Retention of the Cobalt–Cobalt Bond in $[MeN(PF_2)_2]_3Co_2(CO)_2$ Upon Halogenation: the *X*-Ray Crystal Structure of $[MeN(PF_2)_2]_3Co_2Br_4$

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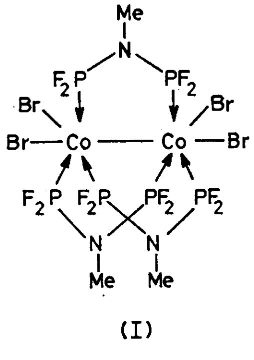
Summary Reaction of $[MeN(PF_2)_2]_3Co_2(CO)_2$ with Br_2 in diethyl ether gives red-brown $[MeN(PF_2)_2]_3Co_2Br_4$ shown by single crystal *X*-ray diffraction to retain the $[MeN(PF_2)_2]_3Co_2$ unit consisting of a cobalt–cobalt bond bridged by three $MeN(PF_2)_2$ ligands.

Recently we have prepared a variety of compounds of the type $[MeN(PF_2)_2]_3Co_2L_2$ (L = two-electron donor ligand[1–3]) and have demonstrated by *X*-ray crystallography the presence of a cobalt–cobalt bond bridged by three $MeN(PF_2)_2$ ligands for the derivatives where L = CO,[1] PF_2NHMe,[1] and Me_2NPF_2.[3] We now show that the $[MeN(PF_2)_2]_3Co_2$ unit is so stable that the cobalt–cobalt bond resists cleavage by halogens under conditions where the metal–metal bond in simple unbridged bimetallic systems such as $[(C_5H_5)Fe(CO)_2]_2$[4] and $M_2(CO)_{10}$ (M = Mn and Re)[5] is cleaved by halogens to form monometallic metal halides.



(I)

The reactions of $[MeN(PF_2)_2]_3Co_2(CO)_2$ with halogens (Cl_2, Br_2, and I_2) at room temperature in organic solvents result in rapid evolution of CO to give complex mixtures of products of stoicheiometries in the range $[MeN(PF_2)_2]_3Co_2X_n$ ($2 \leqslant n \leqslant 4$). A pure product has been obtained in the case of the reaction of $[MeN(PF_2)_2]_3Co_2(CO)_2$ with a large excess of Br_2. Thus treatment of 0·446 g of $[MeN(PF_2)_2]_3Co_2(CO)_2$[1,2] with 1·2 ml of Br_2 in 200 ml of diethyl ether followed by evaporation and crystallization of the residue from dichloromethane–hexane gave 0·521 g (84% yield) of brown $[MeN(PF_2)_2]_3Co_2Br_4$ (I), decomp. 140 °C. In order to establish the nature of the $[MeN(PF_2)_2]_3Co_2$ unit in this complex, its structure was determined by single crystal *X*-ray diffraction.

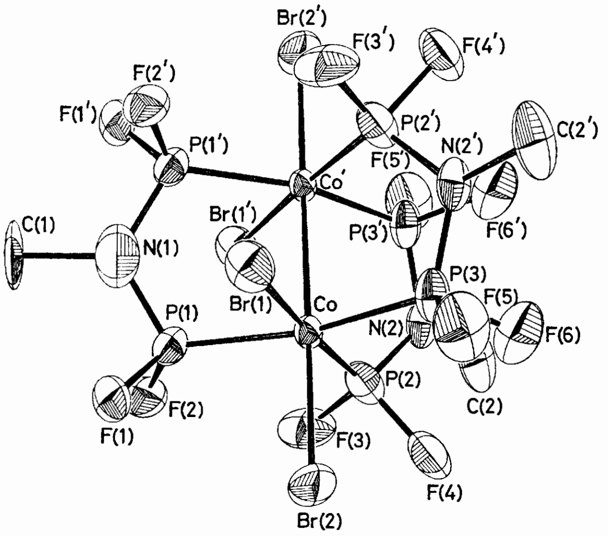


FIGURE. ORTEP drawing of the structure of $[MeN(PF_2)_2]_3Co_2Br_4$. The β_{33} of N(1) was so small that a physically meaningful plot was not possible. The value of β_{33} was thus set at the average of C(1) and P(1) to achieve this plot. These problems most likely arise from uncorrected absorption (μ = 90·76 cm^{-1} for Mo-$K_{\bar{\alpha}}$).

The complex $[MeN(PF_2)_2]_3Co_2Br_4$ forms monoclinic crystals from dichloromethane–hexane: space group *C2/c*; a = 14·429(7), b = 12·080(6), c = 14·185(10) Å, β = 106·14(5)°, Z = 4. Least-squares anisotropic refinement using the 847 observed reflections (R = 0·105, R_w = 0·063) indicates the structure depicted in the Figure.† This structure (I) contains the cobalt–cobalt bond bridged by three bidentate $MeN(PF_2)_2$ ligands similar to the $[MeN(PF_2)_2]_3Co_2$ unit found in the $[MeN(PF_2)_2]_3Co_2L_2$ complexes mentioned above (L = CO, $MeNHPF_2$, and Me_2NPF_2). The co-ordination around each cobalt atom is an only slightly distorted octahedron since the three *trans*-angles Co′–Co–Br(2), Br(1)–Co–P(2), and P(1)–Co–P(3) are 171·1(2), 174·9(3), and 162·7(4)°, respectively, as compared with the ideal 180° and the 12 *cis*-angles Co′–Co–Br(1), Co′–Co–P(1), Co′–Co–P(2), Co′–Co–P(3), Br(2)–Co–Br(1), Br(2)–Co–P(1), Br(2)–Co–P(2), Br(2)–Co–P(3), Br(1)–Co–P(1), Br(1)–Co–P(3), P(1)–Co–P(2), and P(2)–Co–P(3) are 96·2(2), 87·3(3), 85·3(3), 91·8(3), 91·9(2), 90·2(3), 86·9(3), 93·1(3), 82·5(3), 80·4(3), 102·5(4), and 94·7(4)°, respectively, as compared with the ideal 90°. The cobalt–cobalt bond length in $[MeN(PF_2)_2]_3Co_2Br_4$ is 2·717(5) Å as compared with 2·71—2·77 Å for the cobalt–cobalt bond lengths in the $[MeN(PF_2)_2]_3Co_2L_2$ derivatives (L = CO, PF_2NHMe, and PF_2NMe_2). This indicates that the dimensions of the very stable $[MeN(PF_2)_2]_3Co_2$ unit are relatively little affected by the +2 increase in the cobalt formal oxidation state when CO is replaced by 2Br.

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