b	55.6 (55.7)	5.0 (5.0)			1937, 1853	326 (M^+), 298 ($[\mathrm{M-CO}]^+$)
4a	48.9 (48.5)	3.9 (3.9)	5.8 (5.7)		1943, 1859	496 (M^+), 438 ($[\mathrm{M-2CO-2H}]^+$), 417 ($[\mathrm{M-Br}]^+$), 358 ($[\mathrm{M-Br-2CO-2H}]^+$)
4b	48.7 (48.5)	4.2 (3.9)	5.8 (5.7)		1944, 1861	496 (M^+), 440 ($[\mathrm{M-2CO}]^+$), 417 ($[\mathrm{M-Br}]^+$), 359 ($[\mathrm{M-Br-2CO-2H}]^+$)
5a	58.3 (58.6)	4.7 (4.8)			1934, 1841	659 ($[\mathrm{M-Br}]^+$), 629 ($[\mathrm{M-Br-CO-2H}]^+$), 599 ($[\mathrm{M-Br-2CO-4H}]^+$)
5b	58.3 (58.6)	4.7 (4.8)			1935, 1841	738 (M^+), 710 ($[\mathrm{M-CO}]^+$), 680 ($[\mathrm{M-2CO-2H}]^+$), 659 ($[\mathrm{M-Br}]^+$), 629 ($[\mathrm{M-Br-CO-2H}]^+$), 599 ($[\mathrm{M-Br-2CO-4H}]^+$), 575 ($[\mathrm{M-2CO-C_8H_{11}}]^+$)
6a	58.1 (58.1)	4.9 (4.6)			1939, 1848	724 (M^+), 696 ($[\mathrm{M-CO}]^+$), 666 ($[\mathrm{M-2CO-2H}]^+$), 645 ($[\mathrm{M-Br}]^+$), 615 ($[\mathrm{M-Br-CO-2H}]^+$), 585 ($[\mathrm{M-Br-2CO-4H}]^+$)
6b	58.4 (58.1)	4.7 (4.6)			1938, 1845	666 ($[\mathrm{M-2CO-2H}]^+$), 645 ($[\mathrm{M-Br}]^+$), 615 ($[\mathrm{M-Br-CO-2H}]^+$), 585 ($[\mathrm{M-Br-2CO-4H}]^+$), 561 ($[\mathrm{M-2CO-C_8H_{11}}]^+$)
7a	47.7 (47.5)	5.8 (5.8)	5.5 (5.5)	2179	1951, 1867	509 (M^+), 452 ($[\mathrm{M-2CO}]^+$), 427 ($[\mathrm{M-Br}]^+$), 399 ($[\mathrm{M-Br-CO}]^+$), 369 ($[\mathrm{M-Br-2CO-2H}]^+$)
7b	47.4 (47.5)	6.2 (5.8)	5.3 (5.5)	2177	1949, 1868	509 (M^+), 452 ($[\mathrm{M-2CO}]^+$), 427 ($[\mathrm{M-Br}]^+$), 399 ($[\mathrm{M-Br-CO}]^+$), 369 ($[\mathrm{M-Br-2CO-2H}]^+$)
8a	50.4 (50.4)	6.5 (6.4)	6.9 (7.1)	2187, 2170	1981, 1924	510 (M^+), 482 ($[\mathrm{M-CO}]^+$), 452 ($[\mathrm{M-2CO-2H}]^+$), 427 ($[\mathrm{M-CNBu^t}]^+$), 399 ($[\mathrm{M-CNBu^t-CO}]^+$), 369 ($[\mathrm{M-CNBu^t-2CO-2H}]^+$)
8b	50.5 (50.4)	6.7 (6.4)	7.1 (7.1)	2183, 2152	1984, 1931	510 (M^+), 482 ($[\mathrm{M-CO}]^+$), 454 ($[\mathrm{M-2CO}]^+$), 426 ($[\mathrm{M-CNBu^t}]^+$), 399 ($[\mathrm{M-CNBu^t-CO}]^+$), 369 ($[\mathrm{M-CNBu^t-2CO-2H}]^+$)

[a] Calculated values in parentheses. [b] Solution spectra in $\mathrm{CH_2Cl_2}$, unless otherwise stated. [c] *m*/*z* values based on $^{98}\mathrm{Mo}$. [d] In NCMe.

η:4,5-$\mathrm{C_8H_{11}}$ ligand have $\nu(\mathrm{CO})_{\mathrm{average}}$ to high wavenumber of that of the 1–3-η:5,6-$\mathrm{C_8H_{11}}$ analogue by 1 to 2 cm^{-1}. Where comparisons are possible, analogous complexes of the cycloheptadienyl system {for example $[\mathrm{Mo(CO)_2(\eta^3\text{-}C_7H_9)Cp}]$, $\nu(\mathrm{CO})$ 1938, 1856 cm^{-1} ($\mathrm{CH_2Cl_2}$)}[4] exhibit $\nu(\mathrm{CO})_{\mathrm{average}}$ shifted yet slightly further to high wavenumber. The preferred mass spectroscopic technique for these complexes was FAB spectroscopy; electrospray mass spectroscopy was also applied to selected complexes with some success, but the use of solvents such as NCMe, inherent to this technique, led to ligand exchange processes and resultant complications in spectral interpretation. The fragmentation patterns observed were almost independent of the identity of the cyclooctadienyl ligand, but notable features were the lability of halide and NCMe ligands, and (as observed for analogous cycloheptadienyl systems)[4] the loss of 2 or 4 additional mass units which we attribute to fragmentation of the cyclooctadienyl ring. Each of the isocyanide complexes **7a**, **7b**, **8a**, and **8b** exhibit a group of peaks around *m*/*z* = 565, and this may be attributed to the generation of $[\mathrm{Mo(CO)(CNBu^t)_4(\eta^3\text{-}C_8H_{11})}]^+$, the synthesis and isolation of which will be described in a subsequent paper.

The ^{1}H and ^{13}C NMR data for each of the new complexes described in this paper are summarised in Tables 4 and 5, respectively and define characteristic spectra for both types of η^3-bonded cyclooctadienyl ligand. The tables are arranged to group together complexes of one ligand type for ease of comparison, thus complexes **1a** to **8a** are presented first, followed by **1b** to **8b**. The best resolved spectra were obtained for the tris-nitrile cations **2a** and **2b**, and the cyclopentadienyl derivatives **3a** and **3b**. The characteristic chemical shifts and couplings of the assigned resonances aided identification in less straightforward cases, although the majority of spectra were fully assigned by the techniques of [^{1}H–^{1}H] COSY or double irradiation (^{1}H NMR spectra), or [^{1}H–^{13}C] HETCOR (^{13}C{^{1}H} spectra).

The ^{1}H NMR spectra of $[\mathrm{Mo(CO)_2(\eta^3\text{-}R)Cp}]$ (R = 1–3-η:5,6-$\mathrm{C_8H_{11}}$, **3a**; 1–3-η:4,5-$\mathrm{C_8H_{11}}$, **3b**) are illustrated in Fig. 4 and 5 respectively. For both ligands, there are three principal regions of the spectrum: the two protons of the uncoordinated double bond at low field, the three allyl protons and, at high field, the six protons of the three methylene groups. In the 1–3-η:4,5-$\mathrm{C_8H_{11}}$ ligand, one of the protons attached to C^8 (spectroscopic numbering system) is characteristically shifted to high field and consistently appears in the region 0.5 to 1.1 ppm—no proton resonances from the 1–3-η:5,6-$\mathrm{C_8H_{11}}$ ligand are observed in this region. For complexes **2a** and **2b**, selected ^{1}H–^{1}H coupling constants have been determined by double irradiation techniques and these are listed in Table 4. Of particular note is the magnitude of the coupling between the terminal allyl proton (H^3) and the olefinic proton (H^4) [$J(\mathrm{H^3\text{–}H^4})$ = 3 Hz] in the complex $[\mathrm{Mo(CO)_2(NCMe)_3(1\text{–}3\text{-}\eta\text{:}4,5\text{-}C_8H_{11})}]^+$, **2b**; a very similar value (2.4 Hz) is reported for this parameter in $[\mathrm{Mo(CO)_2(BH_2pz_2)}$-

Table 4 ^{1}H NMR data for [MoBr(CO)$_2$(L$_2$)(η^3-C$_8$H$_{11}$)] and [Mo(CO)$_2$(L$_3$)(η^3-C$_8$H$_{11}$)]$^+$ [a]

Complex	H$_{alkene}$	H$_{allyl}$	H$_{methylene}$	L
1a [b]	5.79, 1H, m, H^5; 5.44, 1H, m, H^6	4.52, 1H, m, 4.33, 1H, m, H^1 and H^3; 3.87, 1H, at, H^2, J(H^2–H^3) 8	2.50, 1H, m, 1.92, 1H, m, H^4; 2.40, 1H, m, 1.55, 1H, m, H^8; 2.26, 2H, m, H^7	
2a [b]	5.83, 1H, m, H^5, J(H^5–H^6) 11; 5.49, 1H, m, H^6	4.89, 1H, m, H^3; 4.72, 1H, m, H^1, J(H^1–H^2) 8; 3.86, 1H, at, H^2, J(H^2–H^3) 7	2.62, 1H, m, 2.02, 1H, m, H^4; 2.49, 1H, m, 1.65, 1H, m, H^8; 2.36, 2H, m, H^7	
3a [c]	5.79, 1H, m, H^5, J(H^5–H^6) 11; 5.40, 1H, m, H^6	4.23, 1H, m, 3.99, 1H, m, H^3 and H^1; 3.84, 1H, at, H^2, J(H^2–H^3) 8	2.45, 1H, m, 2.05, 1H, m, H^4; 2.35, 1H, m, 1.67, 1H, m, H^8; 2.24, 2H, m, H^7	5.23, 5H, s, Cp
4a	5.74, 1H, m, H^5; 5.39, 1H, m, H^6	4.20, 1H, m, 3.97, 1H, m, H^3 and H^1; 2.91, 1H, at, H^2, J(H^2–H^3) 8	2.66, 1H, m, H^4; 2.55, 1H, m, 1.79, 1H, m, H^8; 2.27–2.11, 3H, m, H^7 and H^4	8.91, 2H, m, H^A; 8.12, 2H, m, H^D; 8.00, 2H, m, H^C; 7.50, 2H, m, H^B
5a [d,e]	5.73, 1H, m, H^5; 5.40, 1H, m, H^6	4.94, 1H, m, H^3; 4.80, 1H, m, H^1; 3.75, 1H, at, H^2, J(H^2–H^3) 8	2.55, 1H, m, H^4; 2.01, 1H, m, H^8; 2.45–2.18, 6H, m, H^4, H^7, H^8, and CH$_2$ (dppe)	7.63, 8H, m, Ph; 7.42, 12H, m, Ph; 2.98, 2H, m, CH$_2$ (dppe); 2.45–2.18, 6H, m, H^4, H^7, H^8, and CH$_2$ (dppe)
6a	5.64, 1H, m, H^5; 5.29, 1H, m, H^6	4.95, 1H, br, 4.80, 1H, br, H^1 and H^3; 3.86, 2H, m, H^2 and CH$_2$ (dppm)	2.48, 1H, m, 2.26, 1H, m, H^4; 2.40, 1H, m, 1.88, 1H, br, H^8; 2.17, 2H, br, H^7	7.38, 8H, m, Ph; 7.24, 12H, m, Ph; 4.32, 1H, m, CH$_2$ (dppm); 3.86, 2H, m, H^2 and CH$_2$ (dppm)
7a [c]	5.78, 1H, m, H^5; 5.46, 1H, m, H^6	4.91, 2H, br, H^1 and H^3; 4.57, 1H, at, H^2, J(H^2–H^3) 8	2.56, 2H, m, H^4 and H^8; 2.29, 3H, br, H^4 and H^7; 2.00, 1H, m, H^8	1.56, 9H, s, 1.51, 9H, s, CNBu^t
8a [c]	5.70, 1H, m, H^5; 5.42, 1H, m, H^6	4.91, 1H, m, 4.81, 1H, m, H^1 and H^3; 4.49, 1H, at, H^2, J(H^2–H^3) 8	2.62, 1H, m, 2.39, 1H, m, H^4; 2.55, 1H, m, 2.15, 1H, br, H^8; 2.29, 2H, br, H^7	1.60, s, 1.49, s, 1.46, s, 27H, CNBu^t
1b [b]	6.26, 1H, dd, H^4, J(H^4–H^5) 11; 5.33, 1H, m, H^5	4.65, 1H, br, H^3; 4.05, 1H, br, H^1; 4.20, 1H, at, H^2, J(H^2–H^3) 8	2.84, 1H, m, 2.03, 1H, m, H^6; 2.15, 1H, m, 0.58, 1H, m, H^8; 1.65, 1H, m, 1.29, 1H, m, H^7	
2b [b]	6.33, 1H, dd, H^4, J(H^4–H^5) 11; 5.46, 1H, m, H^5	4.93, 1H, dd, H^3, J(H^3–H^4) 3; 4.40, 1H, m, H^1, J(H^1–H^2) 8; 4.13, 1H, at, H^2, J(H^2–H^3) 7	2.77, 1H, m, 2.20, 1H, m, H^6; 2.27, 1H, m, 0.57, 1H, m, H^8; 1.72, 1H, m, 1.35, 1H, m, H^7	
3b [c]	6.22, 1H, m, H^4, J(H^4–H^5) 11; 5.10, 1H, m, H^5	4.11, 1H, at, H^2, J(H^2–H^3) 8; 4.07, 1H, dd, H^3; 3.86, 1H, m, H^1	2.76, 1H, m, 2.06, 1H, m, H^6; 2.12, 1H, m, 0.75, 1H, m, H^8; 1.43, 1H, m, 1.14, 1H, m, H^7	5.25, 5H, s, Cp
4b	6.40, 1H, m, H^4, J(H^4–H^5) 11; 5.30, 1H, m, H^5	4.21, 1H, m; 3.67, 1H, m; H^1 and H^3; 3.21, 1H, at, H^2, J(H^2–H^3) 8	2.67, 1H, m, 2.00, 1H, m, H^6; 2.35, 1H, m, 0.81, 1H, m, H^8; 1.51, 1H, m, 1.28, 1H, m, H^7	8.91, 2H, m, H^A; 8.15, 2H, m, H^D; 8.01, 2H, m, H^C; 7.51, 2H, m, H^B
5b [f]	6.16, 1H, dd, H^4, J(H^4–H^5) 11; 5.34, 1H, m, H^5	5.20, 1H, br, H^3; 4.45, 1H, br, H^1; 4.18, 1H, at, H^2, J(H^2–H^3) 8	2.71, 1H, m, 2.08, 1H, m, H^6; 2.36, m, 3H, CH$_2$ (dppe) and H^8; 1.07, 1H, m, H^8; 1.58, 1H, br, 1.30, 1H, br, H^7	7.71, 7.47, 20H, m, Ph; 3.04, m, 2H, CH$_2$ (dppe); 2.36, m, 3H, CH$_2$ (dppe) and H^8
6b [c]	6.43, 1H, dd, H^4, J(H^4–H^5) 11; 5.38, 1H, m, H^5	5.24, 1H, br, H^3; 4.70, 1H, br, H^1; 4.37, 1H, at, H^2, J(H^2–H^3) 8	2.77, 1H, m, 2.12, 1H, m, H^6; 2.42, m, 1H, 1.13, 1H, m, H^8; 1.60, 1H, br, 1.32, 1H, br, H^7	7.59, 7.43, 7.33, 20H, m, Ph; 4.55, m, 1H, 4.07, m, 1H, CH$_2$ (dppm)
7b	6.38, 1H, m, H^4, J(H^4–H^5) 11; 5.34, 1H, m, H^5	5.16, 1H, br, H^3; 4.30, 1H, br, H^1; 4.79, 1H, at, H^2, J(H^2–H^3) 8	2.75, 1H, m, 2.13, 1H, m, H^6; 2.22, 1H, m, 0.89, 1H, m, H^8; 1.73–1.41, 19H, m, H^7 and CNBu^t, 1.28, 1H, m, H^7	1.54, 1.51, 18H, CNBu^t
8b [d,g]	6.36, m, H^4; 5.43, m, H^5; 5.34, m, H^{5*}	5.19, m, H^3; 4.57, m, H^1; 4.82, at, H^2, J(H^2–H^3) 8 5.06, m, H^{3*}; 4.62, m, H^{1*}; 5.15, at, H^{2*}, J(H^2–H^3) 8	2.53, m, 2.17, m, H^6; 2.37, m, 1.23, m, H^8; 1.73–1.33, m, H^7 and CNBu^t 2.53, m, 2.22, m, H^{6*}; 2.37, m, 1.84, m, H^{8*}; 1.73–1.33, m, H^{7*} and CNBu^t	1.60, 1.59, 1.52, 1.46, CNBu^t

[a] 300 MHz ^{1}H NMR spectra in CD$_2$Cl$_2$ solution, unless otherwise stated; s = singlet, d = doublet, at = apparent triplet, m = multiplet, br = broad; chemical shifts, δ, downfield from SiMe$_4$, coupling constants in Hz; atom numbering as in Scheme 1. All spectra recorded at room temperature, except for **1a** (−30 °C) and **8a** (−10 °C). [b] In CD$_3$CN. [c] In CDCl$_3$. [d] 500 MHz spectrum. [e] ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C): 43.3 (br), 43.0 (br); (−80 °C): isomer 1: 44.1, d, J(P–P) 15; 41.6, d, J(P–P) 15; isomer 2: 42.5, d, J(P–P) 10; 41.9, d J(P–P) 10; isomer ratio 1 : 2 = 45 : 55. [f] ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C): 44.8, d, J(P–P) 13; 43.6, d, J(P–P) 14; (−80 °C): isomer 1: 48.2, d, J(P–P) 23; 43.6, d, J(P–P) 23; isomer 2: 44.0 (br), 40.7, d, J(P–P) 9; isomer ratio 1 : 2 = 75 : 25. [g] Asterisks indicate resonances for minor isomer (isomer ratio *ca.* 65 : 35 major: minor).

Table 5 ^{13}C NMR data for [MoBr(CO)$_2$(L$_2$)(η^3-C$_8$H$_{11}$)] and [Mo(CO)$_2$(L$_3$)(η^3-C$_8$H$_{11}$)]$^{+}$ [a]

Complex	CO	C$_{\text{alkene}}$	C$_{\text{allyl}}$	C$_{\text{methylene}}$	L
1a[b] (−30 °C)	224.9	129.0, 128.9	74.3, 73.7, 71.6	31.7, 30.6, 30.5	
2a[b]	223.6, 223.5	130.6, C^6; 130.0, C^5	82.7, C^1; 81.9, C^3; 75.4, C^2	33.0, C^7; 31.6, C^{4,8}	
3a[c]	238.5, 238.2	130.8, 129.3	65.4, 61.7, 61.4	33.5, 30.5, 30.3	92.0, Cp
4a	—[d]	130.0, 129.8	74.3, 74.1, 73.7	33.2, 32.5, 32.4	153.9, 153.0, C$^{\mathbf{A},\mathbf{A}',\mathrm{E},\mathrm{E}'}$; 139.0, 138.9, C$^{\mathbf{C},\mathbf{C}'}$; 126.2, 122.7, C$^{\mathbf{B},\mathbf{B}',\mathrm{D},\mathrm{D}'}$
5a	226.3, dd, *J*(C–P) 12, 4; 225.5, t, *J*(C–P) 10	[e]	82.6, C^2; 82.4 (br), 79.0 (br) C^1 and C^3	32.8, 31.1, 30.9	135.6–128.4, Ph; 26.5, m, 26.0, m, CH$_2$
6a	226.5–225.5	[e]	82.0, 81 (br), 79 (br)	32.2, 30.5, 30.2	133.0–127.5, Ph, 34.9, m, CH$_2$
6a (−80 °C)	228.0–223.9, m		86.6, 84.5, 81.1, 79.0, 73.5, 70.2	32.5, 32.0, 30.5, 30.1, 29.9	134.3–128.0, Ph, 33.4, m, CH$_2$
7a[c]		129.8, 129.3	79.8	32.4, 31.6, 30.9	151.7 (br), *C*NCMe$_3$; 57.6, 57.3, CN*C*Me$_3$; 30.6, CNC*C*H$_3$
7a[f] (−50 °C)	225.4, 217.3, 224.9*, 217.6*	129.7, 129.1, 129.5*, 129.4*	94.1, 77.8, 69.6, 91.6*, 78.1*, 72.6*	32.3, 31.6, 30.7, 32.4*, 31.1*, 30.5*	149.3 (br), *C*NCMe$_3$; 57.9, 57.0, CN*C*Me$_3$; 30.1, 30.0, CNC*C*H$_3$
8a[c] (−10 °C)	215.4, 214.1	129.8, 128.4	82.3, 81.0, 80.0	32.1, 31.9, 31.5	59.5, 58.6, 58.4, CN*C*Me$_3$; 30.4, 30.3, 30.1, CNC*C*H$_3$
1b[b,f] (−30 °C)	225.6, 224.2, 224.2*, 223.0*	134.3, 125.7, 132.6*, 128.4*	71.9, 68.8, 68.1, 75.5*, 75.4*, 73.7*	31.3, 28.1, 23.8, 30.9*, 28.2*, 23.7*	
2b[b]	225.0, 223.3	134.4, C^4; 130.0, C^5	77.3, C^3; 77.1, C^1; 75.8, C^2	32.5, C^8; 29.8, C^7; 25.3, C^6	
3b[c]	239.1, 235.9	134.6, 124.3	66.1, 63.3, 49.7	31.4, 27.4, 24.8	92.0, Cp
4b	[d]	136.0, 126.1	74.4, 69.0, 68.6	33.0, 29.7, 25.2	153.3, 152.6, C$^{\mathbf{A},\mathbf{A}',\mathrm{E},\mathrm{E}'}$; 139.0, 138.9, C$^{\mathbf{C},\mathbf{C}'}$; 126.4, 122.7, 122.6, C$^{\mathbf{B},\mathbf{B}',\mathrm{D},\mathrm{D}'}$
5b	228.5, dd, *J*(C–P) 11, 16; 224.8, dd, *J*(C–P) 9, 2	[e]	85.4, 76.6, 75.1	31.8, 28.7, 25.2	135.6–128.1, Ph; 26.6, m, CH$_2$
6b[c]	228.2, br; 225.5, br	133.4, C^4; 127.1, C^5[g]	85.5, C^2, 77.0, C^1, 73.7, C^3[g]	31.6, 28.2, 24.7	133.7–128.4, Ph; 36.1, m, CH$_2$
6b (−60 °C)	229.0, m; 224.9, m	[e]	86.9, 78.9, 70.9, 80.5*, 79.5*, 67.8*	31.7, 27.5, 24.5, 31.4*, 29.2*, 24.7*	134.5–127.4, Ph; 34.3, m, CH$_2$
7b	224.7, br; 219.8, br	134.6, C^4; 125.4, C^5	81.0, C^2[h]	32.7, C^8; 29.2, C^7; 25.4, C^6	151.8 (br), *C*NCMe$_3$; 58.2, 57.9, CN*C*Me$_3$; 30.6, CNC*C*H$_3$
7b[f] (−60 °C)	226.4, 215.2, 223.4*, 217.6*	132.7, 126.1, 132.3*, 126.6*	87.6, 77.1, 65.5, 85.0*, 78.6*, 66.0*	31.3, 27.8, 23.8, 30.1*, 26.7*, 23.3*	148.4 (br), *C*NCMe$_3$; 56.8, 55.7, CN*C*Me$_3$; 28.9, CNC*C*H$_3$
8b[f]	218.4, 213.3, 203.6	132.9, C^4; 128.5, C^5, 133.6*, C^4; 127.1*, C^5	87.4, C^2; 80.9, C^3; 77.7, C^1, 96.9*, C^2; 83.4*, C^1; 79.8*, C^3	33.6, C^8; 28.9, C^7; 24.8, C^6; 34.6*, 27.9*, 25.1*	153, br, 150, br, 147, br, *C*NCMe$_3$; 59.8, 59.7, 58.9, 58.4 CN*C*Me$_3$; 30.5, 30.4, CNC*C*H$_3$

[a] 75 MHz ^{13}C NMR spectra in CD$_2$Cl$_2$ solution at room temperature, unless otherwise stated; d = doublet, t = triplet, m = multiplet, br = broad; chemical shifts, δ, downfield from SiMe$_4$, coupling constants in Hz; atom labelling as in Scheme 1. [b] In CD$_3$CN. [c] In CDCl$_3$. [d] Low solubility precluded observation of carbonyl resonances. [e] Alkene carbon resonances obscured by overlap with phenyl carbons of phosphine ligand. [f] Resonances of minor isomer marked with asterisk. [g] HETCOR used to detect obscured (C$_{\text{alkene}}$) or broad (C$_{\text{allyl}}$) resonances. [h] Resonances for C^1 and C^3 not observed.

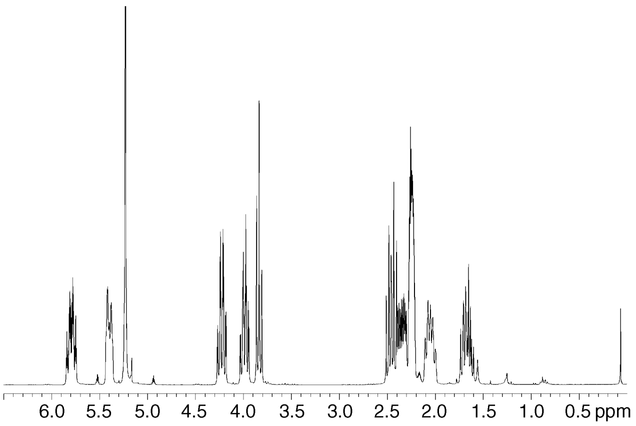


Fig. 4 300 MHz ^{1}H NMR spectrum of [Mo(CO)$_2$(1–3-η:5,6-C_8H_{11})-Cp], **3a**, in $CDCl_3$.

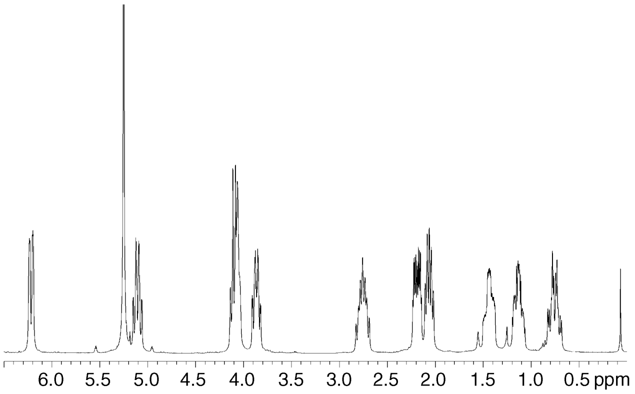


Fig. 5 300 MHz ^{1}H NMR spectrum of [Mo(CO)$_2$(1–3-η:4,5-C_8H_{11})-Cp], **3b**, in $CDCl_3$.

(1–3-η:4,5-C_8H_{11})].[10] The corresponding coupling constant in the analogous cycloheptadienyl complex [Mo(CO)$_2$(NCMe)$_3$-(η^3-C_7H_9)]$^+$ was determined as 6 Hz.[4] We attribute this difference between seven- and eight-membered dienyl rings to additional strain and twisting in the cyclooctadienyl ring system imposed by the extra methylene group, with a resultant increase in the H^3–C^3–C^4–H^4 dihedral angle. There is some evidence for this effect in the solid state, with the dihedral angle H(1)–C(1)–C(8)–H(8) in **8b** (which is equivalent to H^3–C^3–C^4–H^4 in the spectroscopic numbering system) estimated to be 70° based upon location of H(1) by difference Fourier techniques and a calculated position for H(8). The ^{13}C{^{1}H} NMR spectra of **2a**, **2b**, **3a** and **3b** each show eight distinct resonances also divided into olefinic, allylic, and methylene carbons. However the position of the double bond affects the pseudo-symmetry of the ring such that in complexes of the 1–3-η:5,6-C_8H_{11} ligand, pairs of carbons (the olefinic carbons C^5 and C^6 and two of the methylene carbons C^4 and C^8) have very similar chemical shifts. By comparison, the carbon-13 chemical shift pattern in the 1–3-η:4,5-C_8H_{11} ligand is much more similar to the previously reported cycloheptadienyl system, with a separation of *ca.* 10 ppm between the olefinic carbons C^4 and C^5 and well-separated methylene carbons, with C^6 (the methylene carbon adjacent to the double bond) consistently located at the highest field, around 25 ppm.

The NMR spectra of the remaining complexes follow the general trends described above, but the properties of the ancillary ligands and/or asymmetry at the metal centre impose additional complications. The NMR spectra of the complexes [MoBr(CO)$_2$(NCMe)$_2$(η^3-R)] (R = 1–3-η:5,6-C_8H_{11}, **1a**; 1–3-η:4,5-C_8H_{11}, **1b**) were recorded in CD_3CN to avoid solvent-induced decomposition. In the ^{1}H NMR spectrum of **1a**, some broadening associated with the terminal allyl protons H^1 and H^3 was observed at room temperature, but well-resolved resonances were obtained at −30 °C. The spectra of **1b** were further complicated by an additional (possibly isomeric) minor component and the ^{13}C{^{1}H} resonances for this are reported in Table 5 marked with asterisks. The ambient temperature ^{1}H and ^{13}C{^{1}H} NMR spectra of the complexes [MoBr(CO)$_2$-(L_2)(η^3-R)] [L_2 = dppe, **5a**, **5b**; dppm, **6a**, **6b**; 2(CNBu^t), **7a**, **7b**] are characterised by broad resonances for the terminal allyl positions, 1 and 3, although all other resonances were well resolved and readily assigned. The low temperature ^{1}H NMR spectra of these systems proved to be extremely complex, but low temperature ^{13}C{^{1}H} NMR spectra of selected derivatives revealed pairs of resonances indicative of two low temperature forms—where appropriate resonances originating from the minor component are marked with an asterisk in Table 5. In the case of the dppe derivatives **5a** and **5b**, the phenomenon was further explored by variable temperature ^{31}P NMR spectroscopy. As detailed in the footnote to Table 4, the room temperature spectra of both complexes revealed a doublet of doublets pattern indicative of two inequivalent phosphorus atoms and consistent with the X-ray structural work on **5a**. However, on cooling to −80 °C, two pairs of doublets of doublets were observed, suggesting two low temperature isomers. The ratio of isomeric forms, determined by integration of the ^{31}P NMR spectrum, was ligand dependent (**5a** major : minor, 55 : 45; **5b** major : minor, 75 : 25) but was consistent in each case for two independent preparations (and for **5a**, for two independent synthetic methods—see Experimental). Complexes of the type [MoX(CO)$_2$(dppe)(η^3-allyl)] (allyl = C_3H_5, C_7H_7) can exhibit a trigonal twist process which renders equivalent the two phosphorus atoms of the dppe ligand.[32,33] However, as we have shown, some systems of this type show no evidence for the operation of a trigonal twist process[6] and the cyclooctadienyl complexes **5a** and **5b** must be included in this category.

It might have been expected that the tris-isocyanide complexes [Mo(CO)$_2$(CNBu^t)$_3$(η^3-R)][BF$_4$] (R = 1–3-η:5,6-C_8H_{11}, **8a**; 1–3-η:4,5-C_8H_{11}, **8b**) would exhibit simple, single component spectra similar to the tris-nitrile analogues **2a** and **2b**. However, in each case, the NMR spectra were complicated by additional effects. As will be described in a subsequent paper, complex **8a** is a precursor to the η^5-cyclooctadienyl product [Mo(CO)(CNBu^t)$_3$(1–3:5,6-η-C_8H_{11})]$^+$ and the facile conversion process necessitated the synthesis and characterisation of **8a** at low temperature. Even so, the ^{13}C{^{1}H} NMR spectrum of **8a** exhibited some contamination by [Mo(CO)(CNBu^t)$_3$(1–3:5,6-η-C_8H_{11})]$^+$, but the resonances due to this latter complex were readily excluded with reference to data from its independent characterisation. By contrast with **8a**, **8b** is not readily converted to the corresponding η^5-cyclooctadienyl system, but both ^{1}H and ^{13}C{^{1}H} NMR spectra of **8b**, repeated on two independently prepared samples, revealed two components each with resonances characteristic of the trihapto-bonded, 1–3-η:4,5-C_8H_{11} ligand. It is possible that, over time in solution, **8b** forms a mixture with a second, discrete complex, although one probable candidate for this, [Mo(CO)(CNBu^t)$_4$(1–3-η:4,5-C_8H_{11})][BF$_4$] was excluded by comparison of the data with those of an authentic sample. Alternatively, **8b** may exist in solution, as a mixture of two of three possible isomers differing in the arrangement of carbonyl and isocyanide ligands. X-Ray crystallographic studies have established that in the solid state, one form has the three isocyanide ligands arranged facially with the two carbonyl ligands mutually *cis*. However, in solution, the observation of only three carbonyl resonances in the ^{13}C{^{1}H} NMR spectrum is consistent with a mixture of a *cis* carbonyl isomer and a *trans* carbonyl isomer. Moreover, the infrared spectrum of **8b** in the carbonyl region reveals an intensity pattern more typical of *trans* carbonyls, with the high wave-number band of relatively low intensity—this is in total contrast to the typical *cis* carbonyl intensity patterns observed for the analogous complexes **8a** and $[Mo(CO)_2(CNBu^t)_3(\eta^3\text{-}C_7H_7)]^+$,[34] neither of which show any evidence for related component mixtures.

Conclusions

A new route to cyclooctadienyl complexes using bromocyclooctadienes as a source of the cyclooctadienyl ligand has been developed. This has provided an entry into the previously unexplored chemistry of the cyclooctadienylmolybdenum system. Starting from the basic precursors $[MoBr(CO)_2(NCMe)_2(1\text{–}3\text{-}\eta\text{:}5,6\text{-}C_8H_{11})]$, **1a** and $[MoBr(CO)_2(NCMe)_2(1\text{–}3\text{-}\eta\text{:}4,5\text{-}C_8H_{11})]$, **1b**, a wide range of substituted complexes is available for both 1–3-η:5,6-C_8H_{11} and 1–3-η:4,5-C_8H_{11} systems. There are relatively few reports in the literature which address the structure and spectroscopic characteristics of trihapto-bonded cyclooctadienyl systems. X-Ray structural studies reveal that in the solid state, the 1–3-η:4,5-C_8H_{11} ligand is folded into four planes, whereas in the 1–3-η:5,6-C_8H_{11} ligand, the position of the double bond imposes a near planarity upon the five non-allylic carbons. The ^1H and $^{13}C\{^1H\}$ NMR spectral data reveal a clear distinction between the olefinic, allylic, and methylene resonances, and the coupling patterns in the ^1H NMR spectra are particularly characteristic of the two discrete types of η^3-cyclooctadienyl ligand. For the 1–3-η:4,5-C_8H_{11} ligand, the proton–proton coupling constant $J(H^3\text{–}H^4)$ is anomalously small, consistent with a twisting of the ring system. That the η^3-cyclooctadienyl complexes reported in this paper are viable precursors to pentahapto-bonded C_8H_{11} products is demonstrated by the low temperature conversion of $[Mo(CO)_2(CNBu^t)_3(1\text{–}3\text{-}\eta\text{:}5,6\text{-}C_8H_{11})]^+$ to $[Mo(CO)(CNBu^t)^3(1\text{–}3\text{:}5,6\text{-}\eta\text{-}C_8H_{11})]^+$, but a full account of the $\eta^3 \longrightarrow \eta^5$ hapticity interconversion processes of all the new complexes reported in this work will be described in a subsequent paper.

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 chemicals dppe, dppm, $CNBu^t$, 2,2′-bipyridine, and NaCp (2.0 M solution in thf) were supplied by Aldrich Chemical Co. $Ag[BF_4]$, 1,3-cod, and 1,5-cod were obtained from Lancaster Synthesis and alumina (Brockmann activity II) for column chromatography was purchased from Merck. 300 MHz ^1H, 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 ^1H NMR spectra were obtained on a Varian Unity 500 instrument. Infrared spectra were obtained on a Perkin Elmer FT 1710 spectrometer and mass spectra using a Kratos Concept 1S instrument. Microanalyses were carried out by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

Preparations

$[MoBr(CO)_2(NCMe)_2(1\text{–}3\text{-}\eta\text{:}5,6\text{-}C_8H_{11})]$ 1a. $Mo(CO)_6$ (3.08 g, 11.67 mmol) was refluxed in NCMe (40 cm^3) for 5 h, after which time a yellow solution had formed. This was cooled to room temperature and a mixture of 3-Br-1,5-cod and 6-Br-1,4-cod (*ca.* 45: 55) (2.40 g, 12.83 mmol) added, resulting in an orange solution. The solution was stirred for 1 h and then the volume was reduced under vacuum, initiating precipitation of **1a** as a yellow solid. The mother liquors were separated and refrigerated for 24 h, giving further quantities of **1a**; yield 2.30 g (47%).

$[MoBr(CO)_2(NCMe)_2(1\text{–}3\text{-}\eta\text{:}4,5\text{-}C_8H_{11})]$ 1b. Yellow **1b** was prepared by an identical procedure as for **1a** above, starting from $Mo(CO)_6$ (4.23 g, 16.04 mmol) a mixture of 5-Br-1,3-cod and 3-Br-1,4-cod (*ca.* 80 : 20) (3.00 g, 16.04 mmol); yield 3.51 g (52%).

$[Mo(CO)_2(NCMe)_3(1\text{–}3\text{-}\eta\text{:}5,6\text{-}C_8H_{11})]$ 2a. To a stirred NCMe (20 cm^3) suspension of **1a** (0.565 g, 1.34 mmol) was added $Ag[BF_4]$ (0.287 g, 1.48 mmol). This rapidly resulted in the formation of a AgBr precipitate. The reaction mixture was stirred at room temperature for 30 min, filtered through Celite to remove AgBr, and then reduced to a low volume (< 5 cm^3) under vacuum. Addition of diethyl ether (20 cm^3) afforded **2a** as a yellow solid. Subsequent recrystallisation from CH_2Cl_2–Et_2O then NCMe–Et_2O gave the final analytically pure product; yield 0.410 g (65%).

Yellow $[Mo(CO)_2(NCMe)_3(1\text{–}3\text{-}\eta\text{:}4,5\text{-}C_8H_{11})][BF_4]$ **2b** was prepared by an identical procedure, starting from **1b** (1.097 g, 2.34 mmol) and $Ag[BF_4]$ (0.502 g, 2.57 mmol); yield 0.98 g (89%).

$[Mo(CO)_2(1\text{–}3\text{-}\eta\text{:}5,6\text{-}C_8H_{11})Cp]$ 3a. A solution of **1a** (0.50 g, 1.19 mmol) in thf (20 cm^3) was treated with NaCp (0.6 cm^3 of a 2.0 M solution in thf). The reaction mixture was stirred at room temperature for 24 h, then filtered to remove NaBr, and subsequently evaporated to dryness. The residue, dissolved in CH_2Cl_2 (5 cm^3), was transferred to an n-hexane–alumina chromatography column and the product eluted as a yellow band with CH_2Cl_2–n-hexane (1 : 3) as the eluant. The product solution was reduced to low volume and cooled to −20 °C to give **3a** as a yellow crystalline solid; yield 0.176 g (46%).

Yellow $[Mo(CO)_2(1\text{–}3\text{-}\eta\text{:}4,5\text{-}C_8H_{11})Cp]$ **3b** was prepared by an identical procedure, starting from **1b** (0.50 g, 1.19 mmol) and NaCp (0.6 cm^3 of a 2.0 M solution in thf); yield 0.148 g (38%).

$[MoBr(CO)_2(bipy)(1\text{–}3\text{-}\eta\text{:}5,6\text{-}C_8H_{11})]$ 4a. To a thf (20 cm^3) solution of **1a** (0.571 g, 1.36 mmol) was added bipy (0.212 g, 1.36 mmol). This resulted in an immediate colour change from orange to intense dark red. The reaction mixture was stirred at room temperature for 2 h, after which time a dark red precipitate of **4a** had formed. The mother liquors were removed and the product washed with diethyl ether (2 × 10 cm^3); yield 0.525 g (78%).

Dark red $[MoBr(CO)_2(bipy)(1\text{–}3\text{-}\eta\text{:}4,5\text{-}C_8H_{11})]$ **4b** was prepared by an identical procedure, starting from **1b** (0.430 g, 1.02 mmol) and bipy (0.159 g, 1.02 mmol); yield 0.435 g (86%).

$[MoBr(CO)_2(dppe)(1\text{–}3\text{-}\eta\text{:}5,6\text{-}C_8H_{11})]$ 5a. *From 1a.* Compound **1a** (0.418 g, 0.93 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and dppe (0.395 g, 0.99 mmol) quickly added. The resulting red solution was stirred at room temperature for 1 h, then filtered through Celite, reduced in volume (to approximately 5 cm^3), and diethyl ether (20 cm^3) added, giving **5a** as an orange solid. The product was recrystallised from CH_2Cl_2–Et_2O; yield 0.60 g (82%).

Orange–red $[MoBr(CO)_2(dppe)(1\text{–}3\text{-}\eta\text{:}4,5\text{-}C_8H_{11})]$ **5b** was prepared by an identical procedure, starting from **1b** (0.215 g, 0.51 mmol) and dppe (0.203 g, 0.51 mmol); yield 0.19 g (50%).

From $[Mo(CO)_2(dppe)(1\text{–}3\text{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$. To a solution of $[Mo(CO)_2(dppe)(1\text{–}3\text{:}5,6\text{-}\eta\text{-}C_8H_{11})][BF_4]$[9] (0.285 g, 0.383 mmol) in acetone (20 cm^3) was added LiBr (0.034 g, 0.39 mmol). The reaction mixture was stirred for 10 min, then evaporated to dryness. Recrystallisation of the residue from CH_2Cl_2–n-hexane gave **5a** as an orange solid; yield 0.227 g (80%).

$[MoBr(CO)_2(dppm)(1\text{–}3\text{-}\eta\text{:}5,6\text{-}C_8H_{11})]$ 6a. Compound **1a** (1.246 g, 2.96 mmol) was dissolved in CH_2Cl_2 (50 cm^3) and dppm (1.137 g, 2.96 mmol) quickly added. The resulting red solution was stirred at room temperature for 2 h, then filtered

Table 6 Crystal and data collection parameters for complexes **4a**, **5a**, and **8b**

	4a	**5a**	**8b**
Formula	$C_{20}H_{19}N_2O_2BrMo$	$C_{36}H_{35}P_2O_2BrMo$	$C_{25}H_{38}N_3O_2MoBF_4$
Mass	495.23	737.46	595.33
Crystal system	Monoclinic	Triclinic	Monoclinic
Temperature/°C	23	23	22
Space group	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a/Å	35.585(5)	11.437(6)	14.225(4)
b/Å	8.05(1)	13.228(5)	12.497(2)
c/Å	14.512(3)	11.236(7)	18.575(4)
α/°	90.0	103.66(4)	90.0
β/°	112.93(2)	103.62(5)	111.93(2)
γ/°	90.0	76.43(4)	90.0
Volume/Å^3	3829(5)	1576(1)	3063(1)
Z	8	2	4
μ/cm^{-1}	83.16 (Cu-Kα)	17.92 (Mo-Kα)	4.76 (Mo-Kα)
Total data	3138	5846	5641
'Observed' data [$I > 3\sigma(I)$]	2193	2882	3954[a]
R	0.057	0.037	0.047
R_w	0.071	0.041	0.127

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

through Celite, reduced in volume (to approximately 5 cm^3) and diethyl ether (20 cm^3) added, giving **6a** as an orange solid. The product was recrystallised from CH_2Cl_2–Et_2O; yield 1.83 g (86%).

Orange [MoBr(CO)$_2$(dppm)(1–3-η:4,5-C_8H_{11})] **6b** was prepared by an identical procedure, starting from **1b** (0.689 g, 1.64 mmol) and dppm (0.629 g, 1.64 mmol); yield 0.770 g (65%).

[MoBr(CO)$_2$(CNBu^t)$_2$(1–3-η:5,6-C_8H_{11})] 7a. A solution of **1a** (0.955 g, 2.27 mmol) in CH_2Cl_2 (20 cm^3) was cooled to −78 °C. The cooled, stirred solution was treated with CNBu^t (0.376 g, 4.54 mmol) and then allowed to warm to room temperature over a period of 1 h, after which time the red reaction mixture was evaporated to dryness. The residue was dissolved in diethyl ether and the solution filtered, reduced in volume to *ca.* 3 cm^3, and treated with n-hexane to precipitate the product as a red oil. The mother liquors were removed and the product stirred with n-hexane for 1 h, to give **7a** as an orange–red solid; yield 0.694 g (61%).

Orange–red [MoBr(CO)$_2$(CNBu^t)$_2$(1–3-η:4,5-C_8H_{11})] **7b** was prepared by an identical procedure, starting from **1b** (0.580 g, 1.38 mmol) and CNBu^t (0.229 g, 2.76 mmol); yield 0.531 g (76%).

[Mo(CO)$_2$(CNBu^t)$_3$(1–3-η:5,6-C_8H_{11})][BF$_4$] 8a. Compound **2a** (0.268 g, 0.57 mmol) was dissolved in CH_2Cl_2 (25 cm^3) at 0 °C. CNBu^t (0.142 g, 1.71 mmol) was added, resulting in an immediate colour change from yellow to orange–red. The reaction mixture was stirred at 0 °C for 30 min, then filtered through Celite, reduced in volume, and chilled diethyl ether (20 cm^3) added, giving a red oil. This was stirred in diethyl ether at −20 °C for 30 min, to give **8a** as an orange solid; yield 0.208 g (62%).

[Mo(CO)$_2$(CNBu^t)$_3$(1–3-η:4,5-C_8H_{11})][BF$_4$] 8b. Compound **2b** (0.196 g, 0.42 mmol) was dissolved in CH_2Cl_2 (40 cm^3) at 0 °C. CNBu^t (0.104 g, 1.23 mmol) was added resulting in an immediate colour change from yellow to orange–red. The reaction mixture was stirred at 0 °C for 25 min, then reduced in volume and chilled diethyl ether (20 cm^3) added, giving an orange–red precipitate. This was recrystallised from CH_2Cl_2–diethyl ether at 0 °C, to give **8b** as an orange–red solid; yield 0.142 g (57%).

Crystallography

The majority of the details of the structure analyses carried out on **4a**, **5a**, and **8b** are given in Table 6. The diffractometers employed were either a Rigaku AFC5R (**4a** and **8b**) or a Rigaku AFC6S (**5a**) utilising either a Mo-Kα source (λ = 0.71069 Å) (**5a**, **8b**) or a Cu-Kα source (λ = 1.54178 Å) (**4a**). Neutral atom scattering factors were taken from ref. 35 and all calculations were performed using the TEXSAN crystallographic software package,[36] with the exception of the computing structure solution, which was carried out for all complexes with SIR92,[37] and the structure refinement for **8b**, for which SHELXL-97 was employed.[38]

[MoBr(CO)$_2$(bipy)(1–3-η:5,6-C_8H_{11})] 4a. Red, plate crystals of **4a** were grown by crystallisation from CD_2Cl_2 solution at 0 °C. The unit cell dimensions were derived from the setting angles of 20 reflections in the range 30.39 < 2θ < 54.90°. The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by 6.04% 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 0.43 to 1.00, and the data were corrected for Lorentz and polarisation effects. The structure was solved by Patterson methods. All non-hydrogen atoms were refined anisotropically, most hydrogen atoms were included in the structure factor calculation in idealised positions (C–H = 0.95 Å), but hydrogens attached to C(1), C(2), and C(3) were located by difference.

[MoBr(CO)$_2$(dppe)(1–3-η:5,6-C_8H_{11})] 5a. Orange, plate crystals of **5a** 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 16 reflections in the range 15.05 < 2θ < 24.93°. The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by 0.98% 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 0.84 to 1.00, and the data were corrected for Lorentz and polarisation effects. The structure was solved by Patterson methods. All non-hydrogen atoms were refined anisotropically, most hydrogen atoms were included in the structure factor calculation in idealised positions (C–H = 0.95 Å), but hydrogens attached to C(1), C(2), C(3), C(5), C(6), and C(7) were located by difference.

[Mo(CO)$_2$(CNBu^t)$_3$(1–3-η:4,5-C_8H_{11})][BF$_4$] 8b. Orange, tabular crystals of **8b** 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 24 reflections in the range 15.00 < 2θ < 19.86°. The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by 1.4% and a linear correction factor was applied. An empirical absorption correction based on azimuthal scans was applied, which resulted in transmission factors ranging from 0.89 to 1.00, and the data were corrected for Lorentz and polarisation effects. The structure was solved by direct methods, the weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0593\,p)^2 + 2.0988\,p]$, where $p = (F_o^2 + 2F_c^2)/3$. C(18) and C(19) were disordered over two sites, each of whose occupancies were constrained to sum to 1.0. The BF_4 counter ion had to be treated as disordered about B(1)–F(1) and F(2), F(3) and F(4) are interleaved with F(5), F(6) and F(7). The relative occupancies were established by constrained refinement. The non-hydrogen atoms were refined anisotropically, except for the disordered atoms C(18) and C(19). Most hydrogens were included in calculated positions, but those bonded to C(1), C(2), and C(3) were found by difference Fourier techniques and refined isotropically.

CCDC reference numbers 169378–169380.

See http://www.rsc.org/suppdata/dt/b1/b107581k/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the EPSRC for a research studentship (to D. M. S.).

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