

- (8) D. H. Brown, K. D. Crosbie, G. W. Fraser, and D. W. A. Sharp, *J. Chem. Soc. A*, 551 (1969).
 (9) W. Z. Borer and K. Cohn, *Anal. Chim. Acta*, **47**, 355 (1969).
 (10) D. H. Williams, R. S. Ward, and R. G. Cooks, *J. Am. Chem. Soc.*, **90**, 966 (1968).
 (11) D. E. C. Corbridge, *Top. Phosphorus Chem.*, **6**, 235 (1969).
 (12) R. Mathis, L. Lafaille, and R. Burgada, *Spectrochim. Acta, Part A*, **30**, 357 (1974).
 (13) R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964).
 (14) J. G. Morse and K. W. Morse, *J. Am. Chem. Soc.*, **95**, 8469 (1973).
 (15) J. G. Morse, K. W. Morse, and E. R. Falardeau, *Inorg. Chem.*, **13**, 2338 (1974).
 (16) J. G. Morse, K. W. Morse, and E. R. Falardeau, *Inorg. Chem.*, **14**, 132 (1975).
 (17) S. S. Sandhu and A. K. Mehta, *J. Organomet. Chem.*, **77**, 45 (1974).
 (18) G. S. Reddy and R. Schmutzler, *Inorg. Chem.*, **6**, 823 (1967).
 (19) A. H. Cowley and R. P. Pinnell, *J. Am. Chem. Soc.*, **87**, 4454 (1965).
 (20) A. E. Goya, M. D. Rosario, and J. W. Gilje, *Inorg. Chem.*, **8**, 725 (1969).
 (21) G. Mavel, *Annu. Rep. NMR Spectrosc.*, **5**, 1 (1973).
 (22) J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, **13**, 364 (1970).
 (23) V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, 227 (1967).
 (24) E. G. Finer and R. K. Harris, *Prog. Nucl. Magn. Reson. Spectrosc.*, **6**, 61 (1971).
 (25) A. M. Aquiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 229 (1964).
 (26) A. M. Aquiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 5354 (1964).
 (27) R. G. Taylor, R. V. Keiter, and L. W. Cary, *Inorg. Chem.*, **13**, 1928 (1974).
 (28) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).
 (29) C. Kutal, D. Owen, and L. Todd, *Inorg. Synth.*, **11**, 19 (1968).
 (30) H. Noeth and H. J. Vetter, *Chem. Ber.*, **94**, 1505 (1961).
 (31) R. G. Cavell, *J. Chem. Soc.*, 1992 (1964).

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

Metal Complexes of Fluorophosphines. 7. Cocondensations of Some First-Row Transition-Metal Vapors with (Dimethylamino)difluorophosphine and (Methylamino)bis(difluorophosphine)^{1,2}

R. B. KING* and M. CHANG

Received October 6, 1978

Cocondensations of $(\text{CH}_3)_2\text{NPF}_2$ with Cr, Fe, and Ni vapors give the corresponding $\text{M}[(\text{PF}_2\text{N}(\text{CH}_3)_2)_n]$ complexes ($\text{M} = \text{Cr}$, $n = 6$; $\text{M} = \text{Fe}$, $n = 5$; $\text{M} = \text{Ni}$, $n = 4$). Cocondensations of $\text{CH}_3\text{N}(\text{PF}_2)_2$ with Cr, Fe, Co, and Ni vapors give $\text{Cr}[(\text{PF}_2)_2\text{NCH}_3]_3$, $\text{Fe}[(\text{PF}_2)_2\text{NCH}_3]_4$, $\text{Co}_2[(\text{PF}_2)_2\text{NCH}_3]_5$, and $\{\text{Ni}[(\text{PF}_2)_2\text{NCH}_3]_2\}_m$, respectively. Cocondensations of a 4:1 mixture of $(\text{CH}_3)_2\text{NPF}_2$ and $\text{CH}_3\text{N}(\text{PF}_2)_2$, respectively, with Cr, Fe, Co, and Ni vapors give white $\text{Cr}[(\text{PF}_2\text{N}(\text{C}-\text{H}_3)_2)_4[(\text{PF}_2)_2\text{NCH}_3]]$, red-yellow $\text{Fe}[(\text{PF}_2\text{N}(\text{CH}_3)_2)_3[(\text{PF}_2)_2\text{NCH}_3]]$, purple $\text{Co}_2[(\text{PF}_2\text{N}(\text{CH}_3)_2)_2[(\text{PF}_2)_2\text{NCH}_3]]_3$, and a mixture of white $\text{Ni}[(\text{PF}_2\text{N}(\text{CH}_3)_2)_3[(\text{PF}_2)_2\text{NCH}_3]]$ and light yellow $\text{Ni}_2[(\text{PF}_2\text{N}(\text{CH}_3)_2)_2[(\text{PF}_2)_2\text{NCH}_3]]_3$, respectively. No products could be obtained by the cocondensation of Mn vapor with either $(\text{CH}_3)_2\text{NPF}_2$ or $\text{CH}_3\text{N}(\text{PF}_2)_2$.

Introduction

In recent years aminodifluorophosphines of the type R_2NPF_2 have been shown to be good π -acceptor ligands capable of stabilizing low oxidation states of transition metals. The first such observation was the report by Schmutzler³ that $\text{Ni}(\text{CO})_4$ reacts with the (dialkylamino)difluorophosphines R_2NPF_2 ($\text{R} = \text{CH}_3$ or $2\text{R} = -(\text{CH}_2)_5-$) to give homoleptic⁴ zerovalent nickel(0) complexes $\text{Ni}[(\text{PF}_2\text{NR}_2)_4]$ exhibiting relatively high thermal and oxidative stabilities. Subsequent work in our laboratory has shown that the chelating aminodifluorophosphine $\text{CH}_3\text{N}(\text{PF}_2)_2$ is even more effective at stabilizing low oxidation states: for example, the zerovalent derivatives $\text{M}[(\text{PF}_2)_2\text{NCH}_3]_3$ ($\text{M} = \text{Cr}$, Mo , W) exhibit impressive thermal and oxidative stabilities.^{5,6}

Up to the present time the chemistry of derivatives of the types $\text{M}[(\text{PF}_2\text{NR}_2)_m]$ and $\text{M}[(\text{PF}_2)_2\text{NR}]_n$ has been limited to compounds accessible through complete displacement of CO groups from the corresponding metal carbonyls. Syntheses of such compounds by reaction of derivatives containing the metal in a positive formal oxidation state (e.g., a metal halide) with excess aminodifluorophosphine in the presence of strong reducing agents are unattractive because of the potential sensitivity of the P-N and P-F bonds in the ligands toward reductive and/or solvolytic cleavage. A more promising technique for the synthesis of new homoleptic derivatives $\text{M}[(\text{PF}_2\text{NR}_2)_m]$ and $\text{M}[(\text{PF}_2)_2\text{NR}]_n$ is metal-vapor synthesis.^{7,8} Metal-vapor synthesis has already been shown to be a useful method for the synthesis of trifluorophosphine derivatives of the type $\text{M}_m(\text{PF}_3)_n$: e.g., cocondensation of PF_3 with Cr, Fe, and Ni vapors has been reported to give the complexes $\text{Cr}(\text{PF}_3)_6$, $\text{Fe}(\text{PF}_3)_5$, and $\text{Ni}(\text{PF}_3)_4$, respectively.⁹ However, until the work reported here, aminodifluorophosphines of the types R_2NPF_2 and $\text{RN}(\text{PF}_2)_2$ have never been used as ligands in metal-vapor syntheses.

This paper describes the details of our studies on the cocondensations of $(\text{CH}_3)_2\text{NPF}_2$ and $\text{CH}_3\text{N}(\text{PF}_2)_2$ with the first-row transition-metal vapors Cr through Ni, inclusive. These particular aminodifluorophosphines were selected because of their volatility and ease of preparation in the relatively large quantities required for metal-vapor synthesis. The particular metals used were selected on the basis of their ease of evaporation in a simple resistive heating apparatus.

Experimental Section

Microanalyses were performed by Atlantic Microanalytical Laboratory, Atlanta, Ga. Proton NMR spectra were run on a Varian T-60 spectrometer at 60 MHz. Carbon-13 NMR spectra were recorded at 25.0336 MHz on a Jeolco PFT-100 spectrometer operating in the pulsed Fourier transform mode with proton decoupling and a deuterium lock. Melting points were taken in capillaries and are uncorrected.

The ligands $(\text{CH}_3)_2\text{NPF}_2$ ¹⁰ and $\text{CH}_3\text{N}(\text{PF}_2)_2$ ^{6,11} were prepared by the cited published methods.

The Metal-Vapor Reactor. The metal-vapor reactions were run in equipment described below constructed in the shops at the University of Georgia according to previously reported^{8,12} general designs.

The metals were evaporated from commercially available 0.5-mL alumina crucibles (Sylvania Emissive Products, Exeter, N.H.) made from a conical spiral of 1-mm diameter tungsten wire coated with alumina cement. This crucible was mounted between two electrodes inside a 130-mm diameter, 280-mm high, and 4-mm thick Pyrex cylindrical vessel. The electrodes consisted of concentric copper tubes of 4.8 and 13-mm diameters sealed appropriately with silver solder so that they could be cooled by continuously running cold water during an experiment. The electrodes were sealed to the glass top of the reaction vessel by a low vapor pressure resin ("Torr Seal" from Varian Associates, Palo Alto, Calif.). Ligand vapor was admitted to the reaction vessel through a central sample inlet tube so positioned that the vapors from the ligand emerge through numerous small holes 5-15 cm above the crucible of evaporating metal. For easy demountability the electrodes and the ligand inlet tube were attached to a cover which

Table I. Products Obtained by Reactions of Metal Vapors with Aminodifluorophosphines

| metal vapor | products obtained from reaction of the metal vapor with the ligand(s) ^a | | |
|-------------|--|---|--|
| | Me ₂ NPF ₂ | MeN(PF ₂) ₂ | 4:1 Me ₂ NPF ₂ / MeN(PF ₂) ₂ |
| Cr | Cr(PF ₂ -NMe ₂) ₆ (7.1) | Cr(PF ₂) ₂ -NMe ₃ (48) | Cr(PF ₂ NMe ₂) ₄ -[(PF ₂) ₂ NMe] (6.2) |
| Fe | Fe(PF ₂ -NMe ₂) ₅ (14) | Fe(PF ₂) ₂ -NMe ₃ (<1) | Fe(PF ₂ NMe ₂) ₃ -[(PF ₂) ₂ NMe] (~1) |
| Co | no pure product isolated | Co ₂ (PF ₂) ₂ -NMe ₃ (10.5) | Co ₂ (PF ₂ NMe ₂) ₂ -[(PF ₂) ₂ NMe] ₃ (7.5) |
| Ni | Ni(PF ₂ -NMe ₂) ₄ (9.8) | {Ni[(PF ₂) ₂ -NMe] ₂ } _n (9.0) | Ni(PF ₂ NMe ₂) ₃ -[(PF ₂) ₂ NMe] (9.0) + Ni ₂ (PF ₂ NMe ₂) ₂ -[(PF ₂) ₂ NMe] ₃ (6.2) |

^a The yields (%) of isolated products relative to metal evaporated are given in parentheses.

fitted onto the reaction vessel by means of a ground glass joint.

The crucible for evaporating the metals was heated by the current from a power supply which provided continuously variable alternating current up to 100 A at 16 V. The vacuum was maintained by means of a two-stage silicone oil diffusion pump backed by a mechanical pump. The pressure was monitored by a cold cathode vacuum gauge with a range from 10⁻³ to 10⁻⁸ mm (Model K-920000 from Kontes, Vineland, N.J.). At the end of the experiment unused ligand could be recovered by distillation into appropriate traps of the vacuum system.

The results of the metal-vapor syntheses are summarized in Table I. Further details of product isolation and characterization are given below.

Preparation of Cr[PF₂N(CH₃)₂]₆. Approximately 1 g of chromium powder was placed into the crucible. After the whole system was pumped to a pressure of 10⁻⁴ mm or lower, the crucible was preheated to remove volatiles in both the crucible and metal powder. The pressure rose temporarily. The reaction vessel was then immersed in liquid nitrogen. Evaporation of the metal was begun by increasing the output of the power supply. Simultaneously, the (CH₃)₂NPF₂ ligand was allowed to diffuse into the reaction vessel from the sample inlet tube at a rate of 0.3 mL/min. By passing a current of 40 A at 10 V, 0.2 g of chromium metal could be evaporated over a period of 30 min. The power to the crucible was then turned off and the crucible was allowed to cool. Excess ligand was removed from the reaction vessel by pumping at -78 °C. After nitrogen was admitted, the resulting brown slurry was extracted with dichloromethane. The dichloromethane extracts were filtered through a layer of Celite to remove the fine metal powder. Evaporation of the light brown filtrate under vacuum at room temperature gave 0.2 g (7.1% yield) of white Cr[PF₂N(CH₃)₂]₆. Anal. Calcd for C₁₂H₃₆CrF₁₂N₆P₆: C, 19.7; H, 5.0; N, 11.5; mol wt 730. Found: C, 18.9; H, 5.0; N, 10.8; mol wt 721 (in benzene).

This chromium complex is a white solid, stable at -20 °C in the solid state, but turns green in dichloromethane solution upon standing at room temperature. The mass spectrum of this complex even at an inlet temperature of 40 °C exhibited no chromium-containing ions but only ions corresponding to the free (CH₃)₂NPF₂ ligand.

Preparation of Fe[PF₂N(CH₃)₂]₅. The same procedure as in the preparation of Cr[PF₂N(CH₃)₂]₆ was followed. About 0.5 g of iron metal was evaporated. The resulting black slurry was extracted with hexane. The resulting solution was chromatographed on a Florisil column. Elution of the yellow band with hexane followed by evaporation gave 0.8 g (14% yield) of yellow Fe[PF₂N(CH₃)₂]₅, mp 164-165 °C. Proton NMR: τ 7.0 (broad). Anal. Calcd for C₁₀H₃₀F₁₀FeN₅P₅: C, 19.3; H, 4.9; N, 11.3. Found: C, 19.6; H, 4.7; N, 11.1.

Reaction of Cobalt Vapor with (CH₃)₂NPF₂. The same procedure as in the preparation of Cr[PF₂N(CH₃)₂]₆ was followed except that cobalt was used rather than chromium metal. The resulting black product was not sublimable. Extraction of the black product with dichloromethane followed by evaporation of the solvent gave a black oil. This black oil decomposed upon attempted chromatography on both Florisil and silica gel columns. No pure product could be separated.

Preparation of Ni[PF₂N(CH₃)₂]₄ from Nickel Vapor. A procedure

analogous to the preparation of Cr[PF₂N(CH₃)₂]₆ was followed. About 0.5 g of nickel metal was evaporated. The resulting brown slurry was extracted with dichloromethane and the dichloromethane extracts were filtered through Celite. Evaporation of the solvent under vacuum followed by recrystallization of the residue from diethyl ether gave 0.42 g (9.8% yield) of white, rather air-stable Ni[PF₂N(CH₃)₂]₄, mp 109-110 °C (lit.³ mp 110.5-111.5 °C). Proton NMR: τ 7.4 (broad doublet).

Preparation of Cr[(PF₂)₂NCH₃]₃ from Chromium Vapor. An analogous procedure to the preparation of Cr[PF₂N(CH₃)₂]₆ was followed except that CH₃N(PF₂)₂ rather than (CH₃)₂NPF₂ was used as the ligand. About 0.27 g of chromium metal was evaporated. The resulting brown slurry was extracted with dichloromethane followed by evaporation of the solvent. Sublimation of the resulting crude product at 80 °C (0.05 mm) gave 1.38 g (48% yield) of Cr[(PF₂)₂NCH₃]₃ identified by comparison of its proton NMR and mass spectra with those of authentic material prepared by photolysis of Cr(CO)₆ with excess CH₃N(PF₂)₂ according to the published procedure.^{5,6}

Preparation of Fe[(PF₂)₂NCH₃]₄. An analogous procedure to the preparation of Cr[(PF₂)₂NCH₃]₃ was followed. About 0.5 g of iron metal was evaporated during the reaction. The resulting black slurry was extracted with hexane. The resulting hexane solution was chromatographed on a silica gel column. Elution of the yellow band with hexane followed by recrystallization from hexane at -20 °C gave a low yield (~1%) of yellow air-stable crystals. An X-ray diffraction study on these crystals, described elsewhere,^{2a} indicated formulation of this product as Fe[(PF₂)₂NCH₃]₄ containing one bidentate and three monodentate CH₃N(PF₂)₂ ligands.

Preparation of Co₂[(PF₂)₂NCH₃]₅ from Cobalt Vapor. An analogous procedure to the preparation of Cr[(PF₂)₂NCH₃]₃ was followed. About 0.5 g of cobalt metal was evaporated. Chromatography of the resulting product on Florisil using a mixture of dichloromethane and hexane (1:1 by volume) gave a black band from which was isolated 0.8 g (10.5% yield) of deep violet, moisture-sensitive Co₂[(PF₂)₂NCH₃]₅. Anal. Calcd for C₅H₁₅Co₂F₂₀N₅P₁₀: C, 6.3; H, 1.6; N, 7.4. Found: C, 6.7; H, 1.7; N, 7.4. This product was identical with the product Co₂[(PF₂)₂NCH₃]₅ obtained by photolysis of Co₂(CO)₈ with excess CH₃N(PF₂)₂ according to the published procedure.¹

Preparation of {Ni[(PF₂)₂NCH₃]₂}_n from Nickel Vapor. An analogous procedure to the preparation of Cr[(PF₂)₂NCH₃]₃ was followed. About 0.5 g of nickel metal was evaporated. The resulting black slurry was extracted with diethyl ether. Evaporation of the extract gave a black oil. Heating of this black oil in a sublimator at 140 °C (0.1 mm) gave 0.3 g (9.0% yield) of light yellow, insoluble, air-stable {Ni[(PF₂)₂NCH₃]₂}_n, identical with the product of this stoichiometry obtained from Ni(CO)₄ and excess CH₃N(PF₂)₂ according to the published procedure.⁶

Preparation of Cr[PF₂N(CH₃)₂]₄[(PF₂)₂NCH₃]. A procedure analogous to the preparation of Cr[PF₂N(CH₃)₂]₆ was followed. However a 4:1 mixture of the (CH₃)₂NPF₂ and CH₃N(PF₂)₂ ligands was used. About 0.3 g of chromium metal was evaporated. The resulting black slurry was extracted with dichloromethane. Evaporation of the extract followed by sublimation of the residue at 100 °C (0.1 mm) gave 0.24 g (6.2% yield) of white, reasonably air-stable Cr[PF₂N(CH₃)₂]₄[(PF₂)₂NCH₃]. Carbon-13 NMR in CDCl₃: δ 36.6 and 26.8 of approximate relative intensities 8:1, respectively. Anal. Calcd for C₉H₂₇CrF₁₂N₅P₆: C, 16.1; H, 4.0; N, 10.4. Found: C, 14.7; H, 3.7; N, 9.3.

Preparation of Fe[PF₂N(CH₃)₂]₃[(PF₂)₂NCH₃]. A procedure analogous to the preparation of Cr[PF₂N(CH₃)₂]₄[(PF₂)₂NCH₃] was followed. About 0.5 g of iron metal was evaporated. The resulting black slurry was extracted with diethyl ether followed by evaporation of the solvent. Sublimation of the crude product at 110 °C (0.1 mm) gave a low (~1%) yield of reddish yellow gum. Carbon-13 NMR in CDCl₃: δ 36.6 and 28.8 of approximate relative intensities 6:1, respectively. Anal. Calcd for C₇H₂₁F₁₀FeN₄P₅: C, 14.9; H, 3.8; N, 10.0. Found: C, 13.4; H, 3.5; N, 9.1. Because of the low yield further purification of this compound was not feasible.

Preparation of Co₂[PF₂N(CH₃)₂]₂[(PF₂)₂NCH₃]₃ from Cobalt Vapor. A procedure analogous to the preparation of Cr[PF₂N(CH₃)₂]₄[(PF₂)₂NCH₃] was followed. About 0.4 g of cobalt metal was evaporated. Chromatography of the resulting black slurry on Florisil using a mixture of dichloromethane and hexane gave a black band. Elution of this band gave 0.4 g (7.5% yield) of deep violet, air-stable Co₂[PF₂N(CH₃)₂]₂[(PF₂)₂NCH₃]₃, mp 155 °C (lit.¹ mp 156-157 °C),

identical with the product obtained by ultraviolet irradiation of $\text{Co}_2(\text{CO})_2[(\text{PF}_2)_2\text{NCH}_3]_3$ with excess $(\text{CH}_3)_2\text{NPF}_2$ by the published method.¹

Preparations of $\text{Ni}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_3[(\text{PF}_2)_2\text{NCH}_3]$ and $\text{Ni}_2[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]_3$. A procedure analogous to the preparation of $\text{Cr}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]$ was followed. About 0.4 g of nickel metal was evaporated. The resulting black slurry was extracted with dichloromethane. Evaporation of the dichloromethane under vacuum at room temperature followed by sublimation at 55 °C (0.1 mm) gave 0.34 g (9.0% yield) of white $\text{Ni}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_3[(\text{PF}_2)_2\text{NCH}_3]$, mp 76–78 °C. Carbon-13 NMR in CDCl_3 : δ 34.9 and 24.1 of approximate relative intensities 6:1, respectively. Anal. Calcd for $\text{C}_7\text{H}_{21}\text{F}_{10}\text{N}_4\text{NiP}_5$: C, 14.9; H, 3.7; N, 9.9; mol wt 565. Found: C, 14.3; H, 3.6; N, 9.5; mol wt 573 (in benzene).

After the sublimation of $\text{Ni}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_3[(\text{PF}_2)_2\text{NCH}_3]$ was complete, the residue was recrystallized three times from dichloromethane at -78 °C to give 0.35 g (6.2% yield) of light yellow $\text{Ni}_2[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]_3$, mp 143–145 °C. Carbon-13 NMR in CDCl_3 : δ 34.8 and 26.6 of approximate relative intensities 4:3, respectively. Anal. Calcd for $\text{C}_7\text{H}_{21}\text{F}_{16}\text{N}_4\text{Ni}_2\text{P}_8$: C, 10.0; H, 2.5; N, 8.3. Found: C, 10.0; H, 2.4; N, 8.1.

Attempted Cocondensations of Manganese Vapor with $(\text{CH}_3)_2\text{NPF}_2$ and with $\text{CH}_3\text{N}(\text{PF}_2)_2$. Manganese metal was cocondensed with $(\text{CH}_3)_2\text{NPF}_2$ and with $\text{CH}_3\text{N}(\text{PF}_2)_2$ using the general procedure outlined above. However, neither reaction gave any manganese derivatives other than bulk metal. Apparently complexes of the types $\text{Mn}_x[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_m$ and $\text{Mn}_y[(\text{PF}_2)_2\text{NCH}_3]_n$ cannot be prepared by cocondensation of manganese vapor with these ligands using conventional techniques.

Mass Spectra. The following mass spectra were run at 70 eV on a Perkin-Elmer Hitachi RMU-6 single-focusing mass spectrometer with a modified direct inlet system. Only the major metal-containing ions with m/e values above those of the free ligands are listed below. Relative intensities of the ions are given in parentheses.

A. $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_5$: $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_5^+$ (0.3), $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_4^+$ (10), $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_3^+$ (12), $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2^+$ (100), $(\text{CH}_3)_2\text{NPF}_2\text{FeF}^+$ (8), $\text{FePF}_2\text{N}(\text{CH}_3)_2^+$ (27).

B. $\text{Ni}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_4$: $\text{Ni}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_3^+$ (9), $\text{Ni}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2^+$ (44), $\text{NiPF}_2\text{N}(\text{CH}_3)_2^+$ (100).

C. $\text{Fe}[(\text{PF}_2)_2\text{NCH}_3]_4$: $\text{Fe}[(\text{PF}_2)_2\text{NCH}_3]_3^+$ (100), $\text{CH}_3\text{N}(\text{PF}_2)_2(\text{PF})\text{Fe}[(\text{PF}_2)_2\text{NCH}_3]_2^+$ (21), $\text{Fe}(\text{PF}_2)[(\text{PF}_2)_2\text{NCH}_3]_2^+$ (19), $\text{Fe}[(\text{PF}_2)_2\text{NCH}_3]_2^+$ (67), $\text{Fe}(\text{PF}_2)_2\text{NCH}_3^+$ (37).

D. $\text{Co}_2[(\text{PF}_2)_2\text{NCH}_3]_5$: $\text{Co}_2[(\text{PF}_2)_2\text{NCH}_3]_5^+$ (12), $\text{Co}_2[(\text{PF}_2)_2\text{NCH}_3]_4^+$ (54), $\text{Co}_2[(\text{PF}_2)_2\text{NCH}_3]_3^+$ (100), $\text{CH}_3\text{NPF}_2\text{Co}_2[(\text{PF}_2)_2\text{NCH}_3]_2^+$ (19), $\text{Co}_2(\text{PF}_2)[(\text{PF}_2)_2\text{NCH}_3]_2^+$ (17), $\text{Co}_2(\text{PF}_2)_2[(\text{PF}_2)_2\text{NCH}_3]^+$ (38), $\text{Co}_2\text{F}(\text{PF}_2)_2\text{NCH}_3^+$ (18), $\text{Co}_2(\text{PF}_2)_2\text{NCH}_3^+$ (23), $\text{Co}(\text{PF}_2)_2\text{NCH}_3^+$ (65).

E. $\text{Cr}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_4[(\text{PF}_2)_2\text{NCH}_3]$: $\text{Cr}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_4[(\text{PF}_2)_2\text{NCH}_3]^+$ (3), $\text{Cr}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_4^+$ (4), $\text{Cr}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_3^+$ (13), $\text{Cr}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]^+$ (47), $\text{Cr}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2^+$ (90), $\text{Cr}(\text{PF}_2)_2\text{NCH}_3^+$ (53), $\text{CrPF}_2\text{N}(\text{CH}_3)_2\text{F}^+$ (18), $\text{CrPF}_2\text{N}(\text{CH}_3)_2^+$ (100).

F. $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_3[(\text{PF}_2)_2\text{NCH}_3]$: $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_3[(\text{PF}_2)_2\text{NCH}_3]^+$ (22), $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_3(\text{PF})\text{NCH}_3^+$ (11), $\text{Fe}(\text{PF}_2)[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]^+$ (41), $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]^+$ (100), $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2^+$ (54), $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)(\text{PF})\text{NCH}_3]^+$ (21), $\text{Fe}[(\text{PF}_2)_2\text{NCH}_3]^+$ (37), $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]^+$ (46).

G. $\text{Co}_2[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]_3$: $\text{Co}_2[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]_3^+$ (12), $\text{Co}_2[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]_2^+$ (22), $\text{Co}_2[(\text{PF}_2)_2\text{NCH}_3]_3^+$ (100), $\text{Co}_2[(\text{PF}_2)_2\text{NCH}_3]_2(\text{PF})\text{NCH}_3^+$ (19), $\text{Co}_2[(\text{PF}_2)_2\text{NCH}_3]_2\text{PF}_2^+$ (20), $\text{Co}_2(\text{PF}_2)[(\text{PF}_2)_2\text{NCH}_3]^+$ (70), $\text{Co}_2\text{F}[(\text{PF}_2)_2\text{NCH}_3]^+$ (42), $\text{Co}_2(\text{PF}_2)_2\text{NCH}_3^+$ (53), $\text{Co}(\text{PF}_2)_2\text{NCH}_3^+$ (66).

H. $\text{Ni}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_3[(\text{PF}_2)_2\text{NCH}_3]$: $\text{Ni}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]^+$ (31), $\text{Ni}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2^+$ (67), $\text{Ni}[(\text{PF}_2)_2\text{NCH}_3]_2^+$ (85), $\text{Ni}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]^+$ (100), $\text{Ni}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2^+$ (69), $\text{Ni}(\text{PF}_2)_2\text{NCH}_3^+$ (88), $\text{NiPF}_2\text{N}(\text{CH}_3)_2^+$ (80).

I. $\text{Ni}_2[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]_3$: $\text{Ni}_2[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]_3^+$ (47), $\text{Ni}_2[(\text{PF}_2)_2\text{NCH}_3]_3^+$ (99), $\text{Ni}_2[(\text{PF}_2)_2\text{NCH}_3]_2^+$ (100), $\text{Ni}_2[(\text{PF}_2)_2\text{NCH}_3]\text{F}^+$ $\text{Ni}(\text{PF}_2)_2\text{NCH}_3^+$ $\text{Ni}(\text{PF}_2)_2\text{NCH}_3^+$ (18).

Results and Discussion

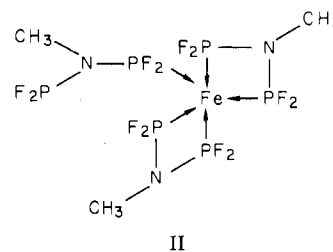
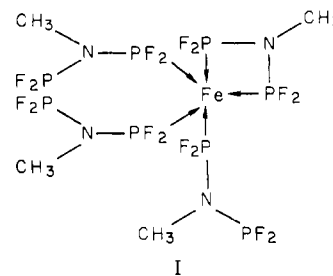
A. Complexes of the Monodentate Ligand $(\text{CH}_3)_2\text{NPF}_2$. The nickel compound $\text{Ni}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_4$ prepared from

$(\text{CH}_3)_2\text{NPF}_2$ and nickel vapor has been previously³ prepared by reaction of $\text{Ni}(\text{CO})_4$ with excess $(\text{CH}_3)_2\text{NPF}_2$. However, the compounds $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_5$ and $\text{Cr}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_6$ have only now been prepared for the first time by using metal-vapor syntheses as described in this paper.

The chromium complex $\text{Cr}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_6$ appears to be appreciably less stable oxidatively and thermally than $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{PF}_3)_6$ evidently owing to steric hindrance between the six $(\text{CH}_3)_2\text{NPF}_2$ ligands which are appreciably bulkier than PF_3 or CO ligands. The iron complex $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_5$, however, appears to be relatively air stable in contrast to most other FeL_5 derivatives, even those containing fairly strong π -acceptor ligands such as $\text{Fe}[\text{P}(\text{OCH}_3)_3]_5$.^{13,14} Even though $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_5$ cannot be sublimed under vacuum without decomposition, its mass spectrum was found to exhibit the complete sequence of ions $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_n^+$ ($n = 5, 4, 3, 2$, and 1) suggesting stepwise loss of the $(\text{CH}_3)_2\text{NPF}_2$ ligands in $\text{Fe}[(\text{PF}_2)_2\text{N}(\text{CH}_3)_2]_5$ analogous to the stepwise loss of carbonyl groups in the mass spectra of most metal carbonyls.¹⁵

B. Complexes of the Bidentate Ligand $\text{CH}_3\text{N}(\text{PF}_2)_2$. The compounds $\text{Cr}[(\text{PF}_2)_2\text{NCH}_3]_3$, $\text{Co}_2[(\text{PF}_2)_2\text{NCH}_3]_5$, and $\text{Ni}[(\text{PF}_2)_2\text{NCH}_3]_n$ prepared by cocondensations of $\text{CH}_3\text{N}(\text{PF}_2)_2$ with chromium, cobalt, and nickel vapors, respectively, have been previously obtained by reactions of excess $\text{CH}_3\text{N}(\text{PF}_2)_2$ with the corresponding metal carbonyls $\text{Cr}(\text{CO})_6$,^{5,6} $\text{Co}_2(\text{CO})_8$,¹ and $\text{Ni}(\text{CO})_4$,⁶ respectively. In these three cases the metal-vapor synthesis appears to offer no particular advantages over previous preparative methods.

The yellow air-stable compound $\text{Fe}[(\text{PF}_2)_2\text{NCH}_3]_4$, obtained from the cocondensation of iron vapor with $\text{CH}_3\text{N}(\text{PF}_2)_2$, has never been obtained from any of the reactions of $\text{CH}_3\text{N}(\text{PF}_2)_2$ with iron carbonyls.^{6,16} However, the yield was so low that the only satisfactory method for its characterization was X-ray diffraction of its crystals that fortunately could readily be grown. This compound was found to have the expected structure I containing one bidentate and three monodentate

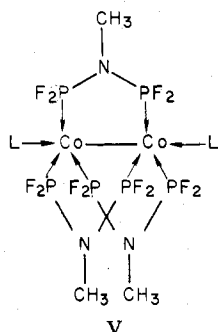
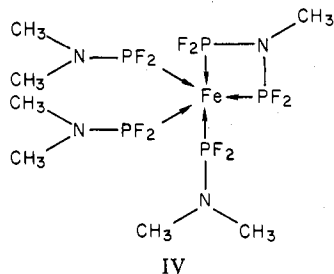
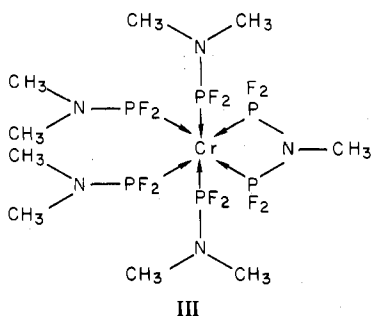


$\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands. However, the highest m/e ion in the mass spectrum of $\text{Fe}[(\text{PF}_2)_2\text{NCH}_3]_4$ is $\text{Fe}[(\text{PF}_2)_2\text{NCH}_3]_3^+$ suggesting facile loss in the mass spectrometer of one of the four $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands to form II.

C. Complexes Containing both $(\text{CH}_3)_2\text{NPF}_2$ and $\text{CH}_3\text{N}(\text{PF}_2)_2$. One of the interesting features of the metal-vapor chemistry described in this paper was the ease with which mixed-ligand complexes could be prepared by cocondensations of metal vapors with mixtures of $(\text{CH}_3)_2\text{NPF}_2$ and $\text{CH}_3\text{N}(\text{PF}_2)_2$. For these experiments, the monodentate ligand $(\text{CH}_3)_2\text{NPF}_2$ was always taken in considerable excess (4:1 by volume) over the bidentate ligand $\text{CH}_3\text{N}(\text{PF}_2)_2$ on the as-

sumption that the bidentate ligand would bond more easily to metals because of the chelate effect. The products from the cocondensations of the ligand mixtures with chromium and with iron were not obtained completely pure. However, analyses of the products by mass spectroscopy and carbon-13 NMR combined with X-ray crystallography of the chromium complex^{2c} leave little doubt as to the identity of these materials. Carbon-13 NMR spectroscopy is particularly useful in characterizing these mixed-ligand complexes since the resonances of the methyl groups in coordinated $(\text{CH}_3)_2\text{NPF}_2$ and coordinated $\text{CH}_3\text{N}(\text{PF}_2)_2$ fall in distinctly different positions (δ 34–37 and 24–29, respectively). Proton NMR spectroscopy is not similarly diagnostic in these cases because of the much smaller chemical shifts.

The reaction of chromium vapor with the $\text{CH}_3\text{N}(\text{PF}_2)_2/(\text{CH}_3)_2\text{NPF}_2$ mixture was found to give white crystalline $\text{Cr}[\text{PF}_2\text{N}(\text{CH}_3)_2]_4[(\text{PF}_2)_2\text{NCH}_3]$ (III) as the major product.



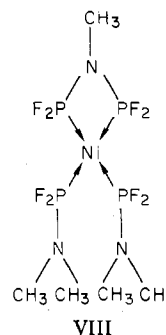
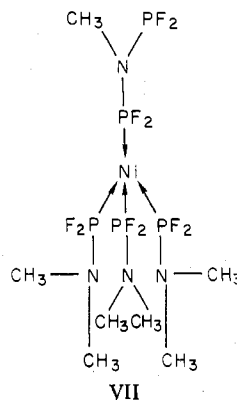
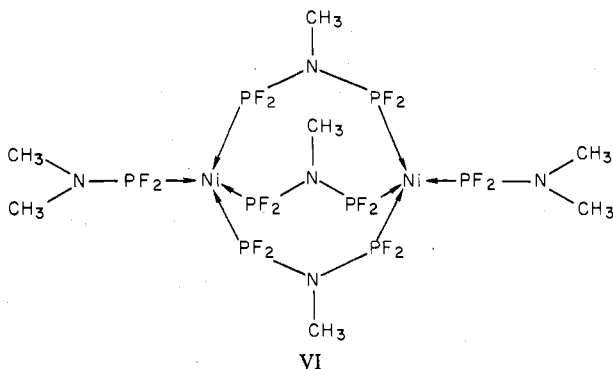
This product is considerably more stable than $\text{Cr}[\text{PF}_2\text{N}(\text{C}_6\text{H}_5)_2]_6$; it can be sublimed under vacuum at 100 °C (0.1 mm) and gives a molecular ion in its mass spectrum. This is in accord with the relief of the steric strain in $\text{Cr}[\text{PF}_2\text{N}(\text{CH}_3)_2]_6$ by replacement of two of the relatively bulky $(\text{CH}_3)_2\text{NPF}_2$ ligands by the single small bite $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligand. The errors in the analyses of $\text{Cr}[\text{PF}_2\text{N}(\text{CH}_3)_2]_4[(\text{PF}_2)_2\text{NCH}_3]$ are consistent with the presence of a small amount of difficultly separable $\text{Cr}[\text{PF}_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]_2$ impurity, which is also consistent with the observation of a small amount of the ion $\text{Cr}[\text{PF}_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]_2^+$ in its mass spectrum.

The cocondensation of iron vapor with the $\text{CH}_3\text{N}(\text{PF}_2)_2/(\text{CH}_3)_2\text{NPF}_2$ mixture was found to give a low yield of a noncrystalline red-yellow volatile wax, which on the basis of its carbon-13 NMR and mass spectrum is formulated as IV. This structure is analogous to that of $\text{Fe}[(\text{PF}_2)_2\text{NCH}_3]_4$ (I) in which the three monodentate $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands are replaced by monodentate $(\text{CH}_3)_2\text{NPF}_2$ ligands.

The cocondensation of cobalt vapor with the $\text{CH}_3\text{N}(\text{PF}_2)_2/(\text{CH}_3)_2\text{NPF}_2$ mixture was found to give a purple, air-stable crystalline solid formulated as $\text{Co}_2[\text{PF}_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]_3$ (V: $\text{L} = (\text{CH}_3)_2\text{NPF}_2$). This complex is also obtained by photochemical replacement of both carbonyl groups in $\text{Co}_2(\text{CO})_2[(\text{PF}_2)_2\text{NCH}_3]_3$ (V: $\text{L} = \text{CO}$) by excess $(\text{CH}_3)_2\text{NPF}_2$ and is one of a series of very stable bimetallic

cobalt derivatives containing a $\text{Co}_2[(\text{PF}_2)_2\text{NCH}_3]_3$ unit consisting of a cobalt–cobalt bond bridged by three $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands.^{1,17}

The cocondensation of nickel vapor with the $\text{CH}_3\text{N}(\text{PF}_2)_2/(\text{CH}_3)_2\text{NPF}_2$ mixture was found to give two products. The less volatile product is a light yellow bimetallic complex $\text{Ni}_2[\text{PF}_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]_3$ of presumed structure VI



analogous to the bimetallic cobalt complex V ($\text{L} = (\text{CH}_3)_2\text{NPF}_2$) but lacking a metal–metal bond. In addition, this reaction gives a sublimable white solid analyzing for $\text{Ni}[\text{PF}_2\text{N}(\text{CH}_3)_2]_3[(\text{PF}_2)_2\text{NCH}_3]$ and formulated as VII in which the single $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligand functions as a monodentate ligand just like the three $(\text{CH}_3)_2\text{NPF}_2$ ligands. The highest m/e ion in the mass spectrum of VII corresponds not to the molecular ion but to the ion $\text{Ni}[\text{PF}_2\text{N}(\text{CH}_3)_2]_2[(\text{PF}_2)_2\text{NCH}_3]^+$. This suggests that VII easily loses one of its $(\text{CH}_3)_2\text{NPF}_2$ ligands in the mass spectrometer to form VIII in which the $\text{CH}_3\text{N}(\text{PF}_2)_2$ has changed from a monodentate to a bidentate ligand.

Acknowledgment. We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AFOSR-75-2869. M.C. is indebted to the University of Georgia Graduate School for a fellowship.

Registry No. $\text{Cr}(\text{PF}_2\text{NMe}_2)_6$, 68474-94-2; $\text{Fe}(\text{PF}_2\text{NMe}_2)_5$, 66058-57-9; $\text{Ni}(\text{PF}_2\text{NMe}_2)_4$, 15053-92-6; $\text{Cr}((\text{PF}_2)_2\text{NMe}_2)_3$, 63404-40-0; $\text{Fe}((\text{PF}_2)_2\text{NMe}_2)_4$, 65829-31-4; $\text{Co}_2[(\text{PF}_2)_2\text{NMe}_2]_5$, 66632-81-3; $\{\text{Ni}[(\text{PF}_2)_2\text{NMe}_2]_2\}_n$, 66632-67-5; $\text{Cr}(\text{PF}_2\text{NMe}_2)_4[(\text{PF}_2)_2\text{NMe}_2]$, 68474-95-3; $\text{Fe}(\text{PF}_2\text{NMe}_2)_3[(\text{PF}_2)_2\text{NMe}_2]$, 68474-96-4; $\text{Co}_2(\text{PF}_2\text{NMe}_2)_2[(\text{PF}_2)_2\text{NMe}_2]_3$, 66674-78-0; $\text{Ni}(\text{PF}_2\text{NMe}_2)_3[(\text{PF}_2)_2\text{NMe}_2]$, 68474-97-5; $\text{Ni}_2(\text{PF}_2\text{NMe}_2)_2[(\text{PF}_2)_2\text{NMe}_2]_3$, 68474-98-6.

References and Notes

- (1) For part 6 of this series see R. B. King, J. Gimeno, and T. J. Lotz, *Inorg. Chem.*, **17**, 2401 (1978).
- (2) For preliminary communications of portions of this work see: (a) M. Chang, R. B. King, and M. G. Newton, *J. Am. Chem. Soc.*, **100**, 998 (1978); (b) M. Chang, M. G. Newton, R. B. King, and T. J. Lotz, *Inorg. Chim. Acta*, **28**, L153 (1975); (c) M. Chang, M. G. Newton, and R. B. King, *ibid.*, **30**, L341 (1978).
- (3) R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964).

- (4) A homoleptic metal complex is a metal complex ML_n , where all of the ligands L are identical (see P. J. Davidson, M. F. Lappert, and R. Pearce, *Acc. Chem. Res.*, **7**, 209 (1974)).
- (5) R. B. King and J. Gimeno, *J. Chem. Soc., Chem. Commun.*, 142 (1977).
- (6) R. B. King and J. Gimeno, *Inorg. Chem.*, **17**, 2390 (1978).
- (7) P. L. Timms and T. W. Turney, *Adv. Organomet. Chem.*, **15**, 53 (1977).
- (8) M. Moskovits and G. A. Ozin, Ed., "Cryochemistry", Wiley-Interscience, New York, 1976.
- (9) P. L. Timms, *Chem. Commun.*, 1033 (1969).
- (10) J. G. Morse, K. Cohn, R. W. Rudolph, and R. W. Parry, *Inorg. Synth.*, **10**, 147 (1967).
- (11) J. F. Nixon, *J. Chem. Soc. A*, 2689 (1968).
- (12) P. L. Timms, *J. Chem. Soc. A*, 2526 (1970).
- (13) E. L. Muetterties and J. W. Rathke, *J. Chem. Soc., Chem. Commun.*, 850 (1974).
- (14) C. A. Tolman, L. W. Yarbrough, II, and J. G. Verkade, *Inorg. Chem.*, **16**, 479 (1977).
- (15) R. B. King, *Top. Curr. Chem.*, **14**, 92 (1970).
- (16) M. G. Newton, R. B. King, M. Chang, and J. Gimeno, *J. Am. Chem. Soc.*, **100**, 326 (1978).
- (17) M. G. Newton, R. B. King, N. S. Pantaleo, and T. J. Lotz, *J. Chem. Soc., Chem. Commun.*, 514 (1978).

Contribution from the Department of Chemistry,
University of New Mexico, Albuquerque, New Mexico 87131

Synthesis and Characterization of Cyclopentadienylfluorophosphine Ligands and Their Borane(3) Complexes

R. T. PAINE,* R. W. LIGHT, and D. E. MAIER

Received June 9, 1978

The reactions of PF_2Br , PF_2Cl , and $PFCl_2$ with thallium(I) salts of cyclopentadiene and methylcyclopentadiene at $-78^\circ C$ produce the organofluorophosphines $\eta^1-C_5H_5PF_2$, $(\eta^1-C_5H_5)_2PF$, $(\eta^1-CH_3C_5H_4)PF_2$, and $(\eta^1-CH_3C_5H_4)_2PF$ in high yields. Each ligand combines with B_2H_6 ; the resulting compounds are classical borane(3) coordination complexes which contain a direct P-B coordinate bond. The ligands and coordination complexes have been characterized by mass, infrared, and 1H , ^{11}B , ^{13}C , ^{19}F , and ^{31}P NMR spectrometries, and these data are presented and discussed.

Introduction

Syntheses for a number of η^1 -cyclopentadienyl derivatives of nonmetal and metal atoms have been reported in the literature. Many of these cyclopentadienyl compounds have been observed to participate in complex intramolecular rearrangements in the liquid phase, and the fluxional motions of several molecules have been successfully explored by 1H and ^{13}C NMR techniques.¹ Despite the attention given specifically to the motional properties of nonmetal η^1 -cyclopentadienyl compounds, the chemistry of these species has received little attention. As an example, several $\eta^1-C_5H_5$ derivatives of group 4A elements have been prepared and extensively characterized by NMR spectroscopy,² but a systematic exploration of their reaction chemistry has not been presented. Further, for the case of group 5A elements only one cyclopentadienyl derivative of a halophosphine, $\eta^1-C_5H_5PF_2$, has been reported.³ The tris(cyclopentadienyl) derivatives Cp_3As , Cp_3Sb , and Cp_3Bi also have been prepared.⁴

For our purposes group 5A cyclopentadienyl derivatives represent a class of ligands of special interest; the ligands are potentially bifunctional and bidentate. It is expected that the lone electron pair localized on the central phosphorus atom should be available for coordination by classical Lewis acceptors and low-valent transition-metal atoms. Furthermore, the cyclopentadienyl ring may be available for coordination by low-valent transition-metal atoms; the $\eta^1-C_5H_5$ might coordinate as a diene or, if the ring is deprotonated, as a η^5 -cyclopentadienyl group. It is also conceivable that both the phosphorus and olefin functions could simultaneously coordinate one transition-metal site or bridge two metal sites.

In this paper we report a much improved synthesis for $\eta^1-C_5H_5PF_2$ and syntheses for the previously unknown ligands $(\eta^1-C_5H_5)_2PF$, $(\eta^1-CH_3C_5H_4)PF_2$, and $(\eta^1-CH_3C_5H_4)_2PF$. These syntheses, for the first time, have permitted convenient studies of the coordination properties of this group of ligands. The coordination chemistry of each ligand toward borane(3) is specifically described here while the coordination chemistry with transition-metal complexes is the subject of another report.⁵

Experimental Section

General Information. Standard high-vacuum synthetic techniques were used for the manipulations of the volatile compounds. Mass

spectra were recorded on a DuPont Model 21-491 spectrometer operating at 70 eV with an inlet temperature of $30^\circ C$ and a source temperature of $100^\circ C$. All samples were introduced as gases. Infrared spectra were recorded on a Perkin-Elmer Model 621 infrared spectrometer using a 10-cm glass cell fitted with KBr windows. The infrared spectra were calibrated with polystyrene film absorptions and fundamental absorptions in the PF_3 spectrum. The NMR spectra were recorded on a Varian XL-100 NMR spectrometer operating at 25.2 MHz (^{13}C), 32.1 MHz (^{11}B), 40.5 MHz (^{31}P), 94.1 MHz (^{19}F), and 100 MHz (1H). The data were collected in the pulse mode using a Nicolet TT-100 data system. Samples were contained in sealed 5-mm tubes rigidly placed in a 12-mm tube containing a deuterated lock sample. Spectra standards were $(CH_3)_4Si$ (^{13}C , 1H), $BF_3 \cdot (C_2H_5)_2O$ (^{11}B), 85% H_3PO_4 (^{31}P), and $CFCl_3$ (^{19}F).

Materials. Thallium cyclopentadienide was prepared by a literature method.⁶ Methylcyclopentadiene dimer was purified and thermally cracked as described in the literature.⁷ Care must be taken to rid the $CH_3C_5H_5$ of C_5H_6 ; otherwise the thallium reagent is contaminated with C_5H_5Tl . Purity of the $CH_3C_5H_5$ was verified by gas chromatograms of the cracked distillate. The $CH_3C_5H_4Tl$ salt was prepared in a fashion similar to C_5H_5Tl except the filtrations and isolation were performed in a nitrogen-filled drybag. Fluorophosphines F_2PBr ,⁸ F_2PCl ,⁸ and FP_2Cl ⁹ and diborane(6)¹⁰ were prepared by literature methods.

Synthesis of $\eta^1-C_5H_5PF_2$ and $\eta^1-CH_3C_5H_4PF_2$. A 5.0-mmol sample of $TlCp$ or $TlMeCp$ was loaded under nitrogen into a 50-mL Schlenk tube. To the evacuated tube, 5.2 mmol of PF_2Cl or PF_2Br was condensed, and the mixture was allowed to warm to $-78^\circ C$. Reaction occurred immediately upon contact of the liquid phosphine and solid thallium salt. To ensure complete reaction the mixture was allowed to remain at $-78^\circ C$ for 2 h. The volatile products were vacuum distilled through -23 , -78 , and $-196^\circ C$ traps. The F_2PCp and $F_2P(MeCp)$ were retained at $-78^\circ C$ as colorless crystals and as a colorless oil, respectively. The yields were 95–98% based upon the fluorophosphine consumed.

Synthesis of $(\eta^1-C_5H_5)_2PF$ and $(\eta^1-CH_3C_5H_4)_2PF$. A 5.0-mmol sample of $TlCp$ or $TlMeCp$ was added to a 50-mL Schlenk tube, and the tube was evacuated. A 2.0-mmol sample of $PFCl_2$ was condensed into the tube at $-196^\circ C$, and the tube was then warmed to $-78^\circ C$. The reactions occurred upon contact of the reagents. After 2 h, the volatile products were vacuum distilled through -23 , -78 , and $-196^\circ C$ traps. The phosphines were retained at $-78^\circ C$ as colorless solids. The yields ranged from 85 to 90% based upon the fluorophosphine consumed.

Synthesis of Borane(3) Complexes. A 2.0-mmol sample of cyclopentadienylphosphine ligand was condensed into a 50-mL Schlenk tube at $-196^\circ C$. A 1.2-mmol sample of B_2H_6 was condensed over