Dalton Communications

Cyclooctadienyl Complexes of Molybdenum: Synthesis and $\eta^5 \longrightarrow \eta^3$ Hapticity Interconversion

Roy L. Beddoes, Dale M. Spencer and Mark W. Whiteley*
Department of Chemistry, University of Manchester, Manchester M13 9PL, UK

The cyclooctadienylmolybdenum complexes $[MoBr(CO)_2(NCMe)_2(\eta^3\text{-}2,5\text{-}C_8H_{11})]$ and $[MoBr(CO)_2(NCMe)_2(\eta^3\text{-}2,4\text{-}C_8H_{11})]$, accessible by reaction of $[Mo(CO)_3(NCMe)_3]$ with bromocyclooctadienes, have been found to be precursors to the pentahapto-bonded complexes $[Mo(CO)_2(L\text{–}L)(\eta^2,\eta^3\text{-}2,5\text{-}C_8H_{11})]^+$ [L–L = $Ph_2PCH_2PPh_2$ (dppm) (crystallographically characterised) or $Ph_2PCH_2CH_2PPh_2$] and $[Mo(CO)_2(dppm)(\eta^5\text{-}C_8H_{11})]^+$; the reactivity of the last three complexes towards $\eta^5 \longrightarrow \eta^3$ hapticity conversion at the dienyl ligand is controlled by the bonding mode of the cyclooctadienyl ligand and the identity of L–L.

The reversible formation of a new co-ordination site at a metal centre, which accompanies $\eta^5 \longrightarrow \eta^3$ 'ring slip' or hapticity interconversion in dienyl complexes, may have important implications for catalysis, but a systematic approach requires the delineation of factors which promote hapticity changes and control the relative stabilities of the discrete bonding modes. Particularly appropriate for such studies is the dienyl chemistry of Mo and W; these metals impart a delicate balance in stability between η^5 and η^3 bonding modes as evidenced by the investigations summarised in equation (1) (M = Mo or W;

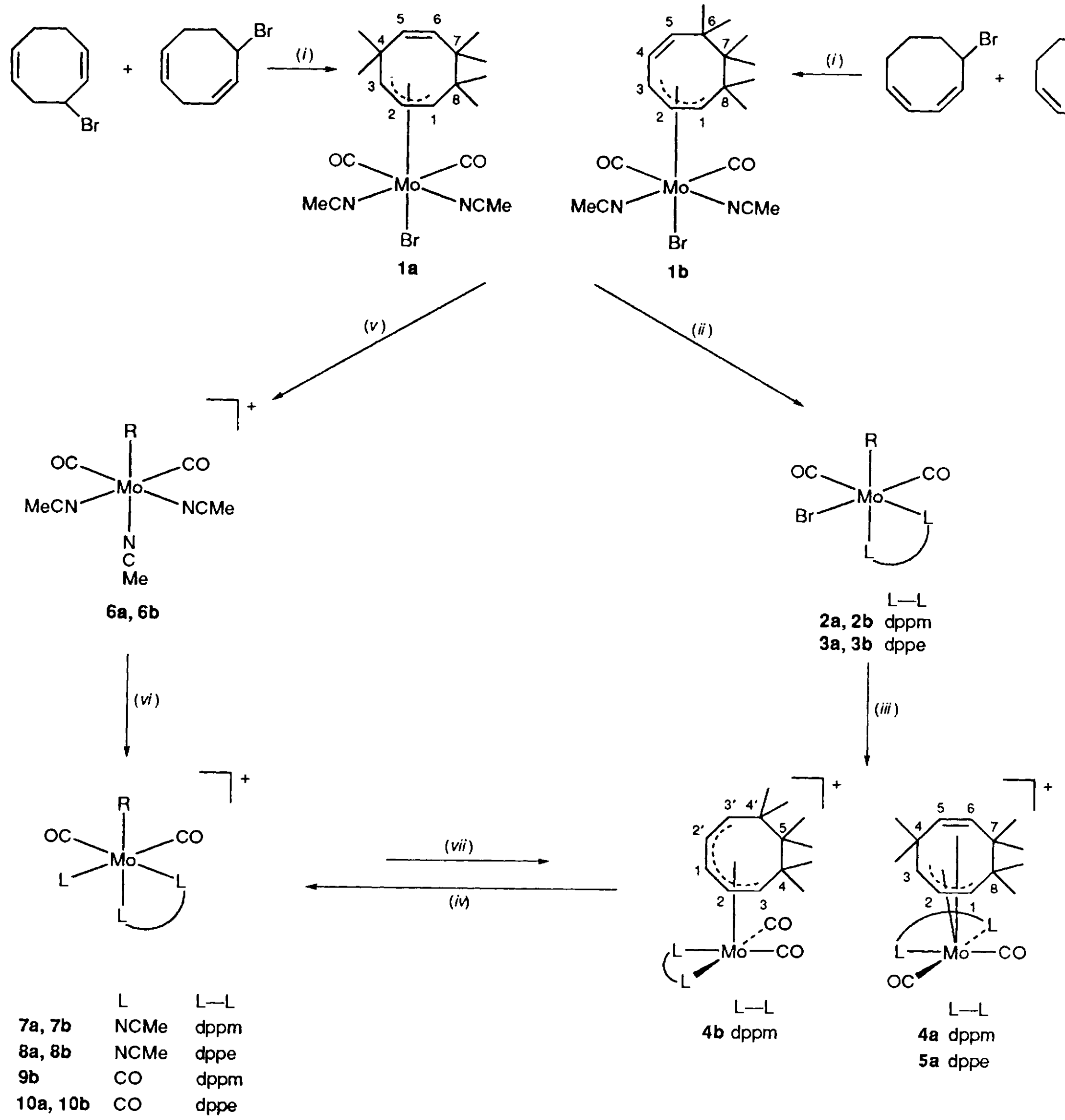
$$[M(CO)_2L_2(\eta^5\text{-}R)]^+ + L' \longrightarrow [M(CO)_2(L')L_2(\eta^3\text{-}R)]^+ \quad (1)$$

L_2 = 2NCMe, $Ph_2P(CH_2)_nPPh_2$ (n = 1, dppm; n = 2, dppe), *etc.*; L′ = NCMe, $CNBu^t$, *etc.*; R = indenyl,[1,2] cycloheptadienyl[3–5] or pentadienyl[3,6,7]). Comparison of analogous complexes, differing only in the identity of R, in reactions of the general type (1), establishes that the propensity to undergo $\eta^5 \longrightarrow \eta^3$ hapticity conversion is strongly R dependent[5] and lies in the order indenyl < cycloheptadienyl < acyclic pentadienyl. This communication, which reports the first examples both of cyclooctadienylmolybdenum complexes and $\eta^5 \longrightarrow \eta^3$ hapticity conversion at a cyclooctadienyl ligand, explores further the R dependence of $\eta^5 \longrightarrow \eta^3$ hapticity conversion with an investigation of the subtle effects of ring size and bonding mode of the dienyl ligand.

Our previous work with cycloheptadienylmolybdenum chemistry[4,5] revealed that the complexes $[Mo(CO)_2(L\text{–}L)(\eta^5\text{-}C_7H_9)]^+$ (L–L = dppm or dppe) are reactive towards addition of a ligand L′ with an accompanying $\eta^5 \longrightarrow \eta^3$ hapticity change at the dienyl ligand. Therefore, the synthesis of analogous cyclooctadienyl complexes $[Mo(CO)_2(L\text{–}L)(\eta^5\text{-}C_8H_{11})]^+$ was explored and accomplished in three steps as outlined in Scheme 1. The first step involves addition of isomeric mixtures of bromocyclooctadienes to $[Mo(CO)_3(NCMe)_3]$. Bromocyclooctadienes were prepared, by the literature procedures,[8,9] from cycloocta-1,5-diene (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 $[Mo(CO)_3(NCMe)_3]$, each separate mixture of bromocyclooctadienes simplified to one product type $[MoBr(CO)_2(NCMe)_2(\eta^3\text{-}2,5\text{-}C_8H_{11})]$ **1a** derived from 1,5-cod and $[MoBr(CO)_2(NCMe)_2(\eta^3\text{-}2,4\text{-}C_8H_{11})]$ **1b** derived from 1,3-cod.† These syntheses parallel those reported by Liu and co-workers[10] as a route to acyclic pentadienyl complexes $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_5H_7)]$ (X = Br or Cl), but the current work is the first example of the addition of a *cyclic* halogenodiene to $[Mo(CO)_3(NCMe)_3]$ and moreover the application of bromocyclooctadienes in the synthesis of cyclooctadienyl complexes is unprecedented. Stage two of the synthesis involves substitution of the NCMe ligands of **1a** and **1b** by the chelate phosphines dppm or dppe to give $[MoBr(CO)_2(L\text{–}L)(\eta^3\text{-}2,5\text{-}C_8H_{11})]$ (L–L = dppm **2a** or dppe **3a**) and $[MoBr(CO)_2(L\text{–}L)(\eta^3\text{-}2,4\text{-}C_8H_{11})]$ (L–L = dppm **2b** or dppe **3b**). In the final step, bromide abstraction from complexes **2** and **3** using $Ag[BF_4]$ in the non-co-ordinating solvent CH_2Cl_2 afforded the cationic, pentahapto-bonded cyclooctadienyl complexes $[Mo(CO)_2(L\text{–}L)(\eta^2,\eta^3\text{-}2,5\text{-}C_8H_{11})]^+$ (L–L = dppm **4a** or dppe **5a**) and $[Mo(CO)_2(dppm)(\eta^5\text{-}C_8H_{11})]^+$ **4b**. However, significantly, attempts to obtain $[Mo(CO)_2(dppe)(\eta^5\text{-}C_8H_{11})]^+$ were unsuccessful; prolonged stirring of a CH_2Cl_2 solution of **3b** with $Ag[BF_4]$ led to the isolation of low yields of the tricarbonyl complex $[Mo(CO)_3(dppe)(\eta^3\text{-}2,4\text{-}C_8H_{11})]^+$ **10b**.

---

† Selected spectroscopic data (numbering as in Scheme 1). **1a**: IR ν(CO) (NCMe) 1944, 1857 cm^{-1}. **1b**: IR ν(CO) (NCMe) 1945, 1858 cm^{-1}. **4a**: IR ν(CO) (CH_2Cl_2) 1998, 1897 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.76–7.09 (Ph, dppm), 5.35 (1 H, H^1), 5.14 (1 H, CH_2, dppm), 5.08 (1 H, H^2), 4.95 (2 H, H^3, H^6), 4.44 (1 H, CH_2, dppm), 3.13 (1 H, H^4), 2.97 (1 H, H^5), 2.62 (2 H, H^7, H^8), 2.32 (3 H, H^4, H^7, H^8); ^{13}C NMR (CD_2Cl_2) δ 227.2, 218.1 (CO), 133.3–128.3 (Ph, dppm), 115.6 (C^6), 103.6 (C^2), 78.9 (C^1), 70.8 (C^3), 64.6 (C^5), 41.7 (CH_2, dppm), 31.1, 27.8 (C^7 and C^8), 21.5 (C^4). **4b**: IR ν(CO) (CH_2Cl_2) 1996, 1930 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.97–6.90 (Ph, dppm), 5.97 (1 H, H^1), 5.81 (1 H, $H^{2'}$), 4.94 (1 H, CH_2, dppm), 4.61 (1 H, H^3), 4.57 (1 H, $H^{3'}$), 4.28 (1 H, CH_2, dppm), 3.96 (1 H, H^2), 2.54 (2 H, $H^{4,4'}$), 2.13 (1 H, H^4), 1.74 (1 H, $H^{4'}$), 1.26 (1 H, H^5), 0.52 (1 H, H^5); ^{13}C NMR ($CDCl_3$) δ 223.7, 221.9 (CO), 134.0–129.3 (Ph, dppm), 106.9 (C^1), 94.2, 93.6, 93.4 ($C^{2,2'}$ and C^3), 69.8 ($C^{3'}$), 40.5 (CH_2, dppm), 28.8 (C^4), 27.0 ($C^{4'}$), 18.7 (C^5). **6a**: IR ν(CO) (NCMe) 1958, 1875 cm^{-1}; ^1H NMR (CD_3CN) δ 5.83 (1 H, H^5), 5.49 (1 H, H^6), 4.89 (1 H, H^3), 4.72 (1 H, H^1), 3.86 (1 H, H^2), 2.62 (1 H, H^4), 2.49 (1 H, H^8), 2.36 (2 H, H^7), 2.02 (1 H, H^4), 1.65 (1 H, H^8); ^{13}C NMR (CD_3CN) δ 223.6, 223.5 (CO), 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 and C^8). **6b**: IR ν(CO) (NCMe) 1958, 1875 cm^{-1}; ^1H NMR (CD_3CN) δ 6.33 (1 H, H^4), 5.46 (1 H, H^5), 4.93 (1 H, H^3), 4.40 (1 H, H^1), 4.13 (1 H, H^2), 2.77 (1 H, H^6), 2.27 (1 H, H^8), 2.20 (1 H, H^6), 1.72 (1 H, H^7), 1.35 (1 H, H^7), 0.57 (1 H, H^8); ^{13}C NMR (CD_3CN) δ 225.0, 223.3 (CO), 134.4 (C^4), 130.0 (C^5), 77.3, 77.1 (C^1 and C^3), 75.8 (C^2), 32.5 (C^8), 29.8 (C^7), 25.3 (C^6). **7b**: IR ν(CO) (NCMe) 1962, 1870 cm^{-1}. **9b**: IR ν(CO) (CH_2Cl_2) 2044, 1983, 1948 cm^{-1}. Satisfactory microanalyses (C, H, N) were obtained for each of complexes **1**–**8**.



Scheme 1 R ≡ C_8H_{11}, **a** indicates 2,5-C_8H_{11}, **b** 2,4-C_8H_{11}, yields (%) in parentheses. (*i*) [$Mo(CO)_3(NCMe)_3$] in NCMe (40 cm^3), 1 h stirring, **1a** (47) from [$Mo(CO)_6$] (3.08 g) and 3-Br-1,5-cod/6-Br-1,4-cod (2.40 g); **1b** (52) from [$Mo(CO)_6$] (4.23 g) and 5-Br-1,3-cod/3-Br-1,4-cod (3.0 g); (*ii*) L–L in CH_2Cl_2, 1 h stirring, **2a** (86), **2b** (65), **3a** (82), **3b** (63); (*iii*) Ag[BF_4] in CH_2Cl_2, 30 min stirring, **4a** (69), **4b** (79), **5a** (69); (*iv*) L = NCMe, **4a**, **4b**, **5a**, dissolution in NCMe, **7a** (64), **7b** (57), **8b** (92); L = CO, CO gas in CH_2Cl_2, **4b**, 30 min, **5a**, 2.5 h; (*v*) Ag[BF_4] in NCMe, 30 min stirring, **6a** (65), **6b** (63); (*vi*) L = NCMe, L–L in CH_2Cl_2, 30 min stirring, **7a**, **7b** and **8a** react further as in (*vii*); (*vii*) L = NCMe, **7a**, **7b** and **8a**, stirring in CH_2Cl_2, **4b** and **5a** formed as equilibrium mixtures with **7b**, **8a** respectively

The spectroscopic data† for complexes **4a**, **4b** and **5a** are consistent with pentahapto-bonded cyclooctadienyl ligands[11] but, further to confirm the η^5 bonding mode, the crystal structure of [$Mo(CO)_2(dppm)(\eta^2,\eta^3\text{-}2,5\text{-}C_8H_{11})$][$BF_4$] **4a** was determined.‡ The molecular structure (Fig. 1) reveals a pentahapto-bonded (1,2,3,5,6-η)-cyclooctadienyl ligand attached to Mo through an η^3-allyl system [C(6), C(7) and C(8) (crystallographic numbering scheme)] and an isolated double bond [C(2), C(3)] with the CH_2 carbons [C(1), C(4) and C(5)] folded away from the Mo. To a good approximation (and in contrast with the conformation adopted by the trihapto-bonded η^3-2,5-C_8H_{11} ligand[13]), C(2), C(3), C(6)–C(8) are coplanar (mean deviation 0.056 Å). A structural feature which may be of significance in explaining the activation of cyclooctadienylmolybdenum complexes to $\eta^5 \longrightarrow \eta^3$ conversion (see below) is the unusually long Mo–C(2) and Mo–C(3) distances by comparison with the average Mo to allyl carbon distance; an analogous effect is not observed for [$Ru(\eta^2,\eta^3\text{-}2,5\text{-}C_8H_{11})(\eta^6\text{-}C_8H_{10})$][$PF_6$], one of the very few structurally characterised complexes containing the η^2,η^3-2,5-C_8H_{11} ligand[11,14] available for comparison.

The reactivity of complexes **4a**, **4b** and **5a** towards $\eta^5 \longrightarrow \eta^3$ conversion of the dienyl system, promoted by ligand addition, was investigated by reactions with NCMe and CO. These investigations permit an assessment, not only of the effect of the co-ligand (dppm *vs.* dppe) but also, exceptionally, the effect of

---

‡ Crystal data: $C_{35}H_{33}BF_4MoO_2P_2$, $M = 730.34$, monoclinic, space group $P2_1/n$ (no. 14), crystal dimensions 0.10 × 0.15 × 0.30 mm, a = 10.182(4), b = 16.698(4), c = 19.141(6) Å, β = 94.86(3)°, U = 3243(2) $Å^3$, $Z = 4$, $D_c = 1.496$ g cm^{-3}, $F(000) = 1488$, Rigaku AFC5R diffractometer, Cu-Kα radiation (λ = 1.541 78 Å), μ(Cu-Kα) 47.83 cm^{-1}, 5005 unique reflections, 3808 with $I > 3.00\sigma(I)$ used in refinement. Solution by direct methods; hydrogen atoms included in the structure-factor calculation in idealised positions (C–H 0.95 Å) and assigned isotropic thermal parameters 20% greater than the equivalent B value of the atom to which they were bonded. The structure was refined to $R = 0.056$, $R' = 0.069$ [$w = 4F_o^2/\sigma^2(F_o^2)$]; calculations performed using the TEXSAN packages.[12] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

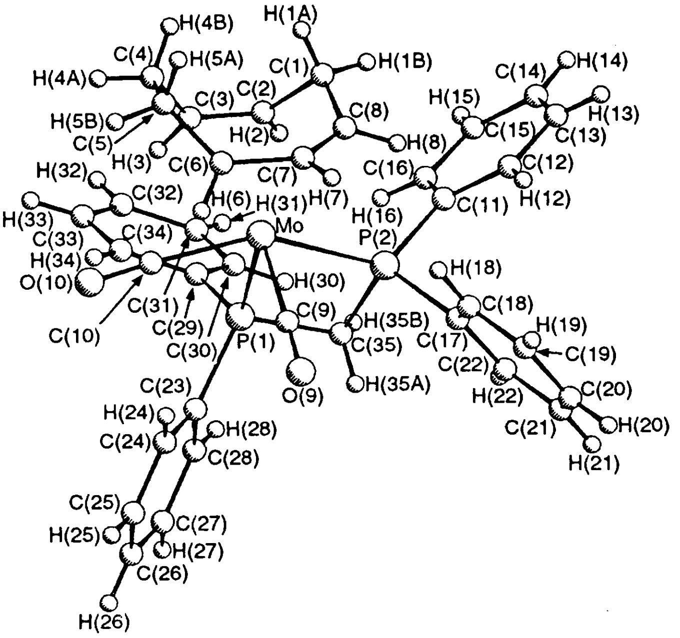


Fig. 1 Molecular structure of complex **4a**. Important bond lengths: Mo–C(2) 2.495(7), Mo–C(3) 2.576(7), Mo–C(6) 2.350(7), Mo–C(7) 2.329(8), Mo–C(8) 2.482(8), C(2)–C(3) 1.32(1), C(6)–C(7) 1.42(1), C(7)–C(8) 1.37(1) Å

a conjugated η^5-dienyl *vs.* an η^5-dienyl ligand with separate allyl and 'ene' components. Furthermore, by comparison with previous work,[4,5] the effect of ring size (C_8 *vs.* C_7) can be evaluated. Dissolution of **4a**, **4b** and **5a** in NCMe led to the immediate and complete formation of the acetonitrile adducts $[Mo(CO)_2(NCMe)(dppm)(\eta^3\text{-}R)]^+$ (R = 2,5-C_8H_{11} **7a**, or 2,4-C_8H_{11} **7b**) and $[Mo(CO)_2(NCMe)(dppe)(\eta^3\text{-}2,5\text{-}C_8H_{11})]^+$ **8a**, respectively. This is in contrast with the cycloheptadienyl analogues $[Mo(CO)_2(L\text{–}L)(\eta^5\text{-}C_7H_9)]^+$, which either do not react with NCMe (L–L = dppm) or, where L–L = dppe, exist in equilibrium with the adduct $[Mo(CO)_2(NCMe)(dppe)(\eta^3\text{-}C_7H_9)]^+$ in solution in NCMe,[5] and suggests that both forms of the cyclooctadienyl ligand have an activating effect on $\eta^5 \longrightarrow \eta^3$ hapticity conversion. Although no discrimination in the reactivity of **4a**, **4b** and **5a** was apparent with NCMe, a clear distinction was observed with CO, a ligand not previously found to induce $\eta^5 \longrightarrow \eta^3$ hapticity conversion in complexes of the type $[M(CO)_2L_2(\eta^5\text{-}R)]^+$ but the use of which was suggested by the enhanced reactivity of the cyclooctadienyl system. Passage of CO gas through CH_2Cl_2 solutions of **4b** and **5a** led to the respective formation of the tricarbonyl complexes $[Mo(CO)_3(dppm)(\eta^3\text{-}2,4\text{-}C_8H_{11})]^+$ **9b** and $[Mo(CO)_3(dppe)(\eta^3\text{-}2,5\text{-}C_8H_{11})]^+$ **10a**, but, by contrast, complex **4a** was inert towards CO. Further information on the relative stabilities of η^5- *vs.* η^3-bonded dienyls can be drawn from the limitations of an alternative route to pentahapto-bonded cyclooctadienyl complexes. As shown in Scheme 1, treatment of **1a** and **1b** with Ag[BF_4] in NCMe affords the *tris*(acetonitrile) products $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}R)]^+$ (R = 2,5-C_8H_{11} **6a** or 2,4-C_8H_{11} **6b**) which are stable towards loss of one NCMe with concomitant $\eta^3 \longrightarrow \eta^5$ conversion at the dienyl ligand, even when dissolved in CH_2Cl_2. However, the outcome of subsequent reactions of **6a** and **6b** with dppm or dppe in CH_2Cl_2 was markedly ligand dependent. Reaction of **6a** with dppm led to the successful isolation of the η^5-dienyl complex **4a**, but treatment of **6a** with dppe or **6b** with dppm produced mixtures of the required pentahapto-bonded complexes together with **7b** and **8a**, respectively. Finally reaction of **6b** with dppe in CH_2Cl_2 gave $[Mo(CO)_2(NCMe)(dppe)(\eta^3\text{-}2,4\text{-}C_8H_{11})]^+$ **8b** almost exclusively.

Based on these observations, we can draw the following conclusions regarding the factors promoting $\eta^5 \longrightarrow \eta^3$ hapticity conversion in cyclooctadienyl complexes. First, all cyclooctadienyl complexes of the type $[Mo(CO)_2L_2(\eta^5\text{-}C_8H_{11})]^+$ are activated towards $\eta^5 \longrightarrow \eta^3$ conversions by comparison with cycloheptadienyl analogues; indeed whilst the dominant bonding mode of the cycloheptadienyl ligand in its complexes with Mo is η^5, that of the cyclooctadienyl ligand is η^3. Secondly, the η^3 bonding mode of both cyclooctadienyl ligands is promoted more effectively by a dppe than by a dppm co-ligand; this result concurs with that reported for cycloheptadienyl complexes.[5] Finally, the conjugated η^5-C_8H_{11} ligand, appears to be less stable than η^2,η^3-2,5-C_8H_{11} when bonded to molybdenum. Using a combination of dppm, dppe and the two discrete types of cyclooctadienyl ligand, the relative stabilities of the η^5 and η^3 bonding modes and reactivity towards ligand addition accompanied by $\eta^5 \longrightarrow \eta^3$ conversion can be fine tuned. Thus, complex **4a**, with a combination of dppm and η^2,η^3-2,5-C_8H_{11} ligands, is the most resistant to ligand addition and does not react with CO. Complexes **4b** and **5a**, which each contain one activating ligand, exhibit increased reactivity towards ligand addition whilst $[Mo(CO)_2(dppe)(\eta^5\text{-}C_8H_{11})]^+$, with a combination of both activating ligands, would be expected to be highly reactive to ligand addition and, consistent with our synthetic studies, correspondingly difficult to isolate.

In conclusion, this communication has demonstrated the potential for the control and fine tuning of reactivity involving $\eta^5 \longrightarrow \eta^3$ hapticity conversion at a dienyl ligand by exploiting subtle variations in the identity of the dienyl ligand and co-ligands at the metal centre.

Acknowledgements

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

References

1 J. M. O'Connor and C. P. Casey, *Chem. Rev.*, 1987, **87**, 307.
2 I. S. Gonçalves and C. C. Romão, *J. Organomet. Chem.*, 1995, **486**, 155.
3 R. D. Ernst, *Chem. Rev.*, 1988, **88**, 1255.
4 R. L. Beddoes, J. R. Hinchliffe and M. W. Whiteley, *J. Chem. Soc., Dalton Trans.*, 1993, 501.
5 R. L. Beddoes, J. R. Hinchliffe, A.-L. A. B. de Souza and M. W. Whiteley, *J. Chem. Soc., Dalton Trans.*, 1994, 2303.
6 G.-H. Lee, S.-M. Peng, I.-C. Tsung, D. Mu and R.-S. Liu, *Organometallics*, 1989, **8**, 2248.
7 S. L. Wu, C.-Y. Cheng, S.-L. Wang and R.-S. Liu, *Inorg. Chem.*, 1991, **30**, 311.
8 S. Moon and C. R. Ganz, *J. Org. Chem.*, 1969, **34**, 465.
9 S. Moon and C. R. Ganz, *J. Org. Chem.*, 1970, **35**, 1241.
10 G.-H. Lee, S.-M. Peng, F.-C. Liu, D. Mu and R.-S. Liu, *Organometallics*, 1989, **8**, 402.
11 T. V. Ashworth, A. A. Chalmers, D. C. Liles, E. Meintjies and E. Singleton, *Organometallics*, 1987, **6**, 1543.
12 TEXSAN-TEXRAY, Structure analysis package, Molecular Structure Corporation, The Woodlands, TX, 1985.
13 G. Vitulli, A. Raffaelli, P. A. Costantino, C. Barberini, F. Marchetti, S. Merlino and P. S. Skell, *J. Chem. Soc., Chem. Commun.*, 1983, 232.
14 T. V. Ashworth, M. J. Nolte, R. H. Reimann and E. Singleton, *J. Chem. Soc., Chem. Commun.*, 1977, 937.

Received 20*th June* 1995; *Communication* 5/04002G