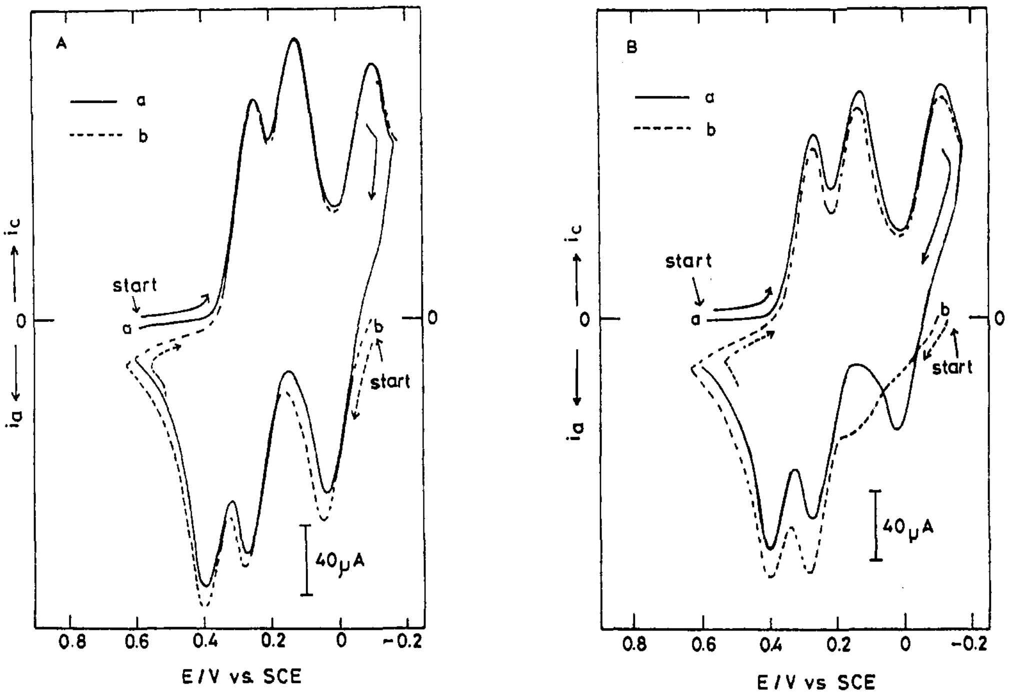

Figure 3. Thin-layer cyclic voltammograms of 12-heteropolymolybdates at a gold-minigrid OTTLE in 50% (w/w) dioxane–water solutions containing 0.36 M H_2SO_4 (scan rate 2 mV s^{-1}): (A) 10^{-3} M $Na_4SiMo_{12}O_{40}$ (a) for initial potential 0.600 V vs. SCE and initial scan direction cathodic and (b) after electrolysis for about 40 min at the potential where 12-molybdosilicate is reduced to the six-electron-reduction product of 12-molybdosilicate and the anodic scan was started; (B) 10^{-3} M $Na_3PMo_{12}O_{40}$ (a) for initial potential 0.600 V vs. SCE and initial scan direction cathodic and (b) after electrolysis for about 40 min at the potential where 12-molybdophosphate is reduced to the six-electron-reduction product of 12-molybdophosphate and the anodic scan was started.

electron-reduction product of 12-MPA. In the case of 12-MSA, the fourth cathodic process seems to be autocatalytic.

The six-electron-reduction product of 12-MPA is more reactive for a homogeneous electron-transfer reaction than that of 12-MSA.

Thin-Layer Voltammetry at a Gold-Minigrid OTTLE. Thin-layer cyclic voltammograms of 12-MSA obtained in 50% (w/w) dioxane–water solutions containing 0.36 M H_2SO_4 are shown in Figure 3A. Curve a in Figure 3A is an ordinary cyclic voltammogram (starting potential +0.600 V vs. SCE). On the other hand, curve b in Figure 3A was obtained by the following procedures. After electrolysis for about 40 min at the potential where the 12-MSA is reduced to the six-electron-reduction product of 12-MSA, the anodic scan was started and the scan was reversed at +0.600 V vs. SCE. Curves a and b in Figure 3A are almost the same. This indicates that the six-electron-reduction product of 12-MSA is very stable in this medium.

Thin-layer cyclic voltammograms of 12-MPA obtained in 50% (w/w) dioxane–water solutions containing 0.36 M H_2SO_4 are shown in Figure 3B. The relationship between curve a and curve b is the same as that in Figure 3A. As seen in curve b, the anodic peak corresponding to the reoxidation of the six-electron-reduction product of 12-MPA was less defined than that of curve a. Spectral changes in the six-electron-reduction product of 12-MPA with time observed by using a gold-minigrid OTTLE had no isosbestic points. These facts indicate that the six-electron-reduction product of 12-MPA is rather unstable even in this medium and that the transformation reaction of the six-electron-reduction product of 12-MPA is not a simple one.[6]

In conclusion, in the case that the electrode reaction processes of 12-heteropolymolybdates are accompanied by chemical reactions and that these chemical reactions cannot be ignored, the influence of a central atom on the electrode reactions of 12-heteropolymolybdates is very significant. The properties of high-reduction products of 12-MPA seem to be very different from those of 12-MSA.

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Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30602

Metal Complexes of Fluorophosphines. 11. Further Observations on Iron Carbonyl Complexes of (Methylamino)bis(difluorophosphine)[1]

R. B. King,* T. W. Lee, and J. H. Kim

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Previous papers of this series[2-4] have described a variety of iron carbonyl derivatives of the small-bite bidentate strong π-acceptor ligand $CH_3N(PF_2)_2$ including the mononuclear complex $[CH_3N(PF_2)_2]_2FeCO$ and two series of binuclear complexes: yellow $[CH_3N(PF_2)_2]_nFe_2(CO)_{10-2n}$ (n = 1 and 2) without an iron–iron bond and yellow to orange $[CH_3N(PF_2)_2]_nFe_2(CO)_{9-2n}$ (n = 1, 2, and 4) with an iron–iron bond. Further work since the publication of these results has resulted in the isolation of two new iron carbonyl complexes of $CH_3N(PF_2)_2$: mononuclear $CH_3N(PF_2)_2Fe(CO)_4$ (I), con-

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[1] For part 10 of this series see: King, R. B.; Lee, T. W. *Inorg. Chem.* **1982**, *21*, 319.

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[3] Newton, M. G.; King, R. B.; Chang, M.; Gimeno, J. *J. Am. Chem. Soc.* **1978**, *100*, 326.

[4] King, R. B.; Gimeno, J. *Inorg. Chem.* **1978**, *17*, 2390.

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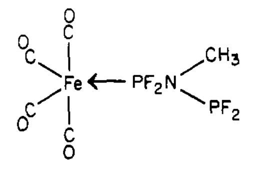

I

taining a monoligate $CH_3N(PF_2)_2$ ligand, and binuclear $[CH_3N(PF_2)_2]_3Fe_2(CO)_3$, which represents the final member of the $[CH_3N(PF_2)_2]_nFe_2(CO)_{9-2n}$ (n = 3) series. This paper describes the preparation and properties of these two new iron carbonyl complexes as well as a solvolysis product of the former complex, namely $CH_3NHPF_2Fe(CO)_4$. In addition, evidence is presented for the formation of the biligate monometallic complex $CH_3N(PF_2)_2Fe(CO)_3$ by the decarbonylation of $CH_3N(PF_2)_2Fe(CO)_4$ (I).

Experimental Section

Except as noted below, general experimental techniques are similar to those described in detail in previous papers of this series.[1,4] Mass spectra were obtained on a Finnegan Model 4023 gas chromatograph–quadrupole mass spectrometer. Ion relative intensities are given in parentheses. Phosphorus-31 NMR spectra were obained on a JEOL PFT-100 spectrometer operating in the pulsed Fourier transform mode with proton noise decoupling and a deuterium lock. The phosphorus-31 NMR chemical shifts (δ) are reported in ppm relative to external 85% H_3PO_4, with positive nos. denoting downfield chemical shifts. The reagents $Fe_2(CO)_9$,[5] $Fe_3(CO)_{12}$,[6] and $CH_3N(PF_2)_2$[4] were prepared by the cited published procedures. Experiments were performed under nitrogen with solvents that had been freshly distilled under nitrogen over suitable drying agents.

Preparation of $CH_3N(PF_2)_2Fe(CO)_4$ (I). A mixture of 5.0 g (13.7 mmol) of $Fe_2(CO)_9$, 10.0 g (59.9 mmol) of $CH_3N(PF_2)_2$, and 150 mL of diethyl ether was stirred for 5 h at room temperature. Removal of solvent from the filtered reaction mixture at ~25 °C (25 mm) followed by vacuum distillation of the liquid residue gave a ~70% yield of yellow $CH_3N(PF_2)_2Fe(CO)_4$ (I): bp 46°C (2 mm) or 68 °C (20 mm); infrared ν(CO) (hexane) 2072 (m), 2046 (w), 2004 (s), 1990 (s), 1984 (s) cm^{-1}; other infrared frequencies (liquid film) 2950 (w), 2890 (vw), 2820 (vw), 1455 (w), 1203 (s), 1193 (s), 1060 (vs), 890–910 (vvs), 780–870 (vvs) cm^{-1}; proton NMR ($CDCl_3$) δ 2.91 (doublet, J = 9 Hz); phosphorus-31 NMR (CH_2Cl_2) δ 189.1 (triplet of doublets, $J_T = |^1J(PP)|$ = 1177 Hz, $J_D = |^2J(PP)|$ = 210 Hz), 136.8 (triplet of doublets, $J_T = |^1J(PP)|$ = 1268 Hz, $J_D = |^2J(PP)|$ = 210 Hz); carbon-13 NMR ($CDCl_3$) δ 210.1 (CO), 26.4 (CH_3); fluorine-19 NMR (CH_2Cl_2) (upfield from CCl_3F) 33.8 (doublet, $J \approx$ 1185 Hz), 73.7 ppm (doublet, $J \approx$ 1258 Hz); mass spectrum $CH_3NP_2F_4Fe(CO)_3^+$ (47), $CH_3NP_2F_3Fe(CO)_3^+$ (6), $CH_3NP_2F_4Fe(CO)_2^+$ (19), $CH_3NP_2F_2Fe(CO)_3^+$ (11), $CH_3NP_2F_3Fe(CO)_2^+$ (2), $CH_3NP_2F_4FeCO^+$ (20), $CH_3NP_2F_2Fe(CO)_2^+$ (6), $CH_3NP_2F_3FeCO^+$ (2), $CH_3NP_2F_4Fe^+$ (39), $CH_3NP_2F_3^+$ (8), $CH_3NP_2F_2^+$ (49), $NP_2F_2^+$ (17), $Fe(CO)_2^+$ (12), $FeCO^+$ (25), CH_2NPF^+ (14), FeF^+ (11), CH_3NP^+ (100), Fe^+ (33). Anal. Calcd for $C_5H_3F_4FeNO_4P_2$: C, 17.9; H, 0.9; N, 4.2. Found: C, 18.7; H, 1.2; N, 4.2.

Preparation of $CH_3NHPF_2Fe(CO)_4$. The crude $CH_3N(PF_2)_2Fe(CO)_4$ (I) obtained from 1.0 g (2.7 mmol) of $Fe_2(CO)_9$ and 2.0 g (12.0 mmol) of $CH_3N(PF_2)_2$ as described above was chromatographed on a Florisil column in hexane solution. After removal of an initial yellow fraction, elution of a pale yellow band followed by vacuum sublimation at room temperature gave 0.25 g (35% yield) of pale yellow crystalline $CH_3NHPF_2Fe(CO)_4$: mp 29 °C; infrared ν(CO) (hexane) 2072 (m), 2008 (s), 1984 (s), 1972 (s) cm^{-1}; ν(NH) 3440 cm^{-1}; proton NMR (CCl_4) δ 2.90 (double doublet, J_1 = 11 Hz, J_2 = 5 Hz); phosphorus-31 NMR (CH_2Cl_2) δ 193.7 (triplet, $J = |^1J(PF)|$ = 1146 Hz); carbon-13 NMR (CH_2Cl_2) δ 211.2 (CO, doublet of triplets, $J_D = |^2J(CP)|$ = 15 Hz, $J_T = |^3J(CF)|$ = 5 Hz), 27.8 (CH_3, doublet, $J = |^2J(CP)|$ = 8 Hz); fluorine-19 NMR (CCl_3F) (upfield from CCl_3F) 19.5 ppm (doublet of doublets, $J = |^1J(PF)|$ = 1156 Hz, $J_2 = |^3J(HF)|$ = 7 Hz); mass spectrum $CH_3NHPF_2Fe(CO)_4^+$ (37), $CH_3NHPFFe(CO)_4^+$ (16), $CH_3NHPF_2Fe(CO)_3^+$ (38), $CH_3NHPFe(CO)_4^+$ (13), $CH_3NHPFFe(CO)_3^+$ (6), $CH_3NHPF_2Fe(CO)_2^+$ (16), $CH_3NHPFe(CO)_3^+$ (16), $CH_3NHPFFe(CO)_2^+$ (2), $CH_3NHPF_2FeCO^+$ (37), $CH_2NHPF_2Fe^+$ (58), $Fe(CO)_3^+$ (3), $FePF_2^+$ (13), $Fe(CO)_2^+$ (17), $CH_3NPF_2^+$ (15), $FeCO^+$ (38), CH_3NHPF^+ (51), FeF^+ (12), PF_2^+ (16), CH_3NHP^+ (100), CH_3NP^+ (51), Fe^+ (53). Anal. Calcd. for $C_5H_4F_2FeNO_4P$: C, 22.5; H, 1.5; N, 5.2. Found: C, 19.8; H, 1.5; N, 4.8. The low carbon analysis is probably a consequence of the volatility and air sensitivity of this compound.

The compound $CH_3NHPF_2Fe(CO)_4$ was also obtained by boiling under reflux a mixture of $Fe_2(CO)_9$ (7.2 g, 20 mmol), $CH_3N(PF_2)_2$ (3.2 g, 20 mmol), and water (3.0 g, 167 mmol) in diethyl ether (30 mL) at room temperature followed by evaporation of the filtered reaction mixture and vacuum distillation; bp 73 °C (25 mm).

Observation of $CH_3N(PF_2)_2Fe(CO)_3$. A mixture of 3.0 g (8.2 mmol) of $Fe_2(CO)_9$ and 6.0 g (35.9 mmol) of $CH_3N(PF_2)_2$ in diethyl ether solution was exposed to ultraviolet irradiation for 5 h. Evaporation of the diethyl ether followed by vacuum distillation gave a yellow liquid, bp 35 °C (0.45 mm), leaving behind in the distillation pot orange solid $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$, identified by its infrared spectrum in the ν(CO) region.[4] The proton NMR spectrum of the yellow liquid exhibited a doublet at δ 2.91 (J = 9 Hz) assigned to $CH_3N(PF_2)_2Fe(CO)_4$ (see above) and a triplet at δ 2.66 (J = 12 Hz) assigned to the unknown $CH_3N(PF_2)_2Fe(CO)_3$. Integration of this NMR spectrum indicated this liquid to contain 56% $CH_3N(PF_2)_2Fe(CO)_4$ and 44% $CH_3N(PF_2)_2Fe(CO)_3$, which was also in approximate agreement with the elemental analyses. (Anal. Calcd for 56% $CH_3N(PF_2)_2Fe(CO)_4$ and 44% $CH_3N(PF_2)_2Fe(CO)_3$: C, 16.9; H, 0.9; N, 4.4. Found: C, 16.2; H, 1.1; N, 4.5). The major iron carbonyl ions in the mass spectrum of this liquid were $CH_3N(PF_2)_2Fe(CO)_n^+$ (n = 3, 2, 1, and 0). Other fragment ions in this mass spectrum were similar to those reported above for the mass spectrum of $CH_3N(PF_2)_2Fe(CO)_4$.

The following attempts to prepare a pure sample of $CH_3N(PF_2)_2Fe(CO)_3$ were unsuccessful: (1) Chromatography of the above mixture on Florisil in hexane solution resulted in hydrolysis of the $CH_3N(PF_2)_2Fe(CO)_4$ into $CH_3NHPF_2Fe(CO)_4$, giving a complex mixture that could not be separated. (2) Heating the above liquid in boiling hexane for 15 h resulted in no change as indicated by the infrared ν(CO) frequencies. (3) Ultraviolet irradiation of the above liquid in hexane for 1 h gave a precipitate of orange $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$, identified by its ν(CO) frequencies. The infrared ν(CO) spectrum of the filtrate indicated no change. (4) Pyrolysis of pure $CH_3N(PF_2)_2Fe(CO)_4$ at 105 °C for 24 h in a sealed evacuated tube resulted in no change indicated by the infrared spectrum in the ν(CO) region.

Preparation of $[CH_3N(PF_2)_2]_3Fe_2(CO)_3$. A mixture of 2.4 g (4.76 mmol) of $Fe_3(CO)_{12}$, 2.0 g (12.0 mmol) of $CH_3N(PF_2)_2$, and 350 mL of diethyl ether was exposed for 130 min to the ultraviolet irradiation from a 450-W Englehard-Hanovia medium-pressure mercury lamp. The green solution was filtered through Celite. Solvent was removed from the filtrate at ~25 °C (25 mm). Chromatography of a concentrated dichloromethane solution of the residue on Florisil followed by elution with hexane and 1:1 hexane/diethyl ether gave a 2% yield of red crystalline $[CH_3N(PF_2)_2]_3Fe_2(CO)_3$: mp 203 °C; infrared ν(CO) (CCl_4) 1977 (s), 1776 (s) cm^{-1}. Anal. Calcd for $C_6H_9F_{12}Fe_2N_3O_3P_6$: C, 9.6; H, 1.2; N, 5.6; mol wt 697. Found: C, 9.7; H, 1.1; N, 5.7; mol wt 700 (benzene).

Results and Discussion

A. New Mononuclear Iron Carbonyl Derivatives. Reaction of equimolar amounts of $CH_3N(PF_2)_2$ and $Fe_2(CO)_9$ in diethyl ether at room temperature was previously[4] found to give yellow liquid $CH_3N(PF_2)_2[Fe(CO)_4]_2$ as the major product as well as a low yield of red-orange crystalline $CH_3N(PF_2)_2Fe_2(CO)_7$. We have now found that a similar reaction of *excess* $CH_3N(PF_2)_2$ with $Fe_2(CO)_9$ (i.e., a 4.4:1 mole ratio) proceeds differently to give the monoligate monometallic complex $CH_3N(PF_2)_2Fe(CO)_4$ as a yellow distillable liquid. The phosphorus-31 NMR spectrum of this product exhibits two triplets of doublets, characteristic[1,7] of monoligate monometallic $CH_3N(PF_2)_2$ complexes. The phosphorus-31 resonances centered at δ 189.1 and 136.8 are assigned to the complexed and uncomplexed PF_2 groups, respectively, since the latter resonance has a chemical shift close to that of the free

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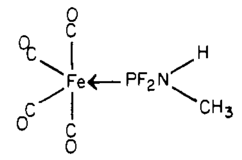
$CH_3N(PF_2)_2$ ligand (δ 141.3). Similarly, the fluorine-19 resonances centered at 33.8 and 73.7 ppm are assigned to the complexed and uncomplexed PF_2 groups, respectively.

The infrared spectra of $LFe(CO)_4$ complexes can be used to distinguish between the axially and equatorially substituted isomers.[8] The positions and relative intensities of the ν(CO) frequencies of $CH_3N(PF_2)_2Fe(CO)_4$ at 2072 (m), 2004 (s), 1990 (s), and 1984 (s) cm^{-1} correspond to the A_1, A_1, B_2, and B_1 frequencies expected for the equatorially substituted isomer as depicted in structure I. The remaining weak ν(CO) frequency at 2046 cm^{-1} may be one of the A_1 frequencies of the axial isomer, which is present in small quantities relative to the equatorial isomer. The other two ν(CO) frequencies (A_1 and E) expected for the axial isomer may be hidden under the three strong lowest ν(CO) frequencies of the much more abundant equatorial isomer. Trivalent phosphorus ligands usually favor axial isomers in their $LFe(CO)_4$ complexes but certain fluorophosphines, including PF_3, are known[9,10] to favor equatorial isomers in their $LFe(CO)_4$ complexes.

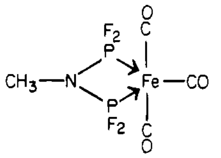
A characteristic feature of monoligate monometallic $CH_3N(PF_2)_2$ complexes is the facile solvolytic cleavage of the uncomplexed PF_2 group to give the corresponding CH_3NHPF_2 metal complex.[7] Such reactions have been observed in the conversion of the monoligate monometallic $CH_3N(PF_2)_2$ complexes $C_5H_5Mo(CO)_2[(PF_2)_2NCH_3]Cl$ and $C_5H_5Fe(CO)[(PF_2)_2NCH_3]Cl$ into the corresponding CH_3NHPF_2 complexes $C_5H_5Mo(CO)_2(PF_2NHCH_3)Cl$ and $C_5H_5Fe(CO)(PF_2NHCH_3)Cl$ by reactions with alcohols.[7] Similarly, the cobalt complex $[CH_3N(PF_2)_2]_5Co_2$, in which two of the $CH_3N(PF_2)_2$ ligands are monoligate monometallic, is converted into $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$ upon chromatography on Florisil.[11] The iron complex $CH_3N(PF_2)_2Fe(CO)_4$ (I) was found to undergo an analogous phosphorus–nitrogen cleavage to $CH_3NHPF_2Fe(CO)_4$ by chromatography on Florisil. The cleavage product $CH_3NHPF_2Fe(CO)_4$ is also obtained from the reaction of $Fe_2(CO)_9$ with $CH_3N(PF_2)_2$ in diethyl ether solution in the presence of added water.

The infrared spectrum of $CH_3NHPF_2Fe(CO)_4$ exhibits four ν(CO) frequencies at 2072 (m), 2008 (s), 1984 (s), and 1972 (s) cm^{-1} corresponding to the A_1, A_1, B_2, and B_1 frequencies, respectively, expected for the equatorially substituted isomer II. The infrared spectrum of $CH_3NHPF_2Fe(CO)_4$ also exhibits a sharp ν(NH) frequency at 3440 cm^{-1}, which is within 5 cm^{-1} of the infrared ν(NH) frequencies of the $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)(L)$ complexes[11] (L = PF_2NHCH_3, CO, $PF_2N(CH_3)_2$, and $P(OC_2H_5)_3$). The proton NMR spectrum of $CH_3NHPF_2Fe(CO)_4$ exhibits a double doublet in the CH_3N region with coupling constants (11 and 5 Hz) similar to those found[7] in $C_5H_5Mo(CO)_2(PF_2NHCH_3)Cl$ and $C_5H_5Fe(CO)(PF_2NHCH_3)Cl$. The phosphorus-31, carbon-13, and fluorine-19 NMR spectra of $CH_3NHPF_2Fe(CO)_4$ support the proposed structure and exhibit splittings that can be assigned to the coupling constants $|^1J(PF)|$, $|^2J(CP)|$, $[^3J(CF)|$, and $|^3J(HF)|$.

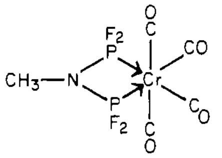


II

Gas chromatography-mass spectrometry was useful for the analysis of mixtures of $CH_3NHPF_2Fe(CO)_4$ and $CH_3N(PF_2)_2Fe(CO)_4$, and the mass spectra provided excellent support of the proposed stoichiometries in view of uncertainties in the combustion analysis data. The mass spectrum of $CH_3NHPF_2Fe(CO)_4$ (II) exhibited the full complement of ions $(CH_3NHPF_2Fe(CO)_n{}^+$ (n = 4, 3, 2, 1, and 0)), but the highest *m/e* ion in $CH_3N(PF_2)_2Fe(CO)_4$ was $CH_3N(PF_2)_2Fe(CO)_3{}^+$, thereby suggesting decarbonylation in the mass spectrometer to the biligate monometallic complex $CH_3N(PF_2)_2Fe(CO)_3$ (III). In the mass spectra of both $CH_3N(PF_2)_2Fe(CO)_4$ (I) and $CH_3NHPF_2Fe(CO)_4$ (II) loss of up to one fluorine per phosphorus was competitive to the usual[12] successive loss of CO groups.



III



IV

The indication of decarbonylation of $CH_3N(PF_2)_2Fe(CO)_4$ (I) to $CH_3N(PF_2)_2Fe(CO)_3$ (III) in the mass spectrometer suggested attempts at the preparation and isolation of the biligate monometallic tricarbonyl III. However, the tetracarbonyl $CH_3N(PF_2)_2Fe(CO)_4$ (I) was recovered unchanged after pyrolysis in a sealed evacuated tube at 105 °C for 24 h. More promising was the exposure to ultraviolet irradiation of the $CH_3N(PF_2)_2/Fe_2(CO)_9$ mixture in diethyl ether used to prepare $CH_3N(PF_2)_2Fe(CO)_4$. The added ultraviolet irradiation had two effects on this reaction: (1) The previously reported[2,4] orange crystalline biligate bimetallic complex $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ was produced and was separated readily from the monometallic derivatives through its much lower solubility in nonpolar organic solvents. (2) The yellow liquid distilled from the reaction mixture exhibited in its proton NMR spectrum not only the doublet at δ 2.91 characteristic of $CH_3N(PF_2)_2Fe(CO)_4$ (I) but also a triplet at δ 2.66 (J = 12 Hz) suggestive of the biligate monometallic complex $CH_3N(PF_2)_2Fe(CO)_3$ (III) since the proton NMR spectrum of the related biligate monometallic chromium carbonyl derivative $CH_3N(PF_2)_2Cr(CO)_4$ (IV) exhibits a triplet at δ 2.75 (J = 10 Hz).[1] Further evidence for the presence of $CH_3N(PF_2)_2Fe(CO)_3$ (III) in this yellow liquid is provided by the following observations: (1) The only iron carbonyl ions observed in the mass spectrum of this liquid are those derived from $CH_3N(PF_2)_2Fe(CO)_3{}^+$, suggesting that the only iron carbonyls present in this liquid have the stoichiometries $CH_3N(PF_2)_2Fe(CO)_4$ and $CH_3N(PF_2)_2Fe(CO)_3$. (2) Integration of the relative areas of the proton NMR resonances at δ 2.91 and 2.66 is consistent with this liquid containing 56% $CH_3N(PF_2)_2Fe(CO)_4$ (I) and 44% $CH_3N(PF_2)_2Fe(CO)_3$ (III), which is in approximate agreement with the combustion analyses on this liquid. Despite this strong evidence for the formation of $CH_3N(PF_2)_2Fe(CO)_3$ (III) in the photolysis of $CH_3N(PF_2)_2$ with $Fe_2(CO)_9$ in a 4.4:1 mole ratio, our efforts to isolate pure $CH_3N(PF_2)_2Fe(CO)_3$ (III) have all failed because of the following difficulties: (1) Attempts to enrich the $CH_3N(PF_2)_2Fe(CO)_3/CH_3N(PF_2)_2Fe(CO)_4$ mixture by photochemical decarbonylation lead to the precipitation of $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ as rapidly as additional tetracarbonyl is decarbonylated, thereby suggesting that $CH_3N(PF_2)_2Fe(CO)_3$ (III) is photosensitive toward further decarbonylation to $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ analogous to the well-known[5] photochemical decarbonylation of $Fe(CO)_5$ to $Fe_2(CO)_9$. (2) Separation of $CH_3N(PF_2)_2Fe(CO)_3/CH_3N(PF_2)_2Fe(CO)_4$ mixtures by chromatography is complicated by similar mobilities of the two iron carbonyl derivatives and the facile

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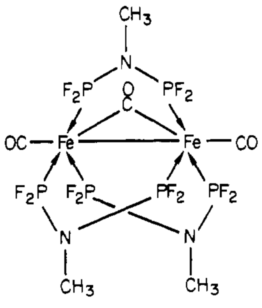
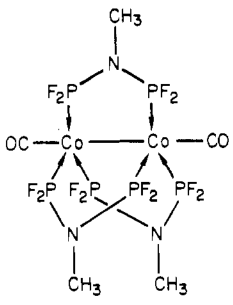
hydrolysis of $CH_3N(PF_2)_2Fe(CO)_4$ (I) to $CH_3NHPF_2Fe(CO)_4$ (II) on the usual chromatographic adsorbents such as Florisil and alumina.

B. The Binuclear Iron Carbonyl Derivative $[CH_3N(PF_2)_2]_3Fe_2(CO)_3$. The thermal reaction of $CH_3N(PF_2)_2$ with $Fe_3(CO)_{12}$ produces $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ as a major product[2,4] whereas the photochemical reaction of excess $CH_3N(PF_2)_2$ with $Fe_3(CO)_{12}$ (i.e., a 6:1 mole ratio) produces $[CH_3N(PF_2)_2]_4Fe_2CO$ in up to 37% yield.[3] These binuclear iron carbonyl complexes are two of the three previously known members of the series $[CH_3N(PF_2)_2]_nFe_2(CO)_{9-2n}$ (n = 1,2, and 4), which may be regarded as formal substitution products of $Fe_2(CO)_9$, although significant structural changes occur upon successive pairwise substitution of CO groups with $CH_3N(PF_2)_2$ ligands. We now report conditions for the isolation of the previously missing member of the $[CH_3N(PF_2)_2]_nFe_2(CO)_{9-2n}$ series, namely $[CH_3N(PF_2)_2]_3Fe_2(CO)_3$ (n = 3), in ~2% yield from the reaction mixture obtained by photolysis of $CH_3N(PF_2)_2$ with $Fe_3(CO)_{12}$ in a 2.5:1 mole ratio.

Several structures for $[CH_3N(PF_2)_2]_3Fe(CO)_3$ are conceivable including a structure with three bridging $CH_3N(PF_2)_2$ ligands as in $[CH_3N(PF_2)_2]_3Co_2(CO)_2$[13] a structure with two bridging $CH_3N(PF_2)_2$ ligands, one bridging PF_2 group, and one terminal CH_3NPF_2 group as in $[CH_3N(PF_2)_2]_4Fe_2CO$[3] and a structure with two bridging $CH_3N(PF_2)_2$ ligands and one terminal $CH_3N(PF_2)_2$ ligand related to that of $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$.[14] Unfortunately, the physically attractive red crystals of $[CH_3N(PF_2)_2]_3Fe_2(CO)_3$ do not appear to be readily suitable for X-ray crystallography.[15] The infrared ν(CO) spectrum of $[CH_3N(PF_2)_2]_3Fe_2(CO)_3$ is distinctive since it exhibits only one terminal ν(CO) frequency (1977 cm^{-1}) and one bridging ν(CO) frequency (1776 cm^{-1}). Structure V is therefore suggested for $[CH_3N(PF_2)_2]_3Fe_2(CO)_3$. This structure has equivalent terminal CO groups on each iron atom and is related to the established structure VI for $[CH_3N(PF_2)_2]_3Co_2(CO)_2$[13] by addition of a bridging carbonyl group across the metal–metal bond.



V



VI

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Registry No. I, 86669-56-9; II, 86669-57-0; III, 86669-58-1; V, 86669-59-2; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 17685-52-8; Fe, 7439-89-6; $CH_3N(PF_2)_2$, 17648-18-9.

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Contribution from the Laboratoire de Chimie Organique
Industrielle ENSCP, 75005 Paris, France

Reduction of Zirconocene Dihalides with Magnesium Studied by ESR. Evidence of Zirconium(III) Hydride Formation by Hydrogen Transfer from the Cyclopentadienyl Ring

Edmond Samuel

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Among the organometallic and coordination compounds of the early transition metals, those of Zr in its 3+ oxidation state are the most poorly documented and remain a scarcity. Their difficult access is due in part to the relatively low potential at which Zr(IV) reduces to Zr(III) ($-E_{1/2}$ = 1.6–2.09 V);[1] they are known also to have a marked tendency to dimerize, giving compounds with low paramagnetism.[2-4] However, very recently a number of cyclopentadienylzirconium compounds have been detected in solution by their ESR spectra as stable radical anions[5] or as intermediates in oxidative-addition reactions.[6,7]

When features due to metal and ligand hyperfine interactions are present, ESR techniques provide an excellent opportunity to monitor reaction sequences involving paramagnetic metal-centered radicals. In this work we report on the identification by ESR of Zr(III) species obtained by chemical reduction of zirconocene dihalides with metallic magnesium and on some of their chemical reactivities.[8] We also demonstrate that the formation of zirconium(III) hydride species proceeds by hydrogen transfer from the cyclopentadienyl ring.

Experimental Section

All manipulations were performed under argon. Grignard-quality magnesium was used for reduction; THF was distilled over sodium naphthalide and then on lithium aluminum hydride before use. ESR spectra were recorded on a JEOL ME SX X-band spectrometer with a Bruker B-A6 accessory for field calibration. $ZrCp_2Cl_2$ (Cp = η^5-C_5H_5) was purchased from Alfa Inorganics. $ZrCp_2Br_2$ was prepared by treating $ZrCp_2(CH_3)_2$ with dry HBr gas in ether.

Results and Discussion

In contrast with titanocene dihalides, which cleanly reduce to the monohalides with Al or Zn metals,[9] zirconocene dihalides are inert toward these reagents and the use of Na amalgam or metallic Li leads to Zr(II) species which have been isolated as zirconocene dicarbonyls or phosphine compounds.[10-12] It has been reported that reduction of $ZrCp_2Cl_2$ with metallic magnesium (0.5 mol) in THF affords a reddish

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