Inorg. Chem. **1986**, *25*, 4699–4704 **4699**

Contribution from the Department of Chemistry,
The University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Hexacoordinate Phosphorus. 3. Neutral Fluoro(trifluoromethyl)(*N*,*N*-dimethylcarbamato-*O*,*O'*)phosphorus(V) Derivatives

Ronald G. Cavell* and Larry Vande Griend

Received May 16, 1986

Three neutral hexacoordinate (*N*,*N*-dimethylcarbamato-*O*,*O'*)phosphorus(V) compounds have been made with the formula $F_{4-n}(CF_3)_nPO_2CN(CH_3)_2$ (n = 1–3). The compounds are stable white crystalline solids. The crystal and molecular structure of $F(CF_3)_3PO_2CN(CH_3)_2$ shows the six-coordinate nature of the phosphorus atom and also that the unique F atom lies in the molecular plane containing that F, a CF_3 group, the phosphorus center, and the planar carbamate ligand. Crystal data: monoclinic, space group $P2_1/c$ (No. 14), a = 7.285 (1) Å, b = 13.063 (1) Å, c = 12.642 (2) Å, β = 93.57 (1)°, V = 1200.78 Å^3, Z = 4. Final R and R_w values were 0.068 and 0.096, respectively. Comparison of NMR parameters of this complex with those of the others in the series suggests that the compound $F_2(CF_3)_2PO_2CN(CH_3)_2$, which shows only one isomer, also has a six-coordinate structure in which both fluorine atoms are coplanar with the carbamate ligand. The compound $F_3(CF_3)PO_2CN(CH_3)_2$ shows a major isomer (relative intensity 2) in which two fluorines are coplanar with the carbamate ligand and a minor isomer (relative intensity 1) in which the single CF_3 lies in the carbamate plane. The compounds are fluxional in solution at ordinary temperatures but static at moderately low temperatures. NMR parameters can be obtained from low-temperature spectra by first-order analysis.

Introduction

Recently we have shown that it is possible to prepare neutral six-coordinate compounds of phosphorus containing the carbamato group as a chelated, bidentate substituent to phosphorus.[1-3] The first syntheses were accomplished by means of the "insertion" reaction of the pentacoordinate aminophosphorane $CH_3(CF_3)_3PN(CH_3)_2$,[1,2] but mechanistic studies[3] showed preformation of the carbamato substituent in solution to be the most likely pathway for the reaction. Accordingly, a rational synthesis was developed from trimethylsilylcarbamate[2] and the appropriate halogeno phosphorus compound, a route that can provide many otherwise inaccessible compounds.[4] Herein we report on the synthesis and characterization of the compounds of the series $F_{4-n}(CF_3)_nPO_2CN(CH_3)_2$.

Experimental Section

Synthesis. All reactions were done in sealed tubes, and standard vacuum techniques were used throughout for the manipulation of volatile compounds. NMR spectra were obtained with Bruker WP400 or WP200 instruments operating in the pulsed FT mode on solutions (ca. 10%) in CCl_3F with CD_2Cl_2 for ^2D lock. Fluorine chemical shifts are given relative to the solvent CCl_3F. Phosphorus chemical shifts (measured relative to the internal lock of the instrument) are quoted relative to 85% H_3PO_4. In both cases negative values indicate resonance to high field of the standard.

1. Preparation of Trifluoro(trifluoromethyl)(*N*,*N*-dimethylcarbamato-*O*,*O'*)phosphorus(V). CF_3PF_4 (0.293 g, 1.66 mmol)[5] and $(CH_3)_3SiO_2CN(CH_3)_2$ (0.203 g, 1.26 mmol)[6] were successively condensed under vacuum into a 50-mL glass tube, which was then sealed. When the vessel was warmed to room temperature, the mixture became liquid. A white solid subsequently formed over a period of a few minutes. After 15 min at room temperature the volatile materials (total 0.186 g) were removed under vacuum and identified as unreacted CF_3PF_4 (38% (NMR) by mass, 0.40 mmol) and a quantitative yield of $(CH_3)_3SiF$ (62% (NMR) by mass, 1.26 mmol). The remaining white solid residue of $F_3(CF_3)PO_2CN(CH_3)_2$ (I) (which moved slowly under a dynamic vacuum) was trapped at 0 °C (0.291 g, 1.19 mmol, 94% yield, mp 58–59 °C). The compound was further purified by sublimation onto a cold finger under vacuum, by gently heating the crude material with an external water bath maintained at 50 °C. This compound was the most air sensitive of the series, fuming visibly on exposure to moist air.

2. Preparation of Difluorobis(trifluoromethyl)(*N*,*N*-dimethylcarbamato-*O*,*O'*)phosphorus(V). $(CF_3)_2PF_3$ (0.601 g, 2.66 mmol)[5] and $(CH_3)_3SiO_2CN(CH_3)_2$[6] (0.340 g, 2.11 mmol) were successively condensed under vacuum into a 50-mL glass tube, which was then sealed. When the reaction vessel was warmed to room temperature, a white solid formed in a slightly exothermic reaction. After 24 h at room temperature the volatile components (total mass 0.320 g) were removed under vacuum to yield excess unreacted $(CF_3)_2PF_3$ (calculated (excess) 0.125 g) and $(CH_3)_3SiF$ (calculated for 100% yield 0.195 g). The white residual solid, $F_2(CF_3)_2PO_2CN(CH_3)_2$ (II, mp 97–98 °C) was purified by sublimation onto a cold finger by heating with an external bath at 60 °C. The yield was 0.568 g (1.93 mmol, 91%). Anal. Calcd for $C_5H_6F_8NO_2P$: C, 20.35; H, 2.05; N, 4.75. Found: C, 21.12; H, 1.94; N, 4.88.

3. Preparation of Fluorotris(trifluoromethyl)(*N*,*N*-dimethylcarbamato-*O*,*O'*)phosphorus(V). $(CF_3)_3PF_2$ (0.607 g, 2.20 mmol)[5] and $(CH_3)_3SiO_2CN(CH_3)_2$[6] (0.302 g, 1.88 mmol) were successively condensed under vacuum into a 50-mL glass tube, which was then sealed under vacuum. A white solid formed quickly when the tube was warmed to room temperature. After 1 h of contact at room temperature, vacuum fractionation of the products yielded only one solid product, which was trapped at −78 °C. Virtually no $(CH_3)_3SiF$ was found in the −196 °C trap. The solid product trapped at −78 °C began to liquefy when brought to room temperature, and over a period of several days at room temperature, visible reaction occurred to deposit white crystals. Vacuum fractionation of the volatile materials at this stage yielded, in the −196 °C trap, a total mass of 0.281 g, which was identified (by NMR) as excess $(CF_3)_3PF_2$ and $(CH_3)_3SiF$ (expected mass 0.261 g, for total reaction on a 1:1 basis) and a white crystalline solid residue identified as $F(CF_3)_3PO_2CN(CH_3)_2$ (III) (0.404 g, 1.17 mmol, 62.5% yield, mp 61–62 °C), which was trapped at 0 °C. Anal. Calcd for $C_6H_6F_{10}NO_2P$: C, 20.88; H, 1.75; N, 4.06. Found: C, 21.47, 21.41; H, 1.78, 1.85; N, 4.02, 3.99.

4. Reaction of a Chlorophosphorane. CF_3PCl_4 (0.405 g, 1.67 mmol)[7] and $(CH_3)_3SiO_2CN(CH_3)_2$ (0.214 g, 1.33 mmol) were combined in a sealed tube as above. A white solid formed immediately on warming the tube to room temperature. This solid then liquified. Fractionation of the volatile products indicated the only products to be $CF_3P(O)Cl_2$[8] (ϕ = 75.3, J = 152 Hz), $ClC(O)N(CH_3)_2$, and $(CH_3)_3SiCl$ along with a small amount of unreacted CF_3PCl_4.

Collection of X-ray Data.[9] A colorless crystal of $F(CF_3)_3PO_2CN(CH_3)_2$ (III) was mounted in a Lindemann glass capillary in a nonspecific orientation on an Enraf-Nonius CAD4 automated diffractometer. All intensity measurements were performed with use of Mo Kα radiation (λ = 0.71073 A) with graphite crystal, incident beam monochromator. The automatic peak search and reflection indexing programs[10] in conjunction with a cell reduction program showed the crystal to be monoclinic, and the space group was determined to be $P2_1/c$ (No. 14).[11] Cell constants

---

(1) The, K. I.; Vande Griend, L.; Whitla, W. A.; Cavell, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 7379.

(2) Cavell, R. G.; The, K. I.; Vande Griend, L. *Inorg. Chem.* **1981**, *20*, 3813.

(3) Cavell, R. G.; Vande Griend, L. *Inorg. Chem.* **1983**, *22*, 2066.

(4) Cavell, R. G.; Vande Griend, L. *Phosphorus Sulfur* **1983**, *18*, 89.

(5) Mahler, W. *Inorg. Chem.* **1963**, *2*, 230.

(6) Breederveld, H. *Recl. Trav. Chim. Pays-Bas* **1962**, *81*, 276.

(7) Emeleus, H. J.; Haszeldine, R. N.; Paul, R. C. *J. Chem. Soc.* **1955**, 563.

(8) Griffiths, J. E. *Spectrochim. Acta, Part A* **1968**, *24A*, 303.

(9) This X-ray crystallographic study was carried out by Dr. R. G. Ball at the Structure Determination Laboratory, Department of Chemistry, University of Alberta. Inquiries regarding the crystallographic results should be directed to the above address quoting report number SR:030122-02-82. See paragraph at the end of paper regarding supplementary material.

(10) The diffractometer programs are those supplied by Enraf-Nonius for operating the CAD4F diffractometer with some local modifications and additions.

0020-1669/86/1325-4699$01.50/0 © 1986 American Chemical Society

Table I. Crystal Data for $F(CF_3)_3PO_2CN(CH_3)_2$

molecular formula	$PF_{10}O_2NC_6H_6$
fw	345.08
cryst shape	blocklike
cryst size, mm	0.30 × 0.18 × 0.09
systematic absences	$h0l$ (l odd), $0k0$ (k odd)
space group	monoclinic, $P2_1/c$ (No. 14)
unit cell parameters	
a, Å	7.285 (1)
b, Å	13.063 (1)
c, Å	12.642 (2)
β, deg	93.57 (1)
V, Å^3	1200.78
Z	4
ρ_{calcd}, g cm^{-3}	1.909
linear abs coeff μ, cm^{-1}	3.50
abs cor factor, Å	none
max 2θ reflcns coll, deg	48.0
takeoff angle, deg	3.05
detector aperture, mm	horizontal: 2.00 + 0.50 tan θ vertical: 4.00
cryst to detector distance, mm	205
scan type	θ–2θ
scan rate, deg min^{-1}	10.1–1.3
scan width, deg	0.70 + 0.35 tan θ
data collection index range	$h,k,\pm l$
std reflcns (esd, %)	3 (1.8, 9.5)
temp, °C	25
no. of indep reflecns (total)	1790 (1897)
no. of reflcns $I > 3\sigma$	1041
final R_1, R_2	0.068, 0.096

were obtained from a least-squares refinement of the setting angles of 22 reflections in the range $17 < 2\theta < 28°$. The various crystal parameters are given in Table I.

The intensity data were collected at room temperature with use of variable ω–2θ scan rates chosen to give $\sigma(I)/I \leq 0.03$ within a time limit of 60 s in order to achieve improved counting statistics for both intense and weak reflections in a minimum time. The scan range and aperture width (Table I) were determined as a function of θ to compensate for the α_1–α_2 wavelength dispersion. Backgrounds for the peaks were measured by extending the scan 25% on either side of the calculated range to give a peak to background counting time of 2:1. Intensity measurements were made to a maximum 2θ of 48.00°. Three reflections, chosen as standards, were remeasured every 60 min of exposure time to monitor crystal and electronic stability over the course of data collection. A linear regression analysis of these standards showed a mean change in intensity of 1.8 (9.5)% over the time of data collection.

X-ray Data Reduction. A total of 1897 reflections were collected, and these were corrected for Lorentz, polarization, and background effects according to the formulas

$$I = \mathrm{SR}(\mathrm{SC} - R^*B)/Lp$$

$$\sigma^2(I) = \{\mathrm{SR}(\mathrm{SC} + R^2B) + (PI)^2\}/Lp^2$$

where SR is the scan rate, SC is the total scan count, R is the ratio of scan time to background time, B is the total background count, P is a factor to downweight intense reflections (chosen as 0.040 in this experiment), and Lp is the Lorentz and polarization correction term. After equivalent forms were averaged and systematically absent data were rejected, 1790 unique reflections remained, which were used for the structure solution and refinement.

Structure Solution and Refinement.[12] The structure was solved with use of the direct methods program SHELX84,[13] which gave the positional parameters for all the non-H atoms in the molecule.

Refinement of atomic parameters was carried out by using full-matrix least-squares techniques on F_o minimizing the function

$$\sum w(|F_o| - |F_c|)^2$$

where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively, and the weighting factor w is given by

$$w = 4F_o^2/\sigma^2(F_o^2)$$

The neutral-atom scattering factors were calculated from the analytical expression for the scattering factor curves.[14] The f' and f'' components of anomalous dispersion[15] were included in the calculations for all nonhydrogen atoms.

Three of the six hydrogens were located in a difference Fourier map and, from these coordinates, idealized positions for all six were calculated by assuming C–H = 0.95 Å and sp^3 geometry. These atoms were then constrained to "ride" on the appropriate C atom with fixed isotropic thermal parameters. The two methyl C atoms and all F atoms were refined with anisotropic thermal parameters while the remaining atoms were constrained to refine isotropically in order to maintain an acceptable (≥7/1) observed data/parameter ratio.

In the final cycle 141 parameters were refined with use of 1041 observations having $I > 3.0\sigma(I)$. The final agreement factors were

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.068$$

$$R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{0.5} = 0.096$$

The largest shift in any parameter was 0.01 times its estimated standard deviation, and the error in an observation of unit weight was 3.37 e. An analysis of R_2 in terms of F_o, λ^{-1} sin θ, and various combinations of Miller indices showed no unusual trends. The highest peak in the final differences Fourier was 0.62 (8) e Å^{-3}.

Results and Discussion

A. Synthesis. The reactions proceed in good yield according to the expected stoichiometry with removal of one fluorine from phosphorus as $(CH_3)_3SiF$:

$$(CF_3)_nPF_{5-n} + (CH_3)_3SiO_2CN(CH_3)_2 \rightarrow F_{4-n}(CF_3)_nPO_2CN(CH_3)_2 + (CH_3)_3SiF \quad (1)$$

$$n = 1\text{–}3$$

The difluorophosphorane $(CF_3)_3PF_2$ reacted most slowly and gave evidence for an intermediate adduct formed by the phosphorane and the silylcarbamate, a reasonable pathway for this reaction. No investigation of this adduct was undertaken.

All of the compounds are crystalline white solids with sharp melting points. They are not unusually air- or moisture-sensitive. All show characteristic high-field phosphorus NMR chemical shifts suggestive of six-coordinate phosphorus[1,2,16] environments, and this was confirmed by a crystal structure analysis for one derivative.

In an attempt to make hexacoordinate chlorophosphorus(V) derivatives, the reaction of CF_3PCl_4 with (trimethylsilyl)carbamate was explored. The reaction proceeded initially to yield a solid product, but this product was unstable and the only chlorophosphorus compound obtained was $CF_3P(O)Cl_2$. The reaction follows the equation

$$CF_3PCl_4 + (CH_3)_3SiOC(O)N(CH_3)_2 \rightarrow CF_3P(O)Cl_2 + (CH_3)_3SiCl + (CH_3)_2NC(O)Cl \quad (2)$$

All of the products can be explained by proposing the formation of an unstable chlorophosphorus carbamate, $Cl_4(CF_3)POC(O)N(CH_3)_2$, which subsequently decomposes by elimination of $(CH_3)_2NC(O)Cl$. In view of this negative result, no further study of chlorophosphoranes was undertaken although it is possible that the more highly trifluoromethylated analogues might yield stable six-coordinate compounds. Related systems[17] have, however, not yielded stable hexacoordinate chlorophosphorus(V) compounds.

B. Crystal and Molecular Structure of $F(CF_3)_3PO_2CN(CH_3)_2$. The crystal and molecular structure of $F(CF_3)_3PO_2CN(CH_3)_2$ (III) was solved and showed the six-coordinate molecular structure (Figure 1) expected by analogy with $CH_3(CF_3)_3PO_2CN(CH_3)_2$.[2]

---

(11) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I.

(12) The computer programs used in this analysis include the Enraf-Nonius Structure Determination Package by B. A. Frenz (*Computing in Crystallography*); Delft University Press: Delft, Holland, 1978; pp 64–71) and several locally written or modified programs.

(13) We would like to thank G. M. Sheldrick for making SHELX84 available at the July 1983 direct methods workshop at the Medical Foundation of Buffalo.

(14) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(15) Reference 14, Table 2.3.1.

(16) Sheldrick, W. S.; Hewson, M. J. C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 834.

(17) Burford, N.; Kennepohl, D.; Cowie, M.; Cavell, R. G. *Inorg. Chem.*, in press.

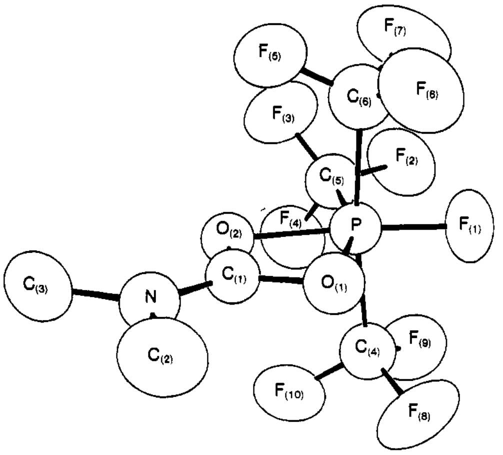

Figure 1. Molecular structure of $F(CF_3)_3PO_2CN(CH_3)_2$ showing the atom-numbering scheme. The atoms (except hydrogen) are shown as 50% probability ellipsoids.

Table II. Final Positional and Thermal Parameters[a,b] for Non-Hydrogen Atoms of $F(CF_3)_3PO_2CN(CH_3)_2$

	x	y	z	U, 10^2 Å^2
P	−0.0224 (3)	−0.0886 (2)	0.2199 (1)	5.46 (5)
O(1)	−0.1635 (7)	−0.0841 (4)	0.0949 (4)	6.1 (1)
O(2)	−0.1525 (6)	−0.2038 (4)	0.2099 (3)	5.4 (1)
N	−0.3355 (8)	−0.2267 (4)	0.0554 (4)	5.3 (2)
C(1)	−0.2269 (9)	−0.1744 (5)	0.1151 (5)	4.9 (2)
C(4)	−0.211 (1)	−0.0144 (7)	0.2849 (6)	6.9 (2)
C(5)	0.088 (1)	−0.1364 (7)	0.3512 (7)	7.6 (2)
C(6)	0.173 (1)	−0.1440 (7)	0.1411 (6)	7.4 (2)
F(1)	0.0780 (7)	0.0189 (3)	0.2119 (4)	8.1 (1)[c]
F(2)	0.2125 (7)	−0.0736 (5)	0.3977 (4)	10.5 (3)[c]
F(3)	0.1668 (8)	−0.2274 (4)	0.3411 (4)	10.1 (3)[c]
F(4)	−0.0390 (7)	−0.1513 (4)	0.4238 (3)	9.4 (3)[c]
F(5)	0.1507 (7)	−0.2404 (4)	0.1125 (4)	9.0 (1)[c]
F(6)	0.1813 (8)	−0.0923 (5)	0.0473 (4)	11.4 (3)[c]
F(7)	0.3340 (7)	−0.1331 (6)	0.1899 (4)	12.0 (3)[c]
F(8)	−0.2853 (8)	0.0587 (4)	0.2211 (4)	11.0 (3)[c]
F(9)	−0.1499 (8)	0.0347 (4)	0.3704 (4)	10.5 (3)[c]
F(10)	−0.3530 (6)	−0.0712 (5)	0.3142 (4)	9.2 (3)[c]
C(2)	−0.407 (1)	−0.1843 (8)	−0.0487 (6)	8.5 (4)[c]
C(3)	−0.392 (1)	−0.3291 (6)	0.0855 (7)	7.6 (3)[c]

[a] Estimated standard deviations given in parentheses. [b] Parameters for hydrogen atoms given as supplementary data. [c] Anisotropic thermal parameters given as supplementary material. The equivalent isotropic U is given by $^1/_3\sum_{i=1}^{3}r_i^2$, where the r_i values are the root-mean-square displacements (supplementary material).

The final refined parameters are given in Tables II and III. CF_3 bond lengths and angles are given as supplementary material. Perhaps somewhat surprising is the fact that the monofluorophosphorus compound is isostructural with the methyl analogue; the unique F occupies the same relative position in the framework, coplanar with the carbamato substituent, as does the CH_3 group. In this context it is also notable that the P–O bond length for the P–O bond trans to F is the shortest of the two, adding support to our previous conclusion[2] that this bond length difference arises as a consequence of the electronegativity of the ligand trans to the P–O bond; thus, CH_3 gives a longer trans P–O bond vs. the P–O bond length trans to CF_3 and in the present case the P–O bond trans to F is the shortest. These differences can be attributed to a trans inductive effect influencing the binding of two equivalent oxygen atoms in the carbamato ligand. The average P–O bond distance is a little shorter (1.805 Å) in the present compound as compared to that in $CH_3(CF_3)_3PO_2CN(CH_3)_2$ (1.855 Å), suggesting that the acidity of the phosphorus which causes the carbamate to chelate is increased by substitution of the more electronegative F for CH_3. Otherwise there is little difference between the two compounds.

A second structural feature of interest is the near-coplanarity of the atoms in the carbamate ligand with P, F, and one of the CF_3 groups, a feature that also appeared in the methyl analogue.[2] Except for the CF_3 (C(5)) carbon atom and one carbon atom of the carbamato ligand (C(3)) the oxygen, phosphorus, nitrogen, C(2), and fluorine (F(1)) atoms lie within 0.04 Å of the plane. An alternate description of the central girdle of the molecule is obtained by defining the carbamato ligand itself as one plane and the central phosphorus atom and the four substituent atoms C(5), F(1), O(1), and O(2) as a second plane. In each of these separate planes, deviation from planarity is 0.009 Å or less except for C(5). These two planes exhibit a small (3.4°) dihedral twist relative to each other. Full coordinates for both approaches are given in the supplementary material.

Table III. Principal Bond Distances and Angles in $F(CF_3)_3PO_2CN(CH_3)_2$[a]

	Bond Distances (Å)[b]		
P–F(1)	1.590 (3)	N–C(1)	1.261 (5)
P–O(1)	1.832 (3)	N–C(2)	1.490 (6)
P–O(2)	1.778 (3)	N–C(3)	1.458 (6)
P–C(4)	1.911 (5)	O(1)–C(1)	1.297 (5)
P–C(5)	1.904 (5)	O(2)–C(1)	1.341 (4)
P–C(6)	1.926 (6)		
	Bond Angles (deg)[b]		
F(1)–P–O(1)	98.8 (2)	C(4)–P–C(5)	93.9 (2)
F(1)–P–O(2)	171.2 (2)	C(4)–P–C(6)	170.9 (2)
F(1)–P–C(4)	85.8 (2)	C(5)–P–C(6)	92.4 (2)
F(1)–P–C(5)	100.0 (2)	P–O(1)–C(1)	89.4 (2)
F(1)–P–C(6)	86.7 (2)	P–O(2)–C(1)	90.3 (2)
O(1)–P–O(2)	72.4 (1)	C(1)–N–C(2)	119.9 (4)
O(1)–P–C(4)	88.5 (2)	C(1)–N–C(3)	121.3 (4)
O(1)–P–C(5)	161.2 (2)	C(2)–N–C(3)	118.8 (4)
O(1)–P–C(6)	87.6 (2)	O(1)–C(1)–O(2)	107.9 (3)
O(2)–P–C(4)	93.7 (2)	O(1)–C(1)–N	126.4 (4)
O(2)–P–C(5)	88.8 (2)	O(2)–C(1)–N	125.7 (4)
O(2)–P–C(6)	93.0 (2)		

[a] Distances and angles for CF_3 substituents given as supplementary material. [b] Numbers in parentheses are estimated standard deviations in the least significant digits.

Another structural feature of interest is the fact that the CF_3–P–CF_3 axis is nearly linear (∠CPC = 170.9°), slightly more bent than in the case of the methylphosphorus(V) derivative.[2] In contrast to the case for the methyl derivative, where the CF_3 groups bend toward the planar carbamato ligand side of the molecule,[2] the axial CF_3 groups in the fluoro derivative bend toward the unique fluorine. The differences in magnitude and direction of the axial bending might be due to differences in electronic effects, but small steric differences might also yield the observed patterns. This structure again provides evidence that the CF_3 groups are however not particularly sterically demanding; a calculated cone angle from the experimental bond lengths and angles indicates that the steric bulk of CF_3 (cone angle 97°) is comparable to that of CH_3 (cone angle 93°).

The only contacts less than 2.95 Å between two molecules are (mol(1) vs. mol(2)) F(5) vs. F(9) (2.945 Å), F(6) vs. O(1) (2.920 Å), and F(7) vs. F(10) (2.806 Å), none of which appear to be significant.

C. NMR Spectra. All three compounds exhibit the characteristic high-field ^{31}P NMR shift indicative of a six-coordinate phosphorus center. All compounds show some fluxionality exhibited as broadening of the lines and loss of some coupling patterns at ordinary temperatures. Limiting spectra for I and III were obtained at temperatures ranging from −30 to −45 °C. The spectrum of II was not very sensitive to temperature, but cooling to −10 °C sharpened all lines in all regions without changing shift or coupling parameters. The static spectra (Figures 2–7) show clearly the presence of appropriate signals for "axial" and "radial" (or equatorial) CF_3 and F substituents in the appropriate numbers. All could be analyzed by first-order methods, although III required a high-field ^{19}F NMR spectrum to achieve first-order analysis because of the pronounced coincidental overlap of CF_3 region signals. The resultant parameters are given in Table IV.

Although all the compounds could possess several isomeric structures (Figure 8), it is notable that $F(CF_3)_3PO_2CN(CH_3)_2$

Table IV. NMR Spectral Parameters for (Carbamato)phosphorus(V) Fluorides

compd	$\sigma(^{31}P)^a$	$\phi(CF_3)^b$	$\phi(F)^b$	$\tau(H)$	$^1J_{PF}$, Hz	$^2J_{PCF}$, Hz	$^2J_{FPF}$, Hz	$^3J_{FPCF}$, Hz
I-B (rel total intens 2)	-145.0^d	-69.7 (a)^{e,f}	-85.1 [2]^{g,h} (r)	...	654.0 [2] (r)	145.0 (a)	62.5	13.8
			-58.9 [1]^i (a)	7.21^j	830.7 [1] (a)			3.0
I-A (rel total intens 1)	-133.9^d	-70.4 (r)^{e,f}	-84.0 [1] (r)	...	936.3 [1]^k (r)	155.6 (r)	55.2	8.5
			-59.6 [2] (a)	7.21^j	921.5 [2]^k (a)			15.0
II	-146.0^l	-70.0^m	-90.9 (r)^n	7.16^o	1057.2 (r)	164.3 (a)	...	14.5
III	-148.5^p	-68.8 [2]^{q,r} (a)	-103.7^t (r)	7.19^u	997.4 (r)^v	141.5 (a)	...	11.0
		-69.1 [1]^{q,s} (r)		7.21^u		97.5 (r)		4.0

[a] Vs. 85% H_3PO_4. Negative values represent shifts to high field (note the use of a different reference compared to that in previous publications[2,3]). [b] Vs. CCl_3F. Negative values indicate shifts to high field. [c] Vs. $(CH_3)_4Si$. τ = 10.0 ppm. [d] At −20 °C, a full first-order pattern of a triplet of doublets of quartets. [e] Legend: a = axial, i.e., perpendicular to carbamate plane; r = radial (or equatorial), i.e., in the carbamate plane. [f] Doublet of triplets of doublets at −30 °C. [g] Relative intensity of signals in brackets. [h] Doublet of doublets of quartets at −30 °C. [i] Doublet of triplets of unresolved quartets at −30 °C. [j] Single at 32 °C, no evidence for two isomers; broad structures with unresolved components at −40 °C. [k] These two values were incorrectly interchanged in ref 4. [l] Triplet of septets at 32 °C. [m] Sharp doublet of triplets at temperatures from +50 to −50 °C. [n] Broad doublet of multiplets at 10 °C, sharp lines (doublet of septets) at −10 °C (fwhm ≈ 6 Hz), through to −50 °C (fwhm ≈ 3 Hz). [o] Singlet at +32 °C. [p] Doublet of septets of quartets at −50 °C. [q] These lines are not first order at temperature from −10 to +80 °C. [r] Doublet of pentets at −50 °C and 376.5 MHz. [s] Doublet of unresolved septets (?) of doublets at −50 °C and 376.5 MHz. [t] Doublet of complex multiplets at −50 °C and 376.5 MHz. [u] Singlet at τ 7.14 at 32 °C. [v] Value given in ref 4 contains a typographical error.

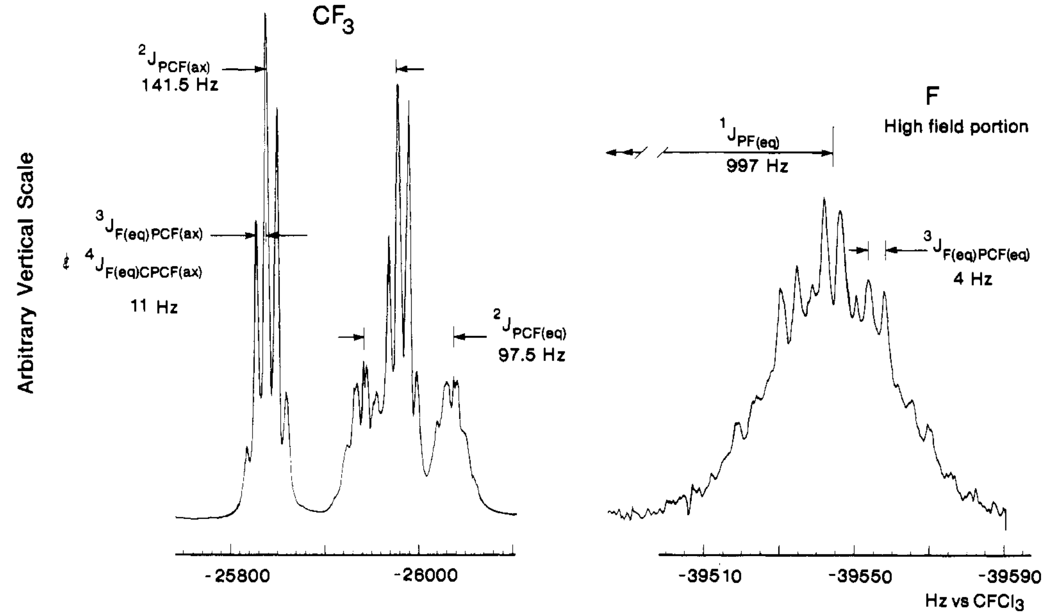

Figure 2. ^{19}F NMR spectrum of $F(CF_3)_3PO_2CN(CH_3)_2$ in $CDCl_2$ at 376.5 MHz and −50 °C.

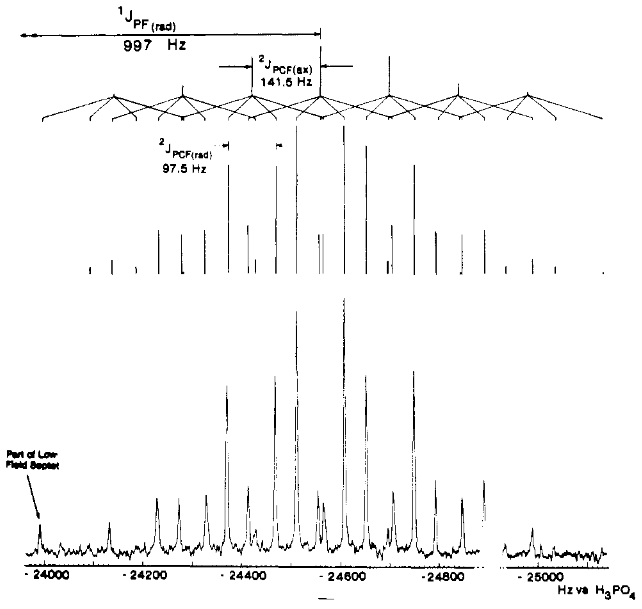

Figure 3. High-field portion of the ^{31}P NMR spectrum of $F(CF_3)_3PO_2CN(CH_3)_2$ in $CDCl_2$ at 162 MHz and −50 °C.

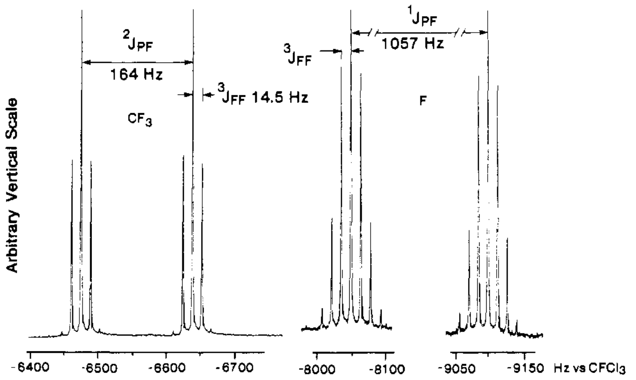

Figure 4. ^{19}F NMR spectrum of $F_2(CF_3)_2PO_2CN(CH_3)_2$ in $CFCl_3$/CD_3CN (1/1) at 94.1 MHz and −50 °C.

(III) and $F_2(CF_3)_2PO_2CN(CH_3)_2$ (II) showed no evidence for more than one structural form in the NMR spectra whereas $F_3(CF_3)PO_2CN(CH_3)_2$ (I) clearly showed two isomeric structures.

To assign the NMR spectra, we make the usual assumption that the structure of $F(CF_3)_3PO_2CN(CH_3)_2$ is the same in both solid and solution states (i.e. III-B). We note also that the unique radial F provided by this case has a very high field chemical shift (Figure 2), the highest of the series (ϕ = −103.7). We therefore associate a high-field chemical shift with a radial (i.e., defined as lying in the carbamate plane of the molecule) location for fluorine, a pattern that has been previously noted for $F_4P(acac)$[16] and that we have observed in related molecules.[17] The limiting

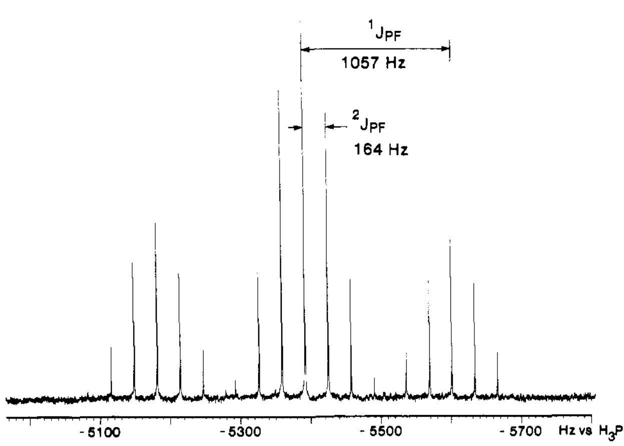

Figure 5. ^{31}P NMR spectrum of $F_2(CF_3)_2PO_2CN(CH_3)_2$ in $CFCl_3$/CD_3CN (1/1) at 36.4 MHz and -50 °C.

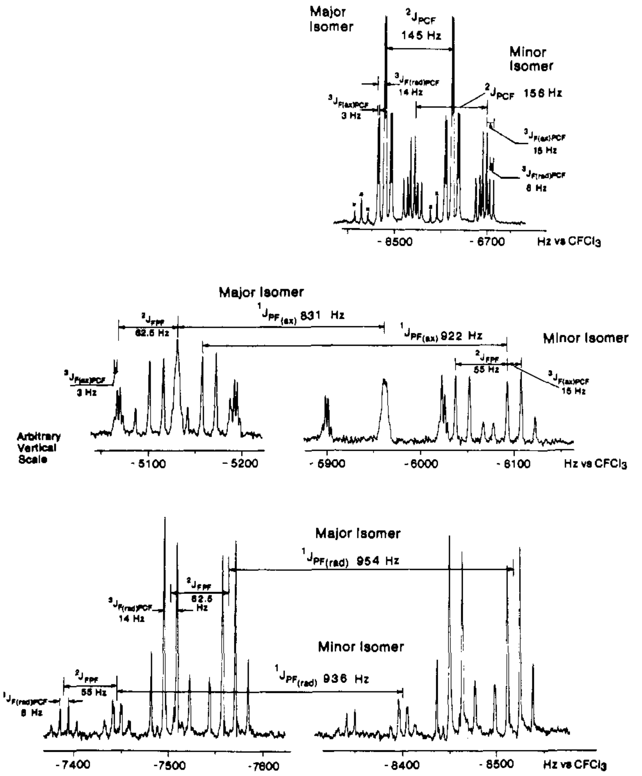

Figure 6. ^{19}F NMR spectrum of the isomeric mixture of $F_3(CF_3)PO_2CN(CH_3)_2$ in $CFCl_3/CD_2CN$ (1/1) at 94.1 MHz and -30 °C. The upper portion shows the CF_3 region and the bottom two portions show the directly bound F signals (intensity scales are arbitrary) with assignments. Peaks marked with an asterisk are due to impurities.

^{31}P NMR spectrum (Figure 3) shows the separate coupling constants clearly.

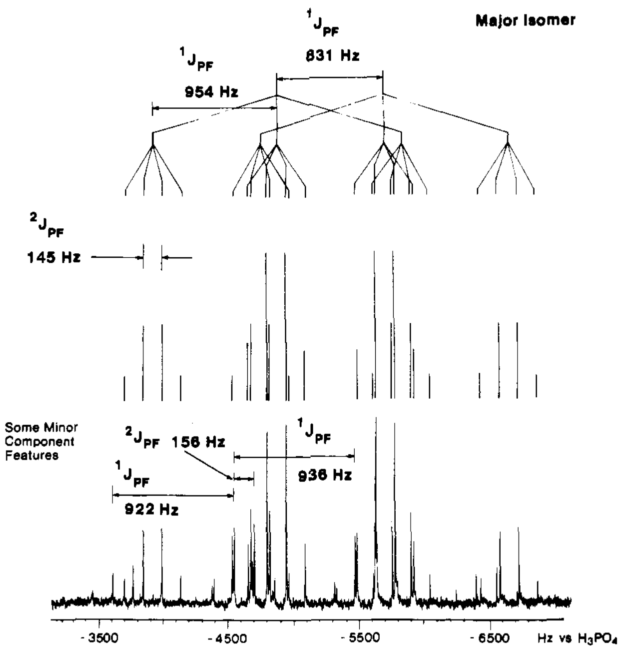

Figure 7. ^{31}P NMR spectrum of the isomeric mixture of $F_3(CF_3)PO_2CN(CH_3)_2$ in $CFCl_3/CD_3CN$ (1/1) at 36.4 MHz and -30 °C. The stick diagram correlates the radial and axial $^1J_{PF}$ and $^2J_{PF}$ coupling constants for the major isomer. In the actual spectrum (lower part) the minor component features are indicated.

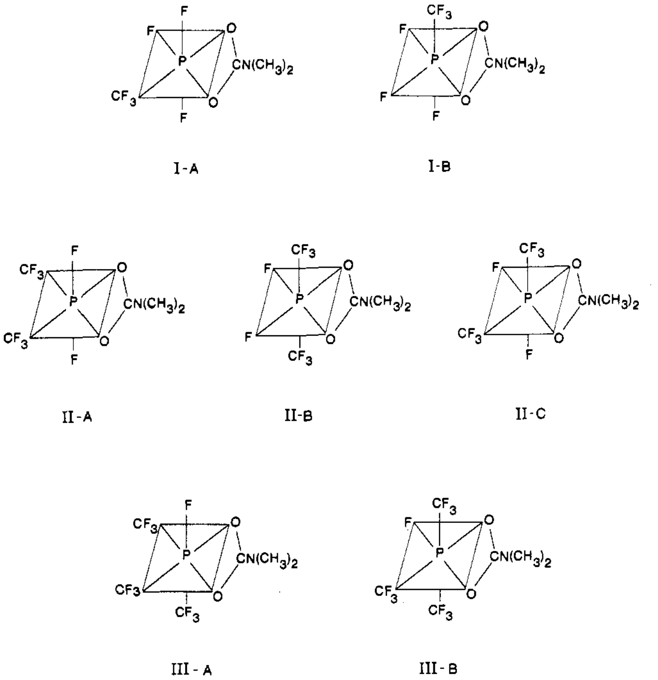

Figure 8. Isomeric structures for six-coordinate (carbamato)phosphorus(V) compounds.

The structure chosen for II, II-B, is consistent with the proposed associations of position and shift in that the F chemical shift value of -90.9 ppm (Figure 4) is a relatively high field value. There is no evidence for the presence of either of the alternate isomeric species II-A and II-C. The former alone would be indistinguishable by NMR, requiring only the reassignment of "axial" and "radial" signals. The latter we think would yield a second-order spectrum unless it were rapidly fluxional. In the case of the acetylacetonate derivative the analogue of structure II-B has been demonstrated by crystallography.[17] Of course, rapid interconversion between all three isomers of II would also be consistent with the observed spectra and cannot be totally ruled out on the basis of the existing NMR measurements, but we think that this situation is unlikely in view of the ready separation of axial and radial environments in the observably fluxional analogues at moderately low temperatures. The ^{31}P NMR spectrum (Figure 5) shows only one isomer with parameters in agreement with those obtained from the ^{19}F NMR spectrum.

The trifluoro derivative $F_3(CF_3)PO_2CN(CH_3)_2$ (I) shows the presence of two isomers with the relative proportions of 2:1. This is most clearly indicated in the CF_3 region of the ^{19}F NMR spectrum (Figure 6). The assignment of the major component to the structure I-B follows from the above assumption because this major component shows a high-field F chemical shift (ϕ = -85) of relative intensity 2 (assigned to two "radial" F atoms) compared to a unit-intensity signal at ϕ = -59, which can be assigned to the "axial" fluorine. Both of these signals correlate, as indicated by comparability of the long-range coupling constants $^3J_{FCPF}$ and $^4J_{FCPCF}$, with the CF_3 signal of total intensity 2. The unit-intensity CF_3 signal correlates with a single F signal at ϕ =

−84 assigned to a "radial" F and a signal for two "axial" fluorines, $\phi = -59.6$, in keeping with the assignment of the structure I-A to the minor component. Although the persistence of the trend demonstrated by the chemical shift of the directly bound fluorine supports these assignments, a completely consistent interpretation of all systems would result if the exactly opposite assignments were made throughout (i.e., if the solution structure of III were not the same as the solid-state structure).

Also supportive of the present assignment is the general consistent association of larger $^1J_{PF}$ values with higher field (radial) fluorine chemical shifts except for the minor isomer I-A. The two $^1J_{PF}$ values in this case are very close (radial 936 Hz, axial 922 Hz) so that the difference is probably not significant. The trend of CF_3 chemical shifts and coupling constants is not fully consistent throughout, although the assignment for III suggests that "axial" CF_3 groups should have substantially larger $^2J_{PF}$ values than "radial" CF_3 groups. This is supported by the value of this parameter indicated for II (assuming structure II-B to be the case). The radial CF_3 coupling constant found for the minor isomer I-A is inconsistent with this trend, being *larger* than the axial value demonstrated by I-B. Again both $^2J_{PF}$ values are close and the small difference may not convey significant information about the location of CF_3 on the framework. We note also that the variation of CF_3 chemical shifts in this series of molecules is very small and this parameter cannot be profitably used to indicate location, a conclusion that has been indicated previously in studies on the analogous five-coordinate systems.[18]

As was the case for the methylphosphorus derivative $CH_3(CF_3)_3PO_2CN(CH_3)_2$, the proton NMR spectrum of III indicates, at −40 °C, nonequivalent environments for the methyl groups on the nitrogen. In both cases this is a chemical shift effect and is not due to coupling with phosphorus. The magnitude of the difference, 0.02 ppm, for the fluoro system is about the same as that observed for the CH_3 analogue.

D. Bonding Properties. These compounds can be considered typical examples of "hypervalent"[19] molecules in which, because of the formal donation of a pair of electrons from oxygen to phosphorus to complete the bidentate binding of the carbamato ligand, there is a formal electron count of 12 electrons (or 6 pairs) around phosphorus (12-P-6).[20] In view of recent interest in such systems[20-22] it is of interest to compare parameters that may reveal details of the bonding in these compounds. The very existence of these compounds seems to require highly electronegative substituents on phosphorus (i.e., F, CF_3, O), suggesting a need to stabilize ionic contributions to the bonding. It is notable that chlorophosphorus(V) compounds have not been successsfully prepared. In addition it is notable that the P–F coupling constants are in general quite large, indicating substantial "s" character in both the P–F and P–CF_3 bonds. The similarity of "axial" and "radial" coupling constant values implies a high degree of spherical symmetry. The large P–F couplings (larger than $^1J_{PF}$ in PF_6^-) suggest that neither axial nor radial bonding can be wholly described in terms of a three-center–two-electron p-orbital bond with substantial ionic character after the model proposed by Rundle;[23] "s" mixing appears to be substantial.

In view of the limited data available for bond lengths and the fact that some CF_3 disorder difficulties have arisen in previous[2] structures the variations in radial and axial C–P bond lengths do not provide a significant and reliable basis for analysis as to the ramifications of "hypervalency". Results on analogous systems presently under investigation[17] may allow us to address this question.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (Ottawa) for support of this work. We also thank Dr. R. Ball of our Structure Determination Laboratory for helpful discussion in addition to the determination of the crystal structure.

Registry No. I-A, 90443-58-6; I-B, 90528-27-1; II, 90443-59-7; III, 90443-60-0; CF_3PF_4, 1184-81-2; $(CH_3)_3SiO_2CN(CH_3)_2$, 32115-55-2; $(CF_3)_2PF_3$, 1184-82-3; $(CF_3)_3PF_2$, 661-45-0; CF_3PCl_4, 1066-48-4.

Supplementary Material Available: Tables of root mean square amplitudes of thermal vibration, derived positional and thermal parameters for hydrogen atoms, weighted least-squares planes, anisotropic thermal parameters, and bond distances and angles for CF_3 substituents (4 pages); a listing of observed ($10F_o$) and calculated ($10F_c$) structure amplitudes (9 pages). Ordering information is given on any current masthead page.

---

(18) Cavell, R. G.; Gibson, J. A.; The, K. I. *J. Am. Chem. Soc.* **1977**, *99*, 7841.

(19) Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54.

(20) Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753. (The notation represents *N* formal electrons on atom X surrounded by *L* ligands.)

(21) Martin, J. C. *Science (Washington, D.C.)* **1983**, *221*, 509. Lee, D. Y.; Martin, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 5745.

(22) Carpenter, L. E.; Verkade, J. G. *J. Am. Chem. Soc.* **1985**, *107*, 7084.

(23) Rundle, R. E. *Surv. Prog. Chem.* **1963**, *1*, 81.