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Hexacoordinate Phosphorus. 1. Preparation and Properties of Neutral Carbamates and Thiocarbamates of Pentavalent Phosphorus and the Crystal and Molecular Structure of (*N,N*-Dimethylcarbamato)methyltris(trifluoromethyl)phosphorane

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The "insertion" of CO₂, COS, or CS₂ into the PN bond of CH₃(CF₃)₃PN(CH₃)₂ yielded neutral compounds containing hexacoordinate phosphorus with the formation of a chelated carbamato or thiocarbamato substituent. The coordination environment was demonstrated by NMR spectral properties, the presence of two distinct CF₃ environments, the very high-field ³¹P NMR chemical shifts, and the crystal and molecular structure of methyltris(trifluoromethyl)(*N,N*-dimethylcarbamato)phosphorane, CH₃(CF₃)₃PO₂CN(CH₃)₂. The crystals were monoclinic belonging to space group *P2₁/c* (*C*_{2h}) with *Z* = 4, *a* = 7.4213 (9) Å, *b* = 13.2327 (24) Å, *c* = 12.6130 (10) Å, and β = 93.84 (1)°. Least-squares refinement of 910 reflections having *F*_o² ≥ 2σ(*F*_o²) gave a conventional *R* factor of 0.051. The molecular structure is characterized by very similar P–O (1.808 (5) and 1.901 (5) Å) and essentially equivalent C–O (1.296 (8) and 1.289 (8) Å) bond lengths, a short C=N bond (1.311 (1) Å), and the near planarity of the framework of the carbamato ligand, the P atom, the CH₃, and one CF₃ substituent. The molecular structure also demonstrates that CF₃ and CH₃ groups are not subject to unusual mutual steric interactions. The monothiocarbamate CH₃(CF₃)₃PO(S)CN(CH₃)₂ occurs as two isomeric forms in 3:2 proportions which result from the same essential molecular structure in which the single sulfur atom is either in the *cis* or the *trans* positions with respect to the CH₃ substituent on phosphorus. The carbamato compounds can also be prepared from CH₃(CF₃)₃PCl (and in one case F) and (CH₃)₃SiE₂CN(CH₃)₂ (E = O, S). The monothiocarbamate compound is quantitatively converted to the dithiocarbamate-phosphorus compound upon treatment with CS₂. Spectroscopic properties of the new compounds are reported.

Introduction

Although many hexacoordinate ions of pentavalent phosphorus are known,^{1,2} few compounds contain pentavalent, hexacoordinate phosphorus in a neutral molecule. The largest single class of such compounds are donor-acceptor adducts of PF₅ and related molecules^{1,2} of which the PF₅·py adduct has been structurally characterized recently.³ A very much smaller class is that which contains monovalent chelates bonded to phosphorus(V). Structurally characterized examples are Cl₄PN(R)C(Cl)N(R),⁴ F₄P(2-Me-8-oxyquinoline),^{5a} F₃-(C₆H₅)P(2-Me-8-oxyquinoline),^{5b} and F₄POC(CH₃)C(H)-C(CH₃)O.⁶ We report herein the preparation and properties of (carbamato)- and (thiocarbamato)phosphorus(V) compounds CH₃(CF₃)₃PE₂CN(CH₃)₂, including the structural characterization of the carbamato derivative, providing examples of a new representative series of neutral molecules containing hexacoordinate phosphorus.⁷

Experimental Section

All reactions were done in sealed tubes, and standard vacuum techniques were used throughout for the manipulation of volatile compounds.

Infrared spectra of volatile materials were recorded with a Perkin-Elmer 457 spectrometer using a 9-cm gas cell fitted with KBr windows. The infrared spectra of the solid complexes were recorded as film casts from CH₂Cl₂ solution on a KBr disk with a Nicolet 7199 FT IR Spectrometer.

Mass spectra were recorded with an AEI MS-9 spectrometer operating at an ionizing voltage of 70 eV.

Proton and ¹⁹F NMR spectra were recorded on solutions of the compound (approximately 10%) in CCl₃F at 100.1 and 94.2 MHz

with a Varian HA 100 instrument in continuous-wave mode. High-field ¹H NMR spectra were measured on a Bruker WP 200 cryospectrometer. Phosphorus-31 NMR spectra were recorded at 36.4 MHz with a Bruker HFX 90 spectrometer in the pulsed Fourier-transform mode with a Nicolet 1085 computer. Samples were prepared in 5-mm o.d. tubes in CCl₃F solvent including CD₂Cl₂ for the heteronuclear reference lock signal. Fluorine chemical shifts were measured relative to internal CCl₃F solvent. Proton shifts were measured relative to an external capillary of (CH₃)₄Si (as a 5% solution in CCl₃F). Phosphorus-31 shifts were measured with respect to the heteronuclear ²D lock signal and converted to the P₄O₆ scale⁸ by means of the appropriate conversion factor.

(I) Preparation of (Carbamato)phosphoranes from (Dimethylamino)methyltris(trifluoromethyl)phosphorane by "Insertion" Reactions of CX₂. (a) The Reaction with Carbon Dioxide. Carbon dioxide (0.060 g, 1.37 mmol) and CH₃(CF₃)₃PN(CH₃)₂⁹ (0.133 g, 0.45 mmol) combined slowly in diethyl ether (0.52 g) when the mixture was shaken at room temperature. Separation of the reaction mixture after 2 days gave CO₂ (0.041 g, 0.92 mmol), trapped at -196 °C, and ether (0.51 g), trapped at -116 and 130 °C, as the only volatile products. The white solid (0.150 g, 0.44 mmol; 98%) remaining in the tube was sublimed and identified as (*N,N*-dimethylcarbamato)tris(trifluoromethyl)methylphosphorane: CH₃(CF₃)₃PO₂CN(CH₃)₂; mp 130–131 °C (uncorrected). Anal. Calcd for C₇H₉F₉O₂NP: C, 24.63; H, 2.64; N, 4.10; F, 50.15, P, 9.09. Found: C, 24.70; H, 2.84; N, 4.02; F, 50.06; P, 9.42.

(b) The Reaction with Carbonyl Sulfide. In a similar fashion COS (0.105 g, 2.51 mmol) combined with CH₃(CF₃)₃PN(CH₃)₂ (0.120 g, 0.40 mmol) in diethyl ether (1.00 g) during 3 days at room temperature with continuous shaking. The products were COS (1.40 g, 2.33 mmol), diethyl ether (1.00 g), unreacted CH₃(CF₃)₃PN(CH₃)₂ (0.063 g, 0.22 mmol), and a white solid (0.063 g, 0.18 mmol, 45%) which after sublimation was identified as a mixture of the two isomers of (*N,N*-dimethylthiocarbamato)methyltris(trifluoromethyl)phosphorane, CH₃(CF₃)₃PS(O)CN(CH₃)₂, mp 113–114 °C (uncorrected), in an approximate 3:2 ratio (by NMR). Repeating this reaction with cyclohexane solvent gave, after 7 days, a yield of 65%. Anal. Calcd for C₇H₉F₉OSP: C, 23.53; H, 2.52; F, 47.89; P, 8.68. Found: C, 23.72; H, 2.67; F, 47.62; P, 8.88.

(c) The Reaction with Carbon Disulfide. Carbon disulfide (0.301 g, 3.97 mmol) slowly combined with CH₃(CF₃)₃PN(CH₃)₂ (0.223

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(8) Chapman, A. C.; Horner, J.; Mowthorpe, D. J.; Jones, K. T. *Chem. Commun.* 1965, 121. The chemical shift of 85% H₃PO₄ is +112 ppm (high field vs. P₄O₆).

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Table I. Mass Measurement Data^a

	calcd	obsd
$\text{CH}_3(\text{CF}_3)_2\text{PS}_2\text{CN}(\text{CH}_3)_2$		
$(\text{CF}_3)_2\text{PS}_2\text{CN}(\text{CH}_3)_2$	303.9818	303.9830
$(\text{CF}_3)_3\text{P}(\text{CH}_3)_2$	252.9829	252.9833
$(\text{CH}_3)_2\text{NCS}_2$	119.9941	119.9945
$\text{CH}_3(\text{CF}_3)_3\text{POSCN}(\text{CH}_3)_2$		
$(\text{CF}_3)_2\text{POSCN}(\text{CH}_3)_2$	288.0046	288.0040
$(\text{CF}_3)_3\text{P}(\text{CH}_3)_2$	252.9829	252.9821
$(\text{CH}_3)_2\text{NCS}$	88.0221	88.0223
$(\text{CH}_3)_2\text{NCO}$	72.0449	72.0451
$\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$		
$(\text{CF}_3)_2\text{PO}_2\text{CN}(\text{CH}_3)_2$	272.0275	272.0271
$(\text{CF}_3)_3\text{P}(\text{CH}_3)_2$	252.9829	252.9821
$(\text{CF}_3)_2\text{P}(\text{F})\text{CH}_3$	202.9861	202.9853

^a Structural formula given for ions merely to aid in recognition.

g, 0.74 mmol) when the materials were shaken together in a sealed tube at room temperature. Separation of the reaction mixture after 3 days gave CS_2 (0.282 g, 3.68 mmol) trapped at -196°C , unreacted $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CH}_3)_2$ (0.130 g, 0.45 mmol), and a solid (0.110 g, 0.29 mmol, 39%) which, following purification by sublimation, was identified as (*N,N*-dimethyldithiocarbamato)methyltris(trifluoromethyl)phosphorane: $\text{CH}_3(\text{CF}_3)_3\text{PS}_2\text{CN}(\text{CH}_3)_2$; mp 157°C . Anal. Calcd for $\text{C}_7\text{H}_9\text{F}_9\text{S}_2\text{NP}$: C, 22.52; H, 2.41; F, 45.84; S, 17.16; N, 3.75; P, 8.31. Found: C, 22.45; H, 2.47; F, 45.47; S, 16.96; N, 3.83; P, 7.95.

(II) **Preparation of Carbamatophosphoranes from Chloromethyltris(trifluoromethyl)phosphorane.** (a) **The Reaction with (*N,N*-Dimethylthiocarbamato)trimethylsilane.** (i) Shaking a mixture of $\text{CH}_3(\text{CF}_3)_3\text{PCl}$ (0.494 g, 1.71 mmol) and $(\text{CH}_3)_3\text{SiO}_2\text{CN}(\text{CH}_3)_2$ (0.242 g, 1.50 mmol) at room temperature for 2 days yielded $(\text{CH}_3)_3\text{SiCl}$ (0.163 g, 1.50 mmol), unreacted $\text{CH}_3(\text{CF}_3)_3\text{PCl}$ (0.030 g, 0.10 mmol), and a white solid (0.50 g, 1.45 mmol, 97% yield) which, after purification by sublimation, was identified as $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ by comparison of its properties with those of the product of I(a) above. (ii) A mixture of $\text{CH}_3(\text{CF}_3)_3\text{PF}$ (0.107 g, 0.39 mmol) and $(\text{CH}_3)_3\text{SiO}_2\text{CN}(\text{CH}_3)_2$ (0.095 g, 0.59 mmol) dissolved in CFCl_3 in an NMR tube was observed by ^{19}F NMR to yield 95% $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ after a slow (4 days) reaction at 60°C .

(b) **The Reaction with (*N,N*-Dimethylthiocarbamato)trimethylsilane.** In a similar fashion, $\text{CH}_3(\text{CF}_3)_3\text{PCl}$ (0.166 g, 0.58 mmol) and $(\text{CH}_3)_3\text{SiO}(\text{S})\text{CN}(\text{CH}_3)_2$ (0.242 g, 1.50 mmol) yielded, after 24 h at room temperature, $(\text{CH}_3)_3\text{SiCl}$ (0.061 g, 0.56 mmol) and unreacted $(\text{CH}_3)_3\text{SiO}(\text{S})\text{CN}(\text{CH}_3)_2$ (0.039 g, 0.23 mmol) as volatile products. The remaining solid product was identified after purification by sublimation as a mixture of the two isomers of $\text{CH}_3(\text{CF}_3)_3\text{POSCN}(\text{CH}_3)_2$, also in 3:2 relative proportions. The total yield was 0.196 g (0.55 mmol, 95%).

(c) **The Reaction with (*N,N*-Dimethyldithiocarbamato)trimethylsilane.** Treatment of $\text{CH}_3(\text{CF}_3)_3\text{PCl}$ (0.965 g, 3.35 mmol) with $(\text{CH}_3)_3\text{SiS}_2\text{CN}(\text{CH}_3)_2$ (0.550 g, 2.85 mmol) in diethyl ether (1.05 g) in a sealed tube for 2 days at room temperature gave, as volatile products, unreacted $\text{CH}_3(\text{CF}_3)_3\text{PCl}$ (0.173 g, 0.60 mmol), trapped at -78°C , an unseparated mixture of diethyl ether and $(\text{CH}_3)_3\text{SiCl}$ (1.35 g) trapped at -113°C , a trace of a very volatile unidentified compound (0.003 g) trapped at -196°C , and, as a solid in the reaction vessel, $\text{CH}_3(\text{CF}_3)_3\text{PS}_2\text{CN}(\text{CH}_3)_2$, which was purified by sublimation. The yield was 0.916 g (2.45 mmol, 86%).

(III) **The Reaction of (*N,N*-Dimethylthiocarbamato)methyltris(trifluoromethyl)phosphorane with Carbon Disulfide.** A mixture of the two isomers of $\text{CH}_3(\text{CF}_3)_3\text{POC}(\text{S})\text{N}(\text{CH}_3)_2$ (0.135 g, 0.38 mmol) was treated with a large excess of CS_2 (0.550 g, 7.22 mmol) for several days at 70°C . Separation of the products gave a mixture of COS and CS_2 (0.545 g) and, as a solid product, $\text{CH}_3(\text{CF}_3)_3\text{PS}_2\text{CN}(\text{CH}_3)_2$ (0.139 g, 0.37 mmol, 97%), which was purified by sublimation.

(IV) **Attempts to Rearrange and Separate Monothiocarbamate**

Isomers. Heating the mixture of isomers of $\text{CH}_3(\text{CF}_3)_3\text{PCO}(\text{S})\text{N}(\text{CH}_3)_2$ to 120° for 2 days did not alter the relative proportions according to NMR spectroscopy. Heating to 150° resulted only in decomposition.

Table II. Hydrolysis of $\text{CH}_3(\text{CF}_3)_3\text{PXYCN}(\text{CH}_3)_2$

X	Y	amt, g (mmol)		
		compd taken	CF_3H	ions in soln
O	O	0.1201 (0.35)	0.0476 (0.68)	$\text{CF}_3(\text{CH}_3)\text{PO}_2^-$ ^a
O	S	0.1101 (0.31)	0.0441 (0.63)	$\text{CF}_3(\text{CH}_3)\text{PO}_2^-$ ^a
S	S	0.1047 (0.28)	0.0392 (0.56)	$\text{CF}_3(\text{CH}_3)\text{PO}_2^-$ ^a

^a NMR parameters in agreement with those given by: Yap, N. T.; Cavell, R. G. *Inorg. Chem.* 1979, 18, 1301.

Table III. NMR Parameters of $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{XY})\text{CN}(\text{CH}_3)_2$

	X = O, Y = S			
	X = Y = O	I ^e	II ^e	X = Y = S
$T, ^\circ\text{C}$	-45		+33	+33
$\tau_{\text{CH}_3\text{P}}^a$	8.77	8.75	8.75	8.37
$\tau_{\text{CH}_3\text{N}}^{a,b}$	7.27, 7.29	6.79, 6.86	6.82, 6.89	6.70, 6.72
$\phi_{\text{CF}_3}^{c,f}$	64.6 (2)	61.6 (2)	65.8 (2)	65.1 (2)
$\delta_{31}\text{P}^d$	63.7 (1)	62.0 (1)	65.8 (1)	62.5 (1)
$\delta_{31}\text{P}^d$	251	261	270	298
$^2J_{\text{PH}}, \text{Hz}$	9.0	7.5	10.0	7.7
$^4J_{\text{FH}}, \text{Hz}$	1.1	1.0	0.6	1.1
$^2J_{\text{PF}}, \text{Hz}^f$	95.5 (2)	95 (2)	97 (2)	98 (2)
$^4J_{\text{FF}}, \text{Hz}$	70.9 (1)	67 (1)	74 (1)	67 (1)
$^4J_{\text{FF}}, \text{Hz}$	10.0	14.9	11.1	13.0

^a τ scale ppm relative to $(\text{CH}_3)_4\text{Si}$ of which $\tau = 10.0$. ^b The two CH_3 groups of the carbamate and thiocarbamate ligands are nonequivalent and not observably coupled to phosphorus at the low-temperature limit (-45°C in the case of the carbamate, $+33^\circ\text{C}$ in the case of all sulfur-containing species) as ascertained by comparison of 100-MHz and 200-MHz NMR spectra. At 60 MHz the carbamate $\text{N}(\text{CH}_3)_2$ peak is a singlet (fwhm 0.8 Hz). Separations and fwhm of the doublets at 100 MHz are as follows: $\text{O}_2\text{CN}(\text{CH}_3)_2$, 0.75 (1.5 Hz); $\text{OSCN}(\text{CH}_3)_2$, I 6.5 Hz, II 6.8 Hz (0.6 Hz); $\text{S}_2\text{CN}(\text{CH}_3)_2$, 1.4 Hz (1.4 Hz). At 200 MHz they are as follows: $\text{O}_2\text{CN}(\text{CH}_3)_2$, 1.55 Hz (0.8 Hz); $\text{OSCN}(\text{CH}_3)_2$, I 13.0 Hz, II 13.7 Hz (0.8 Hz); $\text{S}_2\text{CN}(\text{CH}_3)_2$, 2.6 Hz (0.8 Hz). ^c Given in ppm vs. CFCl_3 ; positive values indicating resonance to high field of standard. ^d Given in ppm vs. P_4O_6 ; positive values indicating resonance to high field of standard. ^e Relative intensity: I 60%; II 40%. ^f Relative intensity given in parentheses.

Additional Characterization. Samples of pure compounds were analyzed by mass spectroscopy, and accurate mass measurement data are given in Table I. Hydrolysis in alkaline and neutral media gave the results in Table II. NMR and IR spectroscopic data are given in Tables III-V.

Collection of X-ray Data. Small amounts of $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ sealed under vacuum in 0.3-mm Lindemann capillaries sublimed as crystals on the capillary walls when placed in a warm oil bath at about 60°C . A small cube-shaped crystal about 0.15 mm on all sides was chosen for analysis.

Preliminary film data showed systematic absences consistent with the space group $P2_1/c$. Crystal and intensity collection data is summarized in Table VI. Unit cell parameters were determined by a least-squares analysis of the setting angles of 12 accurately centered high-angle reflections measured on a Picker FACS-1 diffractometer using $\text{Cu K}\alpha$ radiation. Intensity data were collected on the same diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation by the $\theta/2\theta$ scan technique. Stationary-background counts were measured for 20 s before and after the scan limits. The intensities of three standard reflections, measured after every 50 reflections, decreased linearly about 10% during data collection and were used to scale all data to a common level. Data were collected in the hemisphere $\pm h, \pm k, +l$, and the intensities of equivalent reflections were averaged and reindexed into one consistent set with indices $+h, +k, \pm l$. The data were corrected for Lorentz and polarization effects and reduced to structure factor amplitudes with standard deviations computed by using a p factor¹¹ of 0.04. No correction for absorption ($\mu = 3.19 \text{ mm}^{-1}$) was made since the crystal was small and uniformly shaped. For a sphere of radius 0.075 mm, the above absorption coefficient gave minimum and maximum transmissions differing by about 1% for the range of

Table IV. Infrared Spectral Data of $\text{CH}_3(\text{CF}_3)_3\text{PXYN}(\text{CH}_3)_2^a$

X = Y = O	X = O, Y = S	X = Y = S	assign
3100 m	3040 s	3040 w, br	} ν_{CH}
2920 w	2950 s	2950 m	
2790 m	2750 s, br		
2590 w			
2520 m	2480 s, br		
1639.4 s, shp	1631.5 s, br		$\nu_{\text{asymC=O}}$
		1570 m	
1470 s	1472.1 m		$\nu_{\text{symC=O}}$
1420 m	1423 m	1415 m	
	1341 m		$\delta_{\text{CH}_3(\text{N})}$
1305 m	1306 m		
	1232 s		
1200 s	1209 s	1251 m	
	1175 s		
	1165 s	1172 m, sh	} CS_2 str + $\nu_{\text{CF}} + \nu_{\text{PO}}$
	1155 s		
1170 m	1125 s, sh		
1150 s	1115 vs	1115 sh	
1090 vs, d	1090 vs	1105 vs	
1060 vs	1065 vs	1080 sh	
1020 s	1030 m	1050 m	
945 m	940 m	1000 m	
920 m	920 m	935 m	
	878 m		
850 m	858 m		
745 m	757 m	728 m	
	728 m		
710 s	710 sh	682 s	
700 s	692 m		
	654 m		
	625 w		
	590 w	585 m	
560 s	560 m	550 m	
540 m	540 sh	540 sh	
520 w	505 m	530 sh	
490 s	490 m	468 s	
450 s	456 m	445 s	
	410 w		

^a Film cast from CH_2Cl_2 on KBr disk; values in cm^{-1} . ^b Abbreviations: s = strong, shp = sharp, sh = shoulder, br = broad, m = medium, w = weak, v = very, d = doublet.

Table V. Carbonyl Infrared Region of $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$

state	$\nu_{\text{CO}}, \text{cm}^{-1}$	shift rel to solid	shape ^b
solid	1639.4 ^a		shp, s
CCl_4 soln	1687.2	47.8	br, unresolved sh
CH_2Cl_2 soln	1699.1	59.7	single band
CD_3CN soln	1709.1	69.7	single band
$\text{CD}_3\text{CN}/(\text{CH}_3)_3\text{N}$	1692.6, 1650.8	53.2, 11.4	d, approx equal intensity
$\text{CH}_2\text{Cl}_2/(\text{CH}_3)_3\text{N}$	1689.6, 1651.8	50.4, 12.4	

^a This band appears at 1639.0 cm^{-1} in $\text{CH}_3(\text{CF}_3)_3\text{PO}_2^{13}\text{CN}(\text{CH}_3)_2$.
^b See Table IV.

θ values employed, thus the absorption effects are negligible. A total of 910 reflections of 1828 unique reflections were judged to be above background when the criterion $F_o^2 > 2\sigma(F_o^2)$ was applied.

Solution and Refinement of the Structure. Approximate scale and overall isotropic temperature factors were determined by the Wilson method. The structure was solved by direct methods using MULTAN¹² from 236 reflections with $|E| > 1.50$. An E map calculated with the set of phases having the highest figure of merit (1.38) revealed the positions of the 20 nonhydrogen atoms. An R value of 0.070 was reached after several cycles of refinement of the positional parameters of all the atoms, anisotropic temperature factors for the phosphorus and fluorine atoms, and isotropic temperature factors for the oxygen, nitrogen, and carbon atoms. Reasonable positions for the hydrogen

Table VI. Crystal and Intensity Collection Data for $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$

space group	$P2_1/c (C_2^5h)$
extinctions	$h0l, l = 2n + 1; 0k0, k = 2n + 1$
$a, \text{Å}$	7.4213 (9)
$b, \text{Å}$	13.2327 (24)
$c, \text{Å}$	12.6130 (10)
β, deg	93.84 (1) ^o
$V, \text{Å}^3$	1235.9
Z	4
$d(\text{calcd}), \text{g/cm}^3$	1.833
μ, nm^{-1}	3.19 (Cu $K\alpha$)
radiation	Cu $K\alpha$ ($\lambda = 1.54056 \text{ Å}$ filtered by 0.5 mil thick Ni foil)
scan rate, deg/min	0.5
scan range, deg	0.9 below $K\alpha_1$ to 0.9 above $K\alpha_2$
bkgd count, s	20 (for $5^\circ \leq \theta \leq 120^\circ$)
std reflctns	322, 161, 006
final no. of variables	152
no. of unique reflctns with $F_o^2 \geq 2\sigma(F_o^2)$	910
error in obsn of unit weight	1.30

Table VII. Final Positional and Thermal Parameters^a for $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$

atom	x	y	z	$B, \text{Å}^2$
P	0.0544 (3)	0.4101 (2)	0.2823 (2)	b
F51	-0.1660 (6)	0.4202 (4)	0.0998 (4)	b
F52	-0.1281 (6)	0.2700 (4)	0.1588 (4)	b
F53	0.0810 (6)	0.3416 (4)	0.0802 (4)	b
F61	-0.1428 (6)	0.3899 (4)	0.4547 (4)	b
F62	-0.2929 (5)	0.3530 (4)	0.3105 (4)	b
F63	-0.1068 (6)	0.2459 (4)	0.3831 (4)	b
F71	0.2021 (6)	0.5205 (4)	0.1269 (4)	b
F72	0.3915 (6)	0.4146 (4)	0.1931 (4)	b
F73	0.3265 (7)	0.5470 (4)	0.2795 (4)	b
O1	0.1953 (6)	0.4102 (4)	0.4049 (4)	3.7 (1)
O2	0.1922 (6)	0.2890 (4)	0.2941 (4)	3.6 (1)
N	0.3743 (8)	0.2722 (5)	0.4488 (5)	3.7 (1)
C1	0.2580 (10)	0.3212 (6)	0.3851 (6)	3.7 (2)
C2	0.4337 (12)	0.1733 (8)	0.4217 (7)	5.3 (2)
C3	0.4416 (12)	0.3182 (6)	0.5491 (7)	5.1 (2)
C4	-0.0591 (13)	0.5305 (8)	0.2933 (7)	5.6 (3)
C5	-0.0481 (12)	0.3589 (7)	0.1482 (7)	4.4 (2)
C6	-0.1270 (12)	0.3440 (7)	0.3622 (7)	4.5 (2)
C7	0.2560 (12)	0.4765 (7)	0.2174 (8)	4.9 (2)
H21	0.544 (16)	0.172 (5)	0.440 (8)	
H22	0.386 (15)	0.116 (5)	0.455 (13)	
H23	0.418 (25)	0.155 (6)	0.354 (7)	
H31	0.569 (6)	0.331 (5)	0.535 (3)	
H32	0.404 (9)	0.273 (4)	0.595 (5)	
H33	0.385 (9)	0.394 (4)	0.563 (5)	
H41	-0.025 (16)	0.574 (5)	0.255 (12)	
H42	-0.041 (23)	0.545 (6)	0.366 (4)	
H43	-0.180 (11)	0.515 (5)	0.285 (10)	

^a The estimated standard deviations are in parentheses. ^b Anisotropic thermal parameters in Table VIII.

atoms were located on a difference map. Continued refinement in which the hydrogen atoms of each methyl group were included as hindered rotors¹³ gave final R and R_w values of 0.053 and 0.051, respectively. In the hindered rotor refinement of the methyl hydrogen atoms, the parameters for the position of the center of gravity of the rotor, the angles describing the orientation of the rotor, and the radius of the rotor were varied while the barrier to rotation was held at 2.0 and isotropic temperature factors of 6.0 Å^2 were assigned for the hydrogen atoms. The largest residual electron density peak in a final difference Fourier map corresponded to a density of 0.35 e/Å^3 .

In the full-matrix least-squares refinement, the function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/(\sigma^2(|F_o|))$. R and R_w are defined as $\sum ||F_o| - |F_c||/|F_o|$ and $(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. The atomic scattering factors used for P, F, O, N, and C are from ref 14, those

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Table VIII. Anisotropic Thermal Parameters (\AA^2)^{a,b} for $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$B,^c$
P	0.041 (1)	0.049 (1)	0.043 (1)	0.002 (1)	-0.004 (1)	-0.002 (1)	3.53
F51	0.078 (3)	0.119 (5)	0.063 (3)	0.025 (3)	-0.030 (3)	0.005 (3)	6.89
F52	0.089 (4)	0.086 (4)	0.076 (3)	-0.027 (3)	-0.026 (3)	-0.006 (3)	6.67
F53	0.068 (3)	0.140 (5)	0.056 (3)	0.002 (3)	-0.003 (3)	-0.027 (3)	6.96
F61	0.079 (4)	0.142 (6)	0.072 (4)	0.004 (4)	0.033 (3)	-0.009 (4)	7.66
F62	0.033 (3)	0.160 (5)	0.096 (4)	-0.003 (3)	-0.004 (3)	0.032 (4)	7.66
F63	0.065 (3)	0.082 (4)	0.091 (4)	-0.014 (3)	0.012 (3)	0.022 (3)	6.25
F71	0.083 (4)	0.116 (5)	0.069 (4)	-0.013 (3)	0.001 (3)	0.039 (3)	7.10
F72	0.056 (3)	0.122 (4)	0.085 (4)	0.005 (4)	0.015 (3)	0.019 (4)	6.89
F73	0.106 (4)	0.107 (5)	0.089 (4)	-0.060 (4)	0.006 (3)	-0.005 (4)	8.00

^a The estimated standard deviations are in parentheses. ^b The form of the thermal ellipsoid is $\exp[-2\pi^2(a^*U_{11}h^2 + b^*U_{22}k^2 + c^*U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$. ^c Equivalent isotropic thermal parameter.

Table IX. Bond Distances (\AA) and Bond Angles^a (Deg) of $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$

P-O1	1.808 (5)	C3-H31	0.99 (6)
P-O2	1.901 (5)	C3-H32	0.89 (6)
P-C4	1.812 (11)	C3-H33	1.11 (6)
P-C5	1.930 (9)		
P-C6	1.944 (9)	C4-H41	0.80 (6)
P-C7	1.960 (9)	C4-H42	0.92 (6)
		C4-H43	0.94 (6)
C1-O1	1.296 (8)		
C1-O2	1.289 (8)	C5-F51	1.313 (9)
C1-N	1.311 (8)	C5-F52	1.329 (9)
		C5-F53	1.348 (9)
N-C2	1.430 (11)		
N-C3	1.462 (10)	C6-F61	1.328 (9)
		C6-F62	1.359 (9)
		C6-F63	1.331 (8)
C2-H21	0.84 (6)		
C2-H22	0.95 (6)		
C2-H23	0.89 (6)	C7-F71	1.320 (9)
		C7-F72	1.349 (9)
		C7-F73	1.305 (9)
O1-P-O2	69.9 (2)	C1-N-C2	120.5 (7)
O1-P-C4	100.3 (3)	C1-N-C3	119.8 (6)
O1-P-C5	157.1 (3)	C2-N-C3	119.7 (7)
O1-P-C6	86.4 (3)	F51-C5-F52	107.8 (7)
O1-P-C7	86.7 (3)	F51-C5-F53	106.8 (7)
O2-P-C4	170.2 (3)	F52-C5-F53	104.8 (7)
O2-P-C5	87.2 (3)	P-C5-F51	113.7 (6)
O2-P-C6	88.1 (3)	P-C5-F52	112.0 (6)
O2-P-C7	89.4 (3)	P-C5-F53	111.2 (6)
C4-P-C5	102.6 (4)	F61-C6-F62	104.6 (7)
C4-P-C6	90.8 (4)	F61-C6-F63	106.7 (7)
C4-P-C7	90.5 (4)	F62-C6-F63	105.5 (7)
C5-P-C6	92.9 (4)	P-C6-F61	110.8 (6)
C5-P-C7	93.4 (4)	P-C6-F62	110.4 (6)
C6-P-C7	173.1 (4)	P-C6-F63	118.0 (6)
P-O1-C1	91.7 (4)	F71-C7-F72	105.0 (7)
P-O2-C1	87.8 (4)	F71-C7-F73	106.9 (8)
O1-C1-O2	110.6 (7)	F72-C7-F73	107.2 (7)
O1-C1-N	124.2 (7)	P-C7-F71	111.3 (6)
O2-C1-N	125.2 (7)	P-C7-F72	115.1 (6)
		P-C7-F73	110.9 (6)

^a The numbering corresponds to Figure 1. Estimated standard deviations are given in parentheses.

for H are from ref 15, and the anomalous dispersion terms applied to P and F are from ref 16. The major computer programs used were SFLLS for structure factor and least-squares refinement by C. J. Prewitt, FORDAP for Fourier summation by A. Zalkin, ORFFE for calculating bond lengths, angles, and standard deviations by W. Busing and H. A. Levy, and ORTEP for the plotting routine by C. K. Johnson.

The final atomic positional and thermal parameters are given in Tables VII and VIII, respectively. The observed and calculated structure factors ($10|F_o|$ and $10|F_c|$) in electrons have been tabulated.¹⁷

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Table X. Least-Square Plane Calculation^a for $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$

atoms	Atoms Defining Plane			
	A	B	C	D
P, O1, O2, C1, N	0.7756	0.4342	-0.4581	0.8615
Distances (\AA) of Atoms from Plane				
P	-0.004 (2)	C2	-0.077 (10)	
O1	0.020 (5)	C3	-0.017 (9)	
O2	0.017 (5)	C4	-0.037 (10)	
C1	-0.024 (6)	C5	-0.028 (9)	
N	-0.004 (7)			

^a The equation of the plane is of the form $AX + BY + CZ = D$ where X , Y , and Z are orthogonal coordinates. Estimated standard deviations are given in parentheses.

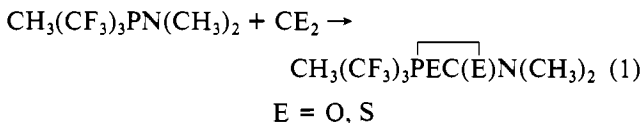
Table XI. Nonbonded Intermolecular Distances (\AA) Less Than 2.95 \AA in $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ ^{a,b}

F61...H31 ^I	2.55 (6)	H33...H42 ^{II}	2.87 (10)
F61...H42 ^{II}	2.70 (6)	F53...H22 ^{III}	2.90 (7)
F72...H32 ^{III}	2.78 (6)	F63...H21 ^I	2.90 (7)
H33...H43 ^{II}	2.80 (10)	F71...H21 ^{IV}	2.91 (7)
F62...F72 ^I	2.806 (6)	F73...H31 ^V	2.91 (7)
F53...H32 ^{III}	2.83 (7)	F73...H33 ^V	2.92 (7)

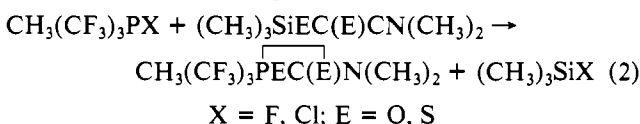
^a The symmetry transformations are as follows: (I) $-1 + x, y, z$; (II) $-x, 1 - y, 1 - z$; (III) $x, 1/2 - y, -1/2 + z$; (IV) $1 - x, 1/2 + y, 1/2 - z$; (V) $1 - x, 1 - y, 1 - z$. ^b Estimated standard deviations are given in parentheses.

Results and Discussion

The addition of CO_2 , COS , or CS_2 to $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CH}_3)_2$ proceeds slowly to give excellent to moderate yields of the carbamate (eq 1). While a solvent facilitates the reactions



of CO_2 and COS , CS_2 serves as its own solvent. The same compounds can be made in faster reactions from the halogenophosphorane and trimethylsilylcarbamates, a reaction which appears to be general (eq 2). The latter reactions are un-



doubtedly facilitated by the separate formation of the carbamate and by the formation of a volatile reaction product, $(\text{CH}_3)_3\text{SiCl}$. The CE_2 "insertion" reactions are probably slow because the rate-limiting step is the formation of carbamate

(17) Supplementary material.

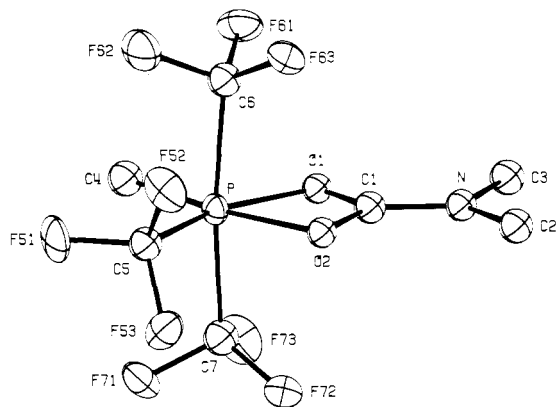


Figure 1. Molecular structure of $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ showing 20% probability ellipsoids for all atoms other than hydrogen.

in solution from CE_2 and free amine, prior to nucleophilic displacement at phosphorus by the carbamate. Detailed discussion of the mechanism will be the subject of a forthcoming paper.

Crystal and Molecular Structure of $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{C}-\text{H}_3)_2$. The final refined values of molecular structural parameters are given in Tables IX and X. Improved reliability relative to the values given in our preliminary communication⁷ arises primarily from the application of hindered rotor models to the alkyl groups. The changes include a small increase in the two P–O bond distances. These bond lengths differ by only 0.093 Å with the bond opposite the electron-donating CH_3 group longer than that opposite the electron-attracting CF_3 group, and so the carbamate group can be regarded as a bidentate chelated substituent. The C–O bonds differ by only 0.007 Å (1 standard deviation) and are significantly (1.293 Å average) shorter than typical C–O single-bond (1.43 Å) distances. The earlier spread⁷ of P–C(F) distances has been reduced.

The most remarkable feature of the molecular structure is the planarity of the chelate ring (Table X). All of the framework atoms of the chelate and the CH_3 and the equatorial CF_3 substituents on P are coplanar with the phosphorus atom. The typical deviation from the plane is 0.02–0.03 Å or less except for one of the terminal carbon atoms attached to N which is 0.077 Å out of plane. This planarity, together with the short C–O and C₁–N bond lengths, suggests significant delocalization in the carbamate fragment. Both P–O distances (1.854 Å average) are significantly longer than the Schomaker–Stevenson corrected single-bond values of 1.71 Å³ and are notably longer than P–O distances (1.717 Å average) observed in the tris(*o*-phenylenedioxy)phosphate ion¹⁸ and the oxyquinoline complexes described elsewhere⁵ perhaps because of the steric requirements of the four-membered chelate ring in the present case. This is further reflected by the reduced O_1PO_2 angle (69.9 (2)°) and the concomitant deviation of the angles in the plane around P from nominal octahedral values. We note that the P–O bond distances of the carbamate correspond to a bond valence of approximately 0.5 for each P–O bond when placed on the “universal” correlation curve for oxygen and atoms of the second row of the periodic table.¹⁹

The “axial” CF_3 groups are nearly collinear (173.1 (4)°), suggesting that the steric requirements of a CF_3 group on phosphorus are not large. We think it likely that large repulsions between a CF_3 group and either of the orthogonal CF_3 or CH_3 groups attached to the phosphorus atom would be readily relieved by the bending of the “axial” CF_3 groups

toward the relatively open side of the molecule. Such steric interactions are probably responsible for the observed 3.5° bend from “vertical” for each of the “axial” CF_3 groups. Further assessment of steric interactions in the molecule is provided by the calculation of CF_3 and CH_3 “cone angles” following the procedure outlined by Tolman²⁰ using the averaged bond parameters obtained herein. The resultant cone angles subtended by CH_3 and CF_3 at phosphorus are quite similar, being 93 and 97°, respectively.

NMR Spectral Properties. All of the compounds show the presence of two CF_3 environments in the ^{19}F and ^{31}P NMR spectra in the ratio of 2:1 at normal temperatures in the case of both the dithio- and monothiocarbamates but only at reduced temperatures in the case of the carbamate. At ordinary temperatures the ^{19}F NMR of the latter shows averaged CF_3 environments. The NMR spectra of the monothiocarbamate shows, in addition, the presence of two isomers, in the ratio 3:2, regardless of the method of preparation. Notably, efforts to separate the isomers have not yet been successful. While all of the above spectral properties and even the presence of two isomeric monothiocarbamates could be rationalized on the basis of a structure containing a five-coordinate phosphorus atom, the most notable feature of the NMR spectra, the very high-field ^{31}P NMR chemical shifts of *all* compounds, strongly suggested a six-coordinate rather than a five-coordinate phosphorus atom.²¹ The phosphorus-31 chemical shift of the carbamate, which undergoes an exchange process at ordinary temperatures, is not notably temperature dependent through the range –45 to –80 °C; therefore, the proportion of phosphorus with a lower coordination number must be small. The presence of hexacoordinate phosphorus is confirmed by the crystal and molecular structure of the carbamate (*vide supra*) which also clearly indicates the reason for two CF_3 environments: two CF_3 groups lie out of the molecular plane and one CF_3 group is in the plane cis to one of the oxygen atoms of the chelated carbamate ligand.

It seems reasonable to suggest that the same structure prevails for all three compounds synthesized herein and that the isomeric nature of the monothiocarbamate is due to the possibility that the single sulfur may adopt two positions, either *cis* or *trans* to the CH_3 group attached to phosphorus.

It is interesting to note that the ^1H NMR signals of the methyl groups of the carbamate ligands are not equivalent. Comparison of the 100- and 200-MHz NMR spectra clearly reveals the chemical shift nature of the doublet pattern assigned to these signals; there is no observable coupling of the nitrogen methyl protons to the ^{31}P , ^{19}F , or other ^1H nuclei in the molecule. Particulars are given in Table III. This inequivalence was observed at ordinary temperatures in the case of the sulfur-containing compounds and at –40 °C in the case of the carbamate. The resolution of the magnetic nonequivalence in the carbamate at this temperature provides further evidence that the fluxional process which operate in this molecule have ceased on the NMR time scale at –40 °C. This magnetic nonequivalence is readily understood since the crystal structure of the carbamate reveals the lack of a plane of symmetry relating the methyl groups on the nitrogen atoms, and this situation will prevail if our postulations regarding the structures of the sulfur containing compounds are correct. In the carbamate structure, the closest nonequivalent atoms are the oxygens, with a difference of 0.093 Å in the P–O bond length, which are three bonds removed from the site of the observed nonequivalence. The in-plane CF_3 and CH_3 groups on phosphorus are well beyond the van der Waals distance, so it seems unlikely that the nonequivalence is transmitted

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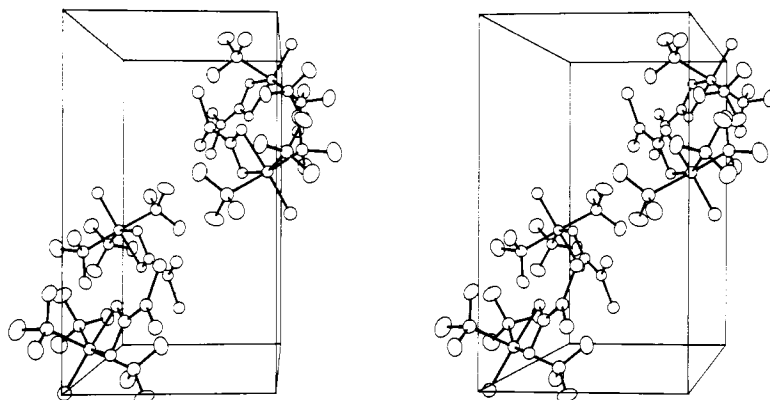


Figure 2. Stereoscopic illustration of the unit cell contents projected along the x axis.

through nonbonded interactions between the CH_3 groups of the carbamate and the coplanar CF_3 and CH_3 substituents on phosphorus.

Infrared Spectral Properties. The principal feature of note in the infrared spectrum of the solid carbamate (Table IV) is the strong sharp band at 1639.4 cm^{-1} . In solution (Table V) this band broadens and in some cases a shoulder appears at higher energy. In the presence of trimethylamine, this band appears as a double band with approximately 40-cm^{-1} separation between components.

The infrared spectra of our carbamate exhibits many features similar to the bidentate carbamate complexes of tin²² and of the chelated and bridging complexes of the transition metals.²³ All possess a strong, sharp band due to the asymmetric CO stretch, the position of which has been associated with the bonding of the carbamate group. In the transition-metal systems, bidentate carbamates show a single sharp band in the $1550\text{--}1580\text{-cm}^{-1}$ region, and in several cases the bidentate character of the carbamate ligand has been supported by X-ray structural analysis.²³ The IR spectrum of $\text{Me}_3\text{SnO}_2\text{CNMe}_2$ shows a strong sharp band at 1555 cm^{-1} which has been assigned to a polymeric structure containing five-coordinate tin and a bifunctional carbamate.²² This same $\text{C}=\text{O}$ region in trimethylsilylon carbamate appears at about 1700 cm^{-1} wherein the ligand is believed to be monodentate. Thus the higher wavenumber band, reasonable assigned to the asymmetric ν_{CO} stretch, appears to shift to lower values in the case of bridging and chelated groups compared to the monodentate species, a behavior which is analogous to the IR spectral behavior of acetates.²⁴ The symmetric stretch at 1470 cm^{-1} is weaker and difficult to identify conclusively among the other bands of this spectrum; however, this vibration does not change appreciably with mode of bonding. It is worth noting that the band frequency observed for the antisymmetric ν_{CO} ($\sim 1640\text{ cm}^{-1}$) is considerably higher in this case than that of metal carbamates^{22,23} wherein this band appears at $1550\text{--}1580\text{ cm}^{-1}$. The difference is not unexpected in view of the different masses and the difference in electronic character between the metals and our phosphorus complex.

In this case, then, the single sharp band displayed by the solid can be assigned to a chelated carbamate group which is supported by the crystal structure. Furthermore, the negligible shift of this band ($<1.0\text{ cm}^{-1}$) in the ^{13}C carbamate (Table V) supports the bidentate chelate structure for the solid.²³ In solution, the broadening of this band and the appearance of the shoulder is consistent with the evidence pro-

vided by NMR that the carbamate is involved in an exchange process, perhaps involving a monodentate carbamate intermediate species, since only at $-40\text{ }^\circ\text{C}$ do we see the NMR spectrum which is consistent with the solid-state structure and which is analogous to the NMR spectra of the monothio- and dithiocarbamates which are nonfluxional. Trimethylamine in solution appears to compete with the carbamate chelation and forms an adduct in which the carbamate ligand is monodentate, possibly therefore giving rise to the second band in the IR spectrum in the CO region. We have not, however, been able to isolate the trimethylamine adduct; removal of solvent leads to loss of the amine and the recovery of the carbamate.

The shift of the CO band in solution to higher wavenumbers is also consistent with the formation of monodentate carbamate in analogy to the behavior of coordinated acetates in which monodentate and bidentate structures apparently occur.²⁴

The monothiocarbamate which appears, according to the NMR spectra, to form two isomers does not show any multiplicity in the ν_{CO} band at 1631.5 cm^{-1} , although this band is considerably broader than the corresponding band in the carbamate. It is possible that isomeric differences have only a small effect in the infrared spectrum in this region. The presence of this single strong band is consistent with the formulation of these complexes as six-coordinate complexes with chelated thiocarbamate ligands.

Chelation of dithiocarbamates is supposedly indicated by the transformation of the doublet infrared band at $\sim 1000\text{ cm}^{-1}$ into a single sharp band.²⁵ In our complexes this region is obscured by strong CF absorptions, and thus the infrared data provide no insight into the structure of the complexes.

The remainder of the spectrum in each case is difficult to assign because of the overlap of group frequencies especially in the region $1300\text{--}900\text{ cm}^{-1}$ where strong CF, PO, and CS stretching frequencies are expected.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (and its predecessor, the National Research Council) for support of this work. We also thank Dr. Alex Whitla for assistance with the crystal preparation and data collection stages of the work.

Registry No. $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$, 65013-32-3; $\text{CH}_3(\text{C-F}_3)_3\text{PS}(\text{O})\text{CN}(\text{CH}_3)_2$ (isomer 1), 78185-53-2; $\text{CH}_3(\text{CF}_3)_3\text{PS}(\text{O})\text{C-N}(\text{CH}_3)_2$ (isomer 2), 78185-54-3; $\text{CH}_3(\text{CF}_3)_3\text{PS}_2\text{CN}(\text{CH}_3)_2$, 78185-55-4; $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CH}_3)_2$, 63715-49-1; $(\text{CH}_3)_3\text{SiO}_2\text{CN}(\text{C-H}_3)_2$, 32115-55-2; $(\text{CH}_3)_3\text{SiO}(\text{S})\text{CN}(\text{CH}_3)_2$, 32115-56-3; $(\text{CH}_3)_3\text{-SiSi}_2\text{CN}(\text{CH}_3)_2$, 18140-13-1; $\text{CH}_3(\text{CF}_3)_3\text{PCl}$, 56420-21-4; $\text{CH}_3(\text{C-F}_3)_3\text{PF}$, 56396-13-5; CO_2 , 124-38-9; COS , 463-58-1; CS_2 , 75-15-0.

Supplementary Material Available: A listing of observed ($10F_o$) and calculated ($10F_c$) structure amplitudes (3 pages). Ordering information is given on any current masthead page.

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