Novel Bimetallic Products from Octacarbonyldicobalt and Methylaminobis(difluorophosphine); *X*-Ray Crystal Structures of $[\{MeN(PF_2)_2\}_3Co_2(PF_2NHMe)_2]$ and $[\{MeN(PF_2)_2\}_3Co_2(CO)_2]$

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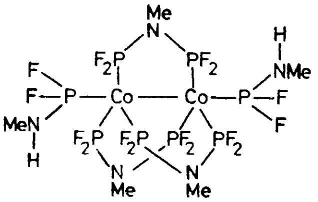
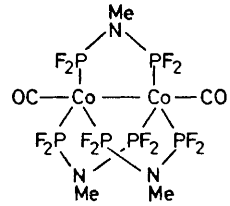
Summary Reactions of $[Co_2(CO)_8]$ with an excess of $MeN(PF_2)_2$ under various conditions give compounds of the general type $[\{MeN(PF_2)_2\}_3Co_2L_2]$ ($L = MeNHPF_2$ or CO) shown by single crystal *X*-ray diffraction to contain a cobalt-cobalt bond bridged by three $MeN(PF_2)_2$ ligands.

Recently we reported that all six carbonyl groups in the metal hexacarbonyls $[M(CO)_6]$ (M = Cr, Mo, or W) are easily replaced by u.v. irradiation with an excess of $MeN(PF_2)_2$ in diethyl ether to give the corresponding $M[(PF_2)_2NMe]_3$ derivatives.[1] We have subsequently investigated similar photochemical reactions of other metal carbonyls with $MeN(PF_2)_2$ as possible routes to other novel zerovalent complexes. This communication reports the preparation and structural characterization of two bimetallic products from $[Co_2(CO)_8]$ and $MeN(PF_2)_2$. Both these complexes contain the unprecedented structural feature of a cobalt–cobalt bond supported by three bridging $MeN(PF_2)_2$ groups.

A mixture of 5 mmol of $[Co_2(CO)_8]$ and 28·4 mmol of $MeN(PF_2)_2$[2] in 250 ml of diethyl ether was exposed to u.v. irradiation (Pyrex filter) for 16 h at room temperature. Removal of solvent from the filtered reaction mixture, followed by chromatography on Florisil in hexane solution using dichloromethane–hexane as eluent, gave 1·29 g (31%) of dark purple $[\{MeN(PF_2)_2\}_3Co_2(PF_2NHMe)_2]$, m.p. 185—190 °C, *M* 913 (in C_6H_6) (calc.817).†



(I)



(II)

Crystal data: The complex (I) forms orthorhombic crystals from dichloromethane–hexane, space group *Aba*2; $a = 14{\cdot}094(3)$, $b = 16{\cdot}999(4)$, $c = 10{\cdot}616(2)$ Å, $Z = 4$. Refinement of intensity data from 1017 observed reflections ($R = 0{\cdot}0288$) indicates structure (I) (Figure). Molecules of (I) occupy the two-fold crystallographic axis which passes through one NMe group and the centre of the Co–Co bond. Of particular interest is the presence of three $MeN(PF_2)_2$ ligands bridging this cobalt–cobalt bond. The environment of each cobalt atom approximates a trigonal bipyramid. The equatorial planes of the interlocked trigonal bipyramids representing the co-ordinations of the two cobalt atoms are staggered by *ca.* 30°.‡

Another unusual feature in structure (I) is the presence of the two terminal PF_2NHMe ligands. Formation of the central $[MeN(PF_2)_2]_3Co_2$ unit in this structure leaves each cobalt atom with only two electrons less than the favoured rare gas electronic configuration. Thus an $MeN(PF_2)_2$ ligand occupying the terminal (axial) positions can only be monodentate. The uncomplexed PF_2 group in such a monodentate $MeN(PF_2)_2$ ligand is apparently very susceptible to hydrolytic removal by traces of adventitious water.

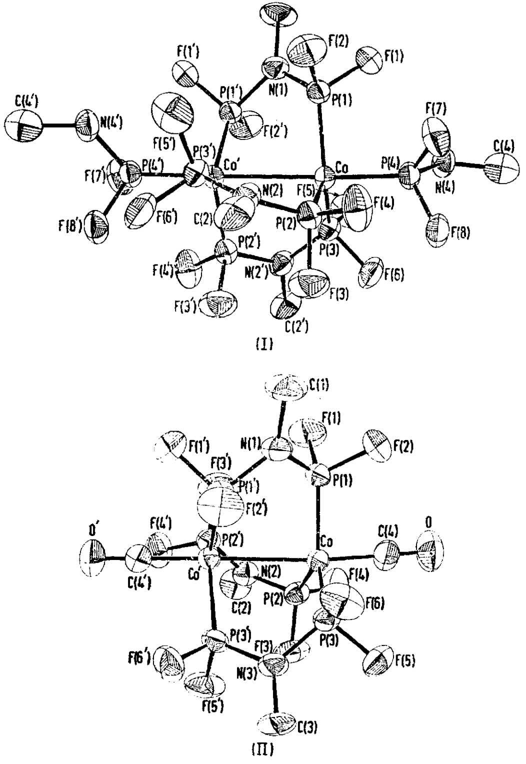


Figure. Structures of (I) and (II).

If the reaction between $[Co_2(CO)_8]$ and $MeN(PF_2)_2$ is carried out in the absence of u.v. irradiation, the central $[MeN(PF_2)_2]_3Co_2$ unit can be generated with retention of the apical carbonyl groups. In a typical such experiment a mixture of 5 mmol of $[Co_2(CO)_8]$, 24 mmol of $MeN(PF_2)_2$, and

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† These compounds gave satisfactory microanalytical data.

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

100 ml of hexane was stirred for 4 h at 0 °C. Removal of solvent followed by dichloromethane extraction and chromatography on Florisil gave 2·43 g (72%) of dark purple $[\{MeN(PF_2)_2\}_3Co_2(CO)_2]$, m.p. 132—133 °C, ν_{CO} (hexane) 2003s and 1978w cm^{-1}, *M* 680 (in C_6H_6) (calc. 675).†

Crystal data: The complex (II) forms monoclinic crystals from dichloromethane–hexane, space group $P2_1/n$; $a = 15{\cdot}657(4)$, $b = 13{\cdot}962(3)$, $c = 9{\cdot}377(2)$ Å, $\beta = 96{\cdot}59(4)°$, $Z = 4$. Refinement of intensity data from 2250 observed reflections ($R = 0{\cdot}0314$) indicates structure (II) (Figure) containing the same type of $[MeN(PF_2)_2]_3Co_2$ unit found in structure (I). The cobalt–cobalt bond in complex (II) is shorter [2·716-(1) Å] than that in complex (I) [2·769(1) Å] for reasons that are not clear.‡

These structural studies on the cobalt complexes $[\{MeN(PF_2)_2\}_3Co_2L_2]$ (L = CO or PF_2NHMe) indicate that $MeN(PF_2)_2$ can act not only as a chelating ligand forming four-membered rings as in $[\{MeN(PF_2)_2\}_3M]$ (M = Cr, Mo, or W)[1] but also as a bridge across a metal–metal bond forming five-membered rings as in structures (I) and (II). The bidentate $MeN(PF_2)_2$ ligand also bridges metal–metal bonds in the compounds $[\{MeN(PF_2)_2\}_nCo_4(CO)_{12-2n}]$ (n = 1, 2, 3, 4, or 5) and $[\{MeN(PF_2)_2\}_nFe_2(CO)_{9-2n}]$ (n = 1 or 2) obtained from various reactions of $MeN(PF_2)_2$ with $[Co_4(CO)_{12}]$ and with appropriate iron carbonyls,[3] respectively.

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