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Metal Complexes of Fluorophosphines. 13.[1] Reaction of *fac*-$(CH_3CN)_3Mo(CO)_3$ with (Methylamino)bis(difluorophosphine). X-ray Crystal Structure Analysis of a Novel Binuclear Molybdenum Fluorophosphine Carbonyl Complex with a Bridging Chlorine Atom: $(CO)_2Mo[\mu\text{-}CH_3N(PF_2)_2]_2(\mu\text{-}PF_2)(\mu\text{-}Cl)Mo(CO)(PF_2NHCH_3)$

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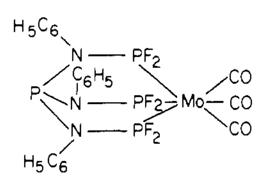
Reaction of *fac*-$(CH_3CN)_3Mo(CO)_3$ with $CH_3N(PF_2)_2$ in acetonitrile solution at room temperature gives white, volatile, crystalline *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$, containing one monodentate and one bidentate $CH_3N(PF_2)_2$ ligand. The same reactants in boiling acetonitrile give yellow $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ in considerably better yield than the previously reported preparation of this binuclear complex from the cycloheptatriene complex $C_7H_8Mo(CO)_3$ and $CH_3N(PF_2)_2$ in boiling methylcyclohexane. Reaction in acetonitrile solution of *fac*-$(CH_3CN)_3Mo(CO)_3$ with $CH_3N(PF_2)_2$ containing about 0.2% HCl (an impurity not known initially to be present) gives brown-red, volatile $(CO)_2Mo[\mu\text{-}CH_3N(PF_2)_2]_2(\mu\text{-}PF_2)(\mu\text{-}Cl)Mo(CO)(PF_2NHCH_3)$, whose composition and structure were established by single-crystal X-ray structure analysis. This novel quadruply bridged binuclear complex is obtained in considerably better yield from the reaction of $[CH_3N(PF_2)_2]_3Mo_2(CO)_5$ with $[(C_2H_5)_3NH]Cl$ in acetonitrile solution. The complex has a Mo–Mo bond 2.975 Å in length. Crystal data: monoclinic, space group $P2_1/c$, $a = 17.546$ (4) Å, $b = 9.725$ (2) Å, $c = 14.558$ (3), $\beta = 107.20$ (2)°, $Z = 4$.

Introduction

A previous paper of this series[3] describes reactions of the norbornadiene complexes $C_7H_8M(CO)_4$ (M = Cr, Mo, W) and the cycloheptatriene complexes $C_7H_8M(CO)_3$ (M = Cr, Mo, W) with the ligands $RN(PF_2)_2$ (R = CH_3, C_6H_5) to give a variety of metal carbonyl derivatives, including the chelates $RN(PF_2)_2M(CO)_4$, the monoligate monometallic complexes $[RN(PF_2)_2]_2M(CO)_4$ (M = Cr, trans isomer; M = Mo and W, cis isomer), and binuclear $M_2(CO)_{11}$ substitution products of the types $[RN(PF_2)_2]_nM_2(CO)_{11-2n}$ (n = 3–5). The extent of this chemistry has led us to investigate reactions of other reactive group 6 metal carbonyl intermediates with the $RN(PF_2)_2$ fluorophosphines. In this connection the reaction of *fac*-$(CH_3CN)_3Mo(CO)_3$ (**1**) with $C_6H_5N(PF_2)_2$ was found[4] to give a novel bicyclo[2.2.2]octane-like cage chelate $P[N(C_6H_5)PF_2]_3Mo(CO)_3$ (**2**), apparently by condensation of three $C_6H_5N(PF_2)_2$ ligands with PF_3 elimination. This paper describes the reaction of *fac*-$(CH_3CN)_3Mo(CO)_3$ with the closely related ligand $CH_3N(PF_2)_2$. Somewhat unexpectedly, the subtle change in the $RN(PF_2)_2$ ligand of the R group from phenyl to methyl appears to prevent PF_3 elimination to give an analogue of **2**. Instead, the reaction of *fac*-$(CH_3CN)_3Mo(CO)_3$ with $CH_3N(PF_2)_2$, depending on the conditions, yields a new compound, *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ (**3**), or provides a greatly improved preparation of the previously reported[3,5] $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$, shown by X-ray crystallography[5] to have the novel structure **4** with an unsymmetrical bridging carbonyl group. In a more unusual reaction, *fac*-$(CH_3CN)_3Mo(CO)_3$ and $CH_3N(PF_2)_2$ in the presence of a mild stoichiometric HCl source were found to give a novel product $(CO)_2Mo[\mu\text{-}CH_3N(PF_2)_2]_2(\mu\text{-}PF_2)(\mu\text{-}Cl)Mo(CO)(PF_2NHCH_3)$ (**5**), hereafter written for brevity as $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$, whose composition and structure were determined only after single-crystal X-ray analysis.



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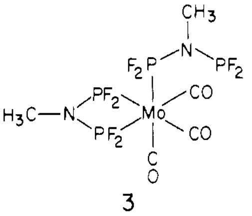

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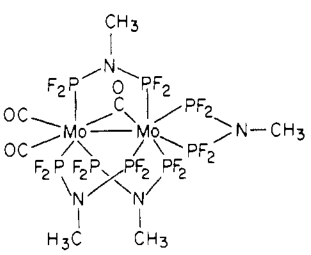

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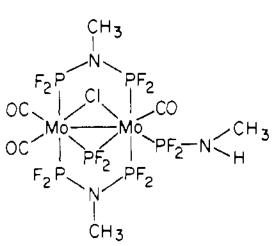

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Experimental Section

Microanalyses were performed by Atlantic Microanalytical Laboratory, Atlanta, GA. Melting points were taken in capillaries and are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 599B spectrometer and calibrated against the 1944- and 1601-cm^{-1} bands of polystyrene film. Proton NMR spectra were run on a Varian EM-390 continuous-wave spectrometer using internal tetramethylsilane as a reference. Carbon-13, phosphorus-31, and fluorine-19 NMR spectra were taken on a JEOL FX-90Q multinuclear pulsed Fourier transform spectrometer using internal tetramethylsilane, external 85% phosphoric acid, and internal fluorotrichloromethane, respectively, as references.

A nitrogen atmosphere was provided for all reactions, for handling of air-sensitive compounds, and for distillation of solvents before use. Acetonitrile was predried over molecular sieves and distilled over calcium hydride before use. The acetonitrile adduct $CH_3CN{\cdot}2HCl$[6] was prepared by saturating dry acetonitrile with hydrogen chloride gas at 0 °C followed by storage in a freezer at −10° for several days, during which time the product separated as colorless crystals. The product was separated by filtration and washed with diethyl ether.

Hexacarbonylmolybdenum was purchased from Pressure Chemical Co., Pittsburgh, PA, and converted to *fac*-$(CH_3CN)_3Mo(CO)_3$,[7] $C_7H_8Mo(CO)_3$,[8] $C_8H_8Mo(CO)_3$,[9] and $[CH_3N(PF_2)_2]_3Mo_2(CO)_5$[3] by the cited published procedures or trivial modifications thereof. The $CH_3N(PF_2)_2$ ligand[10,11] was also prepared by the cited procedure, but

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(1) For part 12 of the series see: King, R. B.; Shimura, M. *J. Organomet. Chem.* **1983**, *256*, 71.

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using decahydronaphthalene rather than methylcyclohexane as the diluent in the final step involving fluorination of $CH_3N(PCl_2)_2$ with SbF_3.

Preparation of *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ (3). (a) From *fac*-$(CH_3CN)_3Mo(CO)_3$ (1). A solution of *fac*-$(CH_3CN)_3Mo(CO)_3$ was prepared by boiling 1.93 g (7.3 mmol) of $Mo(CO)_6$ in 40 mL of acetonitrile for 16 h. After it was cooled to room temperature, this solution was treated with 4.8 g (28.8 mmol) of $CH_3N(PF_2)_2$. After 15 min, solvent was removed at ~25 °C (25 mm). The residue was extracted with 50 mL of pentane in three portions. Evaporation of the pentane extracts gave 1.66 g (44% yield) of crude *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ after washing with a few milliliters of cold hexane. The analytical sample (mp 75–76 °C), obtained by vacuum sublimation at 45 °C (0.3 mm), had infrared ν(CO) frequencies in hexane at 2038, (s), 1982 (vs), and 1976 (vs) cm^{-1}. Anal. Calcd for $C_5H_6F_8MoN_2O_3P_4$: C, 11.7; H, 1.2; N, 5.4. Found: C, 11.8; H, 1.2; N, 5.4.

(b) From the Cycloheptatriene Complex $C_7H_8Mo(CO)_3$. A solution of 2.78 g (17 mmol) of $CH_3N(PF_2)_2$ in 40 mL of hexane was treated dropwise with a solution of 0.59 g (2.2 mmol) of $C_7H_8Mo(CO)_3$ in 70 mL of hexane at 30 °C during 5 h with stirring. The red color of $C_7H_8Mo(CO)_3$ slowly disappeared. After the mixture was allowed to stand overnight at room temperature, solvent was removed at ~25 °C (25 mm). Crystallization of the residue from hexane gave ultimately 0.135 g (12% yield) of *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$, identified by its melting point and infrared spectrum.

(c) From the Cyclooctatetraene Complex $C_8H_8Mo(CO)_3$. A solution of 5.2 g (31 mmol) of $CH_3N(PF_2)_2$ in 50 mL of hexane was treated dropwise with a solution of 1.11 g (3.9 mmol) of $C_8H_8Mo(CO)_3$ in 50 mL of hexane during 30 min with stirring. The red color of $C_8H_8Mo(CO)_3$ disappeared instantly upon contact with the $CH_3N(PF_2)_2$ ligand. A total of 0.101 g (5% yield) of *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ was isolated from the reaction mixture by a procedure similar to that described above and identified by its melting point and infrared spectrum. The residue from the hexane extractions gave 0.005 g of a second slightly yellow product, suggested by its ν(CO) frequencies of 2040 (s), 1952 (vs), and 1900 (s) cm^{-1} in CCl_4 to be the adduct η^4-$C_8H_8Mo(CO)_3(PF_2)_2NCH_3$. However, this product was not fully characterized because of the small amount available.

Preparation of $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ (4). (a) From *fac*-$(CH_3CN)_3Mo(CO)_3$ (1). A solution of *fac*-$(CH_3CN)_3Mo(CO)_3$ was prepared by boiling 1.29 g (4.9 mmol) of $Mo(CO)_6$ in 25 mL of acetonitrile for 16 h. After it was allowed to cool to room temperature, this solution was treated with 2.45 g (14.7 mmol) of $CH_3N(PF_2)_2$. The reaction mixture was boiled under reflux for 3 h. Solvent was removed from the resulting deep orange solution at ~25 °C (25 mm). The yellow solid residue was extracted with 25 mL of diethyl ether in three portions. Evaporation of the filtered combined ether extracts gave 0.76 g (33% yield) of crude $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$, identified by comparison of its ν(CO) frequencies with those reported[3] in the literature. Further purification could be effected by crystallized from diethyl ether.

The time of the reaction between *fac*-$(CH_3CN)_3Mo(CO)_3$ and $CH_3N(PF_2)_2$ in the boiling acetonitrile is rather critical in order to obtain yields similar to those reported above. Comparable yields are obtained with reaction times in the range 1.5–3 h. Reaction times below 40 min or above 7 h gave much lower yields.

(b) From *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$. The crude *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ obtained from 1.1 g (4.2 mmol) of $Mo(CO)_6$ as described above was boiled in 30 mL of heptane for 3.5 h. Cooling the reaction mixture for 3 days at −10 °C precipitated 0.63 g (32% yield) of yellow crystalline $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$, identified by its infrared ν(CO) spectrum.

Conversion of $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ (4) to $[CH_3N(PF_2)_2]_5Mo_2CO$ (6). A mixture of 0.607 g (0.64 mmol) of $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$, 1.33 g (8.0 mmol) of $CH_3N(PF_2)_2$, and 50 mL of heptane was boiled under reflux for 5 h. Cooling the reaction mixture at −10 °C for several hours gave 0.617 g (91% yield) of yellow crystalline $[CH_3N(PF_2)_2]_5Mo_2CO$, which was filtered and washed with hexane. This product was identified by its infrared ν(CO) frequency of 1934 cm^{-1} in CCl_4 (lit.[3] ν(CO) in CCl_4 1923 cm^{-1}) and elemental analyses. The analytical sample was recrystallized from diethyl ether. Anal. Calcd for $C_6H_{15}F_{20}Mo_2N_5OP_{10}$: C, 6.8; H, 1.4; N, 6.6. Found: C, 7.1; H, 1.4; N, 6.6.

Observations on the Chemical Reactivity of $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ (4). In hexane solution, $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ is not converted to any other metal carbonyl derivative by ultraviolet irradiation for several hours; slow decomposition to insoluble products occurs instead. Furthermore, $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ is unreactive toward acetylene in diethyl ether solution at room temperature or toward carbon monoxide in hexane solution at ambient pressure and temperature even in the presence of ultraviolet radiation for 5 h.

Preparation of $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$ (5). (a) From $[CH_3N(PF_2)_2]_3Mo_2(CO)_5$. A mixture of 0.10 g (0.12 mmol) of $[CH_3N(PF_2)_2]_3Mo_2(CO)_5$, 0.0164 g (0.12 mmol) of triethylammonium chloride, and 8 mL of acetonitrile was heated at 35–40 °C for 1 day. The color of the solution gradually turned from yellow through orange to brown. Solvent was removed from the reaction mixture at ~25 °C (25 mm). The brown residue was extracted with 15 mL of hexane in three portions. Removal of the hexane gave 0.047 g (48% yield) of brown crystalline $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$. The analytical sample was obtained by sublimation at 105 °C (0.3 mm).

A similar yield of **5** was obtained from the reaction of 0.10 g (0.12 mmol) of $[CH_3N(PF_2)_2]_3Mo_2(CO)_5$ with 0.0075 g (0.066 mmol) of $CH_3CN{\cdot}2HCl$ in 8 mL of acetonitrile at 40 °C for 1 day using a similar procedure for product isolation.

(b) From $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ (4). A mixture of 0.106 g (0.112 mmol) of $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$, 0.0066 g (0.058 mmol) of $CH_3CN{\cdot}2HCl$, and 8 mL of acetonitrile was heated at 40 °C for 25 h. Solvent was removed from the resulting orange-brown solution at ~25 °C (25 mm). The resulting brown oily solid was extracted with 9 mL of hexane in three portions. Evaporation of the combined hexane extracts gave 0.005 g (5% yield) of brown solid $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$.

(c) From *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ (3). A mixture of 0.10 g (0.29 mmol) of *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$, 0.0197 g (0.14 mmol) of triethylammonium chloride, and 8 mL of acetonitrile was heated at 35–40 °C for 1 day. Solvent was removed from the reaction mixture at ~25 °C (25 mm). Extraction of the residue with 3 mL of pentane in three portions followed by evaporation of the pentane extract gave 0.009 g (8% yield) of brown $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$.

(d) From *fac*-$(CH_3CN)_3Mo(CO)_3$ (1) with $CH_3CN{\cdot}2HCl$. A solution of *fac*-$(CH_3CN)_3Mo(CO)_3$ was prepared by boiling 3.22 g (12.2 mmol) of $Mo(CO)_6$ in 75 mL of acetonitrile for 17 h. This solution was stirred at room temperature with 5.86 g (35 mmol) of $CH_3N(PF_2)_2$ and 0.366 g (3.2 mmol) of $CH_3CN{\cdot}2HCl$ until all of the latter had dissolved. The reaction mixture was then heated at 40 °C for 1 day. During the course of the heating the originally bright yellow solution became dark brown. Solvent was removed from the reaction mixture at ~25 °C (25 mm). The black viscous liquid residue was extracted with 80 mL of hexane in four portions. The hexane extract was concentrated under a vacuum and cooled overnight in a −10 °C freezer. The resulting brown crystals were filtered and washed with pentane to give 0.372 g (7.5% yield) of $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$. The analytical sample, mp 151–152 °C, was obtained by vacuum sublimation at 105 °C (0.3 mm).

(e) From *fac*-$(CH_3CN)_3Mo(CO)_3$ without an External HCl Source. A solution of *fac*-$(CH_3CN)_3Mo(CO)_3$ was prepared by boiling a solution of 7.9 g (30 mmol) of $Mo(CO)_6$ in 150 mL of acetonitrile for 24 h. This solution was heated at 40 °C for 2 days with 15.6 g (93 mmol) of $CH_3N(PF_2)_2$. The reaction mixture gradually became dark brown. Solvent was removed from the reaction mixture at ~25 °C (25 mm). The resulting black oil was extracted with 93 mL of pentane in four portions. The brown pentane solution was concentrated and cooled to 0 °C. The resulting brown-red crystals were filtered and dried to give 0.744 g (6.1% yield based on Mo) of $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$, corresponding to 0.0334 g of HCl or 0.2% HCl impurity in the $CH_3N(PF_2)_2$ ligand. The analytical sample, mp 153–154 °C, was obtained by recrystallization from 120 mL of warm pentane followed by sublimation at 105 °C (0.3 mm). Anal. Calcd for $C_6H_{10}ClF_{12}Mo_2N_3O_3P_6$: C, 8.9; H, 1.2; Cl, 4.4; N, 5.2. Found: C, 8.9; H, 1.2; Cl, 4.4; N, 5.2.

The color of crystalline **5** depends on crystal size. Small crystals are light brown; large ones are ruby red.

Infrared Spectra of $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$ (5). (a) KBr pellet: ν(NH) frequency at 3430 (m) cm^{-1}; ν(CH) frequency at 2950 (w) cm^{-1}; ν(CO) frequencies at 2060 (s),

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2018 (s), 1977 (vs), 1957 (m) cm^{-1}; other bands at 1387 (m), 1378 (w), 1082 (m), 1064 (s), 1057 (sh), 917 (m), 870 (m), 830 (vs), 696 (w), 673 (s), 564 (w), 552 (w), 525 (w), 500 (vw) cm^{-1}.

(b) CCl_4 solution: ν(CO) frequencies at 2050 (m), 2030 (s), 1967 (s) cm^{-1}.

Proton NMR Spectra. (a) *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ (**3**) in $CDCl_3$: δ 2.94 (double doublet, J_1 = 6 Hz, J_2 = 1 Hz, 3 H), δ 2.75 (triplet, J = 10 Hz, 3 H).

(b) $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$ (**5**) in $CDCl_3$: δ 2.82 (double doublet, J_1 = 11 Hz, J_2 = 6 Hz, 3 H), 2.73 (singlet, 6 H).

Carbon-13 NMR Spectra (Proton Decoupled). (a) *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ (**3**) in $CDCl_3$ with $Cr(acac)_3$: δ 212.0 (broad, 2 CO), 206 (broad, 1 CO), 29.1 (singlet, 1 CH_3), 25.3 (singlet, 1 CH_3).

(b) $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3(PF_2)(Cl)$ (**5**) in $CDCl_3$: δ 27.6 (broad, 1 CH_3), 25.7 (2 CH_3); CO resonances not observed.

Phosphorus-31 NMR Spectra (Proton Decoupled). The proton-decoupled phosphorus-31 NMR spectra of *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ (**3**) and $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$ (**5**) are too complicated to be interpreted unequivocally in view of the several types of phosphorus atoms and the large number of possible phosphorus–fluorine and phosphorus–phosphorus coupling constants. A possible partial interpretation of the phosphorus-31 NMR spectrum of *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ follows. (a) Chelating $CH_3N(PF_2)_2$ ligand: resonance centered at δ 143.3 with splittings of ~1230 and ~110 Hz arising from P–F and P–P coupling, respectively. (b) Uncomplexed phosphorus of monodentate $CH_3N(PF_2)_2$ ligand: resonance centered at δ 138.8 with splittings of ~1270 and ~210 Hz arising from P–F and P–P coupling, respectively. (c) Complexed phosphorus of monodentate $CH_3N(PF_2)_2$ ligand: resonance centered at δ 178.7 with splittings of ~1120 and ~210 Hz arising from P–F and P–P coupling, respectively. These chemical shift and coupling constant values are consistent with those previously found[3] for less complicated related fluorphosphine metal carbonyl complexes.

Fluorine-19 NMR Spectra (Proton Decoupled). (a) *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ (**3**) in $CDCl_3$: δ −32.0 (doublet, J = 1135 Hz, 2 F), −50.1 (doublet of multiplets, major splitting 1235 Hz, 2 F), −52.7 (double doublet, J_1 = 1239 Hz, J_2 = 49 Hz, 2 F), −75.1 (doublet, J = 1251 Hz, 2 F).

(b) $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$ (**5**) in $CDCl_3$: δ −6.7 (double doublet, J_1 = 1199 Hz, J_2 = 6 Hz, 2 F), −26.7 (doublet, J = 1102 Hz, 2 F), −39.5 (doublet, J = 1120 Hz, 2 F), −41.2 (doublet, J = 1146 Hz, 2 F), −42.8 (doublet, J = 1152 Hz, 2 F), −44.5 (doublet, J = 1150 Hz, 2 F).

(c) $[CH_3N(PF_2)_2]_3Mo_2(CO)_5$ in $CDCl_3$: δ −33.6 (doublet, J = 1118 Hz, 4 F), −36.8 (doublet, J = 1155 Hz, 4 F), −38.9 (doublet, J = 1155 Hz, 4 F).

(d) $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ (**4**) in $CDCl_3$: δ −24.8 (doublet, J = 1075 Hz, 2 F), −33.4 (doublet, J = 1053 Hz, 2 F), −34.4 (doublet, J = 1118 Hz, 2 F), −35.9 (doublet, J = 1134 Hz, 2 F), −37.2 (doublet, J = 1150 Hz, 2 F), −39.8 (doublet, J = 1137 Hz, 2 F), −50.2 (doublet, J = 1274 Hz, 2 F), −62.7 (doublet, J = 1301 Hz, 2 F).

(e) $CH_3N(PF_2)_2Fe_2(CO)_7$ in acetone: single resonance at δ −44.2 (doublet, J = 1180 Hz).

(f) $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ in $CDCl_3$: single resonance at δ −41.5 (doublet, J = 1147 Hz).

(g) $[CH_3N(PF_2)_2]_4Fe_2CO$ in $CDCl_3$: δ 24.8 (doublet, J = 1138 Hz, 2 F), −21.0 (double doublet, J_1 = 1101 Hz, J_2 = 30 Hz, 2 F), −28.6 (double doublet, J_1 = 1074 Hz, J_2 = 25 Hz, 2 F), −37.7 (doublet, J = 1179 Hz, 6 F), −39.7 (doublet, J = 1140 Hz, 1 F), −41.7 (doublet, J = 1136 Hz, 1 F), −44.9 (doublet, J = 1106 Hz, 1 F), −48.5 (double doublet, J_1 = 1113 Hz, J_2 = 40 Hz, 1 F).

(h) $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ in $CDCl_3$: single resonance at δ −44.9 Hz (doublet, J = 1101 Hz).

(i) $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$ in $CDCl_3$: δ −31.9 (doublet, J = 1145 Hz, 4 F), −42.0 (doublet, J = 1070 Hz, 6 F).

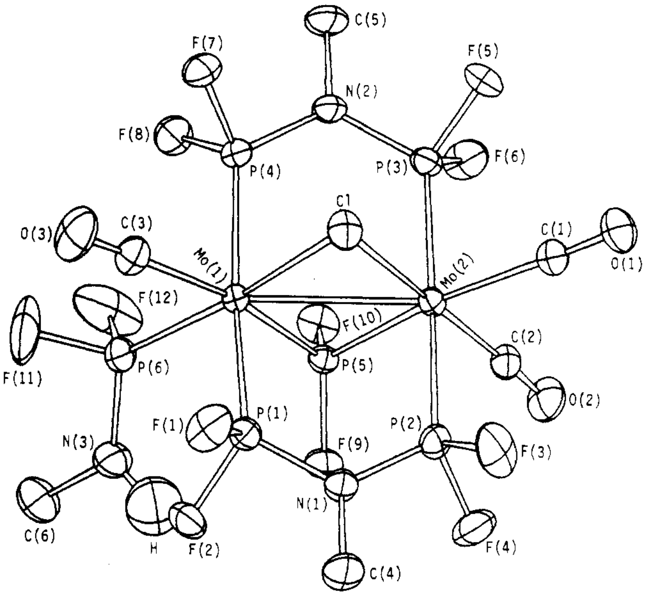

Figure 1. Drawing of the molecule of $[CH_3(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$ (**5**), showing thermal ellipsoids of 10% probability. Methyl hydrogen atoms are not shown.

X-ray Crystal Structure Analysis of $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$ (5). (a) Data. Crystal specimen: irregular chunk with maximum diameter 0.5 mm, cut from larger specimen from preparation e above. Data measurements: Oak Ridge diffractometer,[12] Mo Kα radiation (λ = 0.7107 Å) at 19–21 °C. Unit cell: monoclinic, $P2_1/c$, a = 17.546 (4) Å, b = 9.725 (2) Å, c = 14.558 (3) Å, β = 107.20 (2)°, Z = 4, d_{calcd} = 2.276 g cm^{-3} (mol wt 813.32). Recording of reflection data: θ–2θ step scans; 2θ step = 0.05°; 2θ base width = 1.8° + $\Delta(\alpha_1 - \alpha_2)$; 2-s counts in scan, 40-s background count at each end; niobium filter; three standards every 50 data (no significant deterioration); 5819 observations to 2θ = 55°. Preliminary data processing: Lorentz, polarization, and absorption corrections[13] (μ = 16.5 cm^{-1}, crystal described by 15 faces, maximum and minimum transmission coefficients 0.652 and 0.590); 5475 independent F_o^2 observations after averaging.

(b) Structure Solution and Refinement. The structure solution was obtained by direct methods by use of the program MULTAN;[14] and refinement using Fourier, difference map, and least-squares methods established the structure shown schematically in **5** and to scale in Figure 1. The presence of the unexpected chlorine atom was inferred early in the determination and confirmed by chemical analysis for chlorine, first performed at that time.

The hydrogen atom on N(3) was indicated by a difference map in a late stage of the refinement. For each methyl group, two peaks were also found that could reasonably be used to position in the model the three hydrogen atoms of an idealized methyl group (C–H distance 0.95 Å, tetrahedral angles). Each hydrogen atom was given a thermal parameter B of 10 Å^2. No hydrogen parameters were adjusted.

In the final cycle 4441 F_o^2 values were used, each with a weight of $1/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2)$ is the empirically adjusted variance[15] given by eq 1, where $\sigma_s^2(F_o^2)$ is the variance from counting statistics. The

$$\sigma^2(F_o^2) = \sigma_s^2(F_o^2) + (0.03F_o^2)^2 \qquad (1)$$

996 reflections having $F_o^2 < 2\sigma(F_o^2)$ were given zero weights, as were the 37 reflections having $2\theta < 10°$. The latter were rejected because their lower angle backgrounds had clearly not been properly measured because of the filter-edge effect. For no parameter was the final shift more than 6% of the corresponding esd; in general the shifts were very much smaller. For the 4441 observations included with nonzero weights, the values of the usual measures of goodness of fit are as follows: $R(F)$ = 0.029, $R(F^2)$ = 0.033, $R_w(F^2)$ = 0.064, σ_1 = 1.380.

The standard Oak Ridge National Laboratory crystallographic computer programs were used in this work.[16] The scattering factors used, including the anomalous contributions for Mo, P, and Cl, were from the standard source.[17]

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Table I. Fractional Coordinates of the Atoms (except Methyl Hydrogen Atoms) in $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$ (5)

	x	y	z
Mo(1)	0.311 68 (1)	0.600 40 (2)	0.841 34 (2)
Mo(2)	0.136 32 (1)	0.629 90 (3)	0.803 58 (2)
P(1)	0.313 35 (5)	0.822 58 (8)	0.775 77 (6)
P(2)	0.142 85 (5)	0.847 22 (9)	0.732 20 (7)
P(3)	0.133 85 (5)	0.413 69 (9)	0.876 72 (6)
P(4)	0.304 90 (5)	0.390 34 (8)	0.921 87 (6)
P(5)	0.207 79 (5)	0.528 95 (8)	0.709 49 (5)
P(6)	0.389 93 (6)	0.502 43 (10)	0.752 36 (7)
Cl	0.242 69 (5)	0.710 39 (9)	0.952 57 (5)
F(1)	0.365 34 (13)	0.933 22 (22)	0.845 01 (17)
F(2)	0.353 39 (12)	0.847 26 (23)	0.694 19 (16)
F(3)	0.106 75 (15)	0.975 30 (22)	0.768 66 (22)
F(4)	0.093 58 (13)	0.867 50 (24)	0.625 21 (17)
F(5)	0.095 87 (13)	0.404 28 (24)	0.960 91 (15)
F(6)	0.079 81 (12)	0.298 60 (22)	0.814 98 (15)
F(7)	0.351 38 (12)	0.384 38 (22)	1.031 69 (13)
F(8)	0.343 63 (12)	0.256 05 (20)	0.895 52 (15)
F(9)	0.195 88 (11)	0.579 35 (20)	0.603 40 (12)
F(10)	0.193 69 (12)	0.372 73 (18)	0.680 28 (13)
F(11)	0.479 91 (16)	0.497 17 (48)	0.802 85 (18)
F(12)	0.383 49 (24)	0.342 64 (27)	0.734 60 (25)
O(1)	−0.004 81 (17)	0.716 77 (32)	0.890 32 (20)
O(2)	0.001 30 (14)	0.550 95 (30)	0.616 90 (18)
O(3)	0.479 95 (16)	0.665 92 (34)	0.992 09 (23)
N(1)	0.230 31 (15)	0.912 54 (25)	0.731 41 (19)
N(2)	0.217 42 (15)	0.324 81 (27)	0.923 70 (18)
N(3)	0.384 71 (20)	0.548 95 (37)	0.645 60 (22)
C(1)	0.045 24 (20)	0.689 19 (37)	0.859 10 (25)
C(2)	0.049 73 (18)	0.578 51 (34)	0.686 21 (24)
C(3)	0.420 41 (21)	0.641 44 (37)	0.939 64 (26)
C(4)	0.234 01 (22)	1.051 98 (36)	0.689 47 (28)
C(5)	0.214 12 (24)	0.187 89 (38)	0.969 59 (28)
C(6)	0.435 60 (27)	0.497 15 (51)	0.588 46 (30)
H(N3)	0.349 53	0.620 75	0.612 21

The final coordinates of all atoms except the nine methyl hydrogen atoms are given in Table I. A table of anisotropic thermal parameters, a table of hydrogen atom coordinates, and a listing of observed and calculated structure factor squares with standard errors are available as supplementary material.

Results

Preparative and Spectroscopic Studies. The initial product from the reaction of *fac*-$(CH_3CN)_3Mo(CO)_3$ (**1**) with $CH_3N(PF_2)_2$ is white, air-stable, volatile crystalline *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ (**3**), which was not observed in our earlier work[3] in which olefin–metal carbonyl derivatives were used as the source of $M(CO)_n$ moieties for reactions with $RN(PF_2)_2$ ligands. Nevertheless, we have now shown that reactions of (triene)$Mo(CO)_3$ derivatives (triene = cycloheptatriene, η^6-cyclooctatetraene) with excess $CH_3N(PF_2)_2$ under mild conditions also give *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ (**3**) as the major metal carbonyl product.

The spectroscopic properties of *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ agree with the proposed structure **3**. The infrared $\nu(CO)$ spectrum has the correct pattern for a fac-$L_2L'M(CO)_3$ derivative. The 6-cm^{-1} splitting of the E mode arises from destruction of the C_3 axis of a simple *fac*-$L_3M(CO)_3$ derivative by nonequivalence of L and L′ [here L = bidentate $CH_3N(PF_2)_2$ and L′ = monodentate $CH_3N(PF_2)_2$]. The presence of two nonequivalent types of $CH_3N(PF_2)_2$ ligands is indicated most clearly by the proton and carbon-13 NMR spectra. In the former, the double doublet centered at δ 2.94 and the triplet centered at δ 2.75 can be assigned to the monodentate and bidentate $CH_3N(PF_2)_2$ ligands, respectively, by comparison with the spectra of related compounds.[3] Similarly, in the carbon-13 NMR spectrum the methyl resonances at δ 25.3 and 29.1 can be assigned to the monodentate and bidentate $CH_3N(PF_2)_2$ ligands, respectively. The carbon-13 NMR spectrum also indicates the nonequivalence of carbonyl groups trans to PF_2 groups of monodentate (δ 206) and bidentate (δ 212.0) $CH_3N(PF_2)_2$ ligands.

Reaction of *fac*-$(CH_3CN)_3Mo(CO)_3$ with $CH_3N(PF_2)_2$ in boiling acetonitrile leads to the formation of $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ (**4**) as the only metal carbonyl derivative, although the reaction time is rather critical in order to obtain maximum yields (~33%). This preparation of $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ (**4**) is much better than the reported[3] preparation from the cycloheptatriene complex $C_7H_8Mo(CO)_3$ and $CH_3N(PF_2)_2$, which gives only a 3% yield after a difficult separation from concurrently produced $[CH_3N(PF_2)_2]_5Mo_2CO$ (**6**). The formation of (**6**) as the major metal carbonyl product from the reaction of $C_7H_8Mo(CO)_3$ with $CH_3N(PF_2)_2$ in boiling methylcyclohexane is consistent with our present observation that pure $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ (**3**) reacts with excess $CH_3N(PF_2)_2$ in boiling heptane to give $[CH_3N(PF_2)_2]_5Mo_2CO$ (**6**) in nearly quantitative yield.

In our earlier work[4] we used the reaction of *fac*-$(CH_3CN)_3Mo(CO)_3$ with $C_6H_5N(PF_2)_2$ in acetonitrile for 2 days at 40–45 °C to prepare the cage complex $P[N(C_6H_5)PF_2]_3Mo(CO)_3$ (**2**). A similar reaction of *fac*-$(CH_3CN)_3Mo(CO)_3$ with $CH_3N(PF_2)_2$ gave a volatile brown-red solid, whose structure could not be elucidated by simple analytical and spectroscopic methods. However, a single-crystal X-ray diffraction analysis indicates this solid to be $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$ (**5**), which in terms of its stoichiometry may be regarded as an HCl adduct of the coordinatively unsaturated fragment $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NCH_3)(PF_2)$.

Since no chlorinated solvents were used in the preparation and isolation of **5**, the only possible source of chlorine is the $CH_3N(PF_2)_2$ ligand, which was made by fluorination of $CH_3N(PCl_2)_2$ with SbF_3 in a hydrocarbon solvent. The observed yield of **5** requires the presence of 0.2% HCl in the $CH_3N(PF_2)_2$ ligand, certainly an impurity level that can escape detection by the NMR and mass spectrometry used to check samples of $CH_3N(PF_2)_2$ before use. In a search for more rational preparations of **5**, samples of $[CH_3N(PF_2)_2]_3Mo_2(CO)_5$ and *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ (**3**) were treated with excess HCl gas in acetonitrile solution. However, such reactions led to complete decomposition with no evidence for the formation of significant quantitites of the brown-red compound **5** at any intermediate stage. This, no doubt, is just another example of the susceptibility of the phosphorus–nitrogen bonds in aminophosphines to cleavage by strong acids.

These experiments indicate that a mild source of stoichiometric quantities of HCl is needed for the preparation of **5**. In this connection reactions of *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ (**3**), $[CH_3N(PF_2)_2]_3Mo_2(CO)_5$, and $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ (**4**) with the HCl sources $[(C_2H_5)_3NH]Cl$ and $CH_3CN{\cdot}2HCl$ in stoichiometric quantities were investigated. The best yields of **5** were obtained from $[CH_3N(PF_2)_2]_3Mo_2(CO)_5$ and $[(C_2H_5)_3NH]Cl$, a reaction that can have the following relatively simple stoichiometry:

$$[CH_3N(PF_2)_2]_3Mo_2(CO)_5 + [(C_2H_5)_3NH]Cl \rightarrow [CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl) + (C_2H_5)_3N + 2CO$$

Thus, the effect of the limited quantities of HCl in this reaction is rupture of one of the phosphorus–nitrogen bonds in one of the bridging $CH_3N(PF_2)_2$ ligands in $[CH_3N(PF_2)_2]_3Mo_2(CO)_5$ to form separate PF_2 (bridging) and CH_3NHPF_2 (terminal) units.

The spectroscopic properties of $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$ are consistent with the structure (**5**) established by X-ray crystallography. The solution infrared spectrum exhibits three reasonably strong terminal $\nu(CO)$ frequencies consistent with an unsymmetrical tricarbonyl structure having only terminal carbonyl groups. The infrared

Table II. Bond Lengths (Å) in the Molecule of $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$ (5)

Mo(1)-Mo(2)	2.9750 (3)		
Mo(1)-Cl	2.5280 (8)	Mo(2)-Cl	2.5311 (8)
Mo(1)-P(1)	2.3658 (8)	Mo(2)-P(2)	2.3727 (9)
Mo(1)-P(4)	2.3757 (8)	Mo(2)-P(3)	2.3630 (8)
Mo(1)-P(5)	2.3283 (8)	Mo(2)-P(5)	2.3297 (8)
Mo(1)-P(6)	2.3500 (9)	Mo(2)-C(1)	2.0746 (33)
Mo(1)-C(3)	2.0572 (36)	Mo(2)-C(2)	1.9855 (33)
P(1)-F(1)	1.5691 (21)	P(2)-F(3)	1.5599 (22)
P(1)-F(2)	1.5668 (21)	P(2)-F(4)	1.5544 (23)
P(4)-F(7)	1.5662 (19)	P(3)-F(5)	1.5614 (20)
P(4)-F(8)	1.5712 (20)	P(3)-F(6)	1.5671 (21)
P(6)-F(11)	1.5326 (27)	P(5)-F(9)	1.5743 (18)
P(6)-F(12)	1.5738 (29)	P(5)-F(10)	1.5772 (18)
P(1)-N(1)	1.6579 (26)	P(2)-N(1)	1.6640 (26)
P(4)-N(2)	1.6694 (26)	P(3)-N(2)	1.6648 (27)
P(6)-N(3)	1.5951 (30)	C(1)-O(1)	1.1339 (38)
C(3)-O(3)	1.1221 (39)	C(2)-O(2)	1.1424 (36)
C(4)-N(1)	1.4964 (39)	C(5)-N(2)	1.4985 (40)
C(6)-N(3)	1.4771 (43)		
N(3)-H(N3)	0.96		

Table III. Angles (deg) in the Molecule of $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$ (5)

Mo(1)-Cl-Mo(2)	72.04 (02)	Mo(1)-P(5)-Mo(2)	79.39 (02)
Cl-Mo(1)-Mo(2)	54.03 (02)	Cl-Mo(2)-Mo(1)	53.93 (02)
Cl-Mo(1)-P(5)	104.35 (03)	Cl-Mo(2)-P(5)	104.21 (03)
Cl-Mo(1)-P(1)	86.41 (03)	Cl-Mo(2)-P(2)	88.91 (03)
Cl-Mo(1)-P(4)	86.81 (03)	Cl-Mo(2)-P(3)	89.78 (03)
Cl-Mo(1)-P(6)	173.26 (03)	Cl-Mo(2)-C(2)	176.36 (10)
Cl-Mo(1)-C(3)	89.63 (10)	Cl-Mo(2)-C(1)	92.17 (10)
P(5)-Mo(1)-P(1)	92.29 (03)	P(5)-Mo(2)-P(2)	90.79 (03)
P(5)-Mo(1)-P(4)	90.51 (03)	P(5)-Mo(2)-P(3)	88.55 (03)
P(5)-Mo(1)-P(6)	82.37 (03)	P(5)-Mo(2)-C(2)	78.22 (09)
P(5)-Mo(1)-C(3)	166.01 (10)	P(5)-Mo(2)-C(1)	163.08 (10)
P(5)-Mo(1)-Mo(2)	50.33 (02)	P(5)-Mo(2)-Mo(1)	50.28 (02)
P(1)-Mo(1)-Mo(2)	88.45 (02)	P(2)-Mo(2)-Mo(1)	89.17 (02)
P(4)-Mo(1)-Mo(2)	88.52 (02)	P(3)-Mo(2)-Mo(1)	89.24 (02)
P(1)-Mo(1)-P(4)	173.12 (03)	P(2)-Mo(2)-P(3)	178.35 (03)
P(1)-Mo(1)-P(6)	93.95 (03)	P(2)-Mo(2)-C(2)	88.34 (10)
P(4)-Mo(1)-P(6)	92.64 (03)	P(3)-Mo(2)-C(2)	93.01 (10)
P(6)-Mo(1)-Mo(2)	132.69 (03)	C(2)-Mo(2)-Mo(1)	128.40 (09)
P(1)-Mo(1)-C(3)	89.08 (10)	P(2)-Mo(2)-C(1)	93.76 (10)
P(4)-Mo(1)-C(3)	89.72 (10)	P(3)-Mo(2)-C(1)	87.30 (10)
P(6)-Mo(1)-C(3)	83.65 (10)	C(1)-Mo(2)-C(2)	85.62 (13)
C(3)-Mo(1)-Mo(2)	143.66 (10)	C(1)-Mo(2)-Mo(1)	145.95 (10)
F(1)-P(1)-F(2)	94.37 (13)	F(3)-P(2)-F(4)	94.48 (16)
F(7)-P(4)-F(8)	94.95 (12)	F(5)-P(3)-F(6)	94.70 (13)
F(11)-P(6)-F(12)	93.41 (21)	F(9)-P(5)-F(10)	94.05 (11)
Mo(1)-P(1)-N(1)	121.65 (09)	Mo(2)-P(2)-N(1)	120.47 (09)
Mo(1)-P(4)-N(2)	121.10 (09)	Mo(2)-P(3)-N(2)	121.05 (09)
F(1)-P(1)-Mo(1)	116.19 (09)	F(3)-P(2)-Mo(2)	119.02 (10)
F(2)-P(1)-Mo(1)	120.50 (09)	F(4)-P(2)-Mo(2)	117.86 (10)
F(7)-P(4)-Mo(1)	116.65 (09)	F(5)-P(3)-Mo(2)	118.35 (10)
F(8)-P(4)-Mo(1)	120.38 (08)	F(6)-P(3)-Mo(2)	117.75 (08)
F(1)-P(1)-N(1)	99.52 (13)	F(3)-P(2)-N(1)	99.54 (13)
F(2)-P(1)-N(1)	99.39 (13)	F(4)-P(2)-N(1)	100.68 (13)
F(7)-P(4)-N(2)	99.98 (12)	F(5)-P(3)-N(2)	100.12 (13)
F(8)-P(4)-N(2)	98.79 (13)	F(6)-P(3)-N(2)	100.07 (13)
P(1)-N(1)-P(2)	120.12 (15)	P(3)-N(2)-P(4)	119.83 (15)
P(1)-N(1)-C(4)	119.86 (22)	P(3)-N(2)-C(5)	119.94 (22)
P(2)-N(1)-C(4)	120.01 (22)	P(4)-N(2)-C(5)	120.21 (22)
F(11)-P(6)-Mo(1)	115.85 (12)	F(9)-P(5)-Mo(1)	124.08 (08)
F(12)-P(6)-Mo(1)	117.75 (11)	F(9)-P(5)-Mo(2)	120.48 (08)
N(3)-P(6)-Mo(1)	123.20 (12)	F(10)-P(5)-Mo(1)	122.13 (08)
N(3)-P(6)-F(11)	103.36 (18)	F(10)-P(5)-Mo(2)	119.71 (08)
N(3)-P(6)-F(12)	98.01 (18)	Mo(2)-C(1)-O(1)	177.51 (33)
C(6)-N(3)-P(6)	125.58 (27)	Mo(2)-C(2)-O(2)	177.74 (29)
H(N3)-N(3)-P(6)	123	Mo(1)-C(3)-O(3)	178.59 (35)
C(6)-N(3)-H(N3)	111		

spectrum also exhibits a ν(NH) frequency at 3430 cm^{-1}, close to the ν(NH) frequency of 3435 cm^{-1} found in $[CH_3(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$, which also contains terminal CH_3NHPF_2 ligands.[18] The carbon-13 NMR spectrum exhibits methyl resonances at δ 27.6 and 25.7 that may be assigned to the CH_3NHPF_2 ligand and the two bridging $CH_3N(PF_2)_2$ ligands, respectively, on the basis of their apparent relative intensities. The fluorine-19 NMR spectrum of **5** exhibits six resonances, all with doublet splittings in the range 1100–1200 Hz corresponding to the $|{}^1J(\text{P–F})| - |{}^3J(\text{P–F})|$ coupling constant (derived from the quantity "2*K*" in the literature[19] by realizing that ${}^1J$(P–F) and ${}^3J$(P–F) have opposite signs). The fluorine resonances centered at δ −39.5, −41.2, −42.8, and −44.5 can be assigned to the eight fluorines of the two bridging of $CH_3N(PF_2)_2$ ligands, split into four pairs because of the relatively low symmetry of these systems; similar chemical shifts and coupling constants are observed for all of the fluorine resonances in $[C_3N(PF_2)_2]_3Mo_2(CO)_5$, which necessarily belong to bridging $CH_3N(PF_2)_2$ ligands. The fluorine resonance in the NMR spectrum of **5** at −26.7 can be assigned to the terminal CH_3NHPF_2 ligand on the basis of the similarity of its relative chemical shift to that of the CH_3NHPF_2 fluorines in $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$. The lowest field fluorine resonance in the NMR spectrum of 5 at δ 6.7 may be assigned to the bridging PF_2 group; a similar even lower field (δ 24.8) fluorine resonance is found in $(CO)Fe_2(PF_2NCH_3)[\mu\text{-}CH_3N(PF_2)_2]_3(\mu\text{-}PF_2)$, which also has a bridging PF_2 group and a terminal unprotonated PF_2NCH_3 group.[20] The phosphorus-31 NMR spectrum of **5** is hopelessly complicated because of the large numbers of nonequivalent phosphorus atoms and possible phosphorus–fluorine and phosphorus–phosphorus coupling constants.

The increased availability of $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ (**4**) by the new preparative method described in this paper has allowed us to measure its fluorine-19 NMR spectrum. The resonances centered at δ −50.2 and −62.7 stand out by having splittings around 1300 Hz and can be assigned to the four fluorines in the chelating (biligate monometallic) $CH_3N(PF_2)_2$ ligand, which are split into two pairs because of the asymmetry of **4**. The observed phosphorus–fluorine coupling constants of 1274 and 1301 Hz for the two types of fluorine atoms in the chelating $CH_3N(PF_2)_2$ ligand in **4** are close to the reported[3] $|{}^1J(\text{P–F})|$ of 1291 Hz for the chelating $CH_3N(PF_2)_2$ ligand in $CH_3N(PF_2)_2MO(CO)_4$. The remaining six resonances (δ −24.8, −33.4, −35.9, −37.2, −39.8) can be assigned to the 12 fluorine atoms of the three bridging $CH_3N(PF_2)_2$ ligands in **4**.

Structure of $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$ (5). The geometry of **5** is shown pictorially to scale in Figure 1; the details are specified by the bond lengths and angles in Tables II and III, respectively, and in the description of various least-squares best planes included in the supplementary material.

Although all of the different terminal and bridging ligands in **5** have been known in various combinations in transition-metal complexes, the particular combination in this quadruply bridged structure is unique. The combination of a bridging PF_2 group and a terminal PF_2NHCH_3 group (with no H on the N atom) was already known from the X-ray analysis of the binuclear complex $(CO)Fe_2(PF_2NCH_3)[\mu\text{-}CH_3N(PF_2)_2]_3(\mu\text{-}PF_2)$.[20] In the preparation of this iron compound and in that of **5**, a $CH_3N(PF_2)_2$ molecule cleaves to form two ligands. In compound **5** a Cl atom from HCl takes the place of one of the bridging $CH_3N(PF_2)_2$ ligands in the iron complex, and its accompanying H atom is positioned on atom N(3) of the PF_2NCH_3 group. There is also an additional CO group on each metal atom. The bonding pattern, including the Mo–Mo bond, gives each Mo the effective atomic number of xenon. Presumably the ligand PF_2NHCH_3 is a two-electron donor to Mo(1), and the PF_2 group and the Cl atom are both

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three-electron donors, one donating one electron to Mo(1) and two to Mo(2) and the other donating one to Mo(2) and two to Mo(1). The Mo–Mo distance, 2.975 Å, is clearly a bonding distance, since the Mo–Mo bond in $[(C_5H_5)Mo(CO)_3]_2$, which is not supported by any bridging ligands, is known[21] to have the considerably greater length of 3.235 (1) Å.

As is evident from Figure 1 and Table III, for each Mo atom the coordination geometry is that of a slightly distorted octahedron, if the Mo–Mo bond is excluded from consideration. The two octahedra share the edge defined by the Cl···P(5) line. The Mo–Mo bond approximately bisects the angles Cl–Mo(1)–P(5) and Cl–Mo(2)–P(5), which at 104.4 and 104.2° are the angles in the octahedra that are distorted farthest from ideal 90° angles.

The two Mo–Cl bond lengths, 2.528 (1) and 2.531 (1) Å, are significantly greater than other Mo–Cl bridge bond lengths that have been reliably determined (cf. 2.465 (1) – 2.499 (1) Å in $[Mo_2Cl_8H]^{3-}$ ions of three compounds,[22,23] 2.487 (12) Å in $Cs_3Mo_2Cl_9$,[24] 2.467 (3) Å in Mo_6Cl_{12},[25] 2.478 (8) Å in $(C_5H_5NH)_3[(Mo_6Cl_7S)Cl_6]$[26]). In all of these other binuclear Mo complexes the bridging chlorine atoms are trans to other chlorine atoms, whereas in **5** the bridging chlorine is trans to the C(2)–O(2) carbonyl ligand and to the PF_2NHCH_3 group.

The Mo(2)–C(2) bond length, 1.986 (3) Å, is distinctly shorter than the Mo(1)–C(3) and Mo(2)–C(1) lengths, 2.057 (4) and 2.075 (3) Å. The relative shortening is clearly related to the fact that the C(2)–O(2) carbonyl is the only one of the three carbonyl ligands that is not trans to another strong π-acceptor ligand (CO or PF_2). Since the ligand PF_2NHCH_3 is, like the C(2)–O(2) group, trans to the bridging chlorine, the bond Mo(1)–P(6) might also be expected to be notably short compared with the other Mo–P bonds; but it has the length 2.350 (1) Å, slightly shorter than the Mo–P bonds to the $CH_3N(PF_2)_2$ ligands and slightly longer than the Mo–P bonds to the bridging PF_2 group. We consider that the tendency toward shortening arising from the trans position of P(6) relative to the Cl bridge is compensated by a reduction of π acidity of P(6) relative to that of the other P atoms because P(6) uses π-bonding capacity in forming the bond P(6)–N(3), which from its bond length of 1.595 (3) Å has about the same double-bond character as the corresponding P–N bond in the terminal PF_2NCH_3 ligand of the complex $(CO)Fe(PF_2NCH_3)[\mu\text{-}CH_3N(PF_2)_2]_3(\mu\text{-}PF_2)$. The latter P–N bond, 1.59 (1) Å, is formally a double bond. Thus, the structure $F_2P^-{=}^+NHCH_3$ is apparently a major contributor to the resonance hybrid of the ligand PF_2NHCH_3.

The average length 1.664 Å of the P–N bonds in the $CH_3N(PF_2)_2$ ligands is distinctly less than the value 1.76–1.80 Å expected from the sum of the covalent radii,[27,28] suggesting that these bonds also have substantial double-bond character. That the latter is true is also suggested by the fact that each N atom of the two $CH_3N(PF_2)_2$ ligands has essentially exact trigonal-planar valence geometry. Atoms N(1) and N(2) are displaced only 0.006 (3) and 0.012 (3) Å from the planes of their attached P and C atoms, and the valence angles at N(1) and N(2) are all within one standard error of 120°. The roughly positioned atom H(N3) is 0.07 Å from the plane of P(6), N(3), and C(6).

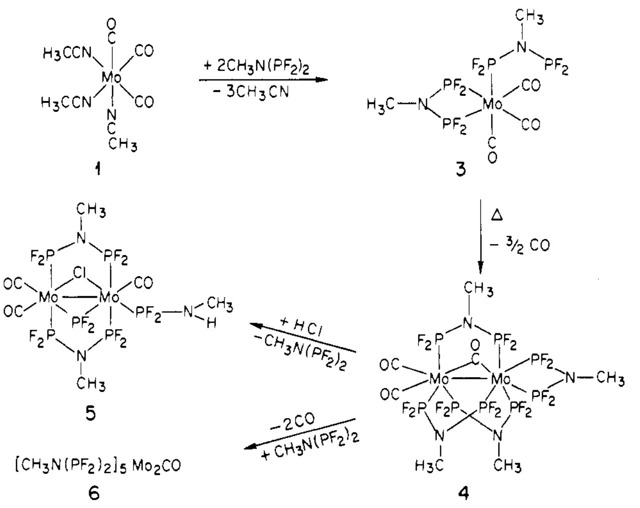

Figure 2. Proposed scheme for the reaction of *fac*-$(CH_3CN)_3Mo(CO)_3$ with $CH_3N(PF_2)_2$.

For describing the shape of the fused-ring structure in **5**, the best least-squares planes were calculated for various approximately plane groups. The maximum deviations (Å) from the planes are as follows: 0.0086 (3) for the group Mo(1), Mo(2), Cl, P(5) (plane a); 0.034 (1) Å for Mo(1), Mo(2), P(1), P(2), N(1) (plane b); 0.048 (1) for Mo(1), Mo(2), P(3), P(4), N(2) (plane c); 0.094 (1) for Mo(1), Mo(2), P(1), P(2), P(3), P(4), N(1), N(2) (plane d). The interplane angles a–b, a–c, a–d, and b–c are 92.66 (3), 90.42 (3), 91.06 (3), and 3.09 (4)°.

The data above for planes b and c make it clear that the two five-membered rings are among the relatively few essentially planar five-membered rings including a metal–metal pair and a bis(phosphine) ligand that have had their structures determined.[28,29] For **5** the shape parameters ϕ, ρ, and D(P···P) used by Schubert et al.[28] in discussing such rings are 2.65 (3)°, 1.71 (15)°, and 2.879 (1) Å for the ring including N(1) and 3.24 (3)°, 3.23 (18)°, and 2.885 (1) Å for the ring including N(2).

Discussion

The experimental data described in this paper support the reaction sequence outlined in Figure 2 for the reaction of *fac*-$(CH_3CN)_3Mo(CO)_3$ with $CH_3N(PF_2)_2$. In the initial step the three acetonitrile ligands in *fac*-$(CH_3CN)_3Mo(CO)_3$ (**1**) are stereospecifically replaced by two $CH_3(PF_2)_2$ ligands to form *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ (**3**). Since these two $CH_3N(PF_2)_2$ ligands must occupy three coordination positions in *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$, one ligand must be bidentate and the other monodentate, in accord with the spectroscopic properties of this complex. The complex *fac*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$ (**3**) next dimerizes to $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ (**4**) with loss of half of its carbonyl groups. A driving force for the dimerization is the stability of the $[CH_3N(PF_2)_2]_3Mo_2$ unit having three five-membered chelate rings with the Mo–Mo edge in common. In this connection the cobalt chemistry of $CH_3N(PF_2)_2$ appears also to be dominated by derivatives containing a very stable $[CH_3N(PF_2)_2]_3Co_2$ unit.[18,30]

In the absence of an HCl source or excess $CH_3N(PF_2)_2$ ligand the binuclear complex $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ (**4**)

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can be the ultimate product from the reaction between *fac*-$(CH_3CN)_3Mo(CO)_3$ and $CH_3N(PF_2)_2$. However, in the presence of limited quantities of hydrogen chloride the course of this reaction can be diverted to $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$ (**5**). In addition, $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ has been shown to react readily with excess $CH_3N(PF_2)_2$ around 100 °C with replacement of two of its three carbonyl groups by a $CH_3N(PF_2)_2$ ligand to give $[CH_3N(PF_2)_2]_5Mo_2CO$ (**6**). In the absence of X-ray crystallographic structural data, we are reluctant to speculate on the structure of $[CH_3N(PF_2)_2]_5Mo_2CO$. However, the presence of an extremely low-field resonance at δ +43.6 (doublet, J = 1111 Hz) in the otherwise very complicated fluorine–19 NMR spectrum of this complex supports our earlier suggestion[3] that $[CH_3N(PF_2)_2]_5Mo_2CO$ has a bridging PF_2 group like $[CH_3N(PF_2)_2]_2Mo_2(CO)_3(PF_2NHCH_3)(PF_2)(Cl)$ (**5**) and $(CO)Fe_2(PF_2NCH_3)[\mu\text{-}CH_3N(PF_2)_2]_3(\mu\text{-}PF_2)$,[20] which also have relatively low-field fluorine-19 resonances.

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Registry No. **1**, 17731-95-2; **3**, 89460-03-7; **4**, 79721-57-6; **5**, 89346-98-5; **6**, 79746-02-4; $C_7H_8Mo(CO)_3$, 12125-77-8; $C_8H_8Mo(CO)_3$, 12108-93-9; η^4-$C_8H_8Mo(CO)_3(PF_2)_2NCH_3$, 89346-99-6; $[CH_3N(PF_2)_2]_3Mo_2(CO)_5$, 79721-55-4; $[(C_2H_5)_3NH]Cl$, 554-68-7; $CH_3N(PF_2)_2$, 17648-18-9; CH_3CN, 75-05-8; Mo, 7439-98-7.

Supplementary Material Available: For compound **5**, listings of anisotropic thermal parameters, hydrogen atom coordinates, least-squares best planes, and observed and calculated values of F^2 with standard errors of the former (27 pages). Ordering information is given on any current masthead page.

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Synthesis, Spectroscopic Characterization, and Magnetic Properties of Unusual 3,5-Dialkyl-1,2,4-triazole Compounds Containing N-Bridging Isothiocyanato Ligands. X-ray Structure of Trinuclear Bis[(μ-thiocyanato-N)bis(μ-3,5-diethyl-1,2,4-triazole-N^1,N^2)bis(thiocyanato-N)(3,5-diethyl-1,2,4-triazole-N^1)nickel(II)-N,N^1,$N^{1'}$]nickel(II) Dihydrate

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The synthesis and characterization of a series of unusual trimeric and polymeric coordination compounds containing 3,5-dialkyl-1,2,4-triazoles are described. The compounds have the general formulas $M_3(LH)_6(NCS)_6(H_2O)_2$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+}; LH = 3,5-dimethyl-1,2,4-triazole and 3,5-diethyl-1,2,4-triazole), $Zn(NCS)(L^-)$ (L^- is the deprotonated ligand LH), and $Cd(NCS)_2(LH)$. The Zn and Cd compounds are polymeric, containing bridging triazole ligands and (bridging) thiocyanato ligands. The Mn, Co, and Ni compounds are mutually isomorphous and contain the linear trinuclear unit $(NCS)_2(LH)M(LH)_2(NCS)M(LH)_2(NCS)M(LH)(NCS)_2$, as deduced from a single-crystal X-ray analysis of the compound with M = Ni(II) and the 3,5-diethyl derivative. The title compound crystallizes in the orthorhombic space group *Pbca* with a = 14.447 (8) Å, b = 23.047 (8) Å, and c = 18.613 (9) Å and Z = 4. The structure was solved with use of Mo Kα diffractometer data and standard heavy-atom and least-squares refinement techniques. Final residuals are 0.058 (R) and 0.063 (R_w). The trinuclear cations all have Ni(II) atoms with a NiN_6 chromophore (Ni–N distances are 2.02 (1)–2.18 (1) Å). The usual structural features are the N-bonding bridging NCS groups between the Ni(II) atoms and the 1,2-bridging triazole ligands (two between each pair of nickel ions). The magnetic-exchange interactions between the metal ions are small but significant. The Mn and Co compounds are antiferromagnetically coupled, but—surprisingly—the nickel trimers are ferromagnetic. The results are discussed on the basis of the structure determined.

Introduction

Triazoles, and in particular 1,2,4-triazole, are versatile ligands that show a very interesting coordination chemistry.[1-5] After deprotonation all three nitrogens have lone pairs available and coordination to metal ions through several modes has been observed. Unsubstituted 1,2,4-triazole is known to yield a chain-type structure through 1,2-bridging in $CuCl_2(trH)$ (trH = 1,2,4-triazole).[2] Changing the anion to NCS^- has led to the discovery of a new class of two-dimensional structures, $M(NCS)_2(trH)_2$, with very interesting magnetic properties.[3] When the experimental conditions were changed, a second isomer was observed, which turned out to be trimeric.[4] Prevention of the deprotonation at N(4) by alkylation led Vos[5] to the discovery of a large group of dimeric and trimeric species, all having the $M(Rtr)_3M$ or the $M(Rtr)_3M(Rtr)_3M$ unit (Rtr = 4-alkyl-1,2,4-triazole).

The use of thiocyanate anions proved to be useful in the above-mentioned studies, and in all cases N-bonded NCS^- groups were found. Thiocyanate is known to be versatile and ambidentate in its coordination behavior,[6] and many other modes of coordination have been reported. In our previous studies we found that bridging occurs between two Cd(II) ions, using only the nitrogens of the NCS ions.[7] Because of the unusual bridging mode of NCS and our interest in the magnetic exchange between transition-metal ions through small

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