Inorg. Chem. **2000,** *39,* 375−377

A Novel Synthesis of Hexakis(trifluoromethyl)cyclotriphosphazene. Single-Crystal X-ray Structures of $N_3P_3(CF_3)_6$ and $N_3P_3F_6$

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Received August 13, 1999

Reaction of hexafluorocyclotriphosphazene ($N_3P_3F_6$) with trimethyl(trifluoromethyl)silane in the presence of a catalytic amount of cesium fluoride in THF produced hexakis(trifluoromethyl)cyclotriphosphazene [$N_3P_3(CF_3)_6$] in 90% isolated yield. $N_3P_3(CF_3)_6$ is fully characterized by melting point, IR, NMR (^{19}F, ^{13}C, ^{31}P), MS, and elemental analysis data. Single-crystal X-ray structures of $N_3P_3(CF_3)_6$ and $N_3P_3F_6$ are reported.

Introduction

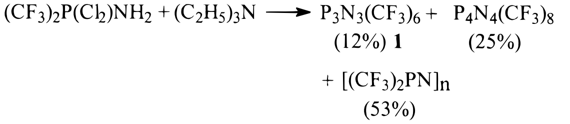
Phosphazenes are an important class of compounds, and their chemistry is well documented in the literature.[1] However, primarily because of the difficulties encountered in their syntheses, fluoroalkyl-substituted phosphazenes have not been studied in detail. Fluoroalkyl-substituted phosphazenes are expected to possess useful properties, e.g., as fire retardants. Moreover, the fluoroalkyl group should decrease the flammability of the phosphazene as compared to nonfluorinated alkyl and aryl derivatives. Hexakis(trifluoromethyl)cyclotriphosphazene [$N_3P_3(CF_3)_6$], **1**, is a promising compound, but its synthesis in the laboratory in good yield has not previously been achieved. The only successful preparation of **1** reported[2] involved a low-yield (12%) cyclization reaction of $(CF_3)_2P(Cl_2)NH_2$ with triethylamine as shown in Scheme 1.

Recently, we and others carried out nucleophilic trifluoromethylation of various substrates by using trimethyl(trifluoromethyl)silane (TMS-CF_3) in the presence of fluoride ion initiators (e.g., KF, (TBA)F, and CsF).[3] By using this methodology, we can now report the synthesis of **1** in excellent isolated yield.

Results and Discussion

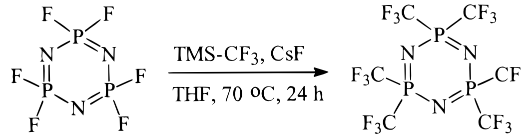
Reaction of **2**[4] with 7 equiv of TMS-CF_3 in tetrahydrofuran (THF) at 70 °C in the presence of catalytic amounts of anhydrous cesium fluoride led to the nearly quantitative formation of **1** (Scheme 2) on the basis of ^{19}F and ^{31}P NMR spectra. To recover compound **1** free of cesium fluoride and THF, the reaction mixture was cooled to −100 °C, which caused components soluble in THF to precipitate. After the THF was decanted at low temperature, the product was agitated vigorously with chloroform at room temperature and the mixture was cooled to −50 °C. The chloroform that contained some residual THF was further decanted at low temperature. This process was repeated once more with chloroform. Finally, the pure product was obtained in 90% yield by low-temperature trap-to-trap distillation. On the basis of spectroscopic data, no other substitution products or ring-opened phosphazenes were observed. Although this separation procedure seems a bit cumbersome, fractional condensation cannot be used because of the ease with which **1** is sublimed.

Scheme 1



$$(CF_3)_2P(Cl_2)NH_2 + (C_2H_5)_3N \longrightarrow \underset{(12\%)\ \mathbf{1}}{P_3N_3(CF_3)_6} + \underset{(25\%)}{P_4N_4(CF_3)_8} + \underset{(53\%)}{[(CF_3)_2PN]_n}$$

Scheme 2



2 **1**

Compound **1** has been characterized previously[2] by melting point, IR, and elemental analysis data and by a molecular weight determination. We have observed the same melting point and IR data for **1** and have also characterized this compound by ^{19}F, ^{31}P, ^{13}C NMR, MS, and single-crystal X-ray analysis. The ^{19}F NMR spectrum showed a doublet at δ −73.6 with a J_{P-F} coupling constant of 130 Hz, indicating magnetically equivalent trifluoromethyl (CF_3) groups. The ^{31}P NMR spectrum showed a well-resolved septet at δ 3.1 with a J_{P-F} coupling constant of 130 Hz. The ^{13}C NMR spectrum appears as a doublet of quartets at δ 118.8 with coupling constants of $J_{C-P} = 150$ Hz and $J_{C-F} = 290$ Hz. In the mass spectrum (electron impact, EI), the parent ion was observed at *m/z* 549 (1% relative intensity). The base peak due to $M^+ - CF_3$ was observed at *m/z* 480. Compound **1** was found to have a vapor pressure of ~0.25 Torr at 22 °C.

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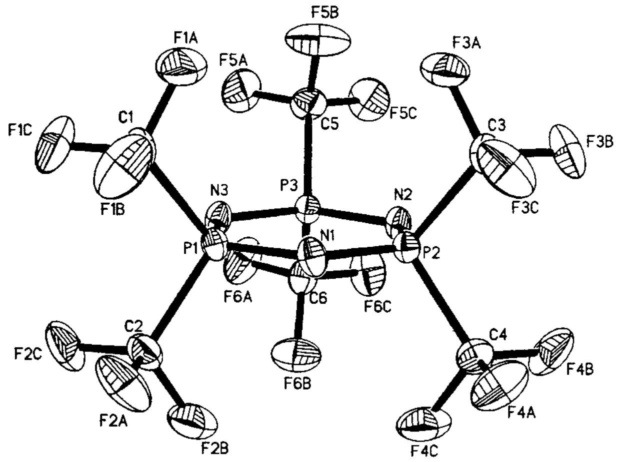

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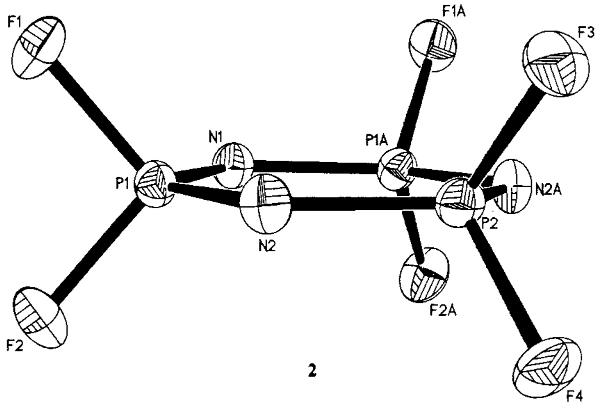

2

Figure 1. ORTEP drawings showing the molecular structures of **1** and **2**.

Table 1. Selected Bond Distances and Angles for **1**

Bond Distances (Å)			
P(1)−N(1)	1.578(4)	P(1)−C(2)	1.827(7)
P(2)−N(1)	1.583(5)	P(3)−N(2)	1.580(4)
P(3)−C(5)	1.859(6)	P(3)−C(6)	1.852(6)
Bond Angles (deg)			
N(1)−P(1)−N(3)	119.7(3)	P(1)−C(1)−F(1A)	109.2(5)
N(1)−P(1)−C(1)	107.9(3)	F(1A)−C(1)−F(1B)	108.6(5)
C(1)−P(1)−C(2)	103.1(3)	P(1)−C(2)−F(2C)	113.9(5)
N(1)−P(2)−C(4)	108.3(3)	F(2A)−C(2)−F(2B)	105.6(5)
P(1)−C(1)−F(1A)	109.2(5)	P(2)−C(3)−F(3B)	111.9(5)
N(2)−P(3)−N(3)	120.0(2)	P(3)−C(5)−F(5B)	109.6(4)
C(5)−P(3)−C(6)	102.3(3)	F(6A)−C(6)−F(6B)	107.6(5)

Table 2. Selected Bond Distances and Angles for **2**

Bond Distances (Å)			
P(1)−N(1)	1.576(8)	P(1)−F(1)	1.526(6)
P(1)−N(2)	1.564(3)	P(2)−F(3)	1.522(2)
P(2)−N(2)	1.568(2)	P(2)−F(4)	1.532(3)
Bond Angles (deg)			
F(1)−P(1)−F(2)	99.11(10)	F(1)−P(1)−N(1)	108.88(14)
F(1)−P(1)−N(2)	109.56(11)	F(2)−P(1)−N(1)	108.99(14)
F(2)−P(1)−N(2)	109.39(13)	N(1)−P(1)−N(2)	119.06(14)
F(3)−P(2)−F(4)	97.71(15)	F(3)−P(2)−N(2)	109.91(11)
F(4)−P(2)−N(2)	109.16(11)	P(1)−N(2)−P(2)	121.21(15)

The structures of heterocyclic rings bearing nitrogen and phosphorus continue to be of great interest.[5] Although the structure of **2** was first determined[6] almost four decades ago, the refinement was grossly inaccurate, with *R* values of ~32%. To date, no attempts have been made to obtain a better structure refinement. To compare the N_3P_3 cores in **1** and **2**, we obtained the X-ray crystal structures of both as shown in Figure 1. (See Tables 1 and 2 for selected bond distances and angles.) In compound **2**, the N_3P_3 core is planar, as seen from the torsion angle value of 0.3(3)° for N1−P1−N2−P2. The atoms P2, N1, F3, and F4 occupy special positions, as they lie on a mirror plane. The P−F bond distance is ~1.524(2) Å, which is much shorter than the reported distances[6] of 1.680−1.861 Å. The N−P−N and P−N−P angles of ~119 and ~121° also show that the ring is undistorted. A search of the Cambridge Structural Database[7] reveals that there is limited structural information for heterocyclic rings containing a P−CF_3 moiety. Among these are hybrid phosphorus, nitrogen, and sulfur/vanadium heterocycles.[8] Substitution of fluorine atoms in **2** by the CF_3 groups to form **1** does not cause any appreciable change in the N_3P_3 core structure. The six CF_3 groups lie above and below the plane of this core (Figure 1). The P−N bond distances in **1** are almost identical to those in **2**, at ~1.580 Å. The N−P−N bond angles of 119.9(2)° (average) are, however, much closer to ideal hexagonal values. The corresponding values for the vanadium metallaphospahzene[8b] are ~118 and 123.1° in the sulfur-containing triazene and tetrazene.[8a,c]

In conclusion, we have developed a new and efficient synthetic procedure to prepare hexakis(trifluoromethyl)cyclotriphosphazene in excellent isolated yield. In general, this method has opened a new facile route to perfluoroalkyl-substituted phosphazenes.

Experimental Section

General Information. Reactions were carried out under a dry nitrogen atmosphere by using standard Schlenk techniques. THF was dried by refluxing over sodium metal and was distilled before use. Trimethyl(trifluoromethyl)silane was prepared by the literature procedure.[9] Cesium fluoride was purchased from Aldrich, was finely powdered, and was used directly from the oven where it was stored at 200 °C. Hexafluorocyclotriphosphazene was prepared by the reaction of hexachlorocyclotriphosphazene with sodium fluoride in acetonitrile as reported in the literature.[4]

^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded in $CDCl_3$ on a spectrometer operating at 200, 50, 188, and 81 MHz, respectively. Chemical shifts are reported in ppm relative to the standards: $CFCl_3$ for ^{19}F; tetramethylsilane for ^1H and ^{13}C; H_3PO_4 for ^{31}P. IR spectra were obtained in a gas cell with KBr windows on a Bio-Rad FTS 3000 spectrometer. Mass spectra were taken by electron impact (70 eV) on a Fininigan GCQ spectrometer.

Preparation of Hexakis(trifluoromethyl)cyclotriphosphazene (1). Hexafluorocyclotriphosphazene, **2** (20 mmol, 4.98 g), and trimethyl(trifluoromethyl)silane (140 mmol, 19.88 g) were dissolved in dry tetrahydrofuran (25 mL) in a two-necked 100 mL flask equipped with a condenser. Anhydrous cesium fluoride (0.5 mmol, 0.075 g) was added directly to the stirred mixture. The resultant reaction mixture was heated to 70 °C under dry nitrogen with stirring for 24 h. Product **1** began precipitating at the end of the reaction. THF was carefully decanted at

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low temperature, and dry chloroform (25 mL) was added. The flask was warmed to room temperature with agitation. (*Caution*! Releasing the stopper for any appreciable time at room temperature will result in loss of product due to the volatility of **1**.) The mixture was again cooled to −50 °C to precipitate the solublized product. Chloroform and residual THF were decanted. This process was repeated once more with an additional 25 mL of chloroform. Purification was finalized by a brief trap-to-trap distillation at − 45 °C. Yield: 9.88 g (90%) of sublimable solid. Mp: 64 °C, sealed capillary tube (lit. 64 °C, sealed capillary tube). IR (KBr, gas phase):[2] ν 1299 s, 1212 vs, 1164 m, 1139 s, 771 cm^{-1}. ^{31}P NMR (CDCl$_3$): δ 3.12, septet ($J_{\mathrm{P-F}} = 130$ Hz). ^{19}F NMR (CDCl$_3$): δ −73.65, doublet ($J_{\mathrm{P-F}} = 130$ Hz). ^{13}C NMR (CDCl$_3$): δ 118.89, doublet of quartets ($J_{\mathrm{C-P}} = 150$ Hz, $J_{\mathrm{C-F}} = 290$ Hz). MS (EI), *m*/*z* (%): 549 (1) [M$^+$], 480 (100) [M$^+$ − CF$_3$], 69 (20) [CF$_3^+$]. Anal. Calcd for $C_6F_{18}N_3P_3$: C, 13.13; N, 7.65; P, 16.93. Found: C, 12.92; N, 7.35; P, 16.77.

X-ray Measurements. Compounds **1** and **2** sublime readily and, therefore, posed a problem during the mounting process. A stream of cold nitrogen gas (∼−50 °C) was directed onto the mounting microscope, and the crystals were covered with mineral oil. A crystal was then mounted on the glass fiber and transported to the goniometer assembly under cold conditions. X-ray diffraction data for **1** were collected on a Siemens SMART three-circle diffractometer by using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) and a CCD detector maintained near −54 °C.[10,11] (See Table 3 for selected X-ray crystallographic data and experimental details.)

Table 3. X-ray Crystallographic Data for **1** and **2**

empirical formula	$C_6F_{18}N_3P_3$	$F_6N_3P_3$
fw	548.98	248.93
crystal system	triclinic	orthorhombic
temp, K	193	293
crystal dimens, mm	0.10 × 0.20 × 0.50	0.10 × 0.20 × 0.55
space group	$P\bar{1}$	*Pnma*
a, Å	8.85891(8)	6.9057(2)
b, Å	8.9195(8)	12.1727(1)
c, Å	12.5198(11)	8.6512(12)
α, deg	86.851(1)	90
β, deg	75.513(1)	90
γ, deg	68.927(2)	90
V, Å^3	865.9(14)	727.23(3)
Z	2	4
ρ_{calcd}, g cm^{-3}	2.106	2.774
F(000)	528	480
R[a]	0.6320	0.0300
R_w[b]	0.1727	0770

[a] $R = \sum||F_o| - |F_o||/\sum|F_o|$. [b] $R_w = [\sum w\delta^2/\sum wF_o^2]^{1/2}$.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-9720635), the Petroleum Research Fund, administered by the American Chemical Society, and the Idaho Space Grant Consortium. We are grateful to the Otsuka Chemical Co., Ltd., for a gift of $P_3N_3Cl_6$.

Supporting Information Available: X-ray crystallographic files, in CIF format, for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Software used: *SMART V 5.0 Software for the CCD Detector System*; Bruker AXS: Madison, WI, 1997. *SAINT V 4.035 Software for the CCD Detector System*; Bruker AXS: Madison, WI, 1997. *SADABS; Siemens Area Detector Absorption Correction Program*; Bruker AXS: Madison, WI, 1997. *SHELXTL 5.10, Program Library for Structure Solution and Molecular Graphics*; Bruker AXS: Madison, WI, 1997.

(11) The frame data were acquired with the SMART software, and the cell constants were determined from 60 frames of 10 s each. A complete hemisphere of data was scanned on ω (0.3°) with a run time of 10 s/frame at 193 K and with a detector resolution of 512 × 512 pixels. A total of 1271 frames were collected in three sets, and a final set of 50 frames, identical to the first 50 frames, were also collected to determine crystal decay. The frames were then processed on an SGI-Indy/Indigo2 workstation by using the SAINT software to give the *hkl* file corrected for Lp/decay. The data were corrected for absorption using the SADABS program. The structures were solved by direct methods and refined by least-squares procedures on F^2 using SHELXTL 5.10. For **2**, the ambiguity between the acentric $Pna2_1$ and the centrosymmetric *Pnma* space group was resolved by considering the intensity statistics.