by volume of THF to 1,2-dimethoxyethane with Na–K alloy at −83 °C is converted[15] at equilibrium to radical anion only to the extent of about 0.1%; toluene under similar conditions forms a radical anion to an even lesser extent.[16] The present results can be rationalized on the basis of the superior reducing power in THF of cesium and cesium alloys over the other alkali metals or alloys. The reaction is evidently promoted by strong electrostatic interaction between cesium cations and benzene or toluene radical anions and the association of ions into insoluble aggregates. These reactions seem to constitute the simplest synthesis of 1,1′,4,4′-tetrahydrobiphenyl and derivatives; dehydrogenation of the latter may in some cases provide a convenient synthesis of certain derivatives of biphenyl. The generality of these reactions is under investigation.

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(4) While reaction at −50 °C was deemed necessary to keep all the alloy in a liquid phase, reaction at this temperature for 1.5 h resulted in some 70% yield of **3**, unreacted 1,1,1-triphenylethane, and unknown product(s) rather than the nearly quantitative yield[1] of **3** found at −70 °C.

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Novel Bimetallic Products from Iron Carbonyls and Methylaminobis(difluorophosphine): an Example of Square Pyramidal Pentacoordinate Iron(0)

Sir:

Recently we reported reactions of $CH_3N(PF_2)_2$ with $Co_2(CO)_8$ to give bimetallic products of the type $[CH_3N(PF_2)_2]_3Co_2L_2$ (L = CO and CH_3NHPF_2) containing a cobalt–cobalt bond supported by three bridging $CH_3N(PF_2)_2$ groups.[1] This communication reports the preparation and structural characterization of bimetallic iron carbonyl derivatives containing pairs of iron atoms bridged by one or two $CH_3N(PF_2)_2$ ligands. Of particular interest is the unambiguous identification by x-ray crystallography of a pentacoordinate iron(0) derivative in which the iron coordination polyhedron is best represented as a square pyramid rather than the more usual trigonal bipyramid.

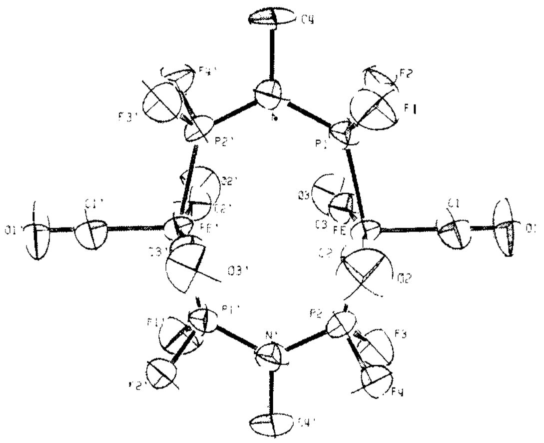


Figure 1. ORTEP drawing of the structure of $[CH_3N(PF_2)_2Fe(CO)_3]_2$ (I).

The ability of $CH_3N(PF_2)_2$ to function as a biligate monometallic ligand[2] as indicated by the formation of $CH_3N(PF_2)_2M(CO)_4$ (M = Cr, Mo, and W)[3] and $[CH_3N(PF_2)_2]_3M$ (M = Cr, Mo, and W)[4] suggested that the iron carbonyl system might form a $CH_3N(PF_2)_2Fe(CO)_3$ complex. In this connection reaction of 2.0 g (4 mmol) of $Fe_3(CO)_{12}$ with 2.0 g (12 mmol) of $CH_3N(PF_2)_2$ in 75 mL of boiling tetrahydrofuran for 20 min followed by rapid removal of solvent and crystallization from dichloromethane gave 0.77 g (20% yield) of yellow crystalline $[CH_3N(PF_2)_2Fe(CO)_3]_n$,[5] mp 128–129 °C; infrared ν(CO) in hexane 2040 (w), 2037 (m), 2033 (m), 2011 (s), 2005 (s), and 1974 (m) cm^{-1}. Molecular weight determinations on freshly prepared benzene solutions of $[CH_3N(PF_2)_2Fe(CO)_3]_n$ by vapor pressure osmometry consistently indicated formulation as a dimer (calcd mol wt for n = 2, 614; found, 627, 583, 618, 572).

The iron complex $[CH_3N(PF_2)_2Fe(CO)_3]_2$ (I) forms monoclinic crystals from n-hexane at −20 °C for 3 h: space group $P2_1/n$; a = 10.473 Å, b = 10.825 Å, c = 9.035 Å; β = 100.127°; Z = 4. Because of crystal decomposition, three crystals were required for collection of x-ray intensity data. Least-squares refinement using the 893 observed reflections (R = 0.0839, R_w = 0.0511) indicates the structure depicted in Figure 1. This structure uses the inversion center. The iron–iron distance is 3.90 Å, clearly a nonbonding distance. The coordination geometry of each iron atom (Figure 1) is best represented as a square pyramid with successive angles between adjacent pairs of the basal ligands of 88.5 (5)°, 88.3 (4)°, 87.4 (4)°, and 88.3 (4)° as compared with 90° for an idealized square pyramid. The successive angles between the apical carbonyl group and the four basal ligands are 98.8 (7)°, 102.6 (4)°, 97.6 (7)°, and 103.5 (4)° corresponding to α values[6] of −9°, −13°, −8°, and −13°, respectively.

The complex $[CH_3N(PF_2)_2Fe(CO)_3]_2$ (I) is unstable upon standing in solution at room temperature with respect to evolution of carbon monoxide to form orange $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ (II),[5] mp 192–193 °C; infrared ν(CO) in hexane 2066 (w), 2026 (s), 1992 (s), 1978 (m), and 1786 (m) cm^{-1}. The relatively stable red-orange $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ (II) is also obtained presumably via $[CH_3N(PF_2)_2Fe(CO)_3]_2$ (I) from the reaction of $Fe_3(CO)_{12}$ with $CH_3N(PF_2)_2$ in boiling diethyl ether or tetrahydrofuran for several hours or in hexane at room temperature for 60 h. The diiron pentacarbonyl II is also obtained in 40% yield by

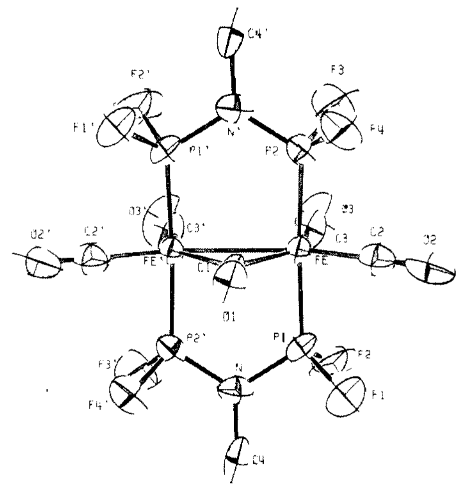


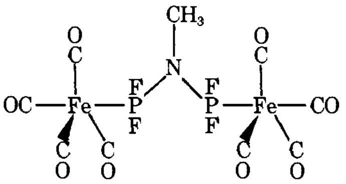
Figure 2. ORTEP drawing of the structure of $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ (II).

the ultraviolet irradiation of equimolar quantities of $Fe(CO)_5$ and $CH_3N(PF_2)_2$ in diethyl ether.

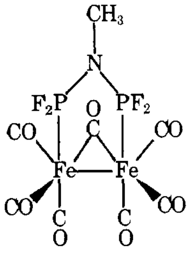
The complex $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ (II) forms orthorhombic crystals from mixtures of 1:1 *n*-hexane-dichloromethane: space group *Pccn*; $a = 10.061$ Å, $b = 9.269$ Å, $c = 19.876$ Å; $Z = 8$. Least-squares refinement using the 978 observed reflections ($R = 0.0411$, $R_w = 0.0414$) indicates the structure depicted in Figure 2 with a twofold axis passing through the bridging carbonyl group and the midpoint of the iron-iron bond. The iron-iron distance is 2.661 (1) Å corresponding to an iron-iron bond. The coordination polyhedron around each iron atom can be derived by appropriate distortions from an octahedron or trigonal bipyramid depending upon whether a coordination position is allocated to the metal-metal bond.

Of particular interest is a comparison between the iron coordination polyhedra in I and II as an indication of the effect of the metal-metal bond in II (see Figures 1 and 2). In $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ (II) the phosphorus-iron-phosphorus angles are 172.5 (1)° which is close to the 180° required for the collinear apical positions in an octahedron or trigonal bipyramid. However, in $[CH_3N(PF_2)_2Fe(CO)_3]_2$ (I) the phosphorus-iron-phosphorus angles are reduced to 153.9 (2)° since the nonbonding iron-iron distance in I is larger than the bite of the $CH_3N(PF_2)_2$ ligand. Thus the repulsion between the nonbonded iron atoms in I forces the five-coordinate iron(0) atoms to adopt the unusual square pyramidal geometry instead of the more usual trigonal bipyramidal geometry. The ability of the simple nonbonded interaction to change the coordination polyhedron of a five-coordinate system is a further indication of the relative nonrigidity of this coordination number and the small energy difference between the trigonal bipyramid and the square pyramid.

Bimetallic iron carbonyl complexes have also been obtained in which only one $CH_3N(PF_2)_2$ ligand bridges the pair of iron atoms. Thus the reaction of $Fe_2(CO)_9$ with $CH_3N(PF_2)_2$ in diethyl ether at 25 to 35 °C gives a mixture of yellow liquid $CH_3N(PF_2)_2[Fe(CO)_4]_2$ (III) (infrared ν(CO) in pentane 2090 (m), 2023 (s), 1996 (s), 1985 (s), and 1976 (s) cm^{-1}) and red-orange $CH_3N(PF_2)_2Fe_2(CO)_7$ (IV) mp 75-77 °C (infrared ν(CO) in pentane 2090 (m), 2040 (s), 2025 (s), 1995 (vs), 1982 (m), and 1805 (s) cm^{-1}) in III:IV ratios ranging from 3:1 to 10:1. Those two compounds can be readily separated by column chromatography on Florisil in hexane solution. The proposed structure of IV is analogous to that reported[7] for the closely related complex $CH_2[P(C_6H_5)_2]_2Fe_2(CO)_7$.



III



IV

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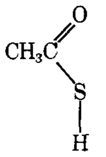
Dynamic Nuclear Magnetic Resonance Spectroscopy. Carbon-Sulfur p-p π-Bonding and Conformational Equilibria in Thioacetic Acid

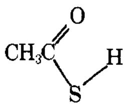
Sir:

Much information about the conformational preferences and carbon-nitrogen π-bonding in amides has been obtained from dynamic nuclear magnetic resonance studies of these compounds,[1] but similar studies of π-bonding between carbon and other heteroatoms have been rare.[2] Application of this method to the bonding in thiol acids is of particular interest because previous studies of carbon-sulfur π-bonding in related systems, using other methods, have resulted in opposite conclusions. The majority[3] of studies cited in a review[4] of divalent sulfur bonding seem to indicate that the mesomeric effect is greater for oxygen than for sulfur.[5] Evidence for the reverse order is presented in this work. In addition, the conformational equilibrium described here has not been detected in previous infrared[6] or electron diffraction studies[7] of thioacetic acid (**1**).

Two planar conformations (*E*-**1** and *Z*-**1**) are possible for the -SH tautomer of thioacetic acid, as shown below. Several bond lengths and bond angles have been reported,[7] but the O-C-S-H dihedral angle was not determined, and the possibility of *E* and *Z* isomers was not discussed. Infrared spectra



E-**1**



Z-**1**