Symmetrical and Unsymmetrical Bridging Carbonyl Groups in Binuclear Molybdenum Carbonyl Complexes of Alkylaminobis(difluorophosphines); *X*-Ray Crystal Structures of Two of the Complexes

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Thermal reactions of the olefin–molybdenum carbonyls $C_7H_8Mo(CO)_n$ (n = 4, C_7H_8 = norbornadiene; n = 3, C_7H_8 = cycloheptatriene) with $RN(PF_2)_2$ ligands (R = Me and Ph) in hydrocarbon solvents at 100—120 °C lead ultimately to binuclear complexes of the type $[RN(PF_2)_2]_nMo_2(CO)_{11-2n}$ (n = 3, 4, and 5); structure determinations by *X*-ray diffraction on $[PhN(PF_2)_2]_3Mo_2(CO)_5$ and $[MeN(PF_2)_2]_4Mo_2(CO)_3$ indicate the presence of symmetrical and unsymmetrical bridging carbonyl groups, respectively.

The small-bite bidentate π-acceptor ligands $RN(PF_2)_2$ (R = Me or Ph)[1] can bridge metal–metal bonds to form five-membered chelate rings (1). Thus binuclear compounds of iron,[2–4] cobalt,[5–7] and nickel[4] have been prepared containing this structural feature. The communication reports the preparations and structures of two binuclear molybdenum carbonyl complexes of $RN(PF_2)_2$ ligands: $[PhN(PF_2)_2]_3Mo_2(CO)_5$ and $[MeN(PF_2)_2]_4Mo_2(CO)_3$, which are of interest in providing a

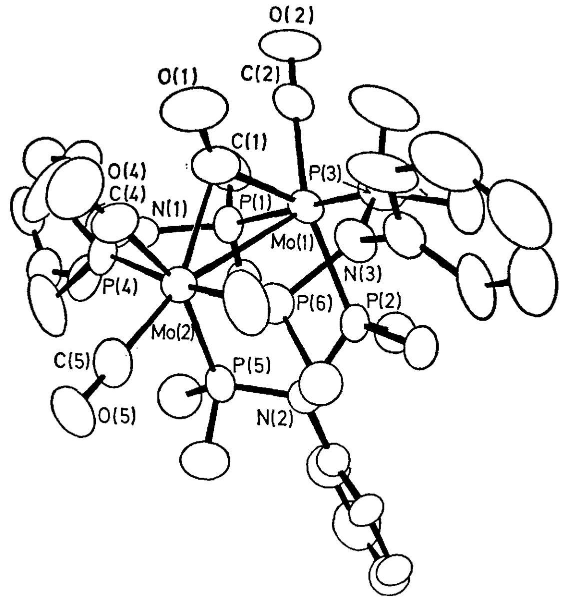
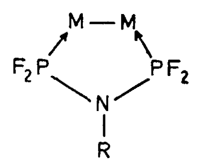


Figure 1. ORTEP diagram of the complex $[PhN(PF_2)_2]_3Mo_2(CO)_5$. The fifth carbonyl group [C(3)–O(3)] is hidden beneath P(3).



(1)

unique example of the transition from a symmetrical to an unsymmetrical bridging carbonyl group through creation of asymmetry in the binuclear system.

The norbornadiene complex $C_7H_8Mo(CO)_4$ has previously been reported[8,9] to react with $RN(PF_2)_2$ ligands at room temperature in a 1:1 ratio to give the mononuclear complexes $RN(PF_2)_2Mo(CO)_4$ (R = Me, Et, and Ph). Pyrolysis of these complexes in hydrocarbon solvents for several hours at 100—120 °C results in a major reorganization of the ligands around the metal atom to give binuclear complexes of the stoicheiometry $[RN(PF_2)_2]_3Mo_2(CO)_5$, (R = Me and Ph).† The i.r. spectra of these complexes exhibit not only the expected terminal ν(CO) bands (*e.g.*, 2037, 2010, 1978, and 1969 cm^{-1} for R = Ph) but also a single bridging ν(CO) band (*e.g.*, 1787 cm^{-1} for R = Ph). The yield of $[PhN(PF_2)_2]_3Mo_2(CO)_5$ was nearly quantitative based on $PhN(PF_2)_2$.

The complex $[PhN(PF_2)_2]_3Mo_2(CO)_5$ forms monoclinic crystals: space group $P2_1/c$; a = 9.635(8), b = 16.608(10), c = 22.282(15) Å, β = 108.801(7)°, Z = 4. Least-squares refinement using the 3456 observed reflections (R = 0.045) indicates the structure depicted in Figure 1 containing equivalent molybdenum atoms. The molybdenum–molybdenum distance is 3.140(1) Å which is clearly a bonding distance in view of the reported[10] molybdenum–molybdenum distance of 3.235 Å in $[(C_5H_5)Mo(CO)_3]_2$. Within experimental error the carbonyl bridge is symmetrical with an average molybdenum–carbon distance of 2.25 Å. The co-ordination polyhedron of each molybdenum can be derived from a *mer*-$P_3Mo(CO)_3$ octahedron by expansion along a bridging carbonyl–phosphorus edge in order to accommodate the molybdenum–molybdenum bond.‡

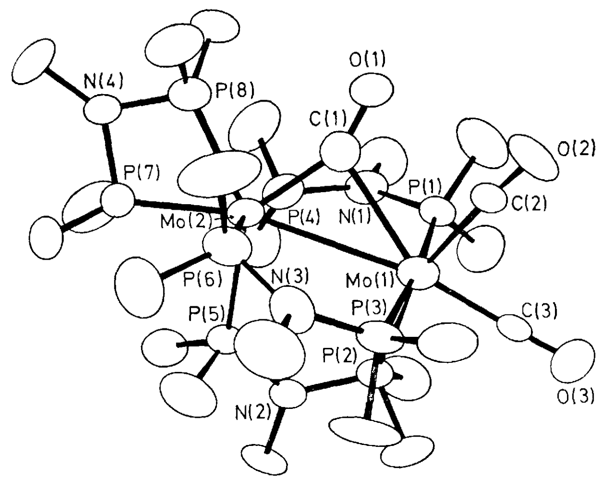


Figure 2. ORTEP diagram of the complex $[MeN(PF_2)_2]_4Mo_2(CO)_3$.

Related reactions can be used to prepare other members of the $[RN(PF_2)_2]_nMo_2(CO)_{11-2n}$ series. Thus reaction of the cycloheptatriene complex $C_7H_8Mo(CO)_3$ with $MeN(PF_2)_2$ in a 2:1 molar ratio in methylcyclohexane, first at 60 °C to form the intermediate *mer*-$[MeN(PF_2)_2]_2Mo(CO)_3$ (identified by its i.r. and ^{31}P n.m.r. spectra), and then at 100 °C for 6 h, gave ultimately a mixture of $[MeN(PF_2)_2]_4Mo_2(CO)_3$ and $[MeN(PF_2)_2]_5Mo_2(CO)$, which could be separated by chromatography on Florisil. The monocarbonyl (11% isolated yield) has not yet been characterized structurally but the presence of a terminal rather than bridging CO group [ν(CO) at 1923 cm^{-1}] suggests analogy with the reported[3] iron carbonyl complex $[MeN(PF_2)_2]_4Fe_2(CO)$. The i.r. spectrum of the tricarbonyl (3% isolated yield) exhibits both terminal (2006 and 1944 cm^{-1}) and bridging (1773 cm^{-1}) ν(CO) frequencies, although the latter is relatively weak.

The tricarbonyl $[MeN(PF_2)_2]_4Mo_2(CO)_3$ forms orthorhombic crystals: space group *Pbca*: a = 10.566(10), b = 15.387(20), c = 34.317(10) Å; Z = 8. Least-squares refinement using the 1645 observed reflections (R = 0.038) indicates the structure depicted in Figure 2. This structure may be derived from that of $[PhN(PF_2)_2]_3Mo_2(CO)_5$ (Figure 1) by replacement of the two terminal carbonyl groups on one metal by a small-bite bidentate $RN(PF_2)_2$ ligand. Thus the two molybdenum atoms become non-equivalent in $[MeN(PF_2)_2]_4Mo_2(CO)_3$. This has no detectable effect on the molybdenum–molybdenum bond distance (3.142 Å). However, in $[MeN(PF_2)_2]_4Mo_2(CO)_3$ the carbonyl bridge is unsymmetrical with molybdenum–carbon distances of 2.02(2) and 2.54(2) Å. The shorter molybdenum–carbonyl (bridging) distance involves the molybdenum atom bearing no terminal carbonyl groups in accord with considerations based on back-bonding.[11]

This work indicates that the ability of an $RN(PF_2)_2$ ligand to stabilize metal–metal bonds by forming five-membered chelate rings (**1**) allows the preparation of the first compounds corresponding to simple substitution products of $Mo_2(CO)_{11}$. Some related binuclear chromium and tungsten compounds are also accessible. However, in view of the stronger bonding of carbonyl groups to chromium and tungsten relative to

† These compounds were characterized by elemental analyses (C, H, and N), i.r. spectra in the ν(CO) region, and n.m.r. spectra (^{1}H, ^{13}C, and ^{31}P).

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

molybdenum,[12] photochemical rather than thermal conditions are preferred for the decarbonylation step leading to the binuclear complex. Thus a simple method for the preparation of $[MeN(PF_2)_2]_3M_2(CO)_5$ (M = Cr and W) involves the u.v. irradiation of $MeN(PF_2)_2$ with $M(CO)_6$ (M = Cr and W) in a 1 : 1 ligand–metal ratio in hexane solution, in contrast with the reported[4,13] preparations of $[MeN(PF_2)_2]_3M$ using a similar photochemical reaction but a 6 : 1 ligand–metal ratio in diethyl ether solution.

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