

Metal Complexes of Fluorophosphines. 6. Reactions of Cobalt Carbonyls with Methylaminobis(difluorophosphine)^{1,2}

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Reaction of $\text{Co}_2(\text{CO})_8$ with $\text{CH}_3\text{N}(\text{PF}_2)_2$ at room temperature in the absence of ultraviolet irradiation gives purple $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$. Ultraviolet irradiation of $\text{Co}_2(\text{CO})_8$ with excess $\text{CH}_3\text{N}(\text{PF}_2)_2$ at room temperature, however, results in complete displacement of all carbonyl groups to give black $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2$, containing three biligate bimetallic and two monoligate monometallic $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands. Chromatography of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2$ on Florisil results in hydrolysis of the two monoligate monometallic $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands to give purple $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{PF}_2\text{NHCH}_3)_2$. Ultraviolet irradiation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ with the ligands $(\text{CH}_3)_2\text{NPF}_2$, $(\text{C}_2\text{H}_5\text{O})_3\text{P}$, $(\text{C}_6\text{H}_5)_3\text{P}$, and $(\text{CH}_3)_3\text{CNC}$ (designated as L) results in the stepwise displacement of the two carbonyl groups to give complexes of the types $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})\text{L}$ and $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2\text{L}_2$. Unsymmetrical complexes of the types $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{PF}_2\text{NHCH}_3)\text{L}$ (L = CO, $(\text{CH}_3)_2\text{NPF}_2$, $(\text{C}_2\text{H}_5\text{O})_3\text{P}$) have been prepared by analogous methods. Reaction of $\text{Co}_4(\text{CO})_{12}$ with $\text{CH}_3\text{N}(\text{PF}_2)_2$ appears to result in the pairwise replacement of CO groups with $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands to give products of the type $[\text{CH}_3\text{N}(\text{PF}_2)_2]_n\text{Co}_4(\text{CO})_{12-2n}$; the products where $n = 2, 3, 4$, and 5 have been isolated in the pure state.

Introduction

A previous paper of this series⁴ describes reactions of $\text{CH}_3\text{N}(\text{PF}_2)_2$ with carbonyls of some transition metals having even atomic numbers such as chromium, molybdenum, tungsten, iron, and nickel. Such metals do not require metal-metal bonds to attain the favored rare-gas electronic configuration in complexes containing exclusively ligands donating an even number of electrons such as CO and $\text{CH}_3\text{N}(\text{PF}_2)_2$. This paper describes the reactions of $\text{CH}_3\text{N}(\text{PF}_2)_2$ with the cobalt carbonyls $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$. Such reactions were found to give products of two general types both of which involve each cobalt atom in an odd number of cobalt-cobalt bonds consistent with the odd atomic number of cobalt: (1) bimetallic derivatives containing a cobalt-cobalt bond bridged by three $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands; (2) cobalt tetrahedra in which $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands bridge one or more edges of the tetrahedron.

Experimental Section

Elemental analyses, melting points, and infrared spectra in the $\nu(\text{CO})$ and $\nu(\text{NH})$ regions of the new metal complexes are given in Tables I and II. In addition, proton and carbon-13 NMR spectra of selected new complexes were obtained using the procedures given in a previous paper of this series.⁴ The ligand $\text{CH}_3\text{N}(\text{PF}_2)_2$ ^{4,5} and the metal carbonyls $\text{M}_4(\text{CO})_{12}$ (M = Co,⁶ Rh⁷) were prepared by the cited published procedures. The $\text{Co}_2(\text{CO})_8$ was purchased from Strem Chemical Co., Danvers, Mass. A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions; (b) handling air-sensitive organometallic compounds, particularly in solution, and including particularly $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$; and (c) filling evacuated vessels containing potentially air-sensitive materials. Ultraviolet irradiations were performed using an Englehard-Hanovia 450-W medium-pressure mercury arc housed in a water-cooled Pyrex immersion well.

Preparation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ and $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})(\text{PF}_2\text{NHCH}_3)$ from $\text{CH}_3\text{N}(\text{PF}_2)_2$ and $\text{Co}_2(\text{CO})_8$. A solution of 12.15 g (35.5 mmol) of $\text{Co}_2(\text{CO})_8$ in 400 mL of hexane was cooled to 0 °C and then treated dropwise with 27.4 g (164 mmol) of $\text{CH}_3\text{N}(\text{PF}_2)_2$. Vigorous gas evolution occurred and the reaction mixture became dark purple. The reaction mixture was allowed to warm spontaneously to room temperature. Solvent was removed from the reaction mixture at ~25 °C (40 mm). The reaction mixture was chromatographed on a 5 × 50 cm Florisil column. Elution of the major purple band with hexane followed by evaporation of the eluate and crystallization from a mixture of hexane and dichloromethane gave 21.1 g (88% yield) of dark purple $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$: mp 131–132 °C; proton NMR (CDCl_3) $\tau(\text{CH}_3)$ 7.08 (broad singlet); carbon-13 NMR (CDCl_3) $\delta(\text{CH}_3)$ 29.1.

After complete removal of the $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$, further elution of the chromatogram with 1:9 dichloromethane-hexane gave 0.70 g (2.6% yield) of dark purple $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})(\text{PF}_2\text{NHCH}_3)$, mp 157–158 °C.

Preparation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2$ from $\text{CH}_3\text{N}(\text{PF}_2)_2$ and $\text{Co}_2(\text{CO})_8$.

A solution of 1.7 g (5 mmol) of $\text{Co}_2(\text{CO})_8$ in 250 mL of diethyl ether was treated with 5.0 g (30 mmol) of $\text{CH}_3\text{N}(\text{PF}_2)_2$. After cessation of gas evolution, the reaction mixture was exposed to ultraviolet irradiation for ~16 h. The black reaction mixture was filtered, and solvent was removed from the filtrate at ~25 °C (40 mm). Recrystallization of the residue from hexane gave 2.27 g (48% yield) of black $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2$, mp 140–142 °C. The analytical sample was purified further by sublimation at 140 °C (0.05 mm).

Preparation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{PF}_2\text{NHCH}_3)_2$ from $\text{CH}_3\text{N}(\text{PF}_2)_2$ and $\text{Co}_2(\text{CO})_8$. A solution of 1.7 g (5 mmol) of $\text{Co}_2(\text{CO})_8$ in 250 mL of diethyl ether was treated with 4.74 g (28 mmol) of $\text{CH}_3\text{N}(\text{PF}_2)_2$. After cessation of the gas evolution, the reaction mixture was exposed to ultraviolet irradiation for ~16 h. After removal of solvent from the filtered reaction solution, a concentrated dichloromethane solution of the black residue was chromatographed on a 3 × 50 cm Florisil column prepared in hexane. Elution of the dark band with a 3:7 mixture of dichloromethane and hexane followed by rechromatography gave a total of 1.29 g (31% yield) of violet $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{PF}_2\text{NHCH}_3)_2$: mp 206–207 °C; proton NMR (CDCl_3) $\tau(\text{CH}_3)$ ~7.1 (broad).

Ultraviolet Irradiation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ with Excess $\text{CH}_3\text{N}(\text{PF}_2)_2$. A mixture of 1.32 g (1.95 mmol) of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$, 0.383 g (2.29 mmol) of $\text{CH}_3\text{N}(\text{PF}_2)_2$, and 300 mL of diethyl ether was exposed to ultraviolet irradiation for 2 h. Solvent was removed from the reaction mixture at ~25 °C (40 mm). A concentrated hexane solution of the residue was chromatographed on a 2 × 50 cm Florisil column to give as successive purple bands 0.418 g (31.7% recovery) of unchanged $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ eluted with pure hexane, 0.587 g (40.3% conversion) of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})(\text{PF}_2\text{NHCH}_3)$ eluted with 2:23 dichloromethane-hexane, and 0.287 g (18.0% conversion) of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{PF}_2\text{NHCH}_3)_2$ eluted with 3:7 dichloromethane-hexane.

Ultraviolet Irradiation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ with $(\text{CH}_3)_2\text{NPF}_2$. A mixture of 0.688 g (1.02 mmol) of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$, 0.150 g (1.33 mmol) of $(\text{CH}_3)_2\text{NPF}_2$,⁸ and 300 mL of diethyl ether was exposed to ultraviolet irradiation for 70 min. After removal of the solvent, a concentrated hexane solution of the residue was chromatographed on a 2 × 50 cm Florisil column. Successive elution gave unchanged $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$, eluted with hexane, 0.288 g (33.4% conversion) of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})(\text{PF}_2\text{N}(\text{CH}_3)_2)$ [mp 124–125 °C; proton NMR (CDCl_3) $\tau(\text{CH}_3)$ 7.0–7.2 (broad)], eluted with 1:9 dichloromethane-hexane, and 0.210 g (24.4% conversion) of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2[\text{PF}_2\text{N}(\text{CH}_3)_2]_2$ [mp 156–157 °C; proton NMR (CDCl_3) $\tau(\text{CH}_3)$ 7.00 (broad), 7.12 (broad)], eluted with 3:7 dichloromethane-hexane.

Ultraviolet Irradiation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ with $(\text{C}_2\text{H}_5\text{O})_3\text{P}$. A mixture of 0.680 g (1.01 mmol) of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$, 1.0 mL (0.96 g, 5.8 mmol) of triethyl phosphite, and 300 mL of diethyl ether was exposed to ultraviolet irradiation for 3 h. After removal of the solvent, a concentrated hexane solution of the residue was chromatographed on a 2 × 50 cm Florisil column. Successive elution with 1:19 dichloromethane-hexane gave 0.084 g (10.3% yield) of dark violet $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})[\text{P}(\text{OC}_2\text{H}_5)_3]$, mp 210–211 °C, and

Table I. Properties of Bimetallic Cobalt Derivatives of Methylaminobis(difluorophosphine)

Compound ^a	Color	Mp, ^b °C	Analyses ^c			Infrared spectrum, cm ⁻¹	
			% C	% H	% N	$\nu(\text{CO})^d$	$\nu(\text{NH})^d$
[MeN(PF ₂) ₂] ₃ Co ₂ (CO) ₂	Dark purple	132–133	Calcd ^e Found ^e	8.9 8.9	1.3 1.4	6.2 6.2	2003 s, 1978 w
[MeN(PF ₂) ₂] ₃ Co ₂	Black	140–142	Calcd Found	6.3 6.6	1.6 1.7	7.3 7.2	None
[MeN(PF ₂) ₂] ₃ Co ₂ (CO)(PF ₂ NHMe)	Dark purple	157–158	Calcd Found	8.1 8.2	1.8 1.7	7.5 7.4	2020
[MeN(PF ₂) ₂] ₃ Co ₂ (PF ₂ NHMe) ₂	Dark purple	206–207	Calcd ^f Found ^f	7.3 7.3	2.1 1.9	8.6 8.4	None
[MeN(PF ₂) ₂] ₃ Co ₂ (CO)(PF ₂ NMe ₂)	Dark purple	124–125	Calcd Found	9.5 9.7	2.0 2.0	7.4 7.3	2021
[MeN(PF ₂) ₂] ₃ Co ₂ (PF ₂ NMe ₂) ₂	Dark purple	156–157	Calcd Found	10.0 10.1	2.5 2.6	8.3 8.2	None
[MeN(PF ₂) ₂] ₃ Co ₂ (PF ₂ NHMe)(PF ₂ NMe ₂)	Dark purple	149–150	Calcd Found	8.7 8.8	2.3 2.3	8.4 8.4	None
[MeN(PF ₂) ₂] ₃ Co ₂ (CO)[P(OEt) ₃]	Dark violet	210–211	Calcd Found	14.8 14.9	3.0 3.0	5.2 5.2	1992
[MeN(PF ₂) ₂] ₃ Co ₂ [P(OEt) ₃] ₂	Red brown	239–240	Calcd Found	18.9 19.2	4.1 4.2	4.4 4.3	
[MeN(PF ₂) ₂] ₃ Co ₂ (PF ₂ NHMe)[P(OEt) ₃]	Dark violet	172	Calcd Found	13.6 13.8	3.2 3.2	6.3 6.2	None
[MeN(PF ₂) ₂] ₃ Co ₂ (PPh ₃) ₂	Dark violet	263	Calcd Found	41.0 40.8	3.4 3.4	3.7 3.6	None
[MeN(PF ₂) ₂] ₃ Co ₂ (CO)(CNCMe ₃)	Red	151–152	Calcd Found	14.8 14.9	2.5 2.5	7.7 7.7	$\nu(\text{CO})$ 2006 $\nu(\text{CN})$ 2153
[MeN(PF ₂) ₂] ₃ Co ₂ (CNCMe ₃) ₂	Red	208–209	Calcd Found	19.9 20.0	3.5 3.5	8.9 8.8	$\nu(\text{CN})$ 2144
[MeN(PF ₂) ₂] ₃ Co ₂ (CO)(Ph ₂ PCH ₂ CH ₂ PPh ₂)	Brown violet	179–180	Calcd Found	34.5 34.7	3.2 3.2	4.0 4.1	2007

^a Me = methyl, Et = ethyl, Ph = phenyl. ^b Melting points were taken in capillaries and are uncorrected. ^c Analyses (C, H, N) were performed by Atlantic Microanalytical Laboratory, Atlanta, Ga. ^d These infrared $\nu(\text{CO})$ frequencies were determined from KBr pellet spectra recorded on a Perkin-Elmer Model 621 spectrophotometer calibrated against the 1601-cm⁻¹ band of polystyrene film. ^e Anal. Calcd for [MeN(PF₂)₂]₃Co₂(CO)₂: F, 33.8; P, 27.5; mol wt 675. Found: F, 33.9; P, 27.7; mol wt 680 (benzene). ^f Anal. Calcd for [MeN(PF₂)₂]₃Co₂(PF₂NHMe)₂: F, 37.2; P, 30.3; mol wt 817. Found: F, 37.8; P, 30.7; mol wt 913 (benzene).

Table II. Properties of Tetrametallic Cobalt Derivatives of Methylaminobis(difluorophosphine)

Compound	Mp, ^a °C	Analyses ^a							$\nu(\text{CO})$ in CH ₂ Cl ₂ , ^a cm ⁻¹
		% C	% H	% N	% F	% P	Mol wt ^a		
[MeN(PF ₂) ₂] ₂ Co ₄ (CO) ₈	132–133	Calcd Found	15.1 15.0	0.7 0.6	3.5 3.7	19.1 19.1	15.6 15.8	794 785	2045 m, 2005 vs, 1835 vs, 1825 vs
[MeN(PF ₂) ₂] ₃ Co ₄ (CO) ₆	178–180	Calcd Found	11.9 11.7	1.0 1.0	4.6 4.6	25.2 25.0	20.5 20.7	904 925	2034 s, 2021 s, 2013 m, 2008 m, 1845 vs
[MeN(PF ₂) ₂] ₄ Co ₄ (CO) ₄	213–215	Calcd Found	9.5 10.0	1.2 1.2	5.5 5.4	29.9 29.9	24.3 24.4	1015 999	2003 s, 1828 vs, 1799 vs
[MeN(PF ₂) ₂] ₅ Co ₄ (CO) ₂	275–277	Calcd Found	7.5 7.1	1.3 1.3	6.2 6.2	33.7 33.6	27.5 27.8	1126 1294	2000 vs

^a See footnotes *b*, *c*, and *d* of Table I.

0.115 g (24% yield) of red-brown [CH₃N(PF₂)₂]₃Co₂[P(OC₂H₅)₃]₂, mp 239–240 °C.

Preparation of [CH₃N(PF₂)₂]₂Co₂[P(C₆H₅)₃]₂. A mixture of 0.684 g (1.01 mmol) of [CH₃N(PF₂)₂]₃Co₂(CO)₂, 0.659 g (2.53 mmol) of triphenylphosphine, and 300 mL of diethyl ether was exposed to ultraviolet irradiation for 140 min. Filtration of the resulting violet precipitate followed by drying at ~25 °C (0.1 mm) gave 0.672 g (58.8% yield) of [CH₃N(PF₂)₂]₂Co₂[P(C₆H₅)₃]₂: mp 263 °C; proton NMR (CDCl₃) $\tau(\text{C}_6\text{H}_5)$ 2.46 and 2.63, $\tau(\text{CH}_3)$ ~7.1 (broad).

Chromatography on Florisil of the filtrate obtained after filtration of the [CH₃N(PF₂)₂]₂Co₂[P(C₆H₅)₃]₂ using a mixture of dichloromethane and hexane gave a dark violet solid suggested by elemental analyses and a $\nu(\text{CO})$ frequency at ~2000 cm⁻¹ to be [CH₃N(PF₂)₂]₂Co₂(CO)P(C₆H₅)₃, contaminated by triphenylphosphine. Anal. Calcd. for C₂₂H₂₄Co₂F₁₂N₃OP₇: C, 29.1; H, 2.7; N, 4.6. Found: C, 31.2; H, 3.3; N, 4.3.

Ultraviolet Irradiation of [CH₃N(PF₂)₂]₃Co₂(CO)₂ with (CH₃)₂CNC. A mixture of 0.684 g (1.01 mmol) of [CH₃N(PF₂)₂]₃Co₂(CO)₂, 0.4 mL (0.3 g, 3.7 mmol) of *tert*-butyl isocyanide,⁹ and 300 mL of diethyl ether was exposed to ultraviolet irradiation for 3 h. Gas evolution occurred immediately and the reaction mixture gradually became more reddish during the reaction period. Chromatography twice on Florisil columns in mixtures of dichloromethane and hexane gave successively

0.10 g (14% yield) of red [CH₃N(PF₂)₂]₂Co₂(CO)[CNC(CH₃)₃] [mp 151–152 °C; proton NMR (CDCl₃) $\tau(\text{CH}_3)$ 7.1 (broad), 8.50 (sharp singlet)] and 0.20 g (25.1% yield) of red [CH₃N(PF₂)₂]₃Co₂[CNC(CH₃)₃]₂ [mp 208–209 °C; proton NMR (CDCl₃) $\tau(\text{CH}_3)$ 7.16 (broad), 8.56 (sharp singlet)].

Ultraviolet Irradiation of [CH₃N(PF₂)₂]₃Co₂(CO)₂ with (C₆H₅)₂PCH₂CH₂P(C₆H₅)₂. A mixture of 0.691 g (1.02 mmol) of [CH₃N(PF₂)₂]₃Co₂(CO)₂, 0.805 g (2.02 mmol) of (C₆H₅)₂PCH₂CH₂P(C₆H₅)₂, and 300 mL of diethyl ether was exposed to ultraviolet irradiation for 1 h. Solvent was removed from the filtered reaction mixture at ~25 °C (40 mm). A concentrated solution of the residue in hexane was chromatographed on a 2 × 50 cm Florisil column. Elution of the chromatogram with mixtures of dichloromethane and hexane followed by two recrystallizations of the product from the first band using mixtures of dichloromethane and hexane at -10 °C gave 0.119 g (11% yield) of purple-brown [CH₃N(PF₂)₂]₃Co₂(CO)-[(C₆H₅)₂PCH₂CH₂P(C₆H₅)₂]₂: mp 180 °C dec; proton NMR (CDCl₃) $\tau(\text{C}_6\text{H}_5)$ 2.44, $\tau(\text{CH}_3)$ 7.16 (broad). The solubility of this complex was too low for the proton NMR resonance from the PCH₂CH₂P bridges to be observed.

Ultraviolet Irradiation of [CH₃N(PF₂)₂]₃Co₂(CO)(PF₂NHCH₃) with (CH₃)₂NPF₂. A mixture of 0.383 g (0.51 mmol) of [CH₃N(PF₂)₂]₃Co₂(CO)(PF₂NHCH₃), 0.078 g (0.69 mmol) of (CH₃)₂NPF₂,

and 300 mL of diethyl ether was exposed to ultraviolet irradiation for 1 h. Solvent was removed at $\sim 25^\circ\text{C}$ (40 mm). A solution of the residue in 5 mL of dichloromethane was chromatographed on a Florisil column. Successive elution gave 0.061 g (15.9% recovery) of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})(\text{PF}_2\text{NHCH}_3)$ eluted with 1:19 dichloromethane-hexane and 0.260 g (60.9% conversion) of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{PF}_2\text{NHCH}_3)[\text{PF}_2\text{N}(\text{CH}_3)_2]$: mp $149\text{--}150^\circ\text{C}$; proton NMR (CDCl_3) $\tau(\text{CH}_3)$ 7.1 (broad), eluted with 3:7 dichloromethane-hexane.

Ultraviolet Irradiation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})(\text{PF}_2\text{NHCH}_3)$ with $(\text{C}_2\text{H}_5\text{O})_3\text{P}$. A mixture of 0.374 g (0.50 mmol) of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})(\text{PF}_2\text{NHCH}_3)$, 0.45 mL (0.36 g, 2.17 mmol) of triethyl phosphite, and 300 mL of diethyl ether was exposed to ultraviolet irradiation for 105 min. Solvent was removed at $\sim 25^\circ\text{C}$ (40 mm). A solution of the residue in 5 mL of dichloromethane was chromatographed on a Florisil column. After removal of a trace of unreacted $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})(\text{PF}_2\text{NHCH}_3)$ by elution with 1:9 dichloromethane-hexane, further elution with 1:3 dichloromethane-hexane gave 0.360 g (81% conversion) of purple $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{PF}_2\text{NHCH}_3)[\text{P}(\text{OC}_2\text{H}_5)_3]$: mp 172°C ; proton NMR (CDCl_3) $\tau(\text{CH}_2)$ 5.9 (broad); $\tau(\text{CH}_3)$ 7.15 (broad), 8.65 (triplet, $J = 7$ Hz).

Preparation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_4(\text{CO})_8$. A solution of 1.14 g (2.0 mmol) of $\text{Co}_4(\text{CO})_{12}$ and 0.71 g (4.2 mmol) of $\text{CH}_3\text{N}(\text{PF}_2)_2$ in 100 mL of hexane was boiled under reflux for 22 h. Solvent was removed from the filtered reaction mixture at $\sim 40^\circ\text{C}$ (40 mm). The residue was chromatographed on a 3×55 cm Florisil column. Elution of the black band with 1:2 dichloromethane-hexane followed by evaporation of this eluate gave 0.80 g (50% yield) of black $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_4(\text{CO})_8$, mp $132\text{--}133^\circ\text{C}$.

Preparation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_4(\text{CO})_6$. A solution of 0.76 g (1.3 mmol) of $\text{Co}_4(\text{CO})_{12}$ and 0.63 g (3.8 mmol) of $\text{CH}_3\text{N}(\text{PF}_2)_2$ in 150 mL of hexane was stirred for 24 h at room temperature and then boiled under reflux for 30 min. The reaction mixture was filtered through Celite. Hexane was removed from the filtrate. A concentrated dichloromethane solution of the residue was chromatographed on a 3×55 cm Florisil column, prepared in hexane. The black band was eluted with 2:3 dichloromethane-hexane. Removal of solvent at 25°C (25 mm) from the eluate gave a black oil. Slow crystallization of this oil from a mixture of dichloromethane and hexane gave 0.65 g (55% yield) of black crystalline $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_4(\text{CO})_6$, mp $178\text{--}180^\circ\text{C}$.

Preparation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Co}_4(\text{CO})_4$. A solution of 0.62 g (1.1 mmol) of $\text{Co}_4(\text{CO})_{12}$ and 2.28 g (13.7 mmol) of $\text{CH}_3\text{N}(\text{PF}_2)_2$ in 100 mL of hexane was boiled under reflux for 22 h. The reaction mixture was then filtered through Celite and hexane was removed from the filtrate. Chromatography of a concentrated dichloromethane solution of the residue on a 3×55 cm Florisil column gave a black band. Elution of this black band with 1:2 dichloromethane-hexane followed by evaporation of the eluate and washing of the residue with pentane gave 0.42 g (38% yield) of black crystalline $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Co}_4(\text{CO})_4$, mp $215\text{--}217^\circ\text{C}$. Further elution of this chromatogram with pure dichloromethane and with diethyl ether gave minor quantities of dark violet products which were not unequivocally identified.

The same product $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Co}_4(\text{CO})_4$ was isolated by a similar chromatographic procedure from the reaction of $\text{Co}_4(\text{CO})_{12}$ or even $\text{Co}_2(\text{CO})_8$ with excess $\text{CH}_3\text{N}(\text{PF}_2)_2$ in boiling benzene.

Preparation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_5\text{Co}_4(\text{CO})_2$. A mixture of 1.14 g (2.0 mmol) of $\text{Co}_4(\text{CO})_{12}$, 4.00 g (24 mmol) of $\text{CH}_3\text{N}(\text{PF}_2)_2$, and 200 mL of redistilled tetrahydrofuran was exposed to ultraviolet irradiation for 5 h. Solvent was then removed from the reaction mixture at 25°C (25 mm). A concentrated solution of the residue in diethyl ether was chromatographed on a 3×55 cm Florisil column, prepared in hexane. After removal of unidentified noncrystalline products by elution first with hexane and then with 1:3 dichloromethane-hexane, the red-black band containing $[\text{CH}_3\text{N}(\text{PF}_2)_2]_5\text{Co}_4(\text{CO})_2$ was eluted with pure diethyl ether. Evaporation of the eluate gave 0.1 g (4.4% yield) of black crystalline $[\text{CH}_3\text{N}(\text{PF}_2)_2]_5\text{Co}_4(\text{CO})_2$, mp $275\text{--}277^\circ\text{C}$.

Reaction of $\text{Rh}_4(\text{CO})_{12}$ with $\text{CH}_3\text{N}(\text{PF}_2)_2$. A solution of 0.74 g (1.0 mmol) of $\text{Rh}_4(\text{CO})_{12}$ and 2.1 g (12.6 mmol) of $\text{CH}_3\text{N}(\text{PF}_2)_2$ in 200 mL of diethyl ether was exposed to ultraviolet irradiation. A yellow solid separated rapidly. After 2 h of irradiation, the yellow solid was filtered, washed successively with hexane and dichloromethane, and dried to give insoluble yellow $\{[\text{CH}_3\text{N}(\text{PF}_2)_2]_6\text{Rh}_4\}_n$, mp 270°C . This product was insoluble in organic solvents and decomposed upon attempted sublimation at 0.5 mm and temperatures

up to 250°C . Anal. Calcd. for $\text{C}_6\text{H}_{18}\text{F}_{24}\text{N}_6\text{P}_{12}\text{Rh}_4$: C, 5.1; H, 1.3; N, 5.9. Found: C 4.9, 5.1; H, 1.4, 1.3; N, 6.1, 6.1.

The same insoluble yellow $\{[\text{CH}_3\text{N}(\text{PF}_2)_2]_6\text{Rh}_4\}_n$ was obtained as a precipitate upon heating 0.37 g (0.5 mmol) of $\text{Rh}_4(\text{CO})_{12}$ with 1.0 g (6.0 mmol) of $\text{CH}_3\text{N}(\text{PF}_2)_2$ in boiling hexane.

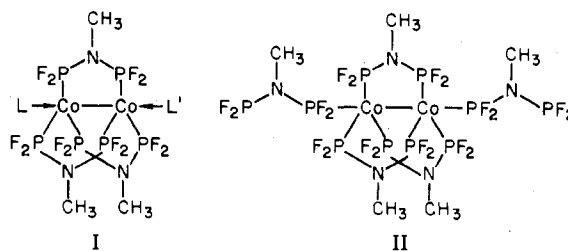
Mass Spectra. The following mass spectra were obtained by Dr. Main Chang at 70 eV on the University of Georgia Perkin-Elmer Hitachi RMU-6 mass spectrometer using the solid inlet probe (intensities of the major ions listed below are given in parentheses relative to $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2^+$ as the base ion):

$[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2$: $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2^+$ (12), $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Co}_2^+$ (55), $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2^+$ (100), $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Co}_2\text{PF}_2\text{NCH}_3^+$ (20), $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Co}_2\text{PF}_2^+$ (18), $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Co}_2\text{F}^+$ (12), $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Co}_2^+$ (4), $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}^+$ (10), $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Co}_2\text{PF}_2^+$ (43), $\text{CH}_3\text{N}(\text{PF}_2)_2\text{Co}_2\text{F}^+$ (20), $\text{CH}_3\text{N}(\text{PF}_2)_2\text{Co}_2^+$ (25), $\text{CH}_3\text{N}(\text{PF}_2)_2\text{Co}^+$ (65).

$[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2[\text{PF}_2\text{N}(\text{CH}_3)_2]$: $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2[\text{PF}_2\text{N}(\text{CH}_3)_2]^+$ (11), $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2\text{PF}_2\text{N}(\text{CH}_3)_2^+$ (20), $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2^+$ (100), $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Co}_2\text{PF}_2\text{NCH}_3^+$ (16), $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Co}_2\text{PF}_2^+$ (18), $\text{CH}_3\text{N}(\text{PF}_2)_2\text{Co}_2\text{PF}_2^+$ (67), $\text{CH}_3\text{N}(\text{PF}_2)_2\text{Co}_2\text{F}^+$ (31), $\text{CH}_3\text{N}(\text{PF}_2)_2\text{Co}_2^+$ (44), $\text{CH}_3\text{N}(\text{PF}_2)_2\text{Co}^+$ (60).

Results and Discussion

The reaction of $\text{Co}_2(\text{CO})_8$ with $\text{CH}_3\text{N}(\text{PF}_2)_2$ at or even below room temperature in the absence of ultraviolet irradiation proceeds rapidly with CO evolution to give a purple crystalline product of stoichiometry $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ in nearly quantitative yield. Structure I ($L = L' = \text{CO}$) for



this complex, containing a cobalt-cobalt bond bridged by three $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands, has been confirmed by X-ray crystallography.²

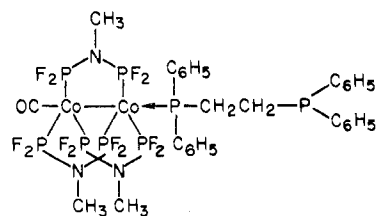
Ultraviolet irradiation of the metal hexacarbonyls $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) with excess $\text{CH}_3\text{N}(\text{PF}_2)_2$ in diethyl ether solution has been shown to result in complete substitution of the carbonyl groups to give the carbonyl-free complexes $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{M}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$).⁴ A similar ultraviolet irradiation of $\text{Co}_2(\text{CO})_8$ with excess $\text{CH}_3\text{N}(\text{PF}_2)_2$ followed by chromatography on Florisil was found to give a purple carbonyl-free product of stoichiometry $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{PF}_2\text{NHCH}_3)_2$. The structure I ($L = L' = \text{PF}_2\text{NHCH}_3$) for this product has been confirmed by X-ray crystallography.² The presence of N-H bonds in $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{PF}_2\text{NHCH}_3)_2$ is also verified spectroscopically by the observation of a sharp infrared $\nu(\text{N-H})$ band at 3435 cm^{-1} .

Formation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{PF}_2\text{NHCH}_3)_2$ by the ultraviolet irradiation of $\text{Co}_2(\text{CO})_8$ with $\text{CH}_3\text{N}(\text{PF}_2)_2$ followed by chromatography on Florisil clearly must involve solvolytic removal of one of the PF_2 groups of the $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligand to give the CH_3NHPF_2 ligand. That this solvolysis occurs during the column chromatography step is demonstrated by the observation that ultraviolet irradiation of $\text{Co}_2(\text{CO})_8$ with excess $\text{CH}_3\text{N}(\text{PF}_2)_2$ in diethyl ether followed by product isolation using vacuum sublimation rather than column chromatography gives the homoleptic¹⁰ complex $[\text{CH}_3\text{N}(\text{PF}_2)_2]_5\text{Co}_2$ apparently with structure II containing three biligate bimetallic $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands and two monoligate monometallic ligands. Thus, $\text{Co}_2(\text{CO})_8$, like $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and $\text{Ni}(\text{CO})_4$ but unlike the iron carbonyls, can be converted to a homoleptic $[\text{CH}_3\text{N}(\text{PF}_2)_2]_5\text{M}_x$ complex upon ultraviolet irradiation with excess $\text{CH}_3\text{N}(\text{PF}_2)_2$. The facile solvolysis of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_5\text{Co}_2$ (II) to $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3$ -

$\text{Co}_2(\text{PF}_2\text{NHCH}_3)_2$ (I: $L = L' = \text{CH}_3\text{NHPF}_2$), which involves only the two monoligate monometallic $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands, is a clear demonstration of the hydrolytic stability of bidentate $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands but the hydrolytic instability of a monodentate $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligand containing an uncomplexed PF_2 group. Such hydrolytic instability of monodentate $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands has also been observed in cyclopentadienylmetal complexes such as $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2[(\text{PF}_2)_2\text{NCH}_3]\text{Cl}$ and $\text{C}_5\text{H}_5\text{Fe}(\text{CO})[(\text{PF}_2)_2\text{NCH}_3]\text{Cl}$.¹

The formation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2$ (II) by ultraviolet irradiation of $\text{Co}_2(\text{CO})_8$ with excess $\text{CH}_3\text{N}(\text{PF}_2)_2$ clearly must involve $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ (I: $L = L' = \text{CO}$) as an intermediate. This suggested that ultraviolet irradiation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ with other ligands might lead to similar $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2\text{L}_2$ complexes I. In order to obtain the necessary $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ for such preparative studies, we carried out the reaction of $\text{Co}_2(\text{CO})_8$ with $\text{CH}_3\text{N}(\text{PF}_2)_2$ in the absence of ultraviolet irradiation on a relatively large scale and isolated the product by chromatography on Florisil. This procedure resulted not only in the isolation of the expected $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ in ~88% yield but also in the isolation of the unsymmetrical complex $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})(\text{PF}_2\text{NHCH}_3)$ (I: $L = \text{CO}$, $L' = \text{CH}_3\text{NHPF}_2$) in low yield. This unsymmetrical complex was obtained along with the symmetrical complex $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{PF}_2\text{NHCH}_3)_2$ (I: $L = L' = \text{CH}_3\text{NHPF}_2$) in somewhat better yield by ultraviolet irradiation of pure $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ with $\text{CH}_3\text{N}(\text{PF}_2)_2$ followed by hydrolytic removal of the uncomplexed PF_2 groups by chromatography on Florisil. However, no reaction conditions could be found which give $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})(\text{PF}_2\text{NHCH}_3)$ in the absence of larger quantities of other $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2\text{L}_2$ derivatives (i.e., $L = L' = \text{CO}$ or CH_3NHPF_2). Therefore, it was not possible to eliminate the chromatographic separation of the unsymmetrical $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})\text{L}$ ($L \neq \text{CO}$) derivatives. This prevented us from obtaining $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Co}_2\text{CO}$ (I: $L = \text{CO}$, $L' = \text{monodentate } \text{CH}_3\text{N}(\text{PF}_2)_2$), containing one monodentate $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligand which would be the precursor to $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})(\text{PF}_2\text{NHCH}_3)$ by hydrolysis.

Ultraviolet irradiations of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ (I: $L = L' = \text{CO}$) with the monodentate ligands $(\text{CH}_3)_2\text{NPF}_2$, $(\text{C}_2\text{H}_5\text{O})_3\text{P}$, and $(\text{CH}_3)_3\text{CNC}$ result in the stepwise replacement of the two carbonyl groups with the monodentate ligand to give the corresponding $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})\text{L}$ and $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2\text{L}_2$ derivatives ($L = (\text{CH}_3)_2\text{NPF}_2$, $(\text{C}_2\text{H}_5\text{O})_3\text{P}$, $(\text{CH}_3)_3\text{CNC}$) which can easily be separated by column chromatography. Ultraviolet irradiation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ with triphenylphosphine in diethyl ether results in the precipitation of the relatively sparingly soluble disubstituted derivative $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$ (I: $L = L' = (\text{C}_6\text{H}_5)_3\text{P}$). Chromatography of the filtrate was found to give the monosubstituted product $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})\text{P}(\text{C}_6\text{H}_5)_3$ (I: $L = \text{CO}$, $L' = (\text{C}_6\text{H}_5)_3\text{P}$), as indicated by its infrared spectrum. However, all of the samples of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]$ obtained in this work were contaminated with unreacted free triphenylphosphine as indicated by the elemental analyses. Ultraviolet irradiation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ with the di(tertiary phosphine) $(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ gives the complex $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]$ (III) containing a monoligate monometallic di(tertiary phosphine). The remaining carbonyl group in $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})(\text{PF}_2\text{NHCH}_3)$ (I: $L = \text{CO}$, $L' = \text{CH}_3\text{NHPF}_2$) is also subject to photolytic replacement with monodentate ligands leading to unsymmetrical complexes of the type $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{PF}_2\text{NHCH}_3)\text{L}$ (I: $L = (\text{C}_2\text{H}_5\text{O})_3\text{P}$, $(\text{CH}_3)_2\text{NPF}_2$, $L' = \text{CH}_3\text{NHPF}_2$).

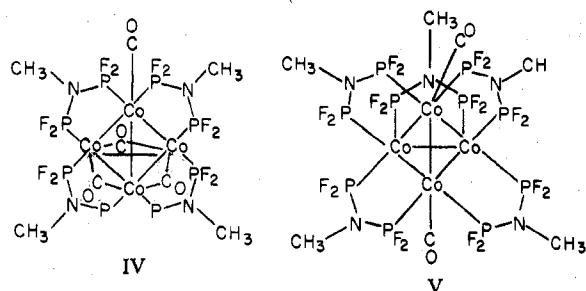


III

The ability to prepare a variety of binuclear cobalt derivatives containing $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2$ units as described in this paper suggests the high stability of this structural unit. The mass spectra of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2$ (II) and $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2[\text{PF}_2\text{N}(\text{CH}_3)_2]$ (I: $L = L' = (\text{CH}_3)_2\text{NPF}_2$) also suggest the high stability of this structural unit since in both spectra the most abundant metal-containing ion is $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2^+$ (m/e 619). Further fragmentation of this ion appears to involve phosphorus–nitrogen bond cleavage to give $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Co}_2\text{PF}_2\text{NCH}_3^+$ and $[\text{CH}_3\text{N}(\text{PF}_2)_2]_n\text{Co}_2\text{PF}_2^+$ ($n = 1, 2$) and fluorine shift from phosphorus to cobalt to give $[\text{CH}_3\text{N}(\text{PF}_2)_2]_n\text{Co}_2\text{F}^+$ ($n = 1, 2$). The mass spectra of both $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2$ and $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2[\text{PF}_2\text{N}(\text{CH}_3)_2]$ exhibit the molecular ions as well as the ions $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2\text{L}^+$ ($L = \text{CH}_3\text{N}(\text{PF}_2)_2$ and $(\text{CH}_3)_2\text{NPF}_2$, respectively) formed by loss of one of the terminal ligands from the molecular ion.

The existence not only of the compounds $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2\text{LL}'$ (I) discussed in this paper but also of the iron derivatives⁴ $\text{CH}_3\text{N}(\text{PF}_2)_2\text{Fe}_2(\text{CO})_7$ and $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Fe}_2(\text{CO})_5$ and the nickel derivative⁴ $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_3$ demonstrate the ability of one or more $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands to bridge metal–metal bonds to form five-membered chelate rings containing two metal atoms, two phosphorus atoms, and one nitrogen atom. This suggests that the $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligand would be a good bridge across metal–metal bonds in metal cluster compounds thereby providing ultimately a new method for the stabilization of new metal clusters including systems of possible significance in catalysis.¹¹ In an elementary attempt to verify such a possibility, the reaction of $\text{Co}_4(\text{CO})_{12}$ with $\text{CH}_3\text{N}(\text{PF}_2)_2$ was investigated under various conditions. Black crystalline products of the type $[\text{CH}_3\text{N}(\text{PF}_2)_2]_n\text{Co}_4(\text{CO})_{12-2n}$ could be isolated in the pure state for $n = 2, 3, 4$, and 5 by appropriate selection of the reaction conditions. In these reactions substitution of CO groups in $\text{Co}_4(\text{CO})_{12}$ by $\text{CH}_3\text{N}(\text{PF}_2)_2$ appears to be relatively easy until the stage $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Co}_4(\text{CO})_4$ is reached, but further substitution to give $[\text{CH}_3\text{N}(\text{PF}_2)_2]_5\text{Co}_4(\text{CO})_2$ appears to require ultraviolet irradiation. These $[\text{CH}_3\text{N}(\text{PF}_2)_2]_n\text{Co}_4(\text{CO})_{12-2n}$ complexes appear to have structures in which two to five of the six edges in the Co_4 tetrahedron of $\text{Co}_4(\text{CO})_{12}$ are bridged by the biligate bimetallic $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands. Infrared spectra in the $\nu(\text{CO})$ region indicate both bridging and terminal groups for the complexes $[\text{CH}_3\text{N}(\text{PF}_2)_2]_n\text{Co}_4(\text{CO})_{12-2n}$ ($n = 2, 3, 4$) suggesting that the fundamental structure¹² of $\text{Co}_4(\text{CO})_{12}$ is preserved upon pairwise replacement of the first eight CO groups with edge-bridging $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands (e.g., structure IV for $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Co}_4(\text{CO})_4$). However, the infrared spectrum in the $\nu(\text{CO})$ region of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_5\text{Co}_4(\text{CO})_2$ indicates that both CO groups are terminal suggesting the obvious structure V.

In most cases 4d and 5d transition metals form more stable metal–metal bonds and, therefore, more stable metal clusters than the corresponding 3d transition metals. For this reason we investigated the reaction of $\text{Rh}_4(\text{CO})_{12}$ with $\text{CH}_3\text{N}(\text{PF}_2)_2$ hoping to obtain a variety of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_n\text{Rh}_4(\text{CO})_{12-2n}$ derivatives. However, this reaction was found to proceed rapidly with complete loss of CO groups to give an insoluble yellow solid of stoichiometry $\{[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Rh}_2\}_n$. This



product may be formulated as a completely substituted $Rh_4(CO)_{12}$ with $CH_3N(PF_2)_2$ bridges along each of the six edges of the Rh_4 tetrahedron (i.e., $[CH_3N(PF_2)_2]_6Rh_4$). However, the extreme insolubility of this product, which precludes, for example, its molecular weight determination in solution, suggests a polymeric structure containing Rh_4 tetrahedra bridged by intertetrahedral bidentate $CH_3N(PF_2)_2$ ligands (i.e., $\{[CH_3N(PF_2)_2]_6Rh_4\}_n$). In any case the facile formation of a carbonyl-free complex $\{[CH_3N(PF_2)_2]_6Rh_4\}_n$ from $Rh_4(CO)_{12}$ and $CH_3N(PF_2)_2$ under conditions milder than those where $Co_4(CO)_{12}$ forms products $[CH_3N(PF_2)_2]_nCo_4(CO)_{12-2n}$ still containing carbonyl groups is a further demonstration of the weaker metal-carbon bonds formed by 4d transition metals relative to corresponding systems involving 3d and 5d transition metals.¹³

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carbon-13 and phosphorus-31 NMR spectra.

Registry No. $[CH_3N(PF_2)_2]_3Co_2(CO)_2$, 64799-21-9; $[CH_3N(PF_2)_2]_3Co_2(CO)(PF_2NHCH_3)$, 66674-80-4; $[CH_3N(PF_2)_2]_5Co_2$, 66632-81-3; $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$, 64799-20-8; $[CH_3N(PF_2)_2]_3Co_2(CO)(PF_2N(CH_3)_2)$, 66632-80-2; $[CH_3N(PF_2)_2]_3Co_2[PF_2N(CH_3)_2]_2$, 66674-78-0; $[CH_3N(PF_2)_2]_3Co_2(CO)(P(OC_2H_5)_3)$, 66632-79-9; $[CH_3N(PF_2)_2]_3Co_2(P(OC_2H_5)_3)_2$, 66632-78-8; $[CH_3N(PF_2)_2]_3Co_2(P(C_6H_5)_3)_2$, 66632-91-5; $[CH_3N(PF_2)_2]_3Co_2(CO)P(C_6H_5)_3$, 66632-90-4; $[CH_3N(PF_2)_2]_3Co_2(CO)[CNC(CH_3)_3]$, 66632-89-1; $[CH_3N(PF_2)_2]_3Co_2(CO)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$, 66674-77-9; $[CH_3N(PF_2)_2]_3Co_2(PF_2NHC_6H_5)(PF_2N(CH_3)_2)$, 66632-88-0; $[CH_3N(PF_2)_2]_3Co_2(PF_2NHC_6H_5)(P(OC_2H_5)_3)$, 66632-87-9; $[CH_3N(PF_2)_2]_3Co_4(CO)_8$, 66687-70-5; $[CH_3N(PF_2)_2]_3Co_4(CO)_6$, 66687-71-6; $[CH_3N(PF_2)_2]_4Co_4(CO)_4$, 66632-86-8; $[CH_3N(PF_2)_2]_5Co_4(CO)_2$, 66702-33-8; $\{[CH_3N(PF_2)_2]_6Rh_4\}_n$, 66687-72-7; $Co_2(CO)_8$, 10210-68-1; $Co_4(CO)_{12}$, 17786-31-1; $Rh_4(CO)_{12}$, 19584-30-6; $[CH_3N(PF_2)_2]_3Co_2(CNC(C_6H_5)_3)_2$, 66632-85-7.

References and Notes

- (1) For part 5 of this series see R. B. King and J. Gimeno, *Inorg. Chem.*, preceding paper in this issue.
- (2) For a preliminary communication of a portion of this work see M. G. Newton, R. B. King, M. Chang, N. S. Pantaleo, and J. Gimeno, *J. Chem. Soc., Chem. Commun.*, 531 (1977).
- (3) On leave from the Department of Chemistry, University of Zaragoza, Zaragoza, Spain.
- (4) R. B. King and J. Gimeno, *Inorg. Chem.*, **17**, 2390 (1978).
- (5) J. F. Nixon, *J. Chem. Soc. A*, 2689 (1968).
- (6) P. Chini, V. Albano, and S. Martinengo, *J. Organomet. Chem.*, **16**, 471 (1969).
- (7) S. Martinengo, P. Chini, and G. Giordano, *J. Organomet. Chem.*, **27**, 389 (1971).
- (8) R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964).
- (9) I. Ugi and R. Meyr, *Chem. Ber.*, **93**, 239 (1960).
- (10) P. J. Davidson, M. F. Lappert, and R. Pearce, *Acc. Chem. Res.*, **7**, 209 (1974).
- (11) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975).
- (12) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966).
- (13) R. B. King, *Inorg. Nucl. Chem. Lett.*, **5**, 905 (1969).

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Synthesis and Characterization of a Series of Thiobenzoate Complexes of Molybdenum(V)

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New dimeric molybdenum(V) complexes of formulas $Mo_2O_4L_2(py)_2$, $Na_2Mo_2O_4L_4$, $Mo_2O_3SL_2(py)_2$, and $Na_2Mo_2O_3SL_4$, where L = monothiobenzoate, have been synthesized. The complexes have been characterized by analytical, spectral, conductivity, and electrochemical measurements. The five-coordinate neutral dimers, $Mo_2O_3XL_2$ (where X = O or S), show a high affinity for electron donors. Strong intermolecular associations occur through terminal oxygen-metal interactions unless a good donor ligand is added. The neutral dimers react with excess sodium thiobenzoate to form molybdenum(V) dimeric anions. Infrared studies indicate that the Mo_2O_3X units of the dimers remain intact in this reaction. The neutral complexes can be regenerated by the addition of 2 equiv of acid. The dissociation behavior of the complexes $Na_2Mo_2O_3XL_4$ in solution is discussed.

Introduction

The coordination chemistry of molybdenum(V) is dominated by the formation of dimeric species with metal ions bridged by one or two oxygen or, in some cases, sulfur atoms. A number of such dimeric units are stabilized by bidentate ligands with oxygen, nitrogen, or sulfur donors.¹ Studies have shown that when di- μ -oxo-molybdenum(V) dimers are converted to monooxo-bridged complexes,² cleaved to form molybdenum(V) monomers,³ or reduced to form lower valent monomeric complexes⁴ very reactive molybdenum species may be produced. Such reactions have led, for example, to the formation of catalytically active species for acetylene,⁴ ni-

trogen,⁴ and nitrate^{3a} reductions. However, relatively few studies of reactions of molybdenum(V) dimers have been reported in which the di- μ -oxo (or μ -oxo, μ -sulfido, or di- μ -sulfido) bridge remains intact.⁵ Electrochemical⁶ and other characterization studies⁷ of molybdenum(V) compounds suggest that the tendency of dimeric complexes to undergo or to resist bridge cleavage reactions can be significantly affected by the nature of the chelating ligand as well as by reaction conditions and the nature of the added reagents.

In order to extend the understanding of the scope of molybdenum coordination chemistry, we are interested in the study of dimeric molybdenum(V) complexes which, because