Further experiments are in progress to prove the existence of soft modes and thus support our view of the nature of the phase transitions.

Acknowledgment. We thank Dr. Nohl and Professor Andersen for many valuable discussions. We are also indebted to Dr. Deiseroth and Mrs. Peters for their help with the structure investigations.

Appendix

We divide all atoms in an unit cell of the l phase ($P2_1cn$) into groups of four atoms that are related to each other by a twofold screw axis or by a pseudoinversion center. At temperature T, the nth group contains four atoms at $(\pm X_n + (\Delta x_n(T)/2), \pm Y_n + (\Delta y_n(T)/2), \pm Z_n + (\Delta z_n(T)/2))$ and $(\pm X_n + (\Delta x_n(T)/2) + {}^1/_2, \pm Y_n - (\Delta y_n(T)/2), \pm Z_n - (\Delta z_n(T)/2) + {}^1/_2)$. When the structure has a true inversion center (then the symmetry is $Pccn$), $\Delta x_n(T)$, $\Delta y_n(T)$, and $\Delta z_n(T)$ are all 0; they increase as the structure deviates from $Pccn$ symmetry, and, in Nb_6I_{11} and HNb_6I_{11}, they are much smaller than 1. The structure factors of the $0kl$ reflections at temperature T are calculated to be $F_{0kl}(T) = 4i\sum_n P_n \sin [2\pi(k\Delta y_n(T) + l\Delta z_n(T))]$ for l = odd and $F_{0kl}(T) = 4\sum_n P_n \cos [2\pi(k\Delta y_n(T) + l\Delta z_n(T))]$ for l = even ($P_n = f_n \cos [2\pi(kY_n + lZ_n)]$).

If all atoms move linearly and uniformly, the ratios $\Delta x_n(T)/\Delta x_n(T_0)$, $\Delta y_n(T)/\Delta y_n(T_0)$, and $\Delta z_n(T)/\Delta z_n(T_0)$ are all equal to the parameter $q(T)$ (see Results). Then we get the following approximation: $F_{0kl} \approx iAq(T)$ for l = odd [$A = 4\sum_n P_n \cdot 2\pi(k\Delta y_n(T_0) + l\Delta y_n(T_0))$]; $F_{0kl} \approx B - Cq(T)^2$ for l = even ($B = 4\sum_n P_n$, $C = 4\sum_n P_n[2\pi(k\Delta y_n(T_0) + l\Delta z_n(T_0)]^2$); for the reflections with odd l, $r_{0kl} = F_{0kl}(T)/F_{0kl}(T_0) \approx q(T)$.

Registry No. Nb_6I_{11}, 12196-47-3; HNb_6I_{11}, 12339-12-7.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (76 pages). Ordering information is given on any current masthead page.

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Metal Complexes of Fluorophosphines. 10. Mononuclear and Binuclear Chromium, Molybdenum, and Tungsten Carbonyl Derivatives of (Alkylamino)bis(difluorophosphines)[1-3]

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Reactions of the (norbornadiene)metal tetracarbonyls $C_7H_8M(CO)_4$ (M = Cr, Mo, and W) with the ligands $RN(PF_2)_2$ (R = CH_3 and C_6H_5) give either the chelates $RN(PF_2)_2M(CO)_4$ or the monoligate monometallic complexes $[RN(PF_2)_2]_2M(CO)_4$ (M = Cr, trans isomer; M = Mo and W, cis isomer) depending on the reaction conditions. Reaction of $CH_3N(PF_2)_2Cr(CO)_4$ with $C_6H_5N(PF_2)_2$ results in opening of the four-membered chelate ring to give *trans*-$[CH_3N(PF_2)_2][C_6H_5N(PF_2)_2]Cr(CO)_4$ containing two different monoligate monometallic $RN(PF_2)_2$ ligands. Reactions of the cycloheptatriene derivative $C_7H_8Cr(CO)_3$ with the ligands $RN(PF_2)_2$ (R = CH_3 and C_6H_5) give *mer*-$[RN(PF_2)_2]_2Cr(CO)_3$ containing one monodentate and one bidentate ligand and the binuclear complex *mer*-$[C_6H_5N(PF_2)_2]_3Cr_2(CO)_6$. Pyrolysis of the molybdenum complexes $RN(PF_2)_2Mo(CO)_4$ at 100–120 °C results in extensive rearrangement to give the binuclear complexes $[RN(PF_2)_2]_3Mo_2(CO)_5$ (R = CH_3 and C_6H_5) containing three biligate bimetallic $RN(PF_2)_2$ ligands. The chromium and tungsten analogues $[CH_3N(PF_2)_2]_3M_2(CO)_5$ (M = Cr and W) can be obtained by photolysis of the corresponding metal hexacarbonyls with $CH_3N(PF_2)_2$ in a 1–1.5/1 ligand/metal mole ratio. Pyrolysis or photolysis of mixtures of the $RN(PF_2)_2$ ligands and the metal carbonyls in a 2–2.5/1 ligand/metal mole ratio gives mixtures of the binuclear complexes $[CH_3N(PF_2)_2]_4M_2(CO)_3$ and $[CH_3N(PF_2)_2]_5M_2CO$ in the case of $CH_3N(PF_2)_2$ (M = Mo and W) and the binuclear complexes $[C_6H_5N(PF_2)_2]_4Mo_2(CO)_3$ and $[C_6H_5N(PF_2)_2]_5Mo_2(CO)_2$ in the case of $C_6H_5N(PF_2)_2$ (M = Mo). The infrared ν(CO) frequencies in the $[RN(PF_2)_2]_4M_2(CO)_3$ complexes indicate one bridging and two terminal CO groups. However, the infrared spectra of the complexes $[CH_3N(PF_2)_2]_5M_2CO$ (M = Mo and W) and $[C_6H_5N(PF_2)_2]_5Mo_2(CO)_2$ indicate the presence of only terminal CO groups. The proton and carbon-13 NMR spectra of the $CH_3N(PF_2)_2$ complexes reported in this paper clearly distinguish between monodentate and bidentate $CH_3N(PF_2)_2$ ligands. The phosphorus-31 and fluorine-19 NMR spectra of the $RN(PF_2)_2$ complexes have been used to estimate the coupling constants $|^1J(PF)|$, $|^2J(PP)|$, $|^3J(PF)|$, and in a few cases $|^4J(FF)|$. Calculation of approximate CO stretching force constants from the combined infrared and Raman ν(CO) frequencies of the *trans*-$[RN(PF_2)_2]_2Cr(CO)_4$ complexes suggests that the ratio between the trans and cis CO stretch–stretch interaction constants is approximately 3 in contrast to the value of 2 usually assumed for this ratio in the standard Cotton–Kraihanzel treatment. With use of this value of 3 the various approximate CO stretching force constants have been calculated for the complexes $RN(PF_2)_2M(CO)_4$, *cis*-$[RN(PF_2)_2]_2M(CO)_4$, and *mer*-$[RN(PF_2)_2]_2M(CO)_3$ reported in this paper.

Introduction

Previous papers of this series have discussed reactions of various metal carbonyls with the chelating strong π acceptors $RN(PF_2)_2$ (R = CH_3[5-7] and C_6H_5[8]). In this connection ultraviolet irradiations of the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, and W) with excess $CH_3N(PF_2)_2$[5,9] or $C_6H_5N(PF_2)_2$[8] were found to result in the complete pairwise replacement of the six carbonyl groups with three bidentate fluorophosphines to give the very stable carbonyl-free complexes $[RN(PF_2)_2]_3M$ (R = CH_3 and C_6H_5; M = Cr, Mo, and W). However, similar reactions of iron and nickel carbonyls

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(1) For part 9 of this series see M. G. Newton, R. B. King, M. Chang, and J. Gimeno, *J. Am. Chem. Soc.*, **101**, 2627 (1979).

(2) Portions of this work were presented at the 9th International Conference on Organometallic Chemistry, Dijon, France, Sept 1979.

(3) For a preliminary communication of a small portion of this work see R. B. King and T. W. Lee, *J. Organomet. Chem.*, **190**, C17 (1980).

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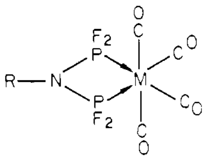
were found to lead to interesting binuclear metal carbonyl complexes including $CH_3N(PF_2)_2Fe_2(CO)_7$,[5,10] $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$,[5,10] $[CH_3N(PF_2)_2Fe(CO)_3]_2$,[5,10] $[CH_3N(PF_2)_2]_4Fe_2CO$,[11] $[CH_3N(PF_2)_2]_2Ni_2(CO)_3$,[5] and $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$.[5]

The research discussed in this paper was directed toward the preparation of similar binuclear metal carbonyl complexes of chromium, molybdenum, and tungsten containing $RN(PF_2)_2$ ligands. Such complexes are of interest for the following reasons: (1) Analogous complexes of corresponding 3d, 4d, and 5d transition metals are potentially readily available, thereby providing a possibility for assessing effects on the properties of $RN(PF_2)_2$-bridged metal–metal bonds upon descending a column of the periodic table. (2) The rigidity of the $RN(PF_2)_2$ bridges could hold together a pair of group 6 metals so that the resulting metal–metal bond could be more readily bridged symmetrically by one or more carbonyl groups; symmetrical CO-bridged metal–metal bonds involving group 6 metals are very rare.[12-14]

The general approach used in this work for the synthesis of binuclear metal complexes involves the preparation of mononuclear derivatives of the general type $[RN(PF_2)_2]_mM(CO)_n$ followed by their decarbonylations to binuclear derivatives by thermal or photochemical methods.

At the time that this work was started the only known $[RN(PF_2)_2]_mM(CO)_n$ derivatives were a series of compounds $C_2H_5N(PF_2)_2M(CO)_4$ (I: R = C_2H_5; M = Cr, Mo, and W) reported by Johnson and Nixon[15] in 1969. For use as possible precursors to novel binuclear complexes we have prepared the related mononuclear complexes $RN(PF_2)_2M(CO)_4$ (I: R = CH_3 and C_6H_5; M = Cr, Mo, and W) as well as several representatives of the new types of mononuclear complexes *trans*-$[RN(PF_2)_2]_2Cr(CO)_4$ (II: R = R′ = CH_3 and C_6H_5), *cis*-$[RN(PF_2)_2]_2M(CO)_4$ (III: R = CH_3 and C_6H_5; M = Mo and W), *mer*-$[RN(PF_2)_2]_2Cr(CO)_3$ (IV: R = CH_3 and C_6H_5), and the novel mixed-ligand complex *trans*-$[CH_3N(PF_2)_2][C_6H_5N(PF_2)_2]Cr(CO)_4$ (II: R = CH_3, R′ = C_6H_5). This paper describes the preparations and spectroscopic properties of these mononuclear complexes as well as their pyrolyses and photolyses to give binuclear complexes of the types $[RN(PF_2)_2]_3M_2(CO)_5$, $[RN(PF_2)_2]_4M_2(CO)_3$, $[CH_3N(PF_2)_2]_5Mo_2CO$, and $[C_6H_5N(PF_2)_2]_5Mo_2(CO)_2$.



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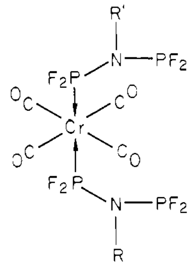

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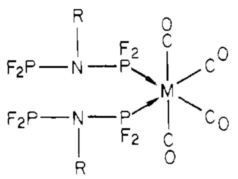

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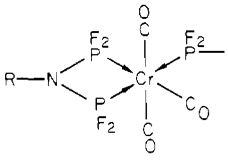

IV

Experimental Section

Microanalyses (Table I) were performed by Atlantic Microanalytical Laboratory, Atlanta, GA (C, H, and N), and Galbraith Laboratories, Inc., Knoxville, TN (P and F). Molecular weights (Table I) were determined in benzene solutions with a Mechrolab Model 301 vapor pressure osmometer located in the laboratory of Professor G. E. Boyd at the University of Georgia. Melting points (Table I) were taken in capillaries and are uncorrected.

Infrared spectra (Table I) were taken in the ν(CO) region in KBr pellets or the indicated solvents (hexane, CCl_4, or CH_2Cl_2) and recorded on a Perkin-Elmer Model 297 or a Perkin-Elmer Model 621 spectrometer with grating optics. Each spectrum was calibrated against the 1601-cm^{-1} band of polystyrene film. Raman spectra were taken on solid samples in sealed capillaries with a Spex 1401 spectrometer located in the laboratory of Professor L. Carreira at the University of Georgia with 20–30-mW power in the 4880-Å line of an argon ion laser as the exciting radiation. Proton NMR spectra (Table II) were recorded in $CDCl_3$ solutions on a Jeolco PFT-100 spectrometer operating in the pulsed Fourier transform mode. Carbon-13 (Table II) and phosphorus-31 (Table III) NMR spectra were taken in the indicated solvents ($CDCl_3$ or CH_2Cl_2) and recorded at 25.0336 and 40.3 MHz, respectively, on a Jeolco PFT-100 spectrometer operating in the pulsed Fourier transform mode with proton-noise decoupling and a deuterium lock. Fluorine-19 NMR spectra (Table III) were taken in CH_2Cl_2 solutions and recorded at 56.456 MHz on a Perkin-Elmer Hitachi R-20 continuous-wave NMR spectrometer. Proton and carbon-13 chemical shifts (δ) are reported *downfield* from internal tetramethylsilane. Phosphorus-31 chemical shifts (δ) are reported in ppm *downfield* from external 85% H_3PO_4 (opposite sign convention from the previous work[5,6]). Fluorine-19 chemical shifts (ϕ) are reported *upfield* from internal CCl_3F.

A nitrogen atmosphere was routinely provided for the following three operations: (a) carrying out reactions; (b) handling air-sensitive organometallic compounds, particularly in solution; (c) filling evacuated vessels containing potentially air-sensitive materials. However, the new (alkylamino)bis(difluorophosphine)metal carbonyls described in this paper appear to be relatively air stable both in solid state and in solution. Ultraviolet irradiations were performed with an immersion Englehard-Hanovia 450-W mercury ultraviolet lamp with a water-cooled Pyrex jacket. Diethyl ether, pentane, and hexane were freshly distilled under nitrogen over sodium benzophenone ketyl.

The metal carbonyls $M(CO)_6$ (M = Cr, Mo, and W) were purchased from Pressure Chemical Co., Pittsburgh, PA, and converted to the norbornadiene complexes $C_7H_8M(CO)_4$ (M = Cr,[16] Mo,[17] and W[18]) and the cycloheptatriene complexes $C_7H_8M(CO)_3$ (M = Cr[19] and Mo[20]) by the cited published procedures. The ligands $RN(PF_2)_2$ (R = CH_3[5,21] and C_6H_5[22]) were also prepared by the cited published procedures.

Reaction of $C_7H_8Cr(CO)_4$ with $CH_3N(PF_2)_2$. (a) In a Closed System with a 2/1 $CH_3N(PF_2)_2/C_7H_8Cr(CO)_4$ Mole Ratio. A mixture of 2.8 g (10.7 mmol) of $C_7H_8Cr(CO)_4$ and 3.6 g (21.5 mmol) of $CH_3N(PF_2)_2$ was sealed in an evacuated tube and allowed to stand at room temperature for 5 days. The tube was opened. Volatile material was removed at 25 °C (20 mm). Distillation of the remaining yellow liquid gave 1.9 g (53% yield) of pale yellow liquid $CH_3N(PF_2)_2Cr(CO)_4$, bp 55 °C (0.007 mm), which solidified upon storing at −10 °C. Further purification by crystallization from pentane at −78 °C followed by sublimation at 25 °C (0.1 mm) gave pale yellow crystals, mp 40–41 °C.

After removal of the $CH_3N(PF_2)_2Cr(CO)_4$ from the first distillation, further distillation of the pot residue gave a deeper yellow liquid, bp ~80 °C (0.001 mm). Heating this liquid in a sublimer at 25 °C (0.001 mm) (static vacuum) with a −78 °C probe resulted in sublimation of some additional $CH_3N(PF_2)_2Cr(CO)_4$. After removal

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Table I. Properties of Chromium, Molybdenum, and Tungsten Carbonyl Derivatives of (Alkylamino)bis(difluorophosphines)

compd[a]	color	mp,[b] °C	bp,[c] °C (*P*, mm)		% C	% H	% N	other	IR/Raman ν(CO),[d] cm^{-1}
			(A) $RN(PF_2)_2M(CO)_4$ Derivatives						
$MeN(PF_2)_2Cr(CO)_4$	white	40–41	30 (8)	Calcd	18.1	0.9	4.3		2053 m, 1992 m, 1980 s, 1967 vs (hex)
				Found	18.5	0.9	4.2		2059 m R, 1984 s R, 1968 m R, 1957 m R (solid)
$PhN(PF_2)_2Cr(CO)_4$	white	52–53	50 (0.1)	Calcd	30.6	1.3	3.6		2055 m, 1995 m, 1982 s, 1967 vs (hex)
				Found	30.4	1.3	3.6		
$MeN(PF_2)_2Mo(CO)_4$	white	47–48	52 (0.001)	Calcd	16.0	0.8	3.7		2060 m, 1997 m, 1984 s, 1975 vs (hex)
				Found	16.3	0.9	3.7		
$PhN(PF_2)_2Mo(CO)_4$	white	85–86	50 (0.01)	Calcd	27.5	1.1	3.2		2061 m, 2000 m, 1985 s, 1977 vs (hex)
				Found	27.4	1.4	3.3		
$MeN(PF_2)_2W(CO)_4$	white	58–59	55 (0.001)	Calcd	13.0	0.6	3.0		2062 m, 1990 s, 1977 vs, 1970 vs
				Found	12.8	0.6	2.9		2060 m R, 1982 s R, 1964 w R, 1946 m R (solid)
$PhN(PF_2)_2W(CO)_4$	white	89–90	80 (0.1)	Calcd	22.9	1.0	2.7		2060 m, 1990 m, 1977 s, 1970 vs (hex)
				Found	23.1	1.0	2.9		
			(B) $[RN(PF_2)_2]_2M(CO)_4$ Derivatives						
trans-$[MeN(PF_2)_2]_2Cr(CO)_4$	white	60–61	~80 (0.001)	Calcd	14.2	1.2	5.5		1957 vs (hex), 1946 vs (KBr)
				Found	14.6	1.2	5.4		2065 s R, 2000 vs R (solid)
trans-$[PhN(PF_2)_2]_2Cr(CO)_4$	white	121–122	95 (0.01)	Calcd	30.9	1.6	4.5		1965 vs (CCl_4), 1935 vs (KBr)
				Found	30.9	1.6	4.4		2065 s R, 2005 s R, 1997 m R, 1978 vw R (solid)
cis-$[MeN(PF_2)_2]_2Mo(CO)_4$	white	liquid	80 (0.001)	Calcd	13.3	1.1	5.2		2062 m, 2000 m, 1986 s, 1977 vs (hex)
				Found	13.4	1.2	4.9		
cis-$[PhN(PF_2)_2]_2Mo(CO)_4$	white	53–55		Calcd	28.8	1.5	4.2		2070 s, 2003 m, 1994 s, 1971 vs (CCl_4)
				Found	28.9	1.7	4.1		
cis-$[MeN(PF_2)_2]_2W(CO)_4$	white	liquid	70 (0.001)	Calcd	11.4	1.0	4.4		2070 m, 1991 m, 1977 s, 1965 vs (hex)
				Found	11.2	0.9	4.3		
trans-$[MeN(PF_2)_2][PhN(PF_2)_2]Cr(CO)_4$	white	67–68	55 (0.001)	Calcd	23.4	1.4	5.0		1969 s
				Found	23.2	1.5	4.8		
			(C) $[RN(PF_2)_2]_2M(CO)_3$ Derivatives						
mer-$[MeN(PF_2)_2]_2Cr(CO)_3$	pale yellow	50–51	25 (0.001)	Calcd	12.8	1.3	6.0		2030 m, 1972 s, 1948 vs (hex)
				Found	12.9	1.2	5.8		
mer-$[PhN(PF_2)_2]_2Cr(CO)_3$	white	67–68	100 (0.01)	Calcd	30.3	1.7	4.7		2031 m, 1972 s, 1949 vs (hex)
				Found	30.3	1.7	4.7		
			(D) Bimetallic Derivatives						
$[PhN(PF_2)_2]_3Cr_2(CO)_6$	white	90–92		Calcd	30.0	1.6	4.4	M_r[g] 959	2032 m, 1975 s, 1951 vs (hex)
				Found	30.0	1.5	4.4	M_r 1025	
$[MeN(PF_2)_2]_3Cr_2(CO)_5$	yellow	158	85 (0.001)	Calcd	12.9	1.2	5.6		2022 s, 2000 s, 1971 s, 1963 s, 1785 m (hex)
				Found	13.6	1.2	5.6		
$[MeN(PF_2)_2]_3Mo_2(CO)_5$	yellow		95 (0.001)	Calcd	11.5	1.1	5.2	M_r 833	2040 s, 2014 s, 1981 s, 1971 s, 1796 m (hex)
				Found	11.6	1.1	5.0	M_r 882	
$[PhN(PF_2)_2]_3Mo_2(CO)_5$	yellow			Calcd	27.1	1.5	4.1		2037 s, 2010 s, 1978 sh, 1969
				Found	26.9	1.7	4.1		1787 w (CCl_4)
$[MeN(PF_2)_2]_3W_2(CO)_5$	yellow			Calcd	9.5	0.9	4.2	*e*	2037 s, 2009 s, 1978 s, 1968 s, 1765 m (hex)
				Found	10.0	0.9	4.1	*e*	
$[MeN(PF_2)_2]_4Mo_2(CO)_3$	pale yellow	~300		Calcd	8.9	1.3	5.9	M_r 944	2006 vs, 1944 vs
				Found	9.7	1.3	5.9	M_r 988	1773 w (hex)
$[MeN(PF_2)_2]_4W_2(CO)_3$	yellow			Calcd	7.5	1.1	5.1		1997 vs, 1932 s
				Found	7.3	1.1	5.0		1751 w (CCl_4)
$[MeN(PF_2)_2]_5Mo_2CO$	yellow			Calcd	6.8	1.4	6.6	M_r 1055	1923 s (CCl_4)
				Found	7.3	1.3	6.8	M_r 1071	
$[PhN(PF_2)_2]_5Mo_2(CO)_2$	yellow			Calcd	27.6	1.8	5.0	*f*	1982 vs, 1930 s (CCl_4)
				Found	27.9	2.0	5.1	*f*	

[a] Me = methyl, Ph = phenyl. [b] Melting points were taken in capillaries and are uncorrected. [c] Sublimation temperatures are given for compounds which remain solid at the indicated temperatures. [d] hex = hexane solution; CCl_4 = CCl_4 solution; KBr = KBr pellet, R = Raman frequency obtained with a solid sample. [e] Calcd: F, 22.6; P, 18.4. Found: F, 21.6; P, 18.7. [f] Calcd: F, 27.3; P, 22.2. Found: F, 27.0; P, 22.0. [g] M_r = molecular weight (relative molecular mass).

Table II. NMR Spectra of Chromium, Molybdenum, and Tungsten Carbonyl Derivatives of (Methylamino)bis(difluorophosphine)

		$^{13}C\{^1H\}$,[b] δ		
compd[a]	^1H NMR,[b] δ(CH_3)	solvent	CO	CH_3
$MeN(PF_2)_2Cr(CO)_4$	2.75 t (10)	$CDCl_3$	220.1 d (23), 215.0 t (18)	29.6
$MeN(PF_2)_2Mo(CO)_4$	2.75 t (10)	$CDCl_3$	~209 br, 203.9 t (13)	29.0
$MeN(PF_2)_2W(CO)_4$	2.73 t (10)	$CDCl_3$	~200 m, 194.8 t (9)	30.3
trans-$[MeN(PF_2)_2]_2Cr(CO)_4$	2.97 dd (8, 1)	$CDCl_3$	213.9 br	25.8
cis-$[MeN(PF_2)_2]_2Mo(CO)_4$	2.89 br, d (6)	$CDCl_3$	206.1 d (47), 203.4 t (12)	25.1
cis-$[MeN(PF_2)_2]_2W(CO)_4$	2.92 ddd (5.6, 3.0, 0.9)	$CDCl_3$	~195 m	25.3
mer-$[MeN(PF_2)_2]_2Cr(CO)_3$	2.89 d (7), 2.75 t (11)	CH_2Cl_2	222.3 br [1], 216.0 q (19) [2]	30.2 [1], 25.8 [1]
mer-$[MeN(PF_2)_2]_2Mo(CO)_3$	2.96 d (6), 2.78 t (10)	$CDCl_3$	~212 br [1], 205 m [2]	29.1 [1], 25.3 [1]
mer-$[MeN(PF_2)_2]_2W(CO)_3$	2.91 d (6), 2.73 t (10)	$CDCl_3$	~202 m [1], 195 m [2]	30.1 [1], 25.5 [1]
$[MeN(PF_2)_2]_3Cr_2(CO)_5$	3.17 t (6) [1], 2.85 t (5) [2]	$CDCl_3$	~221	32.0 [1], 29.3 [2]
$[MeN(PF_2)_2]_3Mo_2(CO)_5$	3.11 t (6) [1], 2.87 [2]	CH_2Cl_2	*c*	31.6 [1], 28.4 [2]
$[MeN(PF_2)_2]_3W_2(CO)_5$	3.02 t (6) [1], 2.87 [2]	CH_2Cl_2	~199.6	33.0 [1], 29.0 [2]
$[MeN(PF_2)_2]_4Cr_2(CO)_3$	3.06 t (6) [1], 2.94 t (12) [1], 2.88 t (6) [2]			
$[MeN(PF_2)_2]_4Mo_2(CO)_3$	2.86 br	CH_2Cl_2	~213	31.4 [1], 29.9 [1], 28.5 [2]
$[MeN(PF_2)_2]_4W_2(CO)_3$	2.87 br			
$[MeN(PF_2)_2]_5Mo_2CO$	2.88	CH_2Cl_2	*c*	31.5 [4], 30.1 [1]
$[MeN(PF_2)_2]_5W_2CO$	2.82	CH_2Cl_2	*c*	31.6 [4], 30.3 [1]
trans-$[MeN(PF_2)_2][PhN(PF_2)_2]Cr(CO)_4$	2.95 d (7) (7.43 from C_6H_5)			

[a] Me = methyl; Ph = phenyl. [b] All proton NMR spectra were taken in $CDCl_3$; d = doublet; dd = doublet of doublets; t = triplet; q = quartet; m = multiplet; br = broad. Splittings in Hz are given in parentheses (); relative intensities are given in brackets [ ]. [c] The signal-to-noise ratio was too weak to detect these carbonyl carbon-13 resonances.

Table III. NMR Spectra of Chromium, Molybdenum, and Tungsten Carbonyl Derivatives of (Alkylamino)bis(difluorophosphines)

	$^{31}P\{^1H\}$ NMR[a]						^{19}F NMR
compd[a]	P type[c]	δ(H_3PO_4)[d]	$\lvert{}^1J(PF)\rvert$[e]	$\lvert{}^2J(PP)\rvert$[e]	$\lvert{}^3J(PF)\rvert$[e]	$\lvert{}^4J(FF)\rvert$[e]	φ($CFCl_3$)
$MeN(PF_2)_2$	U	141.3	1260	442	42	~0	74.7
$MeN(PF_2)_2Cr(CO)_4$	2C	168.5	1295	83	55	8	49.9
$PhN(PF_2)_2$	U	132.2	1278	382	35	~0	68.2
$PhN(PF_2)_2Cr(CO)_4$	2C	165.8	1300	68	51	8	44.8
$MeN(PF_2)_2Mo(CO)_4$	2C	144.5	1291	120	40	7	52.3
$PhN(PF_2)_2Mo(CO)_4$	2C	141.3	1293	117	36	5	47.3
$MeN(PF_2)_2W(CO)_4$	2C	112.4	1275	160	42	5	54.0
$PhN(PF_2)_2W(CO)_4$	2C	109.6	1280	151	42	5	50.3
trans-$[MeN(PF_2)_2]_2Cr(CO)_4$	1C	203.4	1155	212	~0	~0	28.4
	1U	138.2	1275	212	~0	~0	74.7
trans-$\{PhN(PF_2)_2]_2Cr(CO)_4$	1C	199.4	1166	156	~0		
	1U	128.6	1296	151	17		
cis-$[MeN(PF_2)_2]_2Mo(CO)_4$	1C						33.5
	1U						75.5
cis-$[PhN(PF_2)_2]_2Mo(CO)_4$	1C	167.5	1165	~222			
	1U	128.8	1288	228			
mer-$[MeN(PF_2)_2]_2Cr(CO)_3$	1C	208.2	1138	239, 81	~15		24.2
	2C	173.9	1300				48.1
	2C′	167.9	1265				50.4
	1U	139.3	1263	262			74.9
mer-$[PhN(PF_2)_2]_2Cr(CO)_3$	1C	203.8	1151	181, 84			
	2C	171.8	1316	97, 52			
	2C′	163.9	1313				
	1U	128.8	1292	186			
$[PhN(PF_2)_2]_3Cr_2(CO)_6$	BC	208.9	1170	85			
	2C	171.8	1312	101, 51			
	2C′	164.6	~1285				
$[MeN(PF_2)_2]_3Cr_2(CO)_5$	BC	204.0 (1)	~1180				
	BC	200.9 (2)	~1178	~217			
$[MeN(PF_2)_2]_3Mo_2(CO)_5$	BC	182.2 (1)					
	BC	175.2 (2)					

[a] Me = methyl; Ph = phenyl. [b] All phosphorus-31 NMR spectra were taken in CH_2Cl_2 solutions with an external 85% H_3PO_4 standard. [c] 1C = complexed PF_2 phosphorus of a monodentate $RN(PF_2)_2$ ligand. 1U = uncomplexed PF_2 phosphorus of a monodentate $RN(PF_2)_2$ ligand. 2C, 2C′ = (complexed) PF_2 phosphorus of a bindentate (chelating) $RN(PF_2)_2$ ligand; BC = PF_2 phosphorus of a bridging $RN(PF_2)_2$ ligand. [d] Phosphorus-31 chemical shifts are reported in *downfield* from external 85% H_3PO_4. [e] All coupling constants are reported in Hz.

of this $CH_3N(PF_2)_2Cr(CO)_4$, further sublimation at 40–45 °C (0.001 mm) gave 0.35 g of a yellow solid, mp 55 °C. Fractional crystallization of this yellow solid from pentane at −70 °C gave 0.15 g (3% yield) of colorless *trans*-$[CH_3N(PF_2)_2]_2Cr(CO)_4$, mp 61–62 °C.

(b) In an Open System with a 5/1 $CH_3N(PF_2)_2/C_7H_8Cr(CO)_4$ Mole Ratio. A mixture of 0.8 g (3.1 mmol) of $C_7H_8Cr(CO)_4$ and 2.5 g (15 mmol) of $CH_3N(PF_2)_2$ in 50 mL of hexane was boiled under reflux for 22 h. Hexane and other volatile materials were then removed at ~25 °C (25 mm). Sublimation of the resulting solid at 25 °C (0.01 mm) (static vacuum) gave a pale yellow sublimate. Recrystallization of this sublimate from pentane at −70 °C gave 0.30 g (24% yield) of $CH_3N(PF_2)_2Cr(CO)_4$. Three recrystallizations of the yellow sublimation residue from pentane at −78 °C gave 0.17 g (11% yield) of colorless *trans*-$[CH_3N(PF_2)_2]_2Cr(CO)_4$, mp 60–61 °C.

Reaction of $C_7H_8Mo(CO)_4$ with $CH_3N(PF_2)_2$. (a) With a 1.2/1 $CH_3N(PF_2)_2/C_7H_8Mo(CO)_4$ Mole Ratio. A mixture of 2.5 g (8.3

mmol) of $C_7H_8Mo(CO)_4$, 1.7 g (10 mmol) of $CH_3N(PF_2)_2$, and 50 mL of hexane was boiled under reflux for 5 h. Solvent was removed from the nearly colorless reaction mixture at ~25 °C (25 mm). Vacuum distillation of the residue gave 2.2 g (71% yield) of $CH_3N(PF_2)_2Mo(CO)_4$, bp 52 °C (0.001 mm), which solidified upon cooling. The analytical sample was obtained by crystallization from pentane at −70 °C followed by sublimation at 25 °C (0.001 mm).

(b) With a 4/1 $CH_3N(PF_2)_2/C_7H_8Mo(CO)_4$ Mole Ratio. A mixture of 2.0 g (6.7 mmol) of $C_7H_8Mo(CO)_4$, 4.5 g (27 mmol) of $CH_3N(PF_2)_2$, and 50 mL of hexane was boiled under reflux for 4 h. Solvent was then removed from the decolorized reaction mixture at 25 °C (25 mm) to give a pale yellow liquid. This liquid was then transferred to a distillation apparatus which was evacuated to 0.001 mm before immersing the pot into an oil bath preheated to 120 °C. Rapid distillation under these conditions (to minimize thermal decomposition) gave 2.6 g (72% yield) of colorless liquid *cis*-$[CH_3N(PF_2)_2]_2Mo(CO)_4$, bp 80–100 °C (0.4 mm).

Reaction of $C_7H_8W(CO)_4$ with $CH_3N(PF_2)_2$. (a) In a Closed System with a 2/1 $CH_3N(PF_2)_2/C_7H_8W(CO)_4$ Mole Ratio. A mixture of 2.7 g (7.5 mmol) of $C_7H_8W(CO)_4$ and 2.5 g (15 mmol) of $CH_3N(PF_2)_2$ was sealed into an evacuated tube and allowed to stand at ambient temperature for 7 days. The tube was then opened and volatile material removed at ~25 °C (25 mm). Distillation of the remaining liquid gave 1.4 g (41% yield) of $CH_3N(PF_2)_2W(CO)_4$, bp 55 °C (0.001 mm), collected as a colorless liquid which rapidly solidified. The analytical sample was purified further by crystallization from pentane at −70 °C followed by sublimation at 45 °C (0.1 mm).

The residual liquid from the distillation of $CH_3N(PF_2)_2W(CO)_4$ was placed in a sublimer. Residual $CH_3N(PF_2)_2W(CO)_4$ was first removed by sublimation at 25 °C (0.01 mm) (static vacuum) onto a −78 °C probe. After no more solid appeared on the probe, the liquid residue was distilled in vacuum to give 0.25 g (5% yield) of liquid *cis*-$[CH_3N(PF_2)_2]_2W(CO)_4$, bp 70 °C (0.001 mm).

(b) In an Open System with a 4/1 $CH_3N(PF_2)_2/C_7H_8W(CO)_4$ Mole Ratio. A mixture of 1.1 g (2.8 mmol) of $C_7H_8W(CO)_4$, 2.0 g (12 mmol) of $CH_3N(PF_2)_2$, and 50 mL of hexane was boiled under reflux for 14 h. Removal of solvent at 25 °C (25 mm) followed by sublimation at 25 °C (0.001 mm) onto a −78 °C probe and low-temperature crystallization of the sublimate from pentane gave 0.7 g (46% yield) of $CH_3N(PF_2)_2W(CO)_4$. Microdistillation of the liquid remaining from the original sublimation gave 0.15 g (9% yield) of *cis*-$[CH_3N(PF_2)_2]_2W(CO)_4$.

Reaction of $C_7H_8Cr(CO)_4$ with $C_6H_5N(PF_2)_2$. (a) With a 1/1 $C_6H_5N(PF_2)_2/C_7H_8Cr(CO)_4$ Mole Ratio. A mixture of 3.8 g (15 mmol) of $C_7H_8Cr(CO)_4$, 3.9 g (17 mmol) of $C_6H_5N(PF_2)_2$, and 70 mL of hexane was boiled under reflux for 15 h. Removal of solvent at ~25 °C (25 mm) followed by vacuum sublimation at 50 °C (0.1 mm) gave 4.4 g (74% yield) of $C_6H_5N(PF_2)_2Cr(CO)_4$, mp 52–53 °C.

(b) With a 2.5/1 $C_6H_5N(PF_2)_2/C_7H_8Cr(CO)_4$ Mole Ratio. A mixture of 2.6 g (10 mmol) of $C_7H_8Cr(CO)_4$, 5.9 g (25 mmol) of $C_6H_5N(PF_2)_2$, and 50 mL of hexane was boiled under reflux for 25 h. Hexane was removed from the filtered reaction mixture at 25 °C (25 mm). A precipitate appeared during the removal of hexane. Excess liquid was then removed from the residue by pumping at 25 °C (0.1 mm) for 25 min. The semisolid mass was then treated with pentane. The pentane suspension was filtered. The white precipitate was washed with pentane to give 1.7 g (27% yield) of *trans*-$[C_6H_5N(PF_2)_2]_2Cr(CO)_4$.

Solvent was removed from the combined pentane filtrate and washings at 25 °C (25 mm). Excess $C_6H_5N(PF_2)_2$ was removed by sublimation at 25 °C (0.001 mm) onto a −78 °C probe. Continued sublimation after cleaning the probe gave 1.5 g (37% yield) of $C_6H_5N(PF_2)_2Cr(CO)_4$. The residue remaining from this sublimation consisted of an additional 0.8 g (12.8% yield) of colorless *trans*-$[C_6H_5N(PF_2)_2]_2Cr(CO)_4$; the total yield of this substance thus was 2.5 g (40%).

Reaction of $C_7H_8Mo(CO)_4$ with $C_6H_5N(PF_2)_2$. (a) With a 1.2/1 $C_6H_5N(PF_2)_2/C_7H_8Mo(CO)_4$ Mole Ratio. A mixture of 3.1 g (10 mmol) of $C_7H_8Mo(CO)_4$, 2.5 g (12 mmol) of $C_6H_5N(PF_2)_2$, and 50 mL of pentane was boiled under reflux for 24 h. Solvent was then removed at 25 °C (25 mm) followed by excess ligand by pumping at 25 °C (0.1 mm) for 30 min. Sublimation of the colorless solid residue at 50 °C (0.01 mm) gave 3.4 g (78% yield) of $C_6H_5N(PF_2)_2Mo(CO)_4$.

(b) With a 3/1 $C_6H_5N(PF_2)_2/C_7H_8Mo(CO)_4$ Mole Ratio. A mixture of 2.0 g (6.7 mmol) of $C_7H_8Mo(CO)_4$, 4.5 g (20 mmol) of $C_6H_5N(PF_2)_2$, and 50 mL of pentane was boiled under reflux for 6 h. Solvent was then removed at ~25 °C (25 mm) followed by excess ligand by pumping at 25 °C (1 mm) for 1 h. Treatment of the liquid residue with pentane at −78 °C caused solidification; the resulting solid was washed with cold (−70 °C) pentane to give 0.9 g (20% yield) of *cis*-$[C_6H_5N(PF_2)_2]_2Mo(CO)_4$. The analytical sample was purified by low-temperature recrystallization from hexane.

Reaction of $C_7H_8W(CO)_4$ with $C_6H_5N(PF_2)_2$. A mixture of 2.0 g (5 mmol) of $C_7H_8W(CO)_4$, 1.6 g (7 mmol) of $C_6H_5N(PF_2)_2$, and 50 mL of hexane was boiled under reflux for 15 h, after which the yellow solution had completely decolorized. Removal of solvent at 25 °C (25 mm) followed by sublimation of the colorless liquid residue at 80 °C (0.1 mm) gave 2.4 g (91% yield) of $C_6H_5N(PF_2)_2W(CO)_4$, mp 89–90 °C.

Reaction of $CH_3N(PF_2)_2Cr(CO)_4$ with $C_6H_5N(PF_2)_2$. A mixture of 1.0 g (3 mmol) of $CH_3N(PF_2)_2Cr(CO)_4$, 2.75 g (12 mmol) of $C_6H_5N(PF_2)_2$, and 50 mL of hexane was boiled under reflux for 48 h. Removal of solvent at 25 °C (25 mm) followed by sublimation of the waxy solid residue at 55 °C (0.001 mm) gave a white sublimate. Crystallization of this sublimate from pentane at −78 °C gave 0.88 g (52% yield) of white *trans*-$[CH_3N(PF_2)_2][C_6H_5N(PF_2)_2]Cr(CO)_4$, mp 67–68 °C.

Reaction of $C_7H_8Cr(CO)_3$ with $CH_3N(PF_2)_2$. A mixture of 3.0 g (13 mmol) of $C_7H_8Cr(CO)_3$, 6.0 g (36 mmol) of $CH_3N(PF_2)_2$, and 50 mL of hexane was boiled under reflux for 36 h. Volatile materials were removed at 25 °C (25 mm). The resulting liquid was treated with 30 mL of pentane and then cooled in a −78 °C bath. Filtration of the resulting white precipitate gave 3.3 g (54% yield) of *mer*-$[CH_3N(PF_2)_2]_2Cr(CO)_3$. After removal of the solvent from the filtrate followed by sublimation at 25 °C (0.001 mm), an additional 0.7 g (11% yield) of *mer*-$[CH_3N(PF_2)_2]_2Cr(CO)_3$ was obtained, giving a total yield of 4.0 g (65%).

Reaction of $C_7H_8Cr(CO)_3$ with $C_6H_5N(PF_2)_2$. A mixture of 3.0 g (13 mmol) of $C_7H_8Cr(CO)_3$, 6.0 g (26 mmol) of $C_6H_5N(PF_2)_2$, and 125 mL of hexane was boiled under reflux for 3 days. Volatile material was then removed first at 25 °C (25 mm) with use of a rotary evaporator and finally at 25 °C (0.1 mm). The resulting liquid was dissolved in a mixture of 25 mL of hexane and ~10 mL of diethyl ether. Cooling the resulting solution in a −78 °C bath resulted in the crystallization of 3.6 g of a colorless solid, mp 73–86 °C, after the sides of the flask were scratched. This crude product was sublimed at 100 °C (0.02 mm) to give 1.6 g (21% yield) of *mer*-$[C_6H_5N(PF_2)_2]_2Cr(CO)_3$, mp 67–68 °C. The residue from the sublimation was crystallized from hexane to give 1.05 g (17% yield) of colorless $[C_6H_5N(PF_2)_2]_3Cr_2(CO)_6$, mp 90–92 °C.

Preparation of $[CH_3N(PF_2)_2]_3Cr_2(CO)_5$. A mixture of 1.0 g (4.5 mmol) of $Cr(CO)_6$, 0.83 g (5.0 mmol) of $CH_3N(PF_2)_2$, and 400 mL of hexane was exposed to ultraviolet irradiation for 5 h. Solvent was removed from the filtered reaction mixture at 25 °C (25 mm) to give a red-brown liquid residue. This residue was treated with 20 mL of pentane. The resulting mixture was kept at 0 °C. The pentane was decanted off from the oil that separated. This oil was treated further with pentane at room temperature to give a yellow-orange solid, which after recrystallization from hexane gave 0.10 g (8% yield) of $[CH_3N(PF_2)_2]_3Cr_2(CO)_5$.

Preparation of $[CH_3N(PF_2)_2]_3Mo_2(CO)_5$. (a) Thermally. A solution of 2.0 g (5.3 mmol) of $CH_3N(PF_2)_2Mo(CO)_4$ in 40 mL of 2,2,5-trimethylhexane was boiled under reflux for 2 h. After the resulting solution was cooled, the yellow-orange precipitate was filtered, washed with cold hexane, and dried to give 1.27 g of $[CH_3N(PF_2)_2]_3Mo_2(CO)_5$. Concentration of the filtrate followed by cooling to 0 °C gave a further 0.1 g of product bringing the total yield to 1.37 g (93%). This product can be purified further either by recrystallization from mixtures of diethyl ether and hexane or by sublimation at 95–100 °C (0.001 mm).

(b) Photochemically. A solution of 2.6 g (6.9 mmol) of $CH_3N(PF_2)_2Mo(CO)_4$ in 500 mL of hexane was exposed to ultraviolet irradiation for 9 h. Concentration of the resulting solution at 25 °C (25 mm) to 50 mL followed by cooling in a 0 °C bath gave a yellow precipitate which was filtered, washed with cold hexane, and recrystallized from a mixture of diethyl ether and hexane to give 1.1 g (58% yield) of $[CH_3N(PF_2)_2]_3Mo_2(CO)_5$.

Preparation of $[C_6H_5N(PF_2)_2]_3Mo_2(CO)_5$. A solution of 1.6 g (3.7 mmol) of $C_6H_5N(PF_2)_2Mo(CO)_4$ in 50 mL of methylcyclohexane was boiled under reflux for 2.5 h. The reaction mixture was filtered hot. Cooling the filtrate to 0 °C gave 0.22 g of $[C_6H_5N(PF_2)_2]_3Mo_2(CO)_5$, which was removed by filtration. The solvent was then removed from

Table IV. CO Stretching Force Constants (FC) of the Mononuclear Chromium, Molybdenum, and Tungsten Carbonyl Derivatives of (Alkylamino)bis(difluorophosphines)

compd[a]	ν(CO), cm^{-1}	FC, mdyn/Å[b] $k(1)$	$k(2)$	t	c	d
(A) *trans*-$L_2M(CO)_4$ Derivatives						
trans-$[MeN(PF_2)_2]_2Cr(CO)_4$[c]	2065 (A_{1g}), 2000 (B_{2g}), 1946 (E_u)		15.99	0.70	0.27	
trans-$[PhN(PF_2)_2]_2Cr(CO)_4$[c]	2065 (A_{1g}), 2005 (B_{2g}), 1935 (E_u)		15.92	0.80	0.25	
(B) *mer*-$L_3M(CO)_3$ Derivatives						
mer-$[MeN(PF_2)_2]_2Cr(CO)_3$	2030 (A_1), 1972 (A_1), 1948 (B_1)	15.80	15.93	0.61	0.20	
mer-$[PhN(PF_2)_2]_2Cr(CO)_3$	2031 (A_1), 1972 (A_1), 1949 (B_1)	15.80	15.95	0.61	0.20	
(C) *cis*-$L_2M(CO)_4$ Derivatives						
$MeN(PF_2)_2Cr(CO)_4$	2053 (A_1), 1992 (A_1), 1980 (B_2), 1967 (B_1)	15.82	16.43	0.60	0.20	0.20
$PhN(PF_2)_2Cr(CO)_4$	2055 (A_1), 1995 (A_1), 1982 (B_2), 1967 (B_1)	15.83	16.48	0.61	0.21	0.18
$MeN(PF_2)_2Mo(CO)_4$	2060 (A_1), 1997 (A_1), 1984 (B_2), 1975 (B_1)	15.94	16.50	0.61	0.19	0.22
$PhN(PF_2)_2Mo(CO)_4$	2061 (A_1), 2000 (A_1), 1985 (B_2), 1977 (B_1)	15.98	16.52	0.61	0.20	0.21
$MeN(PF_2)_2W(CO)_4$	2062 (A_1), 1990 (A_1), 1977 (B_2), 1970 (B_1)	15.86	16.45	0.67	0.19	0.26
$PhN(PF_2)_2W(CO)_4$	2060 (A_1), 1990 (A_1), 1977 (B_2), 1970 (B_1)	15.86	16.43	0.65	0.19	0.25
cis-$[MeN(PF_2)_2]_2Mo(CO)_4$	2062 (A_1), 2000 (A_1), 1986 (B_2), 1977 (B_1)	15.97	16.55	0.62	0.19	0.21
cis-$[PhN(PF_2)_2]_2Mo(CO)_4$	2070 (A_1), 2003 (A_1), 1994 (B_2), 1971 (B_1)	15.93	16.69	0.64	0.24	0.20
cis-$[MeN(PF_2)_2]_2W(CO)_4$	2070 (A_1), 1991 (A_1), 1977 (B_2), 1965 (B_1)	15.82	16.52	0.74	0.23	0.27

[a] Me = methyl, Ph = phenyl. [b] The notation of Braterman (ref 22, pp 42–43) is used: $k(1)$ = stretching parameter for CO trans to a fluorophosphine ligand; $k(2)$ = stretching parameter for CO trans to CO; t = interaction parameter for mutually trans CO groups; c = interaction parameter for mutually cis CO groups; d = interaction parameter for mutually cis CO groups one of which is trans to CO. [c] From solid-state spectra. The other CO frequencies used for the force constant calculations were obtained from spectra taken in hydrocarbon solvents (Table I).

the filtrate at ~35 °C (25 mm). The residue was treated with 20 mL of hexane and cooled to give another 0.48 g of $[C_6H_5N(PF_2)_2]_3Mo_2(CO)_5$, making the total yield 0.70 g (56%). This product could be purified further by recrystallization from a mixture of diethyl ether and pentane.

Preparation of $[CH_3N(PF_2)_2]_3W_2(CO)_5$. Since $C_7H_8W(CO)_4$ is not particularly readily available in large quantities, this binuclear tungsten complex was prepared directly from $W(CO)_6$.

A mixture of 5.3 g (15 mmol) of $W(CO)_6$, 2.5 g (15 mmol) of $CH_3N(PF_2)_2$, and 350 mL of hexane was exposed to ultraviolet irradiation for 18 h. The resulting yellow solution deposited a yellow precipitate on standing. This precipitate (0.7 g) was removed by filtration. The filtrate was concentrated to 25 mL at ~25 °C (25 mm) to precipitate an additional 1.0 g of crude product. Recrystallization of the combined precipitates from hexane gave 1.3 g (26% yield) of $[CH_3N(PF_2)_2]_3W_2(CO)_5$.

Preparations of $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ and $[CH_3N(PF_2)_2]_5Mo_2CO$. A mixture of 2.7 g (10 mmol) of $C_7H_8Mo(CO)_3$, 3.8 g (22 mmol) of $CH_3N(PF_2)_2$, and 50 mL of methylcyclohexane was heated at ~60 °C until the red solution had decolorized. The resulting solution was then boiled under reflux for 6 h. Cooling the resulting solution precipitated 3.4 g of a yellow solid consisting of a mixture of $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ and $[CH_3N(PF_2)_2]_5Mo_2CO$. A concentrated dichloromethane solution of this solid was chromatographed on a 2 × 30 cm Florisil column. The chromatogram was eluted with 1:1 mixtures of diethyl ether and hexane. The eluates were collected in 20–25-mL fractions. The latter fractions contained pure $[CH_3N(PF_2)_2]_5Mo_2CO$ as indicated by their infrared spectra. The earlier fractions contained mixtures of $[CH_3N(PF_2)_2]_5Mo_2CO$ and $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$. Rechromatography of the combined earlier fractions gave more pure $[CH_3N(PF_2)_2]_5Mo_2CO$ in the latter fractions. The pure $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ was isolated by fractional crystallization from diethyl ether/hexane of the remaining $[CH_3N(PF_2)_2]_4Mo_2(CO)_3/[CH_3N(PF_2)_2]_5Mo_2CO$ mixture. The yield of $[CH_3N(PF_2)_2]_5Mo_2CO$ was 1.0 g (11%) whereas that of $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ was 0.3 g (3%).

Preparations of $[C_6H_5N(PF_2)_2]_4Mo_2(CO)_3$ and $[C_6H_5N(PF_2)_2]_5Mo_2(CO)_2$. A mixture of 2.6 g (10 mmol) of $Mo(CO)_6$, 4.8 g (21 mmol) of $C_6H_5N(PF_2)_2$, and 50 mL of 2,2,5-trimethylhexane was boiled under reflux for 1.5 h. The resulting solution was filtered. The filtrate was treated with 25 mL of hexane to precipitate 0.6 g of a yellow solid consisting of a mixture of $[C_6H_5N(PF_2)_2]_5Mo_2(CO)_2$ and $[C_6H_5N(PF_2)_2]_4Mo_2(CO)_3$ with the former predominating. Recrystallization of this precipitate from diethyl ether gave 0.4 g (7% yield) of pure $[C_6H_5N(PF_2)_2]_5Mo_2(CO)_2$.

The filtrate from the original isolation of this yellow precipitate was treated with additional hexane to precipitate an additional 1.0 g of yellow solid consisting predominantly of $[C_6H_5N(PF_2)_2]_4Mo_2(CO)_3$. Fractional crystallization of this second precipitate from a mixture of diethyl ether and hexane gave 0.2 g (3% yield) of $[C_6H_5N(PF_2)_2]_4Mo_2(CO)_3$.

Preparations of $[CH_3N(PF_2)_2]_4W_2(CO)_3$ and $[CH_3N(PF_2)_2]_5W_2CO$. A mixture of 3.5 g (10 mmol) of $W(CO)_6$, 4.2 g (25 mmol) of $CH_3N(PF_2)_2$, and 450 mL of hexane was exposed to ultraviolet irradiation for 5 h. The resulting yellow precipitate (2.4 g) was removed by filtration and the filtrate concentrated to ~25 mL at 25 °C (25 mm) to give more yellow precipitate (0.6 g). The yellow precipitates were shown by infrared spectroscopy to contain predominantly $[CH_3N(PF_2)_2]_5W_2CO$ with some $[CH_3N(PF_2)_2]_4W_2(CO)_3$. A concentrated dichloromethane solution of the combined yellow precipitates was chromatographed on a Florisil column as described above for the analogous molybdenum system to give directly 1.5 g (28% yield) of pure $[CH_3N(PF_2)_2]_5W_2CO$. Fractional crystallization from a mixture of diethyl ether and hexane of the material obtained from the chromatography eluates enriched in $[CH_3N(PF_2)_2]_4W_2(CO)_3$ gave 0.1 g (1% yield) of pure $[CH_3N(PF_2)_2]_4W_2(CO)_3$.

CO Stretching Force Constant Calculations (Table IV). The procedure pioneered by Cotton and Kraihanzel[23,24] and subsequently discussed in detail by Braterman[25] was used to estimate from the available infrared and Raman data the CO stretching force constants in the new mononuclear complexes of the types *trans*-$L_2M(CO)_4$, *mer*-$L_3M(CO)_3$, and *cis*-$L_2M(CO)_4$ (L = donor phosphorus atoms from the fluorophosphines). Since the systems had some unusual features, the specific methods used are outlined below. The terminology of Braterman[25] is used to designate the various force constants.

(a) *trans*-$[RN(PF_2)_2]_2Cr(CO)_4$ (R = CH_3 and C_6H_5). The system is exactly determined since there are three ν(CO) frequencies (A_{1g}, B_{2g}, and E_u) and three CO stretching force constants ($k(2)$, t, and c). The difficulty is that two of the ν(CO) frequencies (A_{1g}, B_{2g}) are Raman active and infrared inactive and the third ν(CO) frequency (E_u) is Raman inactive and infrared active. Therefore it is necessary to use both infrared and Raman data to obtain the values for the required ν(CO) frequencies; thus the correspondence between the two kinds of vibrational spectra is important. The infrared E_u frequencies used in the force constant calculations were taken from KBr pellet (i.e., solid-state) spectra in order to correspond most closely to the conditions used for the Raman spectra, which were taken on solid samples in sealed capillaries. The trans/cis interaction ratio t/c (assumed to be 2 in the conventional Cotton–Kraihanzel treatment[23,24])

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(23) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).
(24) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).
(25) P. S. Braterman, "Metal Carbonyl Spectra", Academic Press, London, 1975.

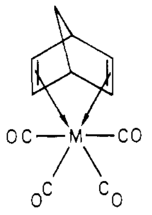
was found to be 2.61 for *trans*-$[CH_3N(PF_2)_2]_2Cr(CO)_4$ and 3.26 for *trans*-$[C_6H_5N(PF_2)_2]_2Cr(CO)_4$. On this basis the ratio t/c (and the related ratio $2t/(c + d)$) was assumed to be 3 in the underdetermined cases discussed below.

(b) *mer*-$[RN(PF_2)_2]_2Cr(CO)_3$ (R = CH_3 and C_6H_5). This system is underdetermined since there are three ν(CO) frequencies (A_1, A_1, and B_1) but four CO stretching force constants ($k(1)$, $k(2)$, t, and c). These force constant calculations were therefore performed by using the "exact" secular equations[24,25] and adjusting $k(1)$ as an "independent variable" in increments of 0.01 mdyn/Å until the ratio t/c approached as closely to 3.0 as possible. The assignment $\nu(A_1) > \nu(A_1) > \nu(B_1)$ was preferred in accord with past experience[24,25] and gave realistic values for the stretching force constants including positive real interaction constants t and c.

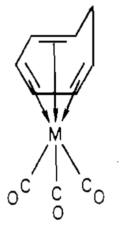
(c) $RN(PF_2)_2M(CO)_4$ (R = CH_3 and C_6H_5; M = Cr, Mo, and W) and *cis*-$[RN(PF_2)_2]_2M(CO)_4$ (R = CH_3 and C_6H_5; M = Mo and W). This system is again underdetermined since there are four ν(CO) frequencies (A_1, A_1, B_2 and B_1) but five CO stretching force constants ($k(1)$, $k(2)$, t, c, and d). Again the force constant calculations were performed by using the "exact" secular equations[23,25] and by adjusting $k(1)$ as an "independent variable" in increments of 0.01 mdyn/Å until the ratio $2t/(c + d)$ (i.e., the ratio of the trans interaction constant t to the mean of the two different cis interaction constants c and d) approached as closely to 3.0 as possible. The assignment $\nu(A_1) > \nu(A_1) > \nu(B_2) > \nu(B_1)$ was preferred over the other conceivable assignment[25] $\nu(A_1) > \nu(B_2) > \nu(A_1) > \nu(B_1)$ since in all cases the former assignment gave more nearly similar values of the two cis interaction constants c and d than the latter assignment (Braterman[25] and Cotton[23,24] interchange the B_1 and B_2 frequencies because of a different assignment of axes).

Results and Discussion

(A) Mononuclear Complexes. The mononuclear metal carbonyl derivatives of the (alkylamino)bis(difluorophosphines) were prepared by displacement of the coordinated olefin from the norbornadiene complexes $C_7H_8M(CO)_4$ (V: M = Cr, Mo, and W) and the cycloheptatriene complex $C_7H_8Cr(CO)_3$ (VI: M = Cr) according to well-established principles.[26-28] Reactions of the acetonitrile complexes *fac*-$(CH_3CN)_3M(CO)_3$ (M = Cr and W)[29] with the $RN(PF_2)_2$ ligands were also investigated but were found to give poorer yields and more complicated product mixtures than the reactions of complexes V and VI with the $RN(PF_2)_2$ ligands.



V



VI

The reactions of the norbornadiene complexes $C_7H_8M(CO)_4$ (V: M = Cr, Mo, and W) with $C_2H_5N(PF_2)_2$ were reported[15] to give the chelates $C_2H_5N(PF_2)_2M(CO)_4$ (I: R = C_2H_5; M = Cr, Mo, and W) according to eq 1 (R = C_2H_5). We have

$$C_7H_8M(CO)_4 + RN(PF_2)_2 \rightarrow RN(PF_2)_2M(CO)_4 + C_7H_8 \quad (1)$$

now found that the reactions of $C_7H_8M(CO)_4$ (V: M = Cr, Mo, and W) with $RN(PF_2)_2$ (R = CH_3 and C_6H_5) can either give the chelates I according to eq 1 or the monoligate mononmetallic complexes $[RN(PF_2)_2]_2M(CO)_4$ according to eq 2. In addition, the complex $CH_3N(PF_2)_2Cr(CO)_4$ was found

$$C_7H_8M(CO)_4 + 2RN(PF_2)_2 \rightarrow [RN(PF_2)_2]_2M(CO)_4 + C_7H_8 \quad (2)$$

to react with $C_6H_5N(PF_2)_2$ to give a novel mixed-ligand complex *trans*-$[CH_3N(PF_2)_2]Cr(CO)_4$ according to eq 3.

$$CH_3N(PF_2)_2Cr(CO)_4 + C_6H_5N(PF_2)_2 \rightarrow [CH_3N(PF_2)_2][C_6H_5N(PF_2)_2]Cr(CO)_4 \quad (3)$$

This reaction clearly involves opening of the four-membered chelate ring in a complex of the type I (R = CH_3, M = Cr) to give a complex of the type II (R = CH_3, R′ = C_6H_5). This observation suggests that the formation of monoligate monometallic products of the stoichiometry $[RN(PF_2)_2]_2M(CO)_4$ by eq 2 proceeds through the chelate ring opening of the corresponding biligate monometallic $RN(PF_2)_2M(CO)_4$ complex formed according to eq 1.

The isomers $[RN(PF_2)_2]_2M(CO)_4$ formed by eq 2 depend upon the transition metal involved. Thus the chromium complexes $[RN(PF_2)_2]_2Cr(CO)_4$ formed by reactions of $C_7H_8Cr(CO)_4$ (V: M = Cr) with excess $RN(PF_2)_2$ ligand are clearly shown to be the trans isomers II by the ν(CO) regions of their infrared spectra (Tables I and IV). However, the molybdenum and tungsten complexes $[RN(PF_2)_2]_2M(CO)_4$ (M = Mo and W) formed by reactions of $C_7H_8M(CO)_4$ (V: Mo and W) with excess $RN(PF_2)_2$ ligands are likewise shown to be the corresponding cis isomers III. This is consistent with the initial stereospecific replacement of the norbornadiene ligand in V by two monodentate $RN(PF_2)_2$ ligands to give the cis isomers III followed by rearrangement to the less sterically hindered trans isomer in the case of the smaller chromium atom. The reactions of $C_7H_8M(CO)_4$ (V) with $RN(PF_2)_2$ to give $[RN(PF_2)_2]_2M(CO)_4$ (eq 2) rather than $RN(PF_2)_2M(CO)_4$ (eq 1) are increasingly favored as the $RN(PF_2)_2/C_7H_8M(CO)_4$ ratios are increased (see the Experimental Section for several actual examples) in accord with the different stoichiometries of these two reaction pathways.

The reactions of the cycloheptatriene complex $C_7H_8Cr(CO)_3$ (VI: M = Cr) with $RN(PF_2)_2$ (R = CH_3 and C_6H_5) result in displacement of the coordinated olefin according to eq 4.

$$C_7H_8Cr(CO)_3 + 2RN(PF_2)_2 \rightarrow [RN(PF_2)_2]_2Cr(CO)_3 + C_7H_8 \quad (4)$$

The products of the stoichiometry $[RN(PF_2)_2]_2Cr(CO)_3$ contain one monoligate monometallic and one biligate monometallic (chelating) $RN(PF_2)_2$ ligand like the previously reported[6] complexes $C_5H_5Mn[(PF_2)_2NCH_3]_2$ and $C_5H_5Mo[(PF_2)_2NCH_3]_2Cl$. The ν(CO) regions of the infrared spectra of these $[RN(PF_2)_2]_2Cr(CO)_3$ products indicate their formulations as the meridional isomers IV (M = Cr, R = CH_3 and C_6H_5) rather than as the corresponding facial isomers. Since stereospecific displacement of the cycloheptatriene ring from $C_7H_8Cr(CO)_3$ (VI: M = Cr) by two $RN(PF_2)_2$ ligands should give the facial rather than the meridional isomer, isomerization of the initial $[RN(PF_2)_2]_2Cr(CO)_3$ product has clearly occurred apparently to minimize the number of $RN(PF_2)_2$ ligands in mutual cis positions. Thus the formation of the meridional rather than the facial isomer of $[RN(PF_2)_2]_2Cr(CO)_3$ from $C_7H_8Cr(CO)_3$ (VI: M = Cr) and two $RN(PF_2)_2$ appears to parallel the formation of the trans rather than the cis isomer of $[RN(PF_2)_2]_2Cr(CO)_4$ from $C_7H_8Cr(CO)_4$ (V: M = Cr) and two $RN(PF_2)_2$. Fluorophosphine ligands thus seem to prefer mutual trans positions to mutual cis positions in octahedral chromium(0) complexes apparently for steric reasons.

The reaction of $C_7H_8Cr(CO)_3$ (VI: M = Cr) with $C_6H_5N(PF_2)_2$ besides forming *mer*-$[C_6H_5N(PF_2)_2]_2Cr(CO)_3$ (IV: M = Cr; R = C_6H_5) also proceeds according to eq 5 to give

$$2C_7H_8Cr(CO)_3 + 3C_6H_5N(PF_2)_2 \rightarrow [C_6H_5N(PF_2)_2]_3Cr_2(CO)_6 + 2C_7H_8 \quad (5)$$

the considerably less volatile binuclear complex $[C_6H_5N(PF_2)_2]_3Cr_2(CO)_6$ again shown by the ν(CO) region of its in-

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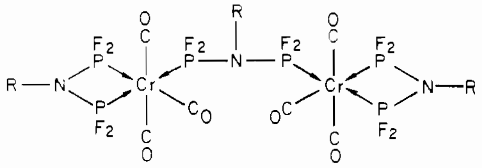
[26] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).
[27] R. B. King, *Inorg. Chem.*, **2**, 936 (1963).
[28] R. B. King and T. F. Korenowski, *Inorg. Chem.*, **10**, 1188 (1971).
[29] D. P. Tate, J. M. Augl, and W. R. Knipple, *Inorg. Chem.*, **1**, 433 (1962).

frared spectrum to have the meridional configuration of the CO groups around each chromium atom. Comparison of the phosphorus-31 NMR spectra of $[C_6H_5N(PF_2)_2]_3Cr_2(CO)_6$ with those of *mer*-$[RN(PF_2)_2]_2Cr(CO)_3$ complexes IV suggests structure VII (R = C_6H_5) for $[C_6H_5N(PF_2)_2]_3Cr_2(CO)_6$.



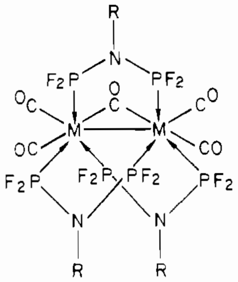
VII

Thus this binuclear complex arises from coordination of the uncomplexed phosphorus atom in *mer*-$[C_6H_5N(PF_2)_2]_2Cr(CO)_3$ (IV: R = C_6H_5) to another chromium atom, thereby making it of a very different type than the more extensive series of binuclear complexes discussed below.

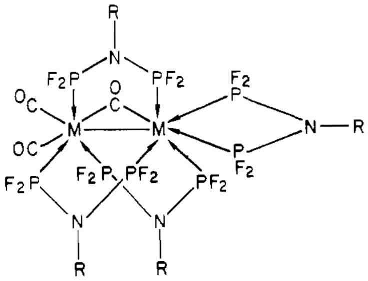
(B) Binuclear Complexes. Photochemical and thermal decarbonylation of the mononuclear $RN(PF_2)_2$ metal carbonyl complexes of chromium, molybdenum, and tungsten provide routes to novel binuclear complexes. Thermal decarbonylation methods work very well in the case of the molybdenum complexes, but photochemical decarbonylations appear preferable in the cases of chromium and tungsten complexes. In many cases, particularly the chromium and tungsten complexes, the preparations of the binuclear complexes can be simplified considerably by generating the mononuclear complex precursor in situ by irradiating the metal hexacarbonyl with the $RN(PF_2)_2$ ligand in an appropriate mole ratio. In any case the type of binuclear metal carbonyl complex produced in such reactions is influenced largely by the $RN(PF_2)_2$/metal ratio present in either the mononuclear metal carbonyl precursor or the $RN(PF_2)_2/M(CO)_6$ system used in the in situ experiments. Furthermore, use of excess $RN(PF_2)_2$ ligand in the photochemical reactions with $M(CO)_6$ must be avoided in order to prevent formation of the previously reported carbonyl-free complexes $[RN(PF_2)_2]_3M$ (M = Cr, Mo, and W; R = CH_3[5] and C_6H_5[8]).

The mononuclear molybdenum complexes $RN(PF_2)_2Mo(CO)_4$ (I: M = Mo; R = CH_3 and C_6H_5) undergo facile pyrolysis in saturated hydrocarbon solvents at 100–130 °C to give binuclear derivatives of the stoichiometry $[RN(PF_2)_2]_3Mo_2(CO)_5$. This reaction clearly must involve a major rearrangement since a mononuclear precursor with a 1/1 $RN(PF_2)_2$/Mo ratio forms a binuclear product with a 1.5/1 $RN(PF_2)_2$/Mo ratio. Thus some of the mononuclear complex is clearly cannibalized to provide enough $RN(PF_2)_2$ ligands for the binuclear complex produced. Analogous binuclear chromium and tungsten complexes $[CH_3N(PF_2)_2]_3M_2(CO)_5$ (M = Cr and W) are best prepared by irradiation of $CH_3N(PF_2)_2$ with the corresponding metal hexacarbonyl in a 1/1 $CH_3N(PF_2)_2$/metal mole ratio. Such reactions clearly involve $CH_3N(PF_2)_2M(CO)_4$ (M = Cr and W) intermediates but appear to be more convenient and efficient than preparing and isolating pure $CH_3N(PF_2)_2M(CO)_4$ derivatives followed by their ultraviolet irradiation.

Spectroscopic properties of the $[RN(PF_2)_2]_3M_2(CO)_5$ complexes relevant to their structure elucidation include the following: (1) Observation of four terminal ν(CO) frequencies and one bridging ν(CO) frequency (1765–1796 cm^{-1}) suggesting a structure containing four terminal carbonyl groups and one bridging carbonyl group. (2) Observation of two methyl resonances in an approximate 2/1 ratio in the proton and carbon-13 NMR spectra (Table II) of the $[CH_3N(PF_2)_2]_3M_2(CO)_5$ complexes (M = Cr, Mo, and W). These observations are consistent with the structure VIII for these complexes. A structure of this type has recently been confirmed by X-ray crystallography[30] for $[C_6H_5N(PF_2)_2]_3Mo_2(CO)_5$. The 2/1 pattern of methyl resonances for $[CH_3N(PF_2)_2]_3M_2(CO)_5$ relates to the inability for all three $CH_3N(PF_2)_2$ bridges to be situated equivalently with respect to the bridging CO group. Instead two of the $CH_3N(PF_2)_2$ bridges can be equivalent and the third unique in accord with the observed proton and carbon-13 NMR spectra.



VIII



IX

Decarbonylation of mononuclear metal carbonyl complexes having a 2/1 $RN(PF_2)_2$/metal ratio leads to a different series of binuclear products. Again pyrolysis is a suitable decarbonylation method for the molybdenum complexes whereas photolysis appears to be necessary for decarbonylation of the tungsten complexes. Pyrolysis of $[RN(PF_2)_2]_2Mo(CO)_3$ complexes (generated in situ from $C_7H_8Mo(CO)_3$ (VI: M = Mo) and two $RN(PF_2)_2$, identified by NMR but not readily isolated in the pure state) in hydrocarbon solvents at 100–130 °C produces mixtures of binuclear complexes separable by combinations of chromatography and fractional crystallization. In both cases investigated (R = CH_3 and C_6H_5), one of the binuclear products has the general stoichiometry $[RN(PF_2)_2]_4Mo_2(CO)_3$. The infrared spectra of these products exhibit two terminal ν(CO) frequencies and one bridging ν(CO) frequency, suggesting corresponding numbers of terminal and bridging carbonyl groups. The carbon-13 NMR spectrum of $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ exhibits three methyl resonances in a 1/1/2 pattern. The observations are consistent with structure IX which has been confirmed by X-ray crystallography[30] for $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$.

The second binuclear product obtained from the decarbonylation of the 2/1 $RN(PF_2)_2$/metal systems appears to depend upon the specific $RN(PF_2)_2$ ligand. The ligand $CH_3N(PF_2)_2$ gives products of the stoichiometry $[CH_3N(PF_2)_2]_5M_2CO$ (M = Mo and W). The infrared spectra of these products exhibit a single *terminal* ν(CO) frequency and no bridging ν(CO) frequencies. This suggests a structure X (R = CH_3) in which one of the five $CH_3N(PF_2)_2$ ligands has undergone phosphorus–nitrogen bond cleavage to give separate PF_2 and CH_3NPF_2 units completely analogous to structure XI shown by X-ray crystallography[11] for the iron carbonyl complex $[CH_3N(PF_2)_2]_4Fe_2CO$ of analogous stoichiometry except for the obvious adjustment in the number of $CH_3N(PF_2)_2$ ligands to give the metals the favored rare gas electronic configuration.

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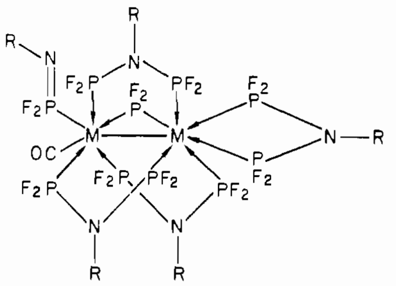
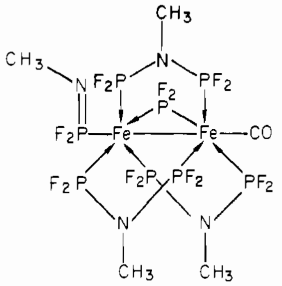
[30] M. G. Newton, R. B. King, T. W. Lee, L. Norskov-Lauritzen, and V. Kumar, *J. Chem. Soc., Chem. Commun.*, in press.

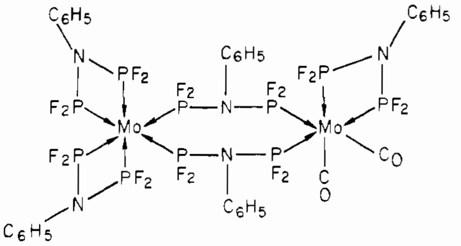


X



XI

The second product obtained by decarbonylation of the $[C_6H_5N(PF_2)_2]_2Mo(CO)_3$ system is not a monocarbonyl but instead appears to be a dicarbonyl of stoichiometry $[C_6H_5N(PF_2)_2]_5Mo_2(CO)_2$. This product has two terminal ν(CO) frequencies and no bridging ν(CO) frequencies. We suggest structure XII for this complex and rationalize the formation of XII rather than X ($R = C_6H_5$) on the basis that phosphorus–nitrogen bond cleavage in $C_6H_5N(PF_2)_2$ reactions is much more difficult than phosphorus–nitrogen bond cleavage in $CH_3N(PF_2)_2$ reactions.[8]



XII

(C) NMR Spectra. The metal carbonyl complexes of the $RN(PF_2)_2$ ligands contain four spin $^1/_2$ nuclei (^1H, ^{13}C, ^{19}F, and ^{31}P) which can be studied by NMR spectroscopy. The proton and carbon-13 NMR spectra (Table II) of $CH_3N(PF_2)_2$ complexes are relatively simple and can be used to identify the various different types of $CH_3N(PF_2)_2$ ligands in the diverse metal complexes. The proton and carbon-13 NMR spectra of the $C_6H_5N(PF_2)_2$ complexes are much less informative because of the complexities of the patterns of the phenyl resonances and their insensitivity toward structural changes. The phosphorus-31 and fluorine-19 NMR spectra (Table III) are considerably more complex owing to the diversity of phosphorus–phosphorus, phosphorus–fluorine, and fluorine–fluorine coupling constants. Elucidation of these coupling constants (a nontrivial matter in any case) was easier in the case of the phosphorus-31 NMR spectra since proton-decoupled pulsed Fourier transform equipment (which enhanced the sensitivity and sharpness of the peaks) was available for the phosphorus-31 NMR spectra whereas only an antiquated continuous wave instrument was available for the fluorine-19 NMR spectra.

The proton NMR spectra (Table II) of the new $CH_3N(PF_2)_2$ complexes prepared during the course of this work are consistent with those previously found in related complexes.[6] Thus biligate monometallic complexes such as $CH_3N(PF_2)_2M(CO)_4$ (I: $R = CH_3$; M = Cr, Mo, and W) exhibit an apparent triplet methyl proton resonance arising from equivalent coupling of the methyl protons with both phosphorus atoms. However, monoligate monometallic complexes such as *trans*-$[CH_3N(PF_2)_2]_2Cr(CO)_4$ (II: $R = R' = CH_3$) and *cis*-$[CH_3N(PF_2)_2]_2M(CO)_4$ (III: $R = CH_3$; M = Mo and W) exhibit a basic doublet methyl resonance pattern arising from coupling of the methyl protons with only the complexed phosphorus atom. This doublet may be further split by longer range couplings with the other phosphorus atoms. Complexes such as *mer*-$[CH_3N(PF_2)_2]_2Cr(CO)_3$ (IV: $R = CH_3$; M = Cr) exhibit both a doublet methyl resonance corresponding to the monodentate $CH_3N(PF_2)_2$ ligand and a triplet methyl resonance corresponding to the bidentate $CH_3N(PF_2)_2$ ligand.

The carbon-13 methyl resonances in the proton-decoupled carbon-13 NMR spectra (Table II) are singlets. Their chemical shifts provide a basis for differentiating between monodentate and bidentate $CH_3N(PF_2)_2$ ligands. Thus the carbon-13 methyl resonances of monoligate monometallic $CH_3N(PF_2)_2$ ligands fall in the range δ 25–26 in accord with previous observations.[6] Similarly the carbon-13 methyl resonances of biligate monometallic $CH_3N(PF_2)_2$ ligands fall in the range δ 29–31 again in accord with previous observations.[6] The carbon-13 methyl resonances of the biligate bimetallic $CH_3N(PF_2)_2$ ligands in the biligate bimetallic $CH_3N(PF_2)_2$ complexes fall in a wider range (δ 28–33) but still do not overlap the monoligate monometallic $CH_3N(PF_2)_2$ range (δ 25–27). The complexes *mer*-$[CH_3N(PF_2)_2]_2M(CO)_3$ (IV: M = Cr, Mo, and W) exhibit two carbon-13 methyl resonances of approximately equal relative intensities in accord with the presence of one monoligate monometallic and one biligate monometallic $CH_3N(PF_2)_2$ ligand.

The chemical shifts of the carbon-13 carbonyl resonances increase in the sequence Cr < Mo < W in accord with previous reports.[31] Some fine structure is evident arising from various phosphorus–carbon couplings. Thus the higher field carbonyl carbon-13 triplets in $CH_3N(PF_2)_2M(CO)_4$ (I: $R = CH_3$; M = Cr, Mo, and W) and *cis*-$[CH_3N(PF_2)_2]_2Mo(CO)_4$ (III: $R = CH_3$; M = Mo) may be assigned to the pair of two mutually trans CO groups coupled equally to the two donor phosphorus atoms. The carbon-13 carbonyl resonances in the $C_6H_5N(PF_2)_2$ metal carbonyl derivatives have essentially identical chemical shifts and fine structures as those in the corresponding $CH_3N(PF_2)_2$ metal carbonyl derivatives and therefore are not reported in detail.

The phosphorus-31 and fluorine-19 NMR spectra (Table III) form an X_2AAX_2 pattern which has been analyzed in some detail;[21,32] nevertheless, the previous papers are vague as to how to extract the relevant coupling constants from the actual spectra. Figure 1a shows the pattern of the proton-decoupled phosphorus-31 NMR spectrum of $CH_3N(PF_2)_2$. The following coupling constants can be extracted from this spectrum: (a) $|^1J(PF)|$, arithmetic mean of the separations between X and E and between X and the midpoint of AB and CD; (b) $|^2J(PP)|$, the separation between AB and CD; (c) $|^3J(PF)|$, half of the difference between the separations between X and E and between X and the midpoint of AB and CD.

The general appearance of the phosphorus-31 NMR spectra of the $RN(PF_2)_2M(CO)_4$ complexes (I: $R = CH_3$ and C_6H_5; M = Cr, Mo, and W) is the same although since the peaks are sharper, additional fine structure can be observed. Figure 1b shows the low-field cluster of peaks in the proton-decoupled phosphorus-31 NMR spectra of $CH_3N(PF_2)_2Cr(CO)_4$ (I: $R = CH_3$; M = Cr). Peaks A and B and peaks C and D are now resolved and peaks B and D are further split into doublets. The

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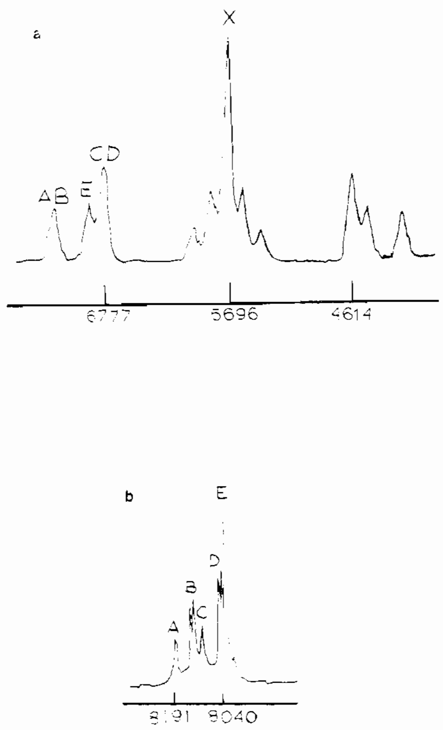


Figure 1. (a) Proton-decoupled phosphorus-31 NMR spectrum of $CH_3N(PF_2)_2$. (b) Low-field cluster of peaks in the proton-decoupled phosphorus-31 NMR spectrum of $CH_3N(PF_2)_2Cr(CO)_4$. The numbers in Figures 1 and 2 refer to the frequency in Hz downfield from external 85% H_3PO_4 at 40.3 MHz.

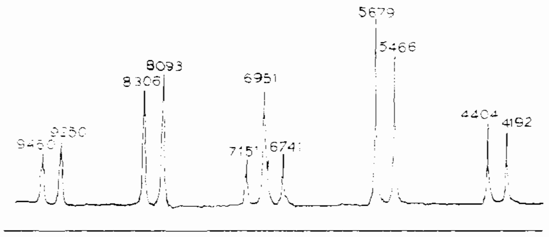


Figure 2. Proton-decoupled phosphorus-31 NMR spectrum of *trans*-$[CH_3N(PF_2)_2]_2Cr(CO)_4$.

splitting of B and D corresponds to $|^4J(FF)|$. The separations A–C and B–D correspond to $|^2J(PP)|$, and the separations A–B and C–D correspond to $|^3J(PF)|$.

The general appearance of the phosphorus-31 NMR spectra of monoligate monometallic $RN(PF_2)_2$ complexes is quite different since the coupling constants $|^3J(PF)|$ are much smaller. Figure 2 shows the proton-decoupled phosphorus-31 NMR spectrum of *trans*-$[CH_3N(PF_2)_2]_2Cr(CO)_4$ (II: R = R′ = CH_3), a representative complex of this type. Each phosphorus atom gives rise to a triplet of doublets with the triplet separation corresponding to $|^1J(PF)|$ and the doublet separation corresponding to $|^2J(PP)|$. The doublet separations for both of the phosphorus resonances thus correspond to the same coupling constant and therefore are equal within experimental error. In all of the monoligate monometallic $RN(PF_2)_2$ complexes the higher field phosphorus-31 resonance is assigned to the uncomplexed phosphorus atom because of the closer proximity of its chemical shift to that of the free ligand.

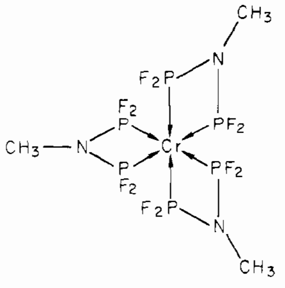
The phosphorus-31 NMR spectra of $RN(PF_2)_2$ complexes containing two or more nonequivalent $RN(PF_2)_2$ ligands (e.g., *mer*-$[RN(PF_2)_2]_2Cr(CO)_3$ (IV) and the binuclear complexes) are considerably more complex. Some attempts are made in Table III to assign the observed resonances and estimate a few of the larger coupling constants for such complexes, but these assignments are less certain than those for the simpler complexes containing only one type of $RN(PF_2)_2$ ligand. Two specific complications in the phosphorus-31 NMR spectra of $RN(PF_2)_2$ complexes containing two or more different types of $RN(PF_2)_2$ ligands are the following: (1) nonequivalence of the two donor phosphorus atoms in a chelating (biligate monometallic) $RN(PF_2)_2$ ligand (e.g., the *mer*-$[RN(PF_2)_2]_2Cr(CO)_3$ derivatives (IV); (2) coupling between phosphorus atoms in nonequivalent $RN(PF_2)_2$ ligands.

The various coupling constants obtainable from the phosphorus-31 NMR spectra (Table III) have the following characteristic features: (a) $|^1J(PF)|$, this coupling constant is significantly less for the complexed phosphorus atom of a monoligate monometallic $RN(PF_2)_2$ ligand (1140–1170 Hz) than for the complexed phosphorus atoms of a biligate monometallic or biligate bimetallic $RN(PF_2)_2$ ligand (1275–1320 Hz). (b) $|^2J(PP)|$, this coupling constant increases in the sequences Cr < Mo < W and biligate monometallic < monoligate monometallic < free ligand. (c) $|^3J(PF)|$, this coupling constant is very small in monoligate monometallic $RN(PF_2)_2$ complexes but otherwise is rather insensitive toward structural changes. (d) $|^4J(FF)|$, this coupling constant, in the rare cases that it is observable, increases in the sequence W < Mo < Cr.

Fluorine-19 NMR spectra of the more soluble complexes were also obtained with an old instrument that was not operative during the earlier work.[5-7] In principle, the same coupling constants obtainable from the phosphorus-31 NMR spectra are also obtainable from the fluorine-19 NMR spectra. However, in practice the signal-to-noise ratio of the fluorine-19 NMR spectra was in general insufficient for observation of all of the weaker peaks required for calculation of the coupling constants. Nevertheless, the coupling constants for the $RN(PF_2)_2M(CO)_4$ complexes were also checked in the fluorine-19 NMR spectra and found to be in agreement within experimental error to the coupling constants listed in Table III which were obtained from the phosphorus-31 NMR spectra.

The fluorine-19 NMR chemical shifts appear to be diagnostic of the types of phosphorus atoms to which the fluorines are bonded as follows: (a) PF_2 groups of uncomplexed phosphorus atoms (ϕ ~75); (b) PF_2 groups of chelating $RN(PF_2)_2$ ligands (ϕ ~40–55); (c) PF_2 groups of complexed phosphorus atoms in monodentate $RN(PF_2)_2$ ligands (ϕ ~ 20–35).

The fluorine-19 NMR spectrometer was not operative when the previous papers[5-7] on $RN(PF_2)_2$ complexes were written. Therefore, attempts were now made to obtain some fluorine-19 NMR spectra of some of these previously reported complexes which were still available. Unfortunately, the spectrometer was too insensitive to obtain spectra of many of these complexes. Of particular interest, however, is the fluorine-19 NMR spectrum of the tris bidentate complex $[CH_3N(PF_2)_2]_3Cr$ (XIII), which exhibits two very broad doublets (J ≈ 1260 Hz) of equal relative intensities at ϕ 34.5 and ϕ 46.7. The six symmetry elements of the D_3 point group of $[CH_3N(PF_2)_2]_3Cr$ divide the 12 fluorine atoms into two symmetry-related sets of six fluorine atoms in accord with the observed fluorine-19 NMR spectrum. In other words, the lack of a



XIII

symmetry plane in $[CH_3N(PF_2)_2]_3Cr$ makes nonequivalent the two fluorine atoms attached to a given phosphorus atom, thereby accounting for the two fluorine doublets of equal relative intensities.

(D) Infrared and Raman Spectra. The approximate CO stretching force constants (Table IV) were calculated by a variation of the Cotton–Kraihanzel method[23,24] as outlined in the Experimental Section. Combination of infrared and Raman data on the *trans*-$[RN(PF_2)_2]_2Cr(CO)_4$ complexes (II) suggested that the trans/cis interaction constant ratio was about 3, a constraint that was used for the force constant calculations for the otherwise underdetermined *cis*-$L_2M(CO)_4$ and *mer*-$L_3M(CO)_3$ derivatives. This contrasts with the trans/cis interaction constant ratio of 2 that was assumed for the original Cotton–Kraihanzel calculations[23,24] as well as in most subsequent treatments. The CO stretching force constants (Table IV) generally fall in the range 15.8–16.0 mdyn/Å except for the mutually trans pair of CO groups in the *cis*-$L_2M(CO)_4$ derivatives of the types I and III, which have appreciably higher stretching force constants (16.4–16.7 mdyn/Å). The magnitudes of these CO stretching force constants suggests that the π-acceptor strength of the donor phosphorus atoms in the $RN(PF_2)_2$ ligands is lower than that of the phosphorus atom in PCl_3 but comparable with the phosphorus atom in $C_2H_5OPCl_2$.[24] The various stretch–stretch interaction constants (t, c, and d in Table IV) appear to be very insensitive toward structural changes. In future analyses of more complicated and highly underdetermined ν(CO) spectra of $RN(PF_2)_2$ metal carbonyls, it probably would not introduce serious errors in the approximate CO stretching constants (corresponding to $k(1)$ and $k(2)$ in Table IV) to use $t = 0.6$ mdyn/Å and $c = d = 0.2$ mdyn/Å as constraints on the calculations provided that such constraints in the stretch–stretch interaction constants were limited to pairs of CO groups on the same metal atom subtending angles of approximately 180 and 90°, respectively.

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Registry No. $CH_3N(PF_2)_2Cr(CO)_4$, 73949-36-7; *trans*-$[CH_3N(PF_2)_2]Cr(CO)_4$, 73949-37-8; $CH_3N(PF_2)_2Mo(CO)_4$, 79734-75-1; *cis*-$[CH_3N(PF_2)_2]_2Mo(CO)_4$, 79721-42-9; $CH_3N(PF_2)_2W(CO)_4$, 79734-76-2; *cis*-$[CH_3N(PF_2)_2]_2W(CO)_4$, 79721-43-0; $C_6H_5N(PF_2)_2Cr(CO)_4$, 79721-44-1; *trans*-$[C_6H_5N(PF_2)_2]_2Cr(CO)_4$, 79721-45-2; $C_6H_5N(PF_2)_2Mo(CO)_4$, 79721-46-3; *cis*-$[C_6H_5N(PF_2)_2]_2Mo(CO)_4$, 79721-47-4; $C_6H_5N(PF_2)_2W(CO)_4$, 79721-48-5; *trans*-$[CH_3N(PF_2)_2][C_6H_5N(PF_2)_2]Cr(CO)_4$, 79721-49-6; *mer*-$[CH_3N(PF_2)_2]_2Cr(CO)_3$, 79721-50-9; *mer*-$[C_6H_5N(PF_2)_2]_2Cr(CO)_3$, 79734-77-3; $[C_6H_5N(PF_2)_2]_3Cr_2(CO)_6$, 79721-51-0; $[CH_3N(PF_2)_2]_3Cr_2(CO)_5$, 79721-52-1; $[CH_3N(PF_2)_2]_3Mo_2(CO)_5$, 79721-55-4; $[C_6H_5N(PF_2)_2]_3Mo_2(CO)_5$, 79721-56-5; $[CH_3N(PF_2)_2]_3W_2(CO)_5$, 79734-78-4; $[CH_3N(PF_2)_2]_5Mo_2CO$, 79746-02-4; $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$, 79721-57-6; $[C_6H_5N(PF_2)_2]_5Mo_2(CO)_2$, 79734-79-5; $[CH_3N(PF_2)_2]_4W_2(CO)_3$, 79721-58-7; *mer*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$, 79721-53-2; *mer*-$[CH_3N(PF_2)_2]_2W(CO)_3$, 79721-54-3; $[CH_3N(PF_2)_2]_4Cr_2(CO)_3$, 79734-80-8; $CH_3N(PF_2)_2$, 17648-18-9; $C_6H_5N(PF_2)_2$, 23611-36-1; $C_7H_8Cr(CO)_4$, 12146-36-0; $C_7H_8Mo(CO)_4$, 12146-37-1; $C_7H_8W(CO)_4$, 12129-25-8; $C_7H_8Cr(CO)_3$, 12125-72-3; $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; $C_7H_8Mo(CO)_3$, 12125-77-8; $Mo(CO)_6$, 13939-06-5; $[C_6H_5N(PF_2)_2]_4Mo_2(CO)_3$, 79721-59-8; $[CH_3N(PF_2)_2]_5W_2CO$, 79769-50-9.

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Trans Isomers of Ruthenium(II) Complexes Containing Two Bipyridine Ligands

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Three different reactions which lead to the formation of complexes of the type *trans*-Ru(2,2′-bipyridine)$_2$XY^{n+} have been investigated. The thermal substitution reactions of *trans*-Ru(2,2′-bipyridine)$_2$(OH$_2$)$_2^{2+}$ appear to offer the most general and efficient synthetic route to this group of compounds. Species containing pyridine, pyrazole, acetonitrile, substituted phosphines, NO_2^-, NO^+, and Cl^- have been prepared.

Introduction

Transition-metal complexes of the type $M(bpy)_2XY^{n+}$ (where bpy = 2,2′-bipyridine) were thought, for many years, to be unstable in the trans geometry. The instability was attributed to the expected unfavorable interaction of the α hydrogens on the opposing bipyridine ligands. The idea seemed to be well-founded in light of the complete lack of examples and the many incorrect isomeric assignments.[1] In 1972, however, the crystal structure of $[Pd(bpy)_2](NO_3)_2$ was reported,[2] followed a few years later by the structures[3,4] of $[Pt(bpy)_2](TCNQ)_2$ and $Cu(bpy)_2(ClO_4)_2$. In recent years two additional examples have appeared. The first was a report, which lacked definitive structural evidence, by Krause[5] concerning the synthesis of *trans*-$[Ru(bpy)_2(py)_2](ClO_4)_2$. The second was the photochemical conversion of *cis*-$Ru(bpy)_2(OH_2)_2^{2+}$ to *trans*-$Ru(bpy)_2(OH_2)_2^{2+}$ reported by one of the authors.[6] In the latter example, the geometry of the oxidized complex *trans*-$[Ru(bpy)_2(OH)(OH_2)](ClO_4)_2$ was verified by an X-ray structure determination. The existence of this collection of complexes suggests that complexes in this geometry are not as unstable as suspected. There remains to be found, however, general synthetic procedures which will enable other species to be produced and studied.

To this end we wish to report some observations dealing with reactions which yield complexes of the general type *trans*-$Ru(bpy)_2XY^{n+}$. The first of these concerns the stereoretentive substitution reactions of *trans*-$Ru(bpy)_2(OH_2)_2^{2+}$. The second

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