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Methylaminobis(difluorophosphine) as a Monoligate Monometallic Ligand

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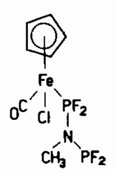
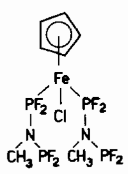
The ability of $CH_3N(PF_2)_2$ [1] to function as a biligate monometallic ligand is indicated by the formation of $CH_3N(PF_2)_2M(CO)_4$ (M = Cr, Mo, and W) [2], $[CH_3N(PF_2)_2]_3M$ (M = Cr, Mo, and W) [3], $C_5H_5V(CO)_2(PF_2)_2NCH_3$ [4], and $C_5H_5V[(PF_2)_2NCH_3]_2$ [4]. The ability of $CH_3N(PF_2)_2$ to function as a biligate bimetallic ligand is indicated by the formation of $[CH_3N(PF_2)_2]_3Co_2L_2$ (L = CO and CH_3NHPF_2) [5], $[CH_3N(PF_2)_2Fe(CO)_3]_2$ [6], and $[CH_3N(PF_2)_2]_nFe_2(CO)_{9-2n}$ (n = 1 and 2) [6]. This Communication reports the first examples of complexes in which $CH_3N(PF_2)_2$ functions as a monoligate monometallic ligand as well as the X-ray crystal structure determination of a novel metal complex containing both biligate monometallic and monoligate monometallic $CH_3N(PF_2)_2$ ligands.

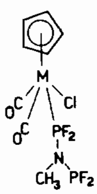
Treatment of $C_5H_5Fe(CO)_2Cl$ [7] with $CH_3N(PF_2)_2$ [1] results in the successive replacement of the two carbonyl groups with monoligate monometallic $CH_3N(PF_2)_2$ ligands to form $C_5H_5Fe(CO)[(PF_2)_2NCH_3]Cl$ (I) and $C_5H_5Fe[(PF_2)_2NCH_3]_2Cl$ (II), respectively.[†] Thus the red–purple complex I, m.p. 85–87 °C, ν(CO) 2000 cm^{-1}, can be obtained in 45 to 55% yields by reaction of $C_5H_5Fe(CO)_2Cl$ with $CH_3N(PF_2)_2$ in a 1:1 mol ratio in boiling hexane for 5 minutes or in boiling diethyl ether for 1 hr. The red complex II, m.p. 62–64 °C, can be obtained in ~ 45% yield by reaction of $C_5H_5Fe(CO)_2Cl$ with excess $CH_3N(PF_2)_2$ in boiling hexane for several hours.



I



II



III

The thermal reactions of $C_5H_5M(CO)_3Cl$ (M = Mo and W) [8], with $CH_3N(PF_2)_2$ in boiling tetrahydrofuran or benzene initially proceed analogously to the formation of I to give the orange complexes[†] $C_5H_5M(CO)_2[(PF_2)_2NCH_3]Cl$ (III: M = Mo, m.p. 90–94 °C, ν(CO) 2026 and 1937 cm^{-1}; M = W, m.p. 109–111 °C (dec.), ν(CO) 2009 and 1927 cm^{-1}) in 50 to 80% yields. However, ultraviolet irradiation of $C_5H_5M(CO)_3Cl$ (M = Mo and W) with excess $CH_3N(PF_2)_2$ in diethyl ether solution gives yellow carbonyl-free complexes of the stoichiometry[†] $C_5H_5M[(PF_2)_2NCH_3]_2Cl$ (M = Mo, m.p. 122–123 °C; M = W, m.p. 123–125 °C (dec.)) in 50% yields.

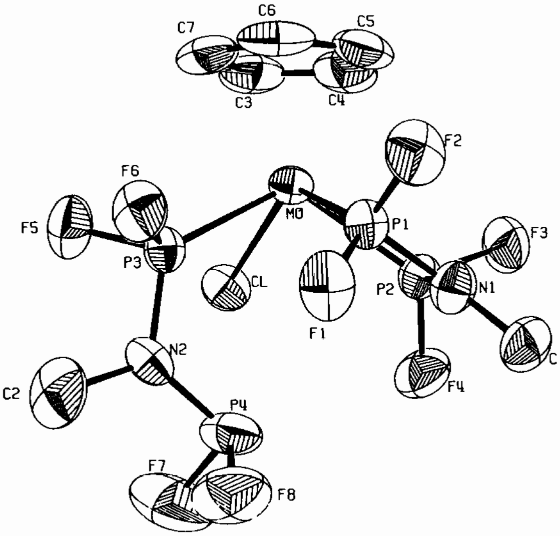


Fig. 1. The molecular structure of $C_5H_5Mo[(PF_2)_2NCH_3]_2Cl$.

The molybdenum complex $C_5H_5Mo[(PF_2)_2NCH_3]_2Cl$ forms monoclinic crystals from a mixture of dichloromethane and cyclohexane: space group C2/c; *a* = 29.481 Å, *b* = 7.991 Å, *c* = 15.833 Å, β = 111.43°, Z = 8. Least squares refinement using the 2160 observed reflections (R = 0.0291, R_w = 0.0310) indicates the structure depicted in Figure 1 containing one biligate monometallic and one monoligate monometallic $CH_3N(PF_2)_2$ ligand. The Mo–Cl distance is 2.510(1) Å as compared with a Mo–Cl distance of 2.542(9) Å found [9] for $C_5H_5Mo(CO)_3Cl$. The P(1)–Mo–P(2) angle involving the biligate monometallic $CH_3N(PF_2)_2$ ligand is 63.09(5)° indicative of the compression associated with the small bite of this bidentate ligand. The remaining lateral (*cis*) ligand bond angles are 83.14(5)°, 76.11(5)°, and 84.01(5)° for the angles P(1)–Mo–P(3), P(3)–Mo–Cl, and Cl–Mo–P(2), respectively. The two diagonal (*trans*) bond angles are 127.38(5)° and 116.42(5)° for the P(1)–Mo–Cl and P(2)–Mo–P(3) angles, respectively. These angles suggest that the

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[†] New compounds were characterized by correct elemental analyses (C, H, N, P, F) and molecular weight determinations (vapor pressure osmometer in benzene). All new compounds were non-electrolytes in acetonitrile solution. The reported infrared ν(CO) frequencies were determined in pentane or hexane solution.

compression in the P(1)–Mo–P(2) angle caused by the small bite of the $CH_3N(PF_2)_2$ ligand is also reflected in the corresponding diagonally situated P(3)–Mo–Cl angle, although to a lesser extent The P(1)–N(1)–P(2) and P(3)–N(2)–P(4) angles are 93 5(2)° and 120 3(3)°, respectively, reflecting the expected geometric differences between biligate monometallic and monoligate monometallic $CH_3N(PF_2)_2$ ligands

Two particularly noteworthy features of the chemistry summarized in this Communication are the tendency of the $CH_3N(PF_2)_2$ ligand to function as a monoligate rather than exclusively as a biligate monometallic ligand in these systems and the extreme reluctance of the $CH_3N(PF_2)_2$ ligand to displace covalently bonded chlorine to form ionic derivatives containing complex cations such as $[C_5H_5M[(PF_2)_2NCH_3]_2]^+$ (M = Mo and W) which would have two biligate monometallic $CH_3N(PF_2)_2$ ligands and would be isostructural with the known [4] $C_5H_5V[(PF_2)_2NCH_3]_2$ In the latter connection all of our attempts to abstract chlorine from $C_5H_5M[(PF_2)_2NCH_3]_2Cl$ with silver hexafluorophosphate to give derivatives of $[C_5H_5M[(PF_2)_2NCH_3]_2]^+$ have given negative results These two features of this $CH_3N(PF_2)_2$ chemistry may be further consequences of the small bite and low basicity of this ligand

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