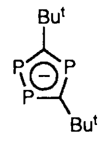
η^3- and η^5-Ligating Modes of 1,3-Diphosphacyclopentadienyl Rings in Structurally Related Molybdenum Complexes. Crystal and Molecular Structure of $[Mo(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}P_2C_3Bu^t_3)(CO)_2]$ and $[Mo(\eta^3\text{-}C_9H_7)(\eta^5\text{-}P_2C_3Bu^t_3)(CO)_2]$ (C_9H_7 = indenyl)

Rainer Bartsch, Peter B. Hitchcock, and John F. Nixon*

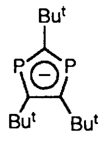
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex, U.K.

The modes of ligation of the two five-membered rings in $[Mo(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}P_2C_3Bu^t_3)(CO)_2]$ and $[Mo(\eta^3\text{-}C_9H_7)(\eta^5\text{-}P_2C_3Bu^t_3)(CO)_2]$ show interesting differences.

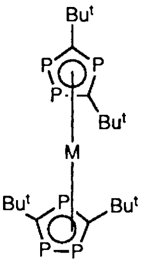
The field of organotransition metal chemistry involving unsaturated organic ligands in which CH fragments are replaced by P is rapidly developing.[1—3] There is considerable current interest in the ligating properties of novel unsaturated ring systems containing two and three phosphorus atoms. In previous publications[4—8] we have shown how the $(P_3C_2Bu^t_2)^-$ and $(P_2C_3Bu^t_3)^-$ ring systems (**1**) and (**2**) can be utilised in the synthesis of 'sandwich' compounds of the type (**3**)—(**6**) analogous to their better known η-cyclopentadienyl analogues. Syntheses and full structural characterisation of the



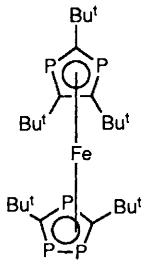
(**1**)



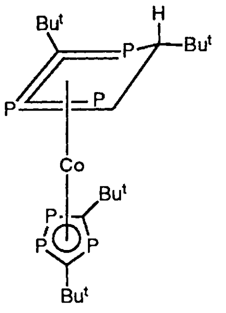
(**2**)



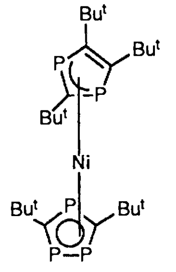
(**3**) M = Fe
(**4**) M = Cr



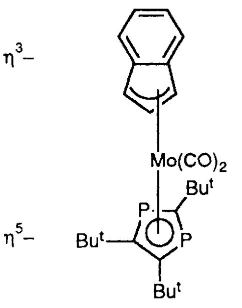
(**5**)



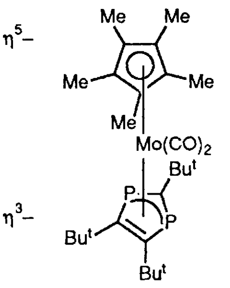
(**6**)



(**7**)



(**8**)



(**9**)

18 e sandwich complexes $[\mathrm{Fe}(\eta^5\text{-}\mathrm{P_3C_2Bu^t_2})_2]$ (**3**) and $[\mathrm{Fe}(\eta^5\text{-}\mathrm{P_3C_2Bu^t_2})(\eta^5\text{-}\mathrm{P_2C_3Bu^t_3})]$ (**5**),[4] and the 16 e paramagnetic compound $[\mathrm{Cr}(\eta^5\text{-}\mathrm{P_3C_2Bu^t_2})_2]$ (**4**)[6] have been reported. Attempts to synthesise the 19 e system $[\mathrm{Co}(\eta^5\text{-}\mathrm{P_3C_2Bu^t_2})_2]$ led instead[7] to the 18 e diamagnetic complex $[\mathrm{Co}(\eta^5\text{-}\mathrm{P_3C_2Bu^t_2})(\eta^4\text{-}\mathrm{P_3C_2Bu^t_2H})]$ (**6**).

Recently[8] we showed that treatment of a mixture of $\mathrm{Li(P_3C_2Bu^t_2)}$ and $\mathrm{Li(P_2C_3Bu^t_3)}$ with $[\mathrm{NiBr_2(monoglyme)_2}]$ afforded the diamagnetic 18 e nickel complex $[\mathrm{Ni(P_3C_2Bu^t_2)(P_2C_3Bu^t_3)}]$ (**7**), in which the $\mathrm{P_2C_3Bu^t_3}$ ring acts as an η^3-ligand. No evidence was obtained for the formation of a paramagnetic 20 e analogue of nickelocene.

We now report that the $\mathrm{P_2C_3Bu^t_3}$ ring can act both as η^3- and as η^5-ligand at the same metal depending on the nature of the other attendant ligands. Treatment of $\mathrm{Li(P_2C_3Bu^t_3)}$ with $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{CO})_2(\mathrm{MeCN})_2]^+\ \mathrm{BF_4}^-$ and $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{CO})_2(\mathrm{MeCN})_2]^+\ \mathrm{CF_3SO_3}^-$ respectively affords the black molybdenum complex $[\mathrm{Mo}(\eta^3\text{-}\mathrm{C_9H_7})(\eta^5\text{-}\mathrm{P_2C_3Bu^t_3})(\mathrm{CO})_2]$ (**8**), and the red–orange molybdenum complex $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5Me_5})(\eta^3\text{-}\mathrm{P_2C_3Bu^t_3})(\mathrm{CO})_2]$ (**9**), in low yields (1 and 5%). No evidence was obtained for the formation of paramagnetic 20 e sandwich complexes. The ^{31}P NMR spectrum of (**9**) shows a singlet for the two equivalent ring phosphorus atoms, and the ^{1}H NMR spectrum two signals for the two sets of inequivalent Bu^t groups in the ratio 2 : 1 as well as a singlet for the $\mathrm{C_5Me_5}$ protons.† No NMR data could be obtained for (**8**) owing to its poor solubility in organic solvents.

Confirmation of the molecular structures of (**8**) and (**9**) came from single crystal *X*-ray diffraction studies (see Figure

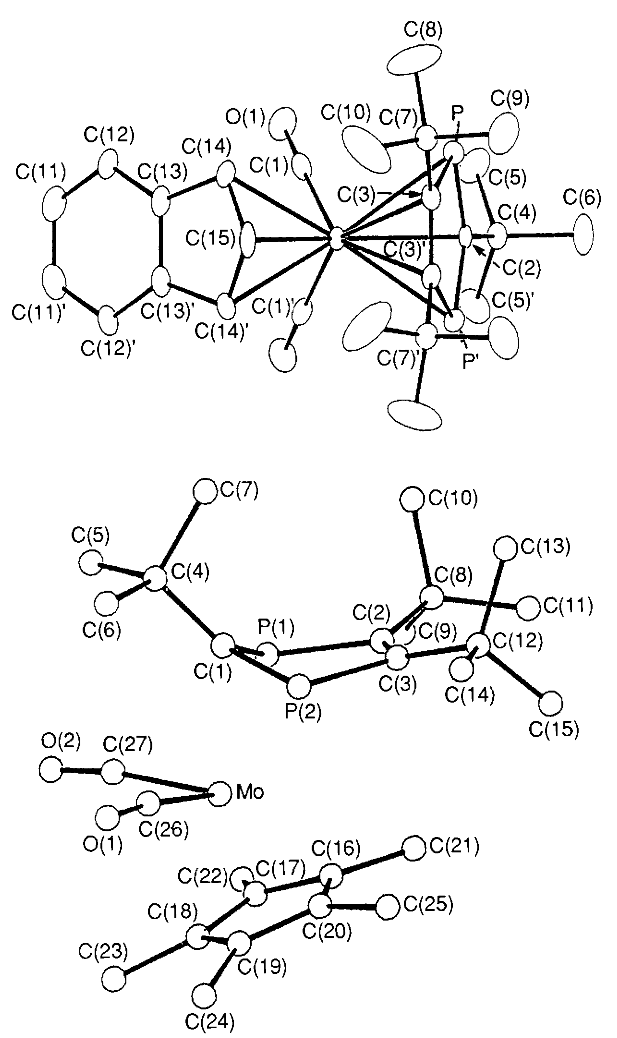


Figure 1. Molecular structures of (**8**) and (**9**). Selected bond lengths (Å) for (**8**): Mo–P 2.557(2), Mo–C(1) 1.941(9), Mo–C(2) 2.393(11), Mo–C(3) 2.537(8), Mo–C(14) 2.434(9), Mo–C(15) 2.222 (12); for (**9**): Mo–M1 2.123, Mo–M2 2.019, Mo–P(1) 2.555(1), Mo–P(2) 2.554(1), Mo–C(1) 2.292(3), Mo–C(16) 2.374(3), Mo–C(17) 2.321(4), Mo–C(18) 2.324(4), Mo–C(19) 2.352(4), Mo–C(20) 2.378(3). M1 and M2 are the centroids of P(1), P(2), C(1), and C(16) to C(20), respectively.

---

† For (**9**), NMR spectra: ^{1}H δ 2.01 (s, $\mathrm{C_5Me_5}$), 1.44 (s, Bu^t), and 1.31 (s, Bu^t) (relative intensity 5 : 3 : 6); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ (relative to phosphoric acid) δ + 66.0 (s) ppm; IR spectrum (carbonyl region): 1927 and 1983 cm^{-1}.

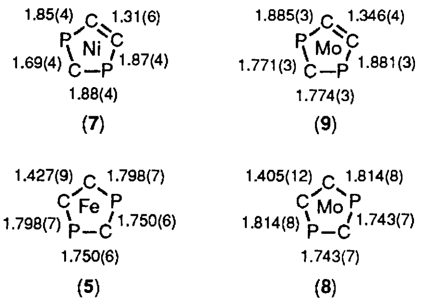


Figure 2. Bond lengths for the C–C–P–C–P system in (**5**), (**7**), (**8**), and (**9**).

1).‡ The ($P_2C_3Bu^t{}_3$) ring is planar and η^5-bonded to the metal in (**8**) whereas it is η^3-ligated and bent along the P(1)–P(2) vector in (**9**) so that the C=C fragment within the ring does not interact with the nickel atom. The indenyl system is η^3-ligated in (**8**) while the C_5Me_5 ring is η^5-bonded to the metal in (**9**).

The bond distances and bond angles in the η^5-1,3-diphosphacyclopentadienyl ring in (**8**) are similar to those previously described for $[Fe(\eta^5\text{-}P_3C_2Bu^t{}_2)(\eta^5\text{-}P_2C_3Bu^t{}_3)]$[4] while the structural parameters in the η^3-$C_3P_2Bu^t{}_3$ system in (**9**) are similar to those in the nickel complex $[Ni(\eta^5\text{-}P_3C_2Bu^t{}_2)(\eta^3\text{-}P_2C_3Bu^t{}_3)]$[8] (see Figure 2). It is well known that indenyl transition metal complexes can undergo more facile η^5- to η^3-ring–metal interaction than their cyclopentadienyl analogues[9,10] and this explains the η^5- to η^3-$P_2C_3Bu^t{}_3$ ring slippage in (**9**) but not in (**8**) where the C_5Me_5 ring prefers η^5-ligation. The non-formation of 20 e molybdenum complexes with the $P_2C_3Bu^t{}_3$ ring systems is in accord with our previous observation on the nickel complex $[Ni(\eta^5\text{-}P_3C_2Bu^t{}_2)(\eta^3\text{-}P_2C_3Bu^t{}_3)]$[8] where the $P_2C_3Bu^t{}_3$ ring undergoes an η^5- to η^3-ring slippage in order to avoid forming a paramagnetic 20 e system similar to nickelocene. This may reflect the higher energy of the antibonding molecular orbitals in both $P_3C_2Bu^t{}_2$ and $P_2C_3Bu^t{}_3$ rings compared with their cyclopentadienyl analogues.

We thank the S.E.R.C. for their continuing support for this work.

Received, 27th November 1989; Com. 9/05057D

---

‡ *Crystal data* for (**8**): $C_{26}H_{34}MoO_2P_2$, M = 536.4, orthorhombic, space group *Pnma*, a = 11.524(4), b = 13.582(6), c = 15.959(4) Å, U = 2498 Å^3, Z = 4, D_c = 1.43 g m^{-3}, $F(000)$ = 1112, $\mu(\text{Mo-}K_\alpha)$ = 6.6 cm^{-1}. A total of 2500 unique reflections were measured on an Enraf-Nonius CAD4 diffractometer, and 1394 reflections $[I > 3\sigma(I)]$ were used in the refinement. The structure was solved by heavy-atom methods and refined by least-squares, with non-hydrogen atoms anisotropic and H atoms fixed, to R = 0.073, R_w = 0.093 using the SDP-Plus program package.

For (**9**): $C_{27}H_{42}MoO_2P_2$, M = 556.5, monoclinic, space group $P2_1/c$, a = 18.452(4), b = 14.533(5), c = 10.523(5) Å, β = 93.98(2)°, U = 2815 Å^3, Z = 4, D_c = 1.31 g m^{-1}, $F(000)$ = 1168, $\mu(\text{Mo-}K_\alpha)$ = 5.9 cm^{-1}. The structure solution and refinement were as for (**8**) except that 2842 reflections were used out of 4087 total measured, and the final residuals were R = 0.028, R_w = 0.040. The diffraction data were weak.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

References

1 R. Appel, F. Knoll, and I. Ruppert, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 731, and references cited therein.
2 J. F. Nixon, *Chem. Rev.*, 1988, **88**, 1327, and references cited therein.
3 M. Regitz and P. Binger, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1484, and references cited therein.
4 R. Bartsch, P. B. Hitchcock, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1987, 1146.
5 R. Bartsch, P. B. Hitchcock, and J. F. Nixon, *J. Organomet. Chem.*, 1988, **344**, C37.
6 R. Bartsch, P. B. Hitchcock, and J. F. Nixon, *J. Organomet. Chem.*, 1988, **356**, C1.
7 R. Bartsch, P. B. Hitchcock, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1988, 819.
8 R. Bartsch, P. B. Hitchcock, and J. F. Nixon, *J. Organomet. Chem.*, 1989, **373**, C17.
9 J. M. O'Connor and C. P. Casey, *Chem. Rev.*, 1987, **87**, 307, and references cited therein.
10 R. M. Kowalewski, A. L. Rheingold, W. C. Trogler, and F. Basolo, *J. Am. Chem. Soc.*, 1986, **108**, 2460.