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Metal Complexes of Fluorophosphines. 5. Reactions of Mononuclear Cyclopentadienylmetal Carbonyls with Methylaminobis(difluorophosphine)[1-3]

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Received December 23, 1977

Ultraviolet irradiation of $C_5H_5Mn(CO)_3$ with $CH_3N(PF_2)_2$ in diethyl ether gives successively $C_5H_5Mn(CO)(PF_2)_2NCH_3$ and $C_5H_5Mn[(PF_2)_2NCH_3]_2$ as distillable yellow liquids. Reaction of $C_5H_5Mo(CO)_2NO$ with $CH_3N(PF_2)_2$ in boiling benzene slowly forms yellow-orange solid $C_5H_5Mo(CO)(NO)(PF_2)_2NCH_3$. Reactions of $C_5H_5M(CO)_3Cl$ (M = Mo, W) with $CH_3N(PF_2)_2$ successively form orange $C_5H_5M(CO)_2[(PF_2)_2NCH_3]Cl$ and yellow $C_5H_5M[(PF_2)_2NCH_3]_2Cl$. Reaction of $C_5H_5Fe(CO)_2Cl$ with $CH_3N(PF_2)_2$ gives successively red-purple $C_5H_5Fe(CO)[(PF_2)_2NCH_3]Cl$ and red $C_5H_5Fe[(PF_2)_2NCH_3]_2Cl$. Reactions of $C_5H_5Mo(CO)_3Cl$ with $CH_3N(PF_2)_2$ in the presence of methanol or ethanol result in the methanolysis of one of the two PF_2 groups from the ligand to give orange $C_5H_5Mo(CO)_2(PF_2NHCH_3)Cl$ and brown-black $C_5H_5Fe(CO)(PF_2NHCH_3)Cl$, respectively. However, reaction of $C_5H_5W(CO)_3Cl$ with $CH_3N(PF_2)_2$ in the presence of the alcohols ROH (R = CH_3, C_2H_5) follows a different pathway to give the orange fluorophosphite complexes $C_5H_5W(CO)_2[PF(OR)_2]Cl$ (R = CH_3, C_2H_5). The complexes $C_5H_5Mn[(PF_2)_2NCH_3]_2$ and $C_5H_5M[(PF_2)_2NCH_3]_2Cl$ (M = Mo, W) are unusual in containing both monoligate monometallic and biligate monometallic $CH_3N(PF_2)_2$ ligands. The proton, carbon-13, and phosphorus-31 NMR spectra of all of the new compounds have been obtained and provide spectroscopic criteria for differentiating between monoligate monometallic and biligate monometallic $CH_3N(PF_2)_2$ ligands.

Introduction

The previous paper of this series[1] discusses reactions of $CH_3N(PF_2)_2$ with mononuclear metal carbonyls such as $M(CO)_6$ (M = Cr, Mo, W), $Fe(CO)_5$, and $Ni(CO)_4$. This paper describes similar reactions of $CH_3N(PF_2)_2$ with the mononuclear cyclopentadienylmetal carbonyl derivatives $C_5H_5Mn(CO)_3$, $C_5H_5Mo(CO)_2NO$, $C_5H_5M(CO)_3Cl$ (M = Mo, W), and $C_5H_5Fe(CO)_2Cl$. In these reactions the cyclopentadienyl–metal bond remains intact. Therefore, fewer coordination positions are available for the $CH_3N(PF_2)_2$ ligand in its reactions with the mononuclear cyclopentadienylmetal carbonyls than in its reactions with the monometallic metal carbonyls mentioned above. Complexes containing fewer $CH_3N(PF_2)_2$ ligands and/or some monoligate monometallic $CH_3N(PF_2)_2$ ligands are, therefore, obtained from the cyclopentadienylmetal carbonyls. These complexes are significant in providing a useful basis for characterizing different bonding types of $CH_3N(PF_2)_2$ ligands from differences in their NMR spectra. In addition, solvolytic cleavage of phosphorus–nitrogen and phosphorus–fluorine bonds has been observed in some reactions of $CH_3N(PF_2)_2$ with the cyclopentadienylmetal carbonyls thereby leading to novel metal complexes of the CH_3NHPF_2 and $(RO)_2PF$ (R = CH_3, C_2H_5) ligands. Such ligands are not readily available in the free state for direct reactions with metal carbonyl derivatives.

Experimental Section

Elemental analyses, melting points, and infrared spectra in the ν(CO) region of the new metal complexes are given in Table I. In addition, the proton (Table II), carbon-13 (Table II), and phosphorus-31 (Table III) NMR spectra of the new complexes are presented in the indicated tables. The general experimental techniques for obtaining such data as well as the general precautions for handling potentially air-sensitive compounds and the preparations of $CH_3N(PF_2)_2$ on a large scale are given in the previous paper of this series.[1] The metal carbonyl derivatives $M(CO)_6$ (M = Mo, W; Pressure Chemical Corp., Pittsburgh, Pa.), $C_5H_5Mn(CO)_3$ (Ethyl Corp., New York, N.Y.), and $Fe(CO)_5$ (GAF Corp., New York, N.Y.) were obtained from the indicated commercial sources. The starting materials $C_5H_5M(CO)_3Cl$ (M = Mo, W),[5,6] $C_5H_5Mo(CO)_2NO$,[5,7] and $C_5H_5Fe(CO)_2Cl$[8] were prepared by the cited published procedures.

Preparation of $C_5H_5Mn(CO)(PF_2)_2NCH_3$. A mixture of 2.03 g (10 mmol) of $C_5H_5Mn(CO)_3$, 1.67 g (10 mmol) of $CH_3N(PF_2)_2$, and 250 mL of diethyl ether was exposed to ultraviolet irradiation for 90 min. The reaction mixture was filtered through Celite and solvent was removed from the filtrate at 25 °C (25 mm). A solution of the residue in hexane was chromatographed on a 2 × 30 cm Florisil column. The single yellow band was eluted with a 1:1 mixture of hexane and diethyl ether. Evaporation of the eluate followed by evaporative distillation at ~80 °C (0.25 mm) gave 1.8 g (57% yield) of air-sensitive yellow liquid $C_5H_5Mn(CO)(PF_2)_2NCH_3$.

Preparation of $C_5H_5Mn[(PF_2)_2NCH_3]_2$. A mixture of 2.03 g (10 mmol) of $C_5H_5Mn(CO)_3$, 6.4 g (38.3 mmol) of $CH_3N(PF_2)_2$, and 400 mL of diethyl ether was exposed to ultraviolet irradiation for 44 h after which time the infrared spectrum showed an absence of metal carbonyl groups. Isolation of the product by the same procedure as used above for the preparation of $C_5H_5Mn(CO)(PF_2)_2NCH_3$ gave 2.16 g (48% yield) of yellow liquid $C_5H_5Mn[(PF_2)_2NCH_3]_2$, bp 70–75 °C (0.5 mm).

Preparation of $C_5H_5Mo(CO)(NO)(PF_2)_2NCH_3$. A mixture of 2.47 g (10 mmol) of $C_5H_5Mo(CO)_2NO$, 1.67 g (10 mmol) of $CH_3N(PF_2)_2$, and ~100 mL of benzene was boiled under reflux for 4 days. Solvent was then removed at ~25 °C (25 mm). The resulting liquid was chromatographed on a 2 × 30 cm Florisil column in hexane solution. The resulting yellow band was eluted with 1:3 dichloromethane–hexane. Removal of solvent from the eluate followed by crystallization from pentane at −78 °C gave 0.3 g (~8% yield) of yellow-orange crystalline $C_5H_5Mo(CO)(NO)(PF_2)_2NCH_3$. Larger crystals could be obtained by slow crystallization from a mixture of pentane and hexane at −10 °C.

Attempts to prepare more highly substituted derivatives of $C_5H_5Mo(CO)_2NO$ by its ultraviolet irradiation with $CH_3N(PF_2)_2$ similar to the preparations of $C_5H_5Mn(CO)(PF_2)_2NCH_3$ and $C_5H_5Mn[(PF_2)_2NCH_3]_2$ outlined above led instead to decomposition.

Preparation of $C_5H_5Mo[(PF_2)_2NCH_3]_2Cl$. A mixture of 1.40 g (5 mmol) of $C_5H_5Mo(CO)_3Cl$, 3.2 g (19 mmol) of $CH_3N(PF_2)_2$, and ~300 mL of diethyl ether was exposed to ultraviolet irradiation for 2 h. Removal of solvent from the resulting yellow solution followed by crystallization from mixtures of dichloromethane and hexane gave 1.6 g (60% yield) of yellow crystalline $C_5H_5Mo[(PF_2)_2NCH_3]_2Cl$. The analytical sample, mp 123–125 °C, molar conductance in CH_3CN 2.0 Ω^{-1} cm^2 mol^{-1}, was obtained by a further low-temperature crystallization from a mixture of dichloromethane and pentane.

Reaction of $C_5H_5Mo(CO)_3Cl$ with excess $CH_3N(PF_2)_2$ in boiling benzene also gave some $C_5H_5Mo[(PF_2)_2NCH_3]_2Cl$, but the yields were considerably lower.

Preparation of $C_5H_5Mo(CO)_2[(PF_2)_2NCH_3]Cl$. A mixture of 2.80 g (10 mmol) of $C_5H_5Mo(CO)_3Cl$, 1.67 g (10 mmol) of $CH_3N(PF_2)_2$, and 100 mL of benzene was heated at 60–70 °C (bath temperature) for 1 h. Solvent was then removed from the reaction mixture at ~25 °C (40 mm). A solution of the oily residue in a minimum of benzene was chromatographed on a 1.5 × 40 cm Florisil column prepared in hexane. A small purple band was first eluted with a 1:1 mixture of diethyl ether and hexane. Evaporation of this eluate gave a negligible quantity of product. Elution of the large orange band with 5:1 diethyl ether–hexane followed by evaporation of the first portion of the eluate gave 0.57 g (13.6% yield) of orange $C_5H_5Mo(CO)_2[(PF_2)_2NCH_3]Cl$.

0020-1669/78/1317-2396$01.00/0

Table I. Properties of Compounds Obtained from Cyclopentadienylmetal Carbonyls and Methylaminobis(difluorophosphine)

Compound[a]	Color	Mp,[b] °C	Analyses[c]								IR
				% C	% H	% N	% Cl	% P	% F	Mol wt[d]	ν(CO),[e] $\mathrm{cm^{-1}}$
			A. Manganese Derivatives								
$\mathrm{CpMn(CO)(PF_2)_2NMe}$	Yellow	Liquid	Calcd	26.7	2.5	4.4					1935
			Found	26.5	2.6	4.4					
$\mathrm{CpMn[(PF_2)_2NMe]_2}$	Yellow	Liquid	Calcd	18.5	2.4	6.2					
			Found	18.6	2.4	6.1					
			B. Molybdenum Derivatives								
$\mathrm{CpMo(CO)(NO)(PF_2)_2NMe}$	Yellow-orange	43–45	Calcd	21.8	2.1	7.2					1970
			Found	22.0	2.1	7.3					1670 (ν(NO))
$\mathrm{CpMo[(PF_2)_2NMe]_2Cl}$	Yellow	122–123	Calcd	15.8	2.1	5.3	6.7	23.4	28.6	530	
			Found	16.0	2.0	5.4	7.3	23.2	28.7	511	
$\mathrm{CpMo(CO)_2[(PF_2)_2NMe]Cl}$	Orange	92–94	Calcd	22.9	1.9	3.3	8.4			419	2020, 1941
			Found	22.7	2.0	3.3	8.6			419	
$\mathrm{CpMo(CO)_2[PF_2NHMe]Cl}$	Orange	98–100	Calcd	27.3	2.6	4.0	10.1	8.8	10.8	352	2029, 1938
			Found	27.7	2.2	4.0	10.0	8.8	10.5	342	
			C. Tungsten Derivatives								
$\mathrm{CpW[(PF_2)_2NMe]_2Cl}$	Yellow	123–125 (dec)	Calcd	13.6	1.8	4.5	5.7	20.0	24.5	618	
			Found	13.7	1.9	4.6	5.5	20.3	24.3	620	
$\mathrm{CpW(CO)_2[(PF_2)_2NMe]Cl}$	Yellow-orange	109–111	Calcd	18.9	1.6	2.7	7.0	12.2	14.9	507	2009, 1927
			Found	19.3	1.5	2.8	6.8	12.0	14.8	503	
$\mathrm{CpW(CO)_2[PF(OMe)_2]Cl}$	Orange	148–150	Calcd	23.9	2.4	0.0	7.7			452	1984, 1904
			Found	22.6	2.4	0.0	8.0			444	
$\mathrm{CpW(CO)_2[PF(OEt)_2]Cl}$	Orange	158–160 (dec)	Calcd	27.5	3.1	0.0	7.4			480	1978, 1899
			Found	26.2	3.1	0.0	7.9			486	
			D. Iron Derivatives								
$\mathrm{CpFe[(PF_2)_2NMe]_2Cl}$	Red	62–64	Calcd	17.1	2.2	5.7	7.2	25.3	30.8	490	
			Found	17.2	2.3	5.6	7.1	25.4	31.0	495	
$\mathrm{CpFe(CO)[(PF_2)_2NMe]Cl}$	Red-purple	85–87	Calcd	24.0	2.3	4.0	10.1	17.6	22.8	351	2003
			Found	24.2	2.3	4.0	10.3	17.7	21.4	326	
$\mathrm{CpFe(CO)[PF_2NHMe]Cl}$	Brown-black	112–114	Calcd	29.6	3.2	4.9	12.5			283	1980
			Found	29.8	3.2	4.9	12.4			276	

[a] Me = methyl, Cp = η^5-cyclopentadienyl. [b] Melting points were taken in capillaries and are uncorrected. [c] Microanalyses were performed by Atlantic Microanalytical Laboratory, Atlanta, Ga. (C, H, N, and Cl), and Galbraith Laboratories, Inc., Knoxville, Tenn. (P and F). [d] Molecular weights were determined by vapor pressure osmometry in benzene solution. [e] Infrared spectra in the ν(CO) region were determined in hexane solution and recorded on a Perkin-Elmer Model 621 spectrophotometer with grating optics. Each spectrum was calibrated against the 1601-$\mathrm{cm^{-1}}$ band of polystyrene film.

Table II. Proton and Proton-Decoupled ^{13}C NMR Spectra of Compounds Obtained from Cyclopentadienylmetal Carbonyls and Methylaminobis(difluorophosphine)

	Proton NMR spectrum,[b,d] τ			Proton-decoupled ^{13}C NMR spectrum,[c,d] δ			
Compound[a]	Solvent	C_5H_5	CH_3	Solvent	CO	C_5H_5	CH_3
$\mathrm{CpMn(CO)(PF_2)_2NMe}$	C_6H_6	5.91 d (3)	8.00 t (11)	C_6H_6	*e*	78.8	29.7
$\mathrm{CpMn[(PF_2)_2NMe]_2}$	$CDCl_3$	5.61	~7.1 br, 7.45 t (12)	$CDCl_3$		78.1	30.1, 26.4
$\mathrm{CpMo(CO)(NO)(PF_2)_2NMe}$	$CDCl_3$	4.44 s	7.08 br, d (7)	$CDCl_3$	230.3 d (12)	93.4	26.0
$\mathrm{CpMo[(PF_2)_2NMe]_2Cl}$	$CDCl_3$	4.59 d (2)	7.06 br, 7, 11 t (11)	$CDCl_3$		92.4	31.0, 25.8
$\mathrm{CpMo(CO)_2[(PF_2)_2NMe]Cl}$	$CDCl_3$	4.37 s	7.08 br, d (8)	$CDCl_3$	246.6 d (41), 228.6	94.7	25.4
$\mathrm{CpMo(CO)_2[PF_2NHMe]Cl}$	$CDCl_3$	4.30 s	7.13 ddt (11, 6, 1, 5)	$CDCl_3$	248.7, 232.5	94.6	26.5
$\mathrm{CpW[(PF_2)_2NMe]_2Cl}$	$CDCl_3$	4.41 d (3)	7.02 t (12), 7.06 br, d (8)	$CDCl_3$		89.5	31.6, 25.6
$\mathrm{CpW(CO)_2[(PF_2)_2NMe]Cl}$	$CDCl_3$	4.17 s	7.09 br, d (8)	$CDCl_3$	236.5 d (29), 219.7	92.8	26.0
$\mathrm{CpW(CO)_2[PF(OMe)_2]Cl}$	$CDCl_3$	4.30 s	6.20 d (12)	$CDCl_3$	241.2 d (31), 227.6 d (11)	92.8	54.6 d (12)
$\mathrm{CpW(CO)_2[PF(OEt)_2]Cl}$	$CDCl_3$	4.27 s	8.64 t (7); CH_2: 5.86 q (7)	$CDCl_3$ + CH_2Cl_2	242.4 d (34), 229.4 d (11)	93.1	16.3; CH_2: 64.6 d (20)
$\mathrm{CpFe[(PF_2)_2NMe]_2Cl}$	$CDCl_3$	5.25 s	6.94 br, d (7)	$CDCl_3$		81.6	26.1
$\mathrm{CpFe(CO)[(PF_2)_2NMe]Cl}$	$CDCl_3$	5.05 s	7.00 br, d (8)	$CDCl_3$	213.9 d (44)	83.5	25.7
$\mathrm{CpFe(CO)[PF_2NHMe]Cl}$	$CDCl_3$	5.09 d (1)	7.24 ddt (12, 6, 1)	$CDCl_3$	215.1 d (44)	82.7	26.6

[a] Me = methyl, Cp = η^5-cyclopentadienyl. [b] Proton NMR spectra were recorded at 60 Hz on a Varian T-60 spectrometer. [c] Carbon-13 NMR spectra were recorded at 25.0336 MHz on a Jeolco PFT-100 spectrometer operating in the pulsed Fourier transform mode with proton noise decoupling and a deuterium lock. Chemical shifts are reported in ppm downfield from tetramethylsilane. [d] s = singlet, d = doublet, t = triplet, q = quartet, br = broad, ddt = double doublet of triplets; coupling constants in Hz are given in parentheses. [e] Not observed.

Preparation of $C_5H_5Mo(CO)_2[PF_2NHCH_3]Cl$. A mixture of 1.68 g (6 mmol) of $C_5H_5Mo(CO)_3Cl$, 1.0 g (6 mmol) of $CH_3N(PF_2)_2$, and 100 mL of chloroform purified by treatment with alumina was boiled under reflux for 2 h. After the solution was cooled to room temperature, 5 mL of methanol was added and the mixture stirred at room temperature for 18 h. During this period the red-orange color became somewhat lighter. Solvent was then removed at ~25 °C (25 mm). The residue was chromatographed on a 3 × 55 cm Florisil column. Elution of the orange band with 2:1 dichloromethane–hexane followed by evaporation of the eluate gave 1.0 g (47% yield) of orange crystalline $C_5H_5Mo(CO)_2[PF_2NHCH_3]Cl$: molar conductance in CH_3CN 0.6 Ω^{-1} $\mathrm{cm^2}$ $\mathrm{mol^{-1}}$; ν(N–H) in KBr 3270 $\mathrm{cm^{-1}}$.

This compound was also obtained in erratic yields from reactions of $C_5H_5Mo(CO)_3Cl$ and $CH_3N(PF_2)_2$ in a 1:1 molar ratio in boiling chloroform in the absence of added alcohol if the chloroform had not been previously freed from the ethanol preservative by alumina treatment.

Preparation of $C_5H_5W[(PF_2)_2NCH_3]_2Cl$. A mixture of 2.19 g (6 mmol) of $C_5H_5W(CO)_3Cl$, 3.10 g (19 mmol) of $CH_3N(PF_2)_2$, and 250 mL of diethyl ether was exposed to ultraviolet irradiation for 18

Table III. ^{31}P NMR Spectra of Compounds Obtained from Cyclopentadienylmetal Carbonyls and Methylaminobis(difluorophosphine)

Compound[a]	Solvent	Proton-decoupled ^{31}P NMR spectrum[b] Phosphorus type[c]	$\delta(H_3PO_4)$	$^1J(PF)$	$^2J(PP)$
$CpMn(CO)(PF_2)_2NMe$	C_6H_6	2C	−168.8	~1270	
$CpMn[(PF_2)_2NMe]_2$	$CDCl_3$	2C	−165.2	~1300	
		1C	−141.6	1235	185
$CpMo(CO)(NO)(PF_2)_2NMe$	$CDCl_3$	1C	−201.4	1156	237
		1U	−139.5	1255	237
$CpMo[(PF_2)_2NMe]_2Cl$	CH_2Cl_2		−200.2	~1170	
			−187.9	~1190	
			−158.1	1300	
			−139.1	1245	190
$CpW[(PF_2)_2NMe]_2Cl$	CH_2Cl_2		−160.7	~1150	
		1U	−142.7	~1240	
			−116.2	~1270	
$CpMo(CO)_2[(PF_2)_2NMe]Cl$	CH_2Cl_2	1C	−192.2	~1150	203
		1U	−138.2	1247	203
$CpW(CO)_2[(PF_2)_2NMe]Cl$	$CHCl_3$	1C	−154.3	1136	~170
		1U	−144.6	1260	~170
$CpMo(CO)_2[PF_2NHMe]Cl$	CH_2Cl_2	1C	−192.2	1134	
$CpW(CO)_2[PF(OMe)_2]Cl$	CH_2Cl_2	1C	−145.6	1157	
$CpW(CO)_2[PF(OEt)_2]Cl$	CH_2Cl_2	1C	−140.9	1155	
$CpFe[(PF_2)_2NMe]_2Cl$	CH_2Cl_2	1C	−194.1	1162	~160
		1U	−135.4	1251	167
$CpFe(CO)[(PF_2)_2NMe]Cl$	CH_2Cl_2	1C	−194.4	1168	165
		1U	−135.6	1258	165
$CpFe(CO)[PF_2NHMe]Cl$	CH_2Cl_2	1C	−195.1	1138	

[a] Me = methyl, Cp = η^5-cyclopentadienyl. [b] Phosphorus-31 NMR spectra were recorded at 40.3 M Hz on a Jeolco PFT-100 spectrometer operating in the pulsed Fourier transform mode with proton noise decoupling and a deuterium lock. [c] 1U = uncomplexed phosphorus atom of monoligate monometallic $CH_3N(PF_2)_2$; 1C = complexed phosphorus atom of monoligate monometallic $CH_3N(PF_2)_2$; 2C = complexed phosphorus atom of biligate monometallic $CH_3N(PF_2)_2$.

h. The resulting yellow solution was filtered through Celite and solvent removed from the filtrate at ~25 °C (25 mm). The residue was dissolved in a minimum of diethyl ether or dichloromethane. Hexane was added to the filtered solution which was then concentrated at ~40 mm to give 3.1 g (84% yield) of yellow crystalline $C_5H_5W[(PF_2)_2NCH_3]_2Cl$; molar conductance in CH_3CN 5.9 Ω^{-1} cm^2 mol^{-1}.

Preparation of $C_5H_5W(CO)_2[(PF_2)_2NCH_3]Cl$. A mixture of 1.82 g (5 mmol) of $C_5H_5W(CO)_3Cl$, 1.1 g (6.6 mmol) of $CH_3N(PF_2)_2$, and 100 mL of benzene was boiled under reflux for 18 h. Solvent was then removed at ~25 °C (25 mm). Crystallization of the residue from a mixture of dichloromethane and hexane gave 2.0 g (78% yield) of yellow-orange $C_5H_5W(CO)_2[(PF_2)_2NCH_3]Cl$. The analytical sample, mp 109–111 °C, molar conductance 1.1 Ω^{-1} cm^2 mol^{-1}, was purified further by a second crystallization from a mixture of dichloromethane and hexane or by chromatography on Florisil in hexane solution using 5:1 diethyl ether–hexane as the eluent.

Preparations of $C_5H_5W(CO)_2[PF(OR)_2]Cl$ (R = CH_3, C_2H_5). A mixture of 2.1 g (6 mmol) of $C_5H_5W(CO)_3Cl$, 1.1 g (6 mmol) of $CH_3N(PF_2)_2$, 30 mL of the appropriate alcohol (methanol for R = CH_3 and ethanol for R = C_2H_5), and 40 mL of hexane was boiled under reflux for 18 h. The resulting orange solution was filtered through Celite and solvent was removed from the filtrate at ~40 °C (25 mm). The residue was chromatographed on a 2 × 30 cm Florisil column in hexane solution. The major orange band of the product was eluted with 3:1 dichloromethane–hexane. Evaporation of the eluate followed by crystallization from a mixture of dichloromethane and hexane gave the orange crystalline $C_5H_5W(CO)_2[PF(OR)_2]Cl$ derivative in 30–55% yields.

Preparation of $C_5H_5Fe[(PF_2)_2NCH_3]_2Cl$. A mixture of 0.8 g (3.8 mmol) of $C_5H_5Fe(CO)_2Cl$, 1.5 g (9.0 mmol) of $CH_3N(PF_2)_2$, and 100 mL of hexane was boiled under reflux for 90 min. The reaction mixture was then filtered and solvent removed at ~25 °C (25 mm). The residue was chromatographed on a Florisil column in hexane solution. The major red band was eluted with a mixture of diethyl ether and hexane. Evaporation of the eluate followed by slow crystallization of the resulting oil from pentane gave 0.88 g (47% yield) of red crystalline $C_5H_5Fe[(PF_2)_2NCH_3]_2Cl$, mp 62–64 °C.

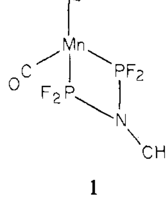
Preparation of $C_5H_5Fe(CO)[(PF_2)_2NCH_3]Cl$. A mixture of 0.8 g (3.8 mmol) of $C_5H_5Fe(CO)_2Cl$, 0.66 g (4.0 mmol) of $CH_3N(PF_2)_2$, and 100 mL of diethyl ether was boiled under reflux for 1 h. Solvent was then removed at ~25 °C (40 mm). The brown-red crystalline residue was chromatographed on a 1 × 25 cm Florisil column in hexane solution. The major red band was eluted with 1:1 diethyl ether–hexane. Evaporation of the eluate gave 0.75 g (56% yield) of red-purple $C_5H_5Fe(CO)[(PF_2)_2NCH_3]Cl$.

Reaction of $C_5H_5Fe(CO)_2Cl$ with $CH_3N(PF_2)_2$ in a 1:1 molar ratio in boiling benzene led to ferrocene as the only isolable product after chromatography.

Preparation of $C_5H_5Fe(CO)[PF_2NHCH_3]Cl$. A mixture of 0.87 g (4.0 mmol) of $C_5H_5Fe(CO)_2Cl$, 0.77 g (4.6 mmol) of $CH_3N(PF_2)_2$, 10 mL of methanol, and 100 mL of benzene was boiled under reflux for 1 h. Solvents were removed at 25 °C (25 mm). The oily residue was chromatographed on a 1.5 × 30 cm Florisil column in hexane solution. Elution of the dark brown band with 3:1 diethyl ether–hexane gave 0.53 g (38% yield) of brown-black crystalline $C_5H_5Fe(CO)[PF_2NHCH_3]Cl$; ν(N–H) in KBr 3220 cm^{-1}.

Results and Discussion

Ultraviolet irradiation of the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) with $CH_3N(PF_2)_2$ is known[1,9] to result in pairwise replacement of the six carbonyl groups with three $CH_3N(PF_2)_2$ ligands to give the carbonyl-free complexes $[CH_3N(PF_2)_2]_3M$ (M = Cr, Mo, W). Similarly, the ultraviolet irradiation of $C_5H_5V(CO)_4$ with $CH_3N(PF_2)_2$ has been shown[10] to result in the successive pairwise replacement of the four carbonyl groups to give the complexes $C_5H_5V(CO)_2(PF_2)_2NCH_3$ and $C_5H_5V[(PF_2)_2NCH_3]_2$, both of which contain only biligate monometallic $CH_3N(PF_2)_2$ ligands. The ultraviolet irradiation of $C_5H_5Mn(CO)_3$ with $CH_3N(PF_2)_2$ has now been shown to give successively the monocarbonyl $C_5H_5Mn(CO)(PF_2)_2NCH_3$ (I) containing a biligate mono-



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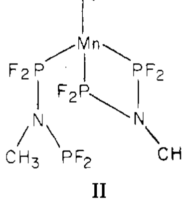

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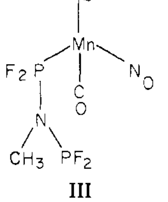
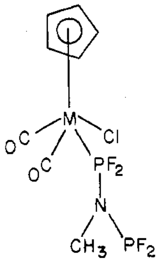


III

metallic $CH_3N(PF_2)_2$ ligand and the carbonyl-free complex $C_5H_5Mn[(PF_2)_2NCH_3]_2$ (II) containing one biligate monometallic and one monoligate monometallic ligand. Both of these complexes are air-sensitive yellow liquids which can be purified by vacuum distillation. In our hands the ultraviolet irradiation of $C_5H_5Co(CO)_2$ with excess $CH_3N(PF_2)_2$ in diethyl ether at room temperature was found to lead only to decomposition giving oily products.

The reaction of $C_5H_5Mo(CO)_2NO$ with $CH_3N(PF_2)_2$ has also been investigated. Ultraviolet irradiation of these compounds in diethyl ether leads to decomposition without the isolation of a $CH_3N(PF_2)_2$ substitution product. However, the thermal reaction of $C_5H_5Mo(CO)_2NO$ with $CH_3N(PF_2)_2$ in boiling benzene very slowly leads to the formation in low yield of orange crystalline $C_5H_5Mo(CO)(NO)(PF_2)_2NCH_3$ (III) containing a monometallic monoligate $CH_3N(PF_2)_2$ ligand. This complex was identified not only by correct elemental analyses but also by the expected single infrared ν(CO) and ν(NO) frequencies.

The initial products formed in the thermal reactions of $CH_3N(PF_2)_2$ with the cyclopentadienylmetal carbonyl chlorides $C_5H_5M(CO)_3Cl$ (M = Mo, W) and $C_5H_5Fe(CO)_2Cl$ are the monosubstituted nonionic derivatives $C_5H_5M(CO)_2[(PF_2)_2NCH_3]Cl$ (IV: M = Mo, W) and $C_5H_5Fe(CO)[(PF_2)_2NCH_3]Cl$ (V) containing a single monoligate monometallic ligand. In the case of the tungsten complex the nonionic character is confirmed by a low molar conductance in acetonitrile. The presence of two carbonyl resonances in the carbon-13 NMR spectra of the complexes $C_5H_5M(CO)_2[(PF_2)_2NCH_3]Cl$ (M = Mo, W) indicate their structures as the depicted lateral isomers IV rather than as the corresponding diagonal isomers.



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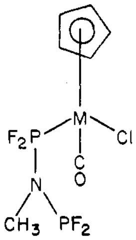

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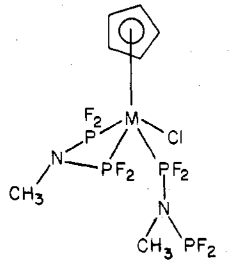
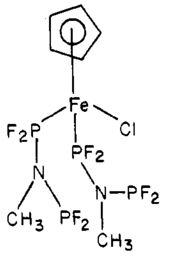


VI

Further substitution of $C_5H_5M(CO)_3Cl$ with $CH_3N(PF_2)_2$ beyond the dicarbonyls IV is most effectively accomplished by ultraviolet irradiation with excess ligand. This gives the yellow carbonyl-free complexes $C_5H_5M[(PF_2)_2NCH_3]_2Cl$ (M = Mo, W). Formulation of these complexes as the nonionic derivatives VI containing one biligate monometallic and one monoligate monometallic ligand rather than as the ionic derivatives $C_5H_5M[(PF_2)_2NCH_3]_2{}^+Cl^-$ containing two biligate monometallic ligands is supported by their low conductances in acetonitrile solution and x-ray crystallography on the molybdenum complex.[2] Attempts to remove the covalently bonded chlorine in $C_5H_5M[(PF_2)_2NCH_3]_2Cl$ with silver hexafluorophosphate in benzene to give the salt $C_5H_5M[(PF_2)_2NCH_3]_2{}^+PF_6{}^-$ containing two biligate monometallic ligands and a cation isostructural with the known[10] $C_5H_5V[(PF_2)_2NCH_3]_2$ gave negative results.

Further substitution of $C_5H_5Fe(CO)_2Cl$ with $CH_3N(PF_2)_2$ beyond the monocarbonyl V is most effectively accomplished by reaction with excess ligand in boiling hexane. The resulting product $C_5H_5Fe[(PF_2)_2NCH_3]_2Cl$ clearly has structure VII containing two monoligate monometallic ligands. Attempts to prepare a complex $C_5H_5Fe[(PF_2)_2NCH_3]Cl$ with a single biligate monometallic $CH_3N(PF_2)_2$ ligand by ultraviolet irradiation of $C_5H_5Fe(CO)[(PF_2)_2NCH_3]Cl$ (V) led instead to decomposition.

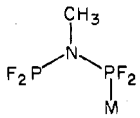


VII

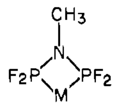
Some interesting examples of solvolyses of $CH_3N(PF_2)_2$ ligands were observed in this work. In general, monoligate monometallic $CH_3N(PF_2)_2$ ligands (VIII) appear to be more susceptible than biligate monometallic $CH_3N(PF_2)_2$ toward solvolyses by proton-donor solvents such as alcohols. Reactions of $C_5H_5Mo(CO)_3Cl$ and $C_5H_5Fe(CO)_2Cl$ with $CH_3N(PF_2)_2$ in the presence of small amounts of an alcohol (methanol or ethanol) can lead to the complexes $C_5H_5Mo(CO)_2(PF_2NHCH_3)Cl$ and $C_5H_5Fe(CO)(PF_2NHCH_3)Cl$, respectively, apparently formed through protonolysis of the nitrogen–phosphorus bond of the monoligate monometallic $CH_3N(PF_2)_2$ involving the phosphorus not bonded to the transition metal. The molybdenum complex $C_5H_5Mo(CO)_2(PF_2NHCH_3)Cl$ was actually first isolated from the thermal reaction of $C_5H_5Mo(CO)_3Cl$ with $CH_3N(PF_2)_2$ in boiling chloroform from which the ethanol preservative had not been removed by alumina treatment. The CH_3NHPF_2 ligand found in these complexes is known[11] but unstable in the uncomplexed state. It is also found in the briefly reported[12] complex $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$ obtained by ultraviolet irradiation of $Co_2(CO)_8$ with excess $CH_3N(PF_2)_2$ followed by chromatography on Florisil. An intermediate $[CH_3N(PF_2)_2]_3Co_2[(PF_2)_2NCH_3]_2$ containing two terminal monoligate monometallic ligands in addition to the three bridging biligate bimetallic ligands has recently[13] been isolated from the ultraviolet irradiation of $Co_2(CO)_8$ with excess $CH_3N(PF_2)_2$ when the chromatography step is omitted. A characteristic feature of the CH_3NHPF_2 ligand in both $C_5H_5Mo(CO)_2(PF_2NHCH_3)Cl$ and $C_5H_5Fe(CO)(PF_2NHCH_3)Cl$ is a sharp ν(NH) infrared frequency at 3245 ± 25 cm^{-1}.

The reaction of $C_5H_5W(CO)_3Cl$ with $CH_3N(PF_2)_2$ in the presence of an alcohol follows a different pathway than the corresponding reaction with $C_5H_5Mo(CO)_3Cl$. In the case of the tungsten derivative solvolysis appears to occur at the phosphorus–nitrogen bond involving the phosphorus bonded to the metal atom. This leads to the complexes $C_5H_5W(CO)_2[PF(OR)_2]Cl$ (R = CH_3, C_2H_5) containing a somewhat unusual fluorophosphite ligand. The presence of only a single fluorine on the single phosphorus atoms in these complexes is confirmed by the doublet in the phosphorus-31 NMR spectrum.

The metal complexes of $CH_3N(PF_2)_2$ described in this paper provide good model compounds for the development of methods for differentiating between monoligate monometallic (VIII) and biligate monometallic (IX) $CH_3N(PF_2)_2$ ligands through their NMR spectra (Tables II and III). In the proton NMR spectra of $CH_3N(PF_2)_2$ complexes containing a single $CH_3N(PF_2)_2$ ligand which is biligate monometallic (IX) the *N*-methyl resonance appears as a sharp triplet (J = 11–12 Hz) apparently owing to coupling of the methyl protons with the two equivalent phosphorus atoms. However, in the proton NMR spectra of $CH_3N(PF_2)_2$ complexes containing a single



VIII



IX

$CH_3N(PF_2)_2$ ligand which is monoligate monometallic (VIII) the *N*-methyl resonance appears as a broad doublet (J = 7–8 Hz). Apparently, the coupling of the methyl protons to the complexed phosphorus atom is appreciable but their coupling to the uncomplexed phosphorus atom is only sufficient to broaden the resonance but not to permit its resolution. These features in the proton NMR spectra of the *N*-methyl group in $CH_3N(PF_2)_2$ complexes are no longer clearly discernible in complexes containing at least two $CH_3N(PF_2)_2$ ligands (e.g., II and VI in this work) possibly because of additional interligand phosphorus–phosphorus virtual coupling.[14] The proton NMR spectra of the *N*-methyl group in the CH_3NHPF_2 complexes $C_5H_5Mo(CO)_2(PF_2NHCH_3)Cl$ and $C_5H_5Fe(CO)(PF_2NHCH_3)Cl$ exhibit a different pattern than either type of $CH_3N(PF_2)_2$ complex VIII or IX, i.e., a double doublet of triplets apparently reflecting the successively decreasing $|^3J(PH)|$, $|^3J(HH)|$, and $|^4J(HF)|$ coupling constants in the coordinated CH_3NHPF_2 ligand.

The carbon-13 NMR spectra of the *N*-methyl groups are much more useful than their proton NMR spectra for identifying the two different types of $CH_3N(PF_2)_2$ ligands VIII and IX in complexes containing two or more ligands. The *N*-methyl groups of the monoligate monometallic $CH_3N(PF_2)_2$ ligands VIII all exhibit carbon-13 NMR resonances in the range δ 25–27 whereas those of the biligate monometallic $CH_3N(PF_2)_2$ ligands IX all exhibit carbon-13 NMR resonances in the range δ 29–31. In compounds containing $CH_3N(PF_2)_2$ ligands of both types VIII and IX such as $C_5H_5Mn[(PF_2)_2NCH_3]_2$ (II) and $C_5H_5M[(PF_2)_2NCH_3]_2Cl$ (VI) two distinct carbon-13 NMR *N*-methyl resonances are observed in the appropriate regions.

The phosphorus-31 NMR spectra (Table III) of the $CH_3N(PF_2)_2$ resonances are considerably more complex since the appreciable $|^1J(PF)|$ couplings of 1100–1300 Hz cause serious overlapping of the phosphorus resonances with different chemical shifts. In the complexes $C_5H_5M[(PF_2)_2NCH_3]_2Cl$ (VI: M = Mo, W), which contain four nonequivalent phosphorus atoms, all four phosphorus resonances could not be located in the exceedingly complex spectrum. The uncomplexed phosphorus atom in a monoligate monometallic $CH_3N(PF_2)_2$ ligand (VIII) appears at δ −135 to −142 with $|^1J(PF)|$ in the range 1235–1260 Hz, close to the reported[15] values of δ −141.5 and 1264 Hz for the free $CH_3N(PF_2)_2$ ligand. The chemical shifts of the coordinated phosphorus atom in the monoligate monometallic $CH_3N(PF_2)_2$ ligand VIII naturally depend upon the coordination chemical shift of the transition-metal system to which this phosphorus atom is bonded. However, the $|^1J(PF)|$ coupling constants of the coordinated phosphorus atom in a monoligate monometallic $CH_3N(PF_2)_2$ ligand fall consistently in the range 1130–1170 Hz, i.e., appreciably lower than those involving the uncomplexed phosphorus atom. The $|^2J(PP)|$ coupling constants between the complexed and uncomplexed phosphorus atoms in a monoligate monometallic $CH_3N(PF_2)_2$ ligand (VIII) are found in the range 160–240 Hz. The chemical shifts of the phosphorus atoms in biligate monometallic $CH_3N(PF_2)_2$ ligands (IX) also vary according to the coordination chemical shift of the transition-metal system, their coupling constants $|^1J(PF)|$ approach 1300 Hz, and their coupling constants $|^2J(PP)|$ in general are not directly observable owing to the equivalence of both phosphorus atoms and insufficient resolution for a second-order[16] X_2AAX_2 analysis.

Acknowledgment. We are indebted to the U.S. Air Force Office of Scientific Research for partial support of this work under Grant AFOSR-75-2869. J.G. is indebted to the Program of Cultural Cooperation between the U.S.A. and Spain, administered by the Fulbright Commission of Spain for a fellowship. We acknowledge the technical assistance of Mr. Courtney Pape in running some of the carbon-13 and phosphorus-31 NMR spectra.

Registry No. $CpMn(CO)(PF_2)_2NMe$, 66610-60-4; $CpMn[(PF_2)_2NMe]_2$, 66610-61-5; $CpMo(CO)(NO)(PF_2)_2NMe$, 66610-62-6; $CpMo[(PF_2)_2NMe]_2Cl$, 66610-63-7; $CpMo(CO)_2[(PF_2)_2NMe]Cl$, 64423-99-0; $CpMo(CO)_2[PF_2NHMe]Cl$, 66610-64-8; $CpW[(PF_2)_2NMe]_2Cl$, 66610-65-9; $CpW(CO)_2[(PF_2)_2NMe]Cl$, 64449-02-1; $CpW(CO)_2[PF(OMe)_2]Cl$, 66610-66-0; $CpW(CO)_2[PF(OEt)_2]Cl$, 66610-67-1; $CpFe[(PF_2)_2NMe]_2Cl$, 64387-50-4; $CpFe(CO)[(PF_2)_2NMe]Cl$, 64387-49-1; $CpFe(CO)[PF_2NHMe]Cl$, 66610-69-3; $CpMn(CO)_3$, 12079-65-1; $CpMo(CO)_2NO$, 12128-13-1; $CpMo(CO)_3Cl$, 12128-23-3; $CpW(CO)_3Cl$, 12128-24-4; $CpFe(CO)_2Cl$, 12107-04-9.

References and Notes

(1) For part 4 of this series see R. B. King and J. Gimeno, *Inorg. Chem.*, preceding paper in this issue.

(2) For a preliminary communication of some of this work see R. B. King, M. G. Newton, J. Gimeno, and M. Chang, *Inorg. Chim. Acta*, **23**, L35 (1977).

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