Polyfluoroalkoxy and Aryloxy Cyclic Phosphazenes: An Alternative Synthetic Route to Substitution Reactions Using Siloxanes in the Presence of Fluoride Ion Catalysts

Anil J. Elias, Robert L. Kirchmeier, and Jean'ne M. Shreeve*

Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343

Received January 21, 1994®

The first detailed investigations on the reactions of polyfluoromono- and dialkoxysilanes with cyclic fluorophosphazenes are carried out and compared with reactions of the nonfluorinated analogues. The method offers an easy and elegant route to the hitherto poorly studied bridged and dangling phosphazene compounds. For the first time a transformation of bridged phosphazene compounds to spiro compounds is observed and monitored by ^{19}F NMR studies. An explanation is offered for the poor yields and inability to isolate bridged derivatives experienced by previous workers. The method offers a convenient way of using $CF_3CH_2OSiMe_3$, which is a byproduct of many polymerization reactions, as a reagent in substitution reactions on fluorophosphazene monomers and polymers with possible extension to chlorophosphazenes as well in the presence of a fluorinating agent. The present study contributes to the explanation of the mechanistic aspects of the possible modes of formation of the various products isolable from reactions of cyclophosphazenes with difunctional reagents. Reactions of $N_3P_3F_6$ with $[CF_2CH_2OSiMe_3]_2$, **1**, and $CF_2[CF_2CH_2OSiMe_3]_2$, **2**, in the presence of CsF as catalyst are found to proceed readily under mild conditions to yield the monospiro and the bridged fluorophosphazene derivatives $(CF_2CH_2O)_2N_3P_3F_4$, **3**, $CF_2(CF_2CH_2O)_2N_3P_3F_4$ **5**, $F_5N_3P_3OCH_2(CF_2)_2CH_2ON_3P_3F_5$ **4**, and $F_5N_3P_3OCH_2(CF_2)_3CH_2ON_3P_3F_5$, **6**, in good yields. Subsequent reactions of the bridged derivative **4** with $4\text{-}FC_6H_4OSiMe_3$, $3\text{-}FC_6H_4OSiMe_3$, $CF_3CH_2OSiMe_3$, and **1** give the additional substitution products $(4\text{-}FC_6H_4O)_5P_3N_3OCH_2CF_2CF_2CH_2ON_3P_3(4\text{-}FC_6H_4O)_5$, **7**, $(3\text{-}FC_6H_4O)_5P_3N_3OCH_2CF_2CF_2CH_2ON_3P_3(3\text{-}FC_6H_4O)_5$, **8**, and $(CF_3CH_2O)_5P_3N_3OCH_2CF_2CF_2CH_2ON_3P_3(CF_3CH_2O)_5$, **9**, and an incompletely characterized dispiro bridged moiety with the facile elimination of Me_3SiF. The reaction of $Me_3SiO(CH_2)_3OSiMe_3$ with $N_3P_3F_6$ in the presence of CsF gives the monospiro, dangling **11** and the bridged **12** derivatives in varying yields depending upon the reaction parameters. Reactions of $N_3P_3F_6$ with excess $CF_3CH_2OSiMe_3$ in the presence of catalytic amounts of CsF or $N_3P_3Cl_6$ with excess KF and $CF_3CH_2OSiMe_3$ in the absence of solvent proceed at 80 °C to yield $[CF_3CH_2O]_6N_3P_3$ and Me_3SiF. The X-ray crystal structures of spiro $[CF_2CH_2O]_2N_3P_3F_4$, **3**, and the bridged $(4\text{-}FC_6H_4O)_5P_3N_3OCH_2CF_2CF_2CH_2ON_3P_3(4\text{-}FC_6H_4O)_5$, **7**, phosphazenes are determined. Compound **3** crystallizes in the monoclinic system, space group $P2_1/c$, with a = 14.695(5) Å, b = 8.532(2) Å, c = 9.600(3) Å, β = 102.38(2)°, V = 1175.6(6) Å^3, D_{calc} 2.096 mg/m^3, Z = 4, and R = 0.0656. Compound **7** crystallizes in the monoclinic system, space group $P2_1/n$, with a = 7.738(2) Å, b = 46.849(9) Å, c = 9.516(2) Å, β = 108.65(3)°, V = 3262.8(13) Å^3, D_{calc} = 1.568 mg/m^3, Z = 2, and R = 0.740. The bridged phosphazene derivatives **4** and **6** are found to undergo a facile transformation to the spiro phosphazenes **3** and **5**, respectively, on heating at 82 °C in the presence of CsF in THF which is monitored by variable-temperature/-time ^{19}F NMR.

Introduction

A major contribution to the burgeoning interest in inorganic macromolecules in recent years is attributable to developments in the synthesis of phosphazene polymers and their versatile applications.[1] Among these polymers, those that contain polyfluoroalkoxy, especially CF_3CH_2O, and aryloxy groups dominate, primarily because of their high thermal and hydrolytic stability and inertness in biological applications. In addition, recent studies indicate that polyfluoroalkoxy- and aryloxy-substituted phosphazene monomers are potential candidates for use as high-temperature lubricants in aircraft gas turbine engines, as additives to lubricants in various specialty applications, and as fire resistant fluids.[2] Unlike the nonfluorinated materials, these compounds do not undergo alkoxyphosphazene–oxophosphazane rearrangement reactions at high temperatures that lead to P=O bond formation.

The chemistry of siloxanes and their polymers developed considerably faster into a much wider and more versatile arena. This is attributable mainly to properties, such as the inherent flexibility of the siloxane chain, coupled with the hydrophobicity and thermooxidative stability associated with the Si–O bond, and with the alkyl and aryl substituents linked to silicon.[3] Attempts to bridge the chemistry of phosphazenes and siloxanes are the focal point of research of various leading phosphazene research groups and are being carried out successfully by Allcock,[4] Wisian-Neilson,[5] and Federov[6] on both cyclic- and polyphosphazenes. Although polyfluoroalkoxysilanes are reported to react with pentacoordinated fluorophosphoranes,[7] the potential use of such siloxanes as reagents in substitution reactions on cyclic and polyphosphazenes is not determined. In fact, a variety of synthetic routes leading to polyphosphazenes and poly(alkyl/aryloxothia-

* Abstract published in *Advance ACS Abstracts*, May 15, 1994.

(1) (a) Mark, J. E.; Allcock, H. R.; West, R. C. *Inorganic Polymers*; Prentice Hall: Englewood Cliffs, NJ, 1992; p 61. (b) Zeldin, M.; Wynne, K. J.; Allcock, H. R. *ACS Symp. Ser.* **1988**, *No. 360*.

(2) (a) Nader, B. S.; Kar, K. K.; Morgan, T. A.; Pawloski, C. E.; Dilling, W. L. *Tribol. Trans.* **1992**, *35*, 37. (b) Novikova, I. A.; Apryatkin, A. D.; Taranova, N. V.; Nikonorov, E. M.; Federov, S. G. *Khim. Technol. Topliv. Masel.* **1991**, *10*, 22. (c) Singer, R. E.; Deome, A. J.; Dunn, D. A.; Bierbach, M. J. *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, *25*, 46.

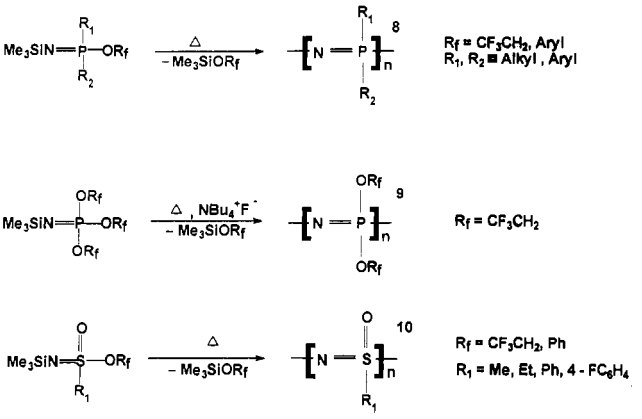
(3) Silicon-Based Polymer Science, A Comprehensive Resource. Zeigler, J. M., Fearon, F. W. G., Eds.; *Advances in Chemistry Series*; American Chemical Society: Washington, DC, 1990; Vol. 224.

(4) (a) Allcock, H. R.; Coggio, W. D.; Masood, P.; Turner, M. L. *Organometallics* **1991**, *10*, 677. (b) Allcock, H. R.; Nelson, C. J.; Coggio, W. D. *Organometallics* **1991**, *10*, 3819. (c) Allcock, H. R.; Coggio, W. D. *Macromolecules* **1990**, *23*, 1626. (d) Allcock, H. R.; Coggio, W. D.; Archibald, R. S.; Brennan, D. J. *Macromolecules* **1989**, *22*, 3571. (e) Allcock, H. R.; Brennan, D. J.; Dunn, B. S. *Macromolecules* **1989**, *22*, 1534. (f) Allcock, H. R.; Brennan, D. J. *J. Organomet. Chem.* **1988**, *341*, 231 and references therein.

(5) (a) Wisian-Neilson, P.; Islam, M. S. *Macromolecules* **1989**, *22*, 2026. (b) Wisian-Neilson, P.; Schaefer, M. A.; Islam, M. S. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1989**, *30*, 183. (c) Wisian-Neilson, P.; Ford, R. R.; Neilson, R. H.; Roy, A. K. *Macromolecules* **1986**, *19*, 2089.

0020-1669/94/1333-2727$04.50/0

Scheme 1



zenes) involves the facile elimination of polyfluoroalkyl- and arylsiloxanes as stable side products. (Scheme 1).[8-10]

Our interest in cyclic fluorophosphazene chemistry stems in part from our recent success in the reactions of perfluoroaromatic compounds with cyclic and acyclic polyfluoroalkoxy- and aryloxysiloxanes. These reactions show the formation of stable C–O bonds in the presence of fluoride ion as catalyst with concomitant facile elimination of silyl fluorides.[11,12] In this paper, we discuss the synthetic potential of the reactions of mono- and bifunctional polyfluoroalkoxysilanes and polyfluoroaryloxysilanes with cyclic fluorophosphazenes to obtain polyfluoroalkoxy and aryloxy derivatives of phosphazenes. The bridged derivatives are described as model compounds for condensation polymerization studies involving phosphazenes.[13] The transformation of bridged cyclic phosphazenes to spiro phosphazenes is documented for the first time and is followed by ^{19}F NMR studies. A dangling species is isolated, and its role as an intermediate in the formation of the bridging and spiro compounds is suggested.

Results and Discussion

Among nucleophilic substitution reactions on cyclic halophosphazenes, those involving bi- and polyfunctional reagents are the focus of greatest interest in recent years. A major section of these studies involves reactions of the cyclic hexachlorophosphazene with polyfunctional alcohols[13-18] and amines.[19] Recently the reactions of silylated nitrogen compounds and some organometallic species are reported.[20] Although four different types of products are possible in these reactions, most result primarily in the formation of spirocyclic compounds. Recently stepwise preparation and structural characterization of a set of ansa derivatives by Allcock[21] helped to elucidate the spiro vs ansa dilemma by providing an easy synthetic approach to the latter compounds. However, the synthesis and chemistry of bridged and dangling substituted phosphazenes are still little studied and insufficiently understood as exemplified by the recent conflicting reports on the formation of bridged species.[22,23]

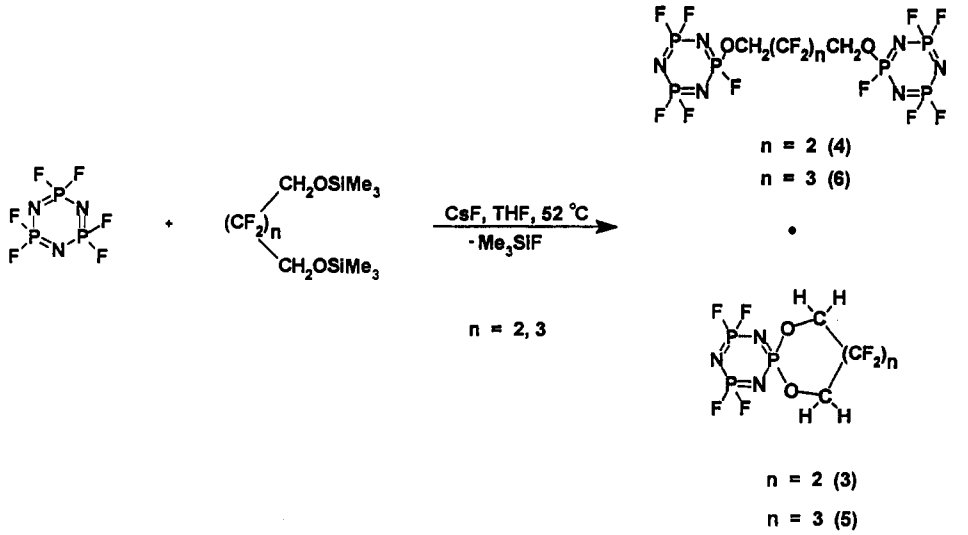
In contrast to the well-known strategy of activating the hydroxy group by metalation prior to reaction with P–Cl bonds in phosphazenes, our approach involves a hitherto untried method of silylation of the attacking species to form a stable siloxy bond followed by reaction with P–F bonds of fluorophosphazenes. A catalyst, preferably fluoride ion, is used to induce the reaction. The reaction is driven by the formation of a very strong Si–F bond with the concomitant elimination of a highly volatile silyl fluoride. The method helps to explain the mechanistic processes involved in these reactions. Also, the effect of reaction parameters on the nature and yield of possible products is better understood. The reactions of fluorinated phosphazenes and bifunctional polyfluoroalkoxy systems can be easily followed, and products can be readily identified by ^{19}F NMR. In contrast to the surfeit of CF_3CH_2O-substituted phosphazenes known in the literature, only a few reports exist on bifunctional polyfluoroalkoxy derivatives of phosphazenes.[15b,24] Reactions of the polyfluoroalkoxysilanes $[CF_2CH_2OSiMe_3]_2$, **1**, and $CF_2[CF_2CH_2OSiMe_3]_2$, **2**, with 2.5 mmol of $N_3P_3F_6$ proceed under mild conditions to yield a mixture of bridged (**4** and **3**) and spiro (**6** and **5**) compounds, respectively, with concomitant elimination of Me_3SiF (Scheme 2). In the case of the nonfluorinated disiloxane, $Me_3SiO(CH_2)_3OSiMe_3$, the formation of the dangling species **11**, in addition to the spiro[16] and the bridged **12** compounds (Scheme 3), is observed.

The ratio and yields of the products are found to be sensitive to the reaction temperature, amount, and nature of catalyst used and the reaction time. Temperatures in the range 50–60 °C and lesser amounts of CsF favor formation of higher yields of the bridged species. A comparatively high yield of the bridged derivative is obtained when potassium *tert*-butoxide is used as the catalyst (ratio of bridged to spiro 93:7). However, an increased amount of the catalyst results in the formation of a mixture of both bridged and spiro products in almost equal yields. Surprisingly, after separation by sublimation, a changed distribution of the products is found with a larger quantity of the spiro and less of the bridged species being isolated. This is in comparison with the product ratio obtained from the ^{19}F NMR spectra of the reaction mixture, which suggests that the bridged species decomposes to form the spiro material during the procedure.

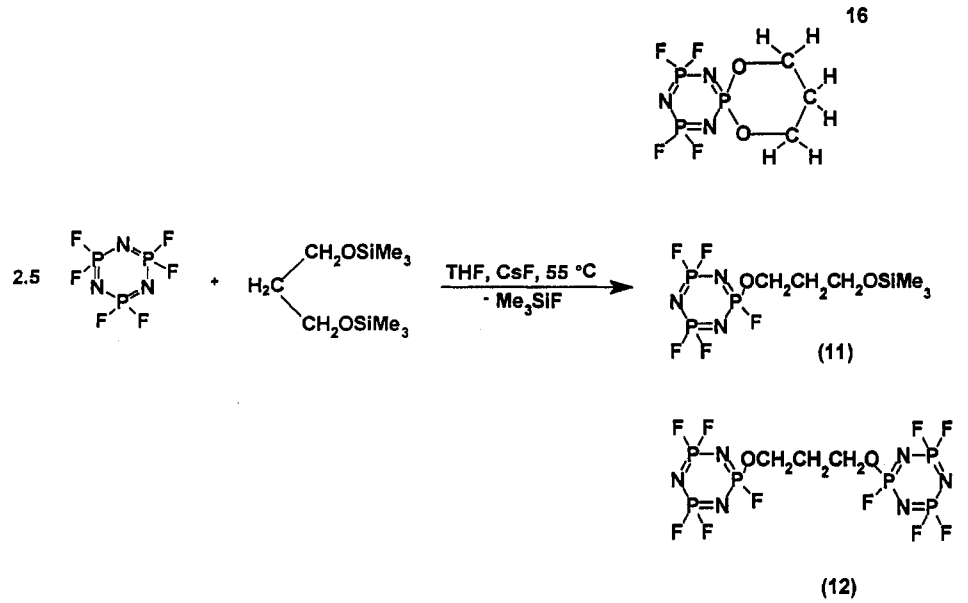
The synthetic method consistently favors the formation of the bridged species which are described as model systems for

(6) (a) Federov, S. G.; Gol'din, G. S.; Nikitina, G. S.; Rusakov, V. A. *Zh. Prikl. Khim. (Leningrad)* **1985**, *58*, 1357. (b) Federov, S. G.; Gol'din, G. S.; Nikitina, G. S. *Nov. Napravleniya Khim. Kremniorg. Soedin.* **1981**, 53. (c) Federov, S. G.; Gol'din, G. S.; Nikitina, G. S.; Kisin, A. V.; Nosova, V. M. *Vysokomol. Soedin., Ser. A* **1980**, *22*, 2070. (d) Federov, S. G.; Gol'din, G. S.; Nikitina, G. S. *Vysokomol. Soedin., Ser. A* **1976**, *18*, 376.
(7) (a) Poulin, D. D.; Demay, C.; Riess, J. G. *Inorg. Chem.* **1977**, *16*, 2278. (b) Jeanneaux, F.; Riess, J. G. *Tetrahedron Lett.* **1978**, *48*, 4845. (c) Peake, S. C.; Schmutzler, R. *Chem. Commun.* **1968**, 665. (d) Riess, J. G.; Robert, D. V. *Bull. Soc. Chim. Fr.* **1975**, 425.
(8) (a) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Synth.* **1989**, *25*, 69. (b) Neilson, R. H.; Hani, R.; Scheide, G. M.; Wettermark, U. G.; Wisian-Neilson, P.; Ford, R. R.; Roy, A. K. *ACS Symp. Ser.* **1988**, *360*, 283. (c) Roy, A. K.; Hani, R.; Neilson, R. H.; Wisian-Neilson, P. *Organometallics* **1987**, *6*, 378. (d) Wisian-Neilson, P.; Roy, A. K.; Xie, Z. M.; Neilson, R. H. *ACS Symp. Ser.* **1983**, 232. (e) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541 and references therein.
(9) Montague, R. A.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1990**, *112*, 6721.
(10) Roy, A. K.; Burns, G. T.; Lie, G. C.; Grigoras, S. *J. Am. Chem. Soc.* **1993**, *115*, 2604.
(11) Zhang, Y. F.; Kirchmeier, R. L.; Shreeve, J. M. *J. Fluorine Chem.*, in press.
(12) Elias, A. J.; Kirchmeier, R. L.; Shreeve, J. M.; Hope, H. *Inorg. Chem.* **1994**, *33*, 415.
(13) Chandrasekhar, V.; Muralidhara, M. G. R.; Selvaraj, I. I. *Heterocycles* **1990**, *31*, 2231.
(14) Schmutzler, R. *Inorg. Synth.* **1967**, *9*, 75.
(15) (a) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709. (b) Rätz, R.; Schroeder, H.; Ulrich, H.; Kober, E.; Grundmann, C. *J. Am. Chem. Soc.* **1962**, *84*, 551.
(16) Kumaraswamy, K. C.; Krishnamurthy, S. S. *Ind. J. Chem.* **1984**, *23A*, 717.
(17) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(18) (a) Shaw, R. A. *Phosphorus Sulfur* **1986**, *28*, 203. (b) Shaw, R. A. *Pure Appl. Chem.* **1980**, *52*, 1063.
(19) Labarre, J. F. *Top. Curr. Chem.* **1985**, *129*, 173.
(20) (a) Gieren, A.; Dederer, B.; Roesky, H. W.; Janssen, E. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 783. (b) Pittman, C. U.; Sheats, J.; Carraher, C. E.; Zeldin, M.; Currel, B. *Prepr., ACS Div. Polym. Mater. Sci. Engin.* **1989**, *61*, 91.
(21) Allcock, H. R.; Turner, M. L.; Visscher, K. B. *Inorg. Chem.* **1992**, *31*, 4354.
(22) Perly, B.; Berthault, P.; Bonnet, J. P.; Labarre, J. F. *J. Mol. Struct.* **1988**, *176*, 285.
(23) Chandrasekhar, V.; Muralidhara, M. G. R.; Reddy, N. S. *Heterocycles* **1992**, *33*, 111.
(24) (a) Sharov, V. N.; Prons, V. N.; Korolko, V. V.; Klebanskii, A. L.; Kondratenkov, G. P. *Zh. Obsch. Khim.* **1975**, *45*, 1953. (b) Koralko, V. V.; Sharov, V. N.; Sokolov, E. I.; Klebanskii, A. L. *Vysokomol Soedin., Ser. B* **1975**, *17*, 64. (c) Allcock, H. R.; Moore, G. Y. *Macromolecules* **1972**, *5*, 231. (d) Allcock, H. R. *US Patent* 3732175, **1973**.

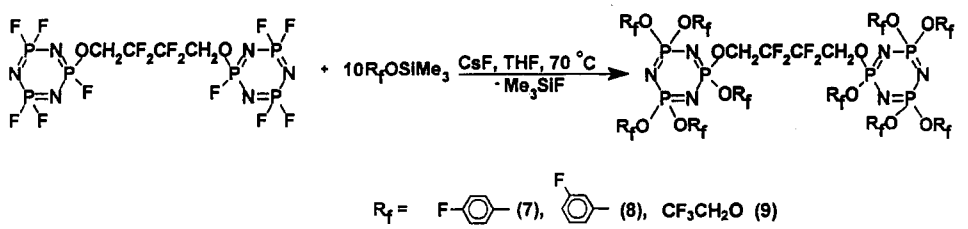
Scheme 2



Scheme 3



Scheme 4

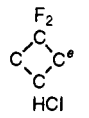


condensation polymerization studies of phosphazenes. The reaction of **4** with 4-$FC_6H_4OSiMe_3$ and 3-$FC_6H_4OSiMe_3$ readily yields the fully substituted derivatives (Scheme 4). However, the reaction of $CF_3CH_2OSiMe_3$ with **4** at 82 °C in the presence of excess CsF gives a spirocyclic compound, $(CF_2CH_2O)_2N_3P_3(OCH_2CF_3)_4$, in addition to the fully substituted bridged species **9**. On reduction of the reaction temperature to 54 °C and by use of potassium *tert*-butoxide as catalyst, the bridged product **9** is obtained exclusively.

Of more interest is the reaction of excess $CF_3CH_2OSiMe_3$ with $N_3P_3F_6$ which, in the presence of CsF and the siloxane as the solvent media, yields the fully substituted derivative $(CF_3CH_2O)_6N_3P_3$ almost quantitatively. This reaction, however, does not occur in the absence of the catalyst. Reaction of $N_3P_3Cl_6$ with $CF_3CH_2OSiMe_3$ does not take place even after 48 h at 80 °C. On adding of excess KF, the fully substituted derivative is formed. The analysis of the reaction mixture via ^{19}F NMR spectra during the course of the reaction shows the presence of a P–F species (^{19}F, δ 69 ppm) with concomitant formation of Me_3SiF. This indicates that the reaction proceeds through the initial fluorination of the P–Cl bonds followed by fluoride ion-induced reaction with the siloxane. Interestingly, no reaction is observed between hexamethyldisiloxane and $N_3P_3F_6$ under similar reaction conditions.

In contrast to ^{31}P and ^1H NMR spectral data, ^{19}F NMR spectral data are exceedingly useful for identification and characterization of the bridged and spiro polyfluorodialkoxy compounds. For the bridged as well as the dangling species, the P–F regions in the

Table 1. ^{19}F NMR Data for CF_2 Groups in the Seven- and Eight-Membered Cyclic and Acyclic Derivatives of $HOCH_2(CF_2)_nCH_2OH$ (n = 2, 3)

X	Y	$YOCH_2(CF_2)_2CH_2OY$	$YOCH_2(CF_2)_3CH_2OY$	$OCH_2(CF_2)_2CH_2OX$	$OCH_2(CF_2)_3CH_2OX$
PCl[a]	PCl_2	−120.76			−126.02
P(O)Cl	$P(O)Cl_2$	−122.30			−125.70
$CF_3N{=}S$[b]					−128.6, −129.0
CH_2[c]					−127.90–115.40 (4F)
					−128.80 (2F)
$SiMe_2$[d]	$SiMe_3$	−123.90	−122.10, −126.21	−127.99	−117.75 (4F)
					−123.90 (2F)
				−126.91 (A, AB m)	−116.65 (4F)
				−131.21 (B, AB m)	−126.60 (2F)
$F_4N_3P_3$[f]	$F_5N_3P_3$	−121.59	−120.76, −125.36	−127.50	−116.84 (4F)
					−125.35 (2F)

[a] Reference 27a. [b] Reference 27b. [c] Reference 30. [d] Reference 12. [e] Reference 31. [f] This work.

Table 2. X-ray Crystallography Parameters for **3** and **7**

param	**3**	**7**
formula	$C_4H_4F_8N_3O_2P_3$	$C_{64}H_{44}F_{14}N_6O_{12}P_6$
fw	371.0	1540.9
space group	$P2_1/c$	$P2_1/n$
cryst system	monoclinic	monoclinic
a, Å	14.695(5)	7.738(2)
b, Å	8.532(2)	46.849(9)
c, Å	9.600(3)	9.516(2)
β, deg	102.38(2)	108.95(3)
V, Å^3	1175.6(6)	3262.8(13)
d_c, mg m^{-3}	2.096	1.568
Z	4	2
F(000)	728	1564
cryst size, mm	0.09 × 0.12 × 0.64	0.3 × 0.2 × 0.4
abs coeff, mm^{-1}	5.823	0.273
2θ range, deg	0.0–108.5	3.0–113.5
scan type	2θ–θ	ω
scan range ω, deg	1.80 + Kα separation	1.10
scan speed/min in ω	constant 30.00°	variable 3.00–60.00°
index ranges	$-15 \le h \le 15, 0 \le k \le 8, 0 \le l \le 10$	$-1 \le h \le 8, -1 \le k \le 49, -10 \le l \le 10$
no. of measd reflns	1439	5658
no. of unique reflns (R_{int}, %)	1439 (undet)	4270 (3.73)
no. of obsd reflns	1295, $I > 6.0\sigma(I)$	2497, $I > 3.0\sigma(I)$
no. of params refined	181	461
weighting scheme, ω^{-1}	$\sigma^2(F) + 0.0134F^2$	$\sigma^2(F) + 0.0010F^2$
R	0.0656	0.0740
R_w	0.0899	0.0774
goodness of fit	0.80	1.35
largest diff peak, hole, e Å^{-3}	0.97, −0.61	0.43, −0.39

^{19}F NMR are almost identical with two sets of doublets of multiplets observed in the ratio 1:4 ($^1J_{P-F}$ = 870–970 Hz). The fluorine atoms bound to the phosphorus atom involved in bridge formation are deshielded by δ 4.80 ± 0.03 ppm for **4** and **6** and δ 3.65 ± 0.1 ppm for **11** and **12**. The spiro compounds show a single set of doublets of multiplets for the PF_2 group, similar to $N_3P_3F_6$. Although the ^1H NMR spectral data for **12** are consistent with the chloro analogue reported earlier, chemical shifts of the CH_2 groups attached to the siloxy moiety on the dangling derivative **11** differ slightly from the analogous chlorinated compound.[25] As was observed by previous workers for fluorophosphazene derivatives, the ^{31}P NMR spectra for the compounds are complex due to second-order effects.[16,26] However, on decoupling the fluorine atoms, the complexity of the spectra is considerably reduced and similar splitting patterns are observed for the bridging and the dangling species which are clearly distinguishable from the spiro species. In these decoupled spectra the phosphorus chemical shifts for PF_2 appear in the range δ 9.10–9.99 ppm, while PF(OR) shifts are observed at δ 13.37–14.16 ppm. The chemical shifts of the phosphorus atoms attached to the spiro moiety appear at δ 19.07 and 17.90 ppm for compounds **3** and **5**, respectively, which are clearly in the range reported for various spirocyclic phosphazenes.[13] The $^2J_{P-P}$ values vary over the range from 126 to 140 Hz.

Interestingly, the ^{19}F chemical shifts of the CF_2 groups bonded to CH_2 groups of the fluoroalkoxy moieties are found to be distinctly unique in the case of the seven-membered and eight-membered spirocyclic compounds. Although no noticeable difference is observed for the siloxanes **1** and **2** and the bridged species **4** and **6**, the CF_3 groups of **3** are slightly more shielded (δ −127.50 ppm), while the corresponding CF_2 groups of **5** are deshielded (δ −117.84 ppm). This observation is consistent with ^{19}F chemical shifts of similar cyclic species prepared in our laboratory[27] (Table 1) and is a useful tool for the identification and estimation of relative amounts of bridged and spiro compounds in reaction mixtures.

The yields of bridged and spiro compounds vary under different reaction conditions, e.g., more of the bridged species is formed under mild reaction conditions, and a spiro derivative results in the attempted substitution on **4** with $CF_3CH_2OSiMe_3$ at 80 °C in the presence of CsF. Study of the thermal behavior of the bridged species **4** and **6** in the presence of a nucleophile is of interest. Cesium fluoride in THF is used to mimick the reaction

(25) Alkubaisi, A. H.; Parkes, H. G.; Shaw, R. A. *Heterocycles* **1989**, *28*, 347.
(26) Chivers, T.; Hedgeland, R. *Can. J. Chem.* **1972**, *50*, 1017.
(27) (a) Mahmood, T.; Shreeve, J. M. *Inorg. Chem.* **1986**, *25*, 4081. (b) Marsden, H. M.; Shreeve, J. M. *Inorg. Chem.* **1986**, *25*, 4021.

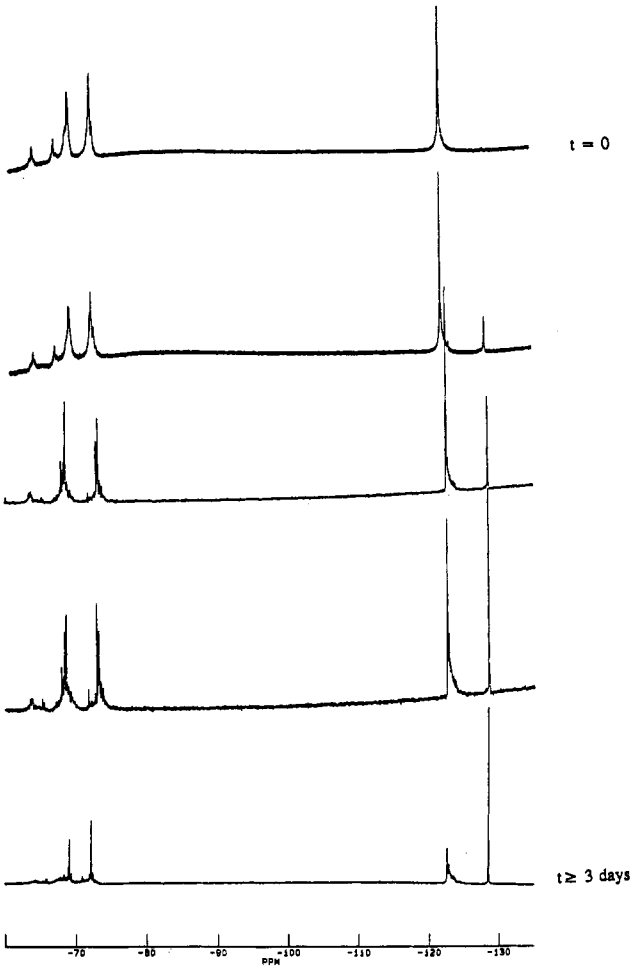


Figure 1. ^{19}F variable-time/-temperature NMR spectra of the transformation of the bridged $F_5N_3P_3OCH_2(CF_2)_2CH_2OP_3N_3F_5$ (**4**) to spiro-$(CF_2CH_2O)_2N_3P_3F_4$ (**3**) at 82 °C.

conditions. Indeed, the difference in the chemical shifts of the CF_2 groups of the bridged compounds **4** and **6** and the corresponding spiro compounds **3** and **5** (Table 1) is useful in the study of the transformation of these compounds from bridged to spiro. On examination of the ^{19}F NMR spectrum of a mixture **4** and CsF in THF–C_6D_6 in the variable-time/temperature mode, no change is observed below 82 °C. When this temperature is maintained for about 5 h, a peak at δ −127.50 ppm which is typical of **3** appears and begins to grow in intensity with time (Figure 1). After 3 days the resonance peak corresponding to the CF_2 in the bridging group is greatly reduced. A similar observation is noted for **6** with a resonance band appearing at δ −117.85 ppm and increasing in intensity with time at 82 °C. Although a decrease in intensity is apparent for the peak corresponding to the bridged species, even after 5 days it is does not disappear fully. In both cases, additional new peaks are found to appear with time in the ^{19}F NMR. Noticeable among these are the peaks very close to δ −124 ppm and the complex doublet observed at δ −50 and −49 ppm for **4** and **6** (J = 870 Hz) which is attributable to a new P–F-bonded species formed during the transformation. Separate decomposition studies carried out on **4** and **6** indicate the formation of the corresponding spiro compounds whose identities are confirmed by spectral studies. A similar study on **12** in C_6D_6 shows that spirolization does not proceed even after 6 days. However, on addition of THF, transformation sets in slowly indicating the necessity of a polar solvent for these transformations.

Although about a dozen crystal structures of monospiro phosphazene compounds are available, none with PF_2 groups is known.[13] The structure of **3**[28] (Figure 2) resembles those of $Cl_4N_3P_3(OCH_2CH_2)_2$[29] and $Cl_4N_3P_3(NHCH_2CH_2)_2$.[19] The

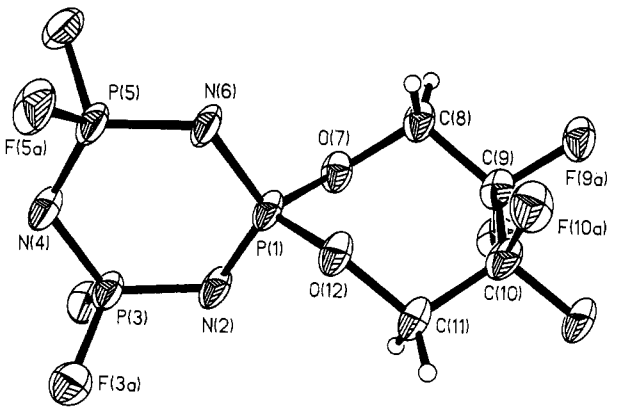


Figure 2. X-ray crystal structure of $(CF_2CH_2O)_2N_3P_3F_4$ (**3**).

Table 3. Selected Bond Distances (Å) and Angles (deg) of **3**

P(1)–N(2)	1.570(4)	P(1)–N(6)	1.581(4)
P(1)–O(7)	1.574(3)	P(1)–O(12)	1.582(3)
N(2)–P(3)	1.574(4)	P(3)–N(4)	1.572(4)
P(3)–F(3A)	1.521(3)	P(3)–F(3B)	1.517(3)
N(4)–P(5)	1.566(5)	P(5)–N(6)	1.565(4)
P(5)–F(5A)	1.534(3)	P(5)–F(5B)	1.518(3)
C(8)–C(9)	1.502(6)	C(9)–C(10)	1.522(7)
C(9)–F(9A)	1.370(6)	C(9)–F(9B)	1.367(5)
C(10)–C(11)	1.500(7)	C(10)–F(10A)	1.371(5)
C(10)–F(10B)	1.358(5)		

N(2)–P(1)–N(6)	118.2(2)	N(2)–P(1)–O(7)	105.4(2)
N(6)–P(1)–O(7)	112.1(2)	N(2)–P(1)–O(12)	111.6(2)
N(6)–P(1)–O(12)	104.5(2)	O(7)–P(1)–O(12)	104.3(2)
P(1)–N(2)–P(3)	121.3(2)	N(2)–P(3)–N(4)	119.1(2)
N(2)–P(3)–F(3A)	109.1(2)	N(4)–P(3)–F(3A)	108.4(2)
N(2)–P(3)–F(3B)	109.9(2)	N(4)–P(3)–F(3B)	109.1(2)
F(3A)–P(3)–F(3B)	99.4(2)	P(3)–N(4)–P(5)	120.1(3)
N(4)–P(5)–N(6)	119.9(2)	N(4)–P(5)–F(5A)	109.1(2)
N(6)–P(5)–F(5A)	108.3(2)	N(4)–P(5)–F(5B)	109.4(2)
N(6)–P(5)–F(5B)	109.7(2)	F(5A)–P(5)–F(5B)	98.3(2)
P(1)–N(6)–P(5)	121.0(3)	C(8)–C(9)–C(10)	117.3(4)
C(8)–C(9)–F(9A)	108.0(4)	C(10)–C(9)–F(9A)	107.3(3)
C(8)–C(9)–F(9B)	109.9(3)	C(10)–C(9)–F(9B)	107.7(4)
F(9A)–C(9)–F(9B)	106.1(3)	C(9)–C(10)–C(11)	116.6(4)
C(9)–C(10)–F(10A)	107.1(4)	C(11)–C(10)–F(10A)	109.7(4)
C(9)–C(10)–F(10B)	108.3(4)	C(11)–C(10)–F(10B)	108.0(4)
F(10A)–C(10)–F(10B)	106.6(3)		

fluorinated phosphazene ring is slightly distorted at the phosphorus atom attached to the perfluoroalkoxy group as indicated by the deviation from trigonal planarity observed at the N–P–N angle (116.5°) (Table 3). The P–N bond distances are slightly shorter than those reported for the nonfluorinated analogues. The fact that no structures are known for purely alkoxy bridged, fully substituted phosphazene compounds makes the crystal structure of **7** unique (Figures 3 and 4). The 4-fluoroaryloxy substituents are distributed on the phosphazene skeleton with maximum separation, and the *p*-fluorophenyl rings lie almost perpendicular

(28) A rather unusual observation is noted in the independent structural analyses of separate samples of **3**. In contrast to the simple structure of **3** at 120 K, structural analysis of the same compound but a different crystal at 25 °C gives a completely different result. The latter shows six crystallographically different but chemically identical structures in the unit cell (Z = 12). The crystals have a lower density and belong to the triclinic system ($P\bar{1}$). The crystal volume is 3677.9(12) Å^3 as compared with 1175.6(6) Å^3 for **3**. In both structures the molecules lie in layers with the phosphazene rings positioned roughly parallel to the plane of the layers. In the 120 K structure, these layers lie in the *ab* plane, while in the room temperature structure they lie in the *ac* plane. In contrast to the regular arrangement of N_3P_3 layers found in **3**, the 25 °C structure exhibits two crystallographically independent layers. The arrangement is very different from that found at 120 K. Details of these structural studies will be published elsewhere.

(29) Contractor, S. R.; Hursthouse, M. B.; Shaw, L. S.; Shaw, R. A.; Yilmaz, H. *Acta Crystallogr.* **1985**, *B41*, 122.
(30) Patel, N. R.; Kirchmeier, R. L.; Shreeve, J. M. Unpublished results.
(31) Guo, C. Y.; Elias, A. J.; Kirchmeier, R. L.; Shreeve, J. M. Manuscript in preparation.

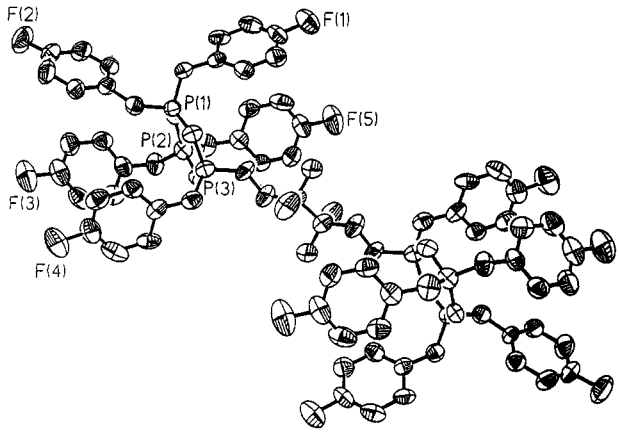


Figure 3. X-ray crystal structure of $(4\text{-}FC_6H_4O)_5P_3N_3OCH_2(CF_2)_2CH_2OP_3N_3(4\text{-}FC_6H_4O)_5$ (**7**).

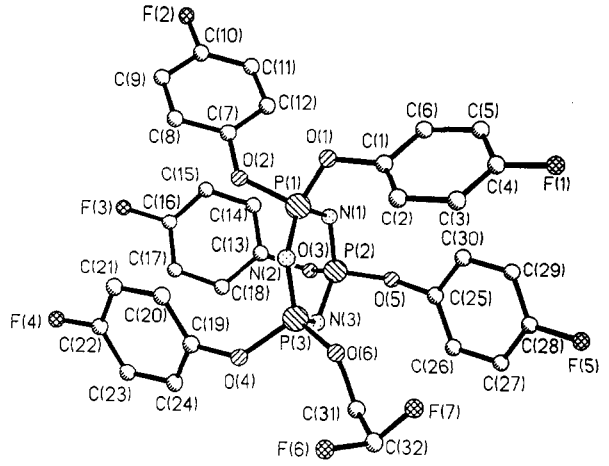


Figure 4. More detailed X-ray crystal structure of half of **7**.

Table 4. Selected Bond Distances (Å) and Angles (deg) of **7**

P(1)–O(1)	1.586(6)	C(4)–C(3)	1.369(12)
P(1)–N(2)	1.572(6)	C(2)–C(3)	1.382(13)
P(3)–O(4)	1.606(5)	O(6)–C(31)	1.403(13)
O(1)–C(1)	1.411(10)	C(1)–C(2)	1.348(13)
O(2)–C(7)	1.393(10)	F(1)–C(4)	1.368(12)
C(1)–C(6)	1.366(11)	C(6)–C(5)	1.379(14)
F(7)–C(32)	1.348(12)	C(4)–C(5)	1.345(16)
C(32)–C(31)	1.487(14)		
O(1)–P(1)–O(2)	98.3(3)	O(4)–P(3)–O(6)	98.9(3)
O(2)–P(1)–N(2)	106.0(3)	O(6)–P(3)–N(3)	111.6(4)
O(2)–P(1)–N(1)	113.3(3)	O(5)–P(2)–O(3)	94.3(4)
O(4)–P(3)–N(2)	111.2(4)	O(1)–C(1)–C(6)	117.1(8)
N(2)–P(3)–O(6)	105.8(4)	C(6)–C(1)–C(2)	122.5(8)
N(2)–P(3)–N(3)	118.9(4)	F(7)–C(32)–F(6)	105.1(9)
N(1)–P(2)–N(3)	115.5(4)	F(6)–C(32)–C(31)	109.0(8)
N(3)–P(2)–O(5)	110.3(4)	C(1)–C(6)–C(5)	117.9(9)
P(1)–O(1)–C(1)	121.9(6)	F(1)–C(4)–C(5)	118.5(8)
P(1)–O(2)–C(7)	128.7(5)	C(1)–C(2)–C(3)	120.1(8)
P(1)–N(1)–P(2)	123.6(4)	F(1)–C(4)–C(3)	117.9(9)
O(1)–C(1)–C(2)	120.3(7)	C(3)–C(4)–C(5)	123.6(10)
O(1)–P(1)–N(2)	110.8(4)	C(4)–C(3)–C(2)	116.8(9)
O(1)–P(1)–N(1)	110.1(3)	C(6)–C(5)–C(4)	119.2(8)

to the plane of the phosphazene rings. The P–N bond distances are comparable to those in the analogous monomers (Table 4). Noticeably different from the others is the P(1)–O(2)–C(7) angle (128.7(5)°) which is bent even more than the bridging P–O–C angle.

This study has shown that the initial formation of a dangling phosphazene species, followed by its conversion to spiro and the bridged species, can be envisaged (Scheme 5). The observations that the dangling species can be isolated only from the reaction of nonfluorinated disiloxanes with $N_3P_3F_6$ carried out in THF and that the yield of this species is diminished with respect to the other two with time favor this view. The reaction of **11** with CsF in the presence of acetonitrile at 80 °C also shows the formation of the spirocyclic compound $CH_2(CH_2O)_2N_3P_3F_4$. An additional route to the formation of spiro compounds is from the transformation of the bridged species. Although we can conclusively prove the formation of the spiro compounds from the bridged species, we have only a partial understanding of the nature of the other products resulting from such a transformation. Detailed investigations are under way to identify these species and provide a more complete mechanistic view of these transformations.

Experimental Section

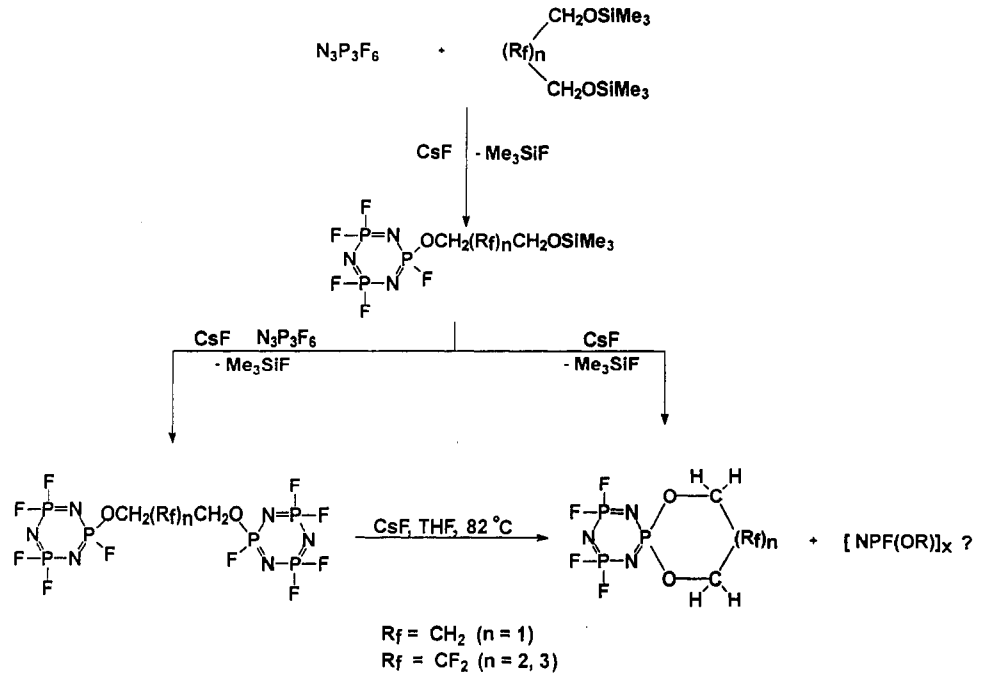
Materials. $[CF_2CH_2OH]_2$ (gift from 3M) and $CF_2[CF_2CH_2OH]_2$ (PCR) are purified by sublimation prior to use. Hexamethyldisilazane, 2,2,2-trifluoroethanol, 1,3-propanediol, $N_3P_3Cl_6$, 3-FC_6H_4OH (Aldrich), and 4-FC_6H_4OH (PCR) are used as received. The preparation of the siloxanes is described elsewhere.[12] $N_3P_3F_6$ is made by the literature method.[14] The solvents, THF and acetonitrile, are dried and distilled prior to use according to standard procedures.

General Procedures. A conventional vacuum system comprised of a Pyrex glass vacuum line equipped with Heise Bourdon tube and Televac thermocouple gauges is used to handle gases and volatile liquids. Reactions are performed in thick-walled 50-mL-bottomed flasks fitted with Teflon stopcocks or in 25-mL stainless steel vessels. Products are separated and purified by distillation or vacuum sublimation. Infrared spectra are recorded on a Perkin-Elmer 1710 FTIR spectrometer equipped with an IBM PS-2 data station by using KBr disks, Nujol mulls, or a 10-cm gas cell equipped with KBr disks. The ^1H, ^{19}F, and ^{31}P NMR (^{19}F coupled and decoupled) spectra are obtained with a Bruker AC200 or AC300 Fourier transform NMR spectrometers using $CDCl_3$, C_6D_6, or CD_3CN as solvent and Me_4Si, CCl_3F, and 85% H_3PO_4 as references. Mass spectra are obtained with a VG 7070HS GC/MS spectrometer by using electron impact or chemical ionization techniques. Elemental analyses are performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Reaction of $N_3P_3F_6$ with $[CF_2CH_2OSiMe_3]_2$ in a 2.5:1 Molar Ratio. Into an oven-dried 25-mL round-bottomed flask fitted with a Kontes Teflon stopcock is sublimed $N_3P_3F_6$ (1.63 g, 6.55 mmol). After addition of CsF (0.08 g), $[CF_2CH_2OSiMe_3]_2$ (0.81 g, 2.65 mmol) is introduced by syringe. The contents of the flask are frozen and degassed, and 10 mL of dry THF is transferred. The mixture is brought to 25 °C, and the flask is filled with nitrogen at 1 atm. The mixture is then kept in an oil bath at 55 °C for 48 h. Analysis of the reaction mixture by IR and ^{19}F NMR shows the complete reaction of the siloxane as well as the formation of two new products in addition to Me_3SiF. The reaction flask is held in a −10 °C bath, and all volatile materials are pumped off. The residue at 25 °C is vacuum sublimed into a U tube in liquid nitrogen for 6 h (0.04 Torr) to collect a crystalline solid. It is identified as the monospirotetrafluorophosphazene $[CF_2CH_2O]_2P_3N_3F_4$, **3** (0.33 g, 34%), mp 51 °C. IR (Nujol): 1396 m, 1281 vs, 1240 m, 1149 s, 1095 s, 1055 s, 1006 w, 950 s, 924 m, 846 s, 806 s, 708 vw, 672 s, 590 w, 572 w, 566 w, 515 m, 488 m, 464 m, 405 m cm^{-1}. NMR: ^1H, δ 4.31 (m, CH_2); ^{19}F, δ −127.88 (s, CF_2, 4F), −69.28 (m, PF_2, 4F), $^1J_{P-F}$ = 879 Hz; $^{31}P\{^{19}F\}$, δ PF_2 9.69, $^2J_{P-P}$ = 129 Hz; P_{spiro} 19.07, $^2J_{P-P}$ = 126 Hz. MS (EI) [*m*/*e* (species), intensity]: 371 (M^+), 9; 351 (M^+ − HF), 10; 331 (M^+ − 2HF), 4; 228 ($N_3P_3F_4OH^+$), 50; 86 (PF_2OH^+), 100. Anal. Calcd for $C_4H_4F_8O_2N_3P_3$: C, 12.95; F, 40.97; N, 11.32. Found: C, 13.07; F, 41.20; N, 11.28. After removal of **3**, a fresh U tube is placed between the reaction flask and the vacuum line and the flask is warmed under vacuum using an oil bath (62–64 °C, 0.035 Torr). A needlelike crystalline compound is found to sublime to the sides of the U tube. It is identified as $F_5N_3P_3OCH_2CF_2CF_2CH_2OP_3N_3F_5$, **4** (0.58 g, 29%), mp 55 °C. IR (Nujol): 1410 m, 1293 vs, 1200 s, 1159 s, 1092 s, 1018 m, 989 s, 952 s, 926 s, 890 s, 851 s, 828 s, 745 w, 723 w, 673 w, 573 w, 528 m, 511 s, 484 m, 468 s, 458 m, 432 w cm^{-1}. NMR: ^1H, δ 4.55 (m); ^{19}F, δ −121.59 (s, CF_2, 4 F), −64.26 (m, PF, 2 F), $^1J_{P-F}$ = 876 Hz, −69.03 (m, PF_2, 8 F), $^1J_{P-F}$ = 892 Hz; $^{31}P\{^{19}F\}$, δ PF_2 9.35, $^2J_{P-P}$ = 126 Hz, PF(OR) 14.14. MS (EI) [*m*/*e* (species), intensity]: 620 (M^+), 3; 599 ($M^+ - H_2F$), 50; 310 ($N_3P_3F_5OCH_2CF_2^+$), 10; 260 ($N_3P_3F_5OCH_2^+$), 45; 230 ($N_3P_3F_5^+$), 100. MS (CI) [*m*/*e* (species), intensity]: 620 (M^+), 60; 599 ($M^+ - H_2F$), 100. Anal. Calcd for $C_4H_4F_{14}O_2N_6P_6$: C, 7.75; F, 42.90; N, 13.56. Found: C, 7.96; F, 43.1; N, 13.64.

Reaction of $N_3P_3F_6$ with $[CF_2CH_2OSiMe_3]_2$ in the Presence of Potassium *tert*-Butoxide. $N_3P_3F_6$ (0.80 g, 3.21 mmol) and $(CF_2CH_2OSiMe_3)_2$ (0.39

Scheme 5



g, 1.28 mmol) are stirred in THF (5 mL) at 80 °C for 24 h in a reaction vessel identical to the conditions described above for the reaction of $N_3P_3F_6$ with $[CF_2CH_2OSiMe_3]_2$. Potassium *tert*-butoxide (0.04 g) is added to the mixture and stirring is continued for 24 h at 80 °C. Analysis of the reaction mixture shows formation of bridged **4** and spiro **3** phosphazenes in a ratio of 93:7 in addition to Me_3SiF and traces of Me_3SiOBu^t. Upon sublimation, 0.07 g (15%) of spiro **3** and 0.34 g (43%) of bridged **4** derivatives are isolated.

Reaction of $N_3P_3F_6$ with $CF_2[CF_2CH_2OSiMe_3]_2$ in 2.5:1 Molar Ratio. The reaction of $N_3P_3F_6$ (0.95 g, 3.82 mmol) with $CF_2[CF_2CH_2OSiMe_3]_2$ (0.54 g, 1.52 mmol) is performed in the presence of CsF (0.05 g) and worked up as described above to yield two new products. The first one is separated by vacuum sublimation and is identified as the monospirofluorophosphazene $CF_2[CF_2CH_2O]_2N_3P_3F_4$, **5** (0.29 g, 45%), mp 51 °C. IR (neat): 2976 w, 1461 w, 1402 w, 1336 s, 1279 vs, 1239 vs, 1218 s, 1165 vs, 1139 s, 1124 s, 1099 s, 1073 vs, 1013 s, 997 s, 953 vs, 921 s, 847 vs, 813 vs, 736 m, 708 m, 648 m, 622 m, 605 m, 592 m, 520 s, 511 s, 466 s, 449 s, 438 m, 429 w cm^{-1}. NMR: ^1H, δ 4.45 (m, 4 H), ^{19}F, δ −116.81 (t, CF_2, 4 F), −125.35 (t, CF_2, 2 F), −69.28 (m, PF_2, 4 F), $^1J_{P-F}$ = 870 Hz; $^{31}P\{^{19}F\}$, δ PF_2, $^2J_{P-P}$ = 127 Hz, P_{spiro} 17.9. MS (CI) [*m/e* (species), intensity]: 422 ($M^+ + 1$), 90; 402 ($M^+ - F$), 100; 230 ($N_3P_3F_4OH^+$), 12; 211 ($N_3P_3F_4^+$), 8. Anal. Calcd for $C_5H_4F_{10}O_2N_3P_3$: F, 45.07; N, 9.97. Found: F, 44.5; N, 9.67. The second compound is a viscous oil and is identified as the bridged species $F_5N_3P_3OCH_2(CF_2)_3CH_2OP_3N_3F_5$, **6** (0.23 g, 23%). IR (neat): 2975 w, 1779 w, 1535 w, 1458 w, 1407 w, 1284 vs, 1206 s, 1167 s, 1108 s, 1019 s, 955 vs, 911 s, 849 vs, 782 w, 770 w, 751 w, 730 vw, 671 w, 515 vs, 466 vs cm^{-1}. NMR: ^1H, δ 4.54 (m, 4 H); ^{19}F, δ −120.76 (t, CF_2, 4 F), −125.36 (t, CF_2, 2 F), −64.51 (m, PF, 2 F), $^1J_{P-F}$ = 878 Hz, −69.34 (m, PF_2, 8 F), $^1J_{P-F}$ = 906 Hz; $^{31}P\{^{19}F\}$, δ PF_2 9.29, $^2J_{P-P}$ = 140 Hz, PF(OR) 14.16, $^2J_{P-P}$ = 123 Hz. MS (EI) [*m/e* (species), intensity]: 670 (M^+), 2; 650 ($M^+ - HF$), 50; 631 ($M^+ - HF_2$), 8; 340 ($N_3P_3F_5OCHCFCF_2^+$), 10; 310 ($N_3P_3F_5OCH_2CF_2^+$), 25; 260 ($N_3P_3F_5OCH_2^+$), 70; 230 ($N_3P_3F_5^+$), 100. Anal. Calcd for $C_5H_4F_{16}O_2N_6P_6$: C, 8.96; F, 45.38; N, 12.54. Found: C, 9.60; F, 44.7; N, 12.38.

Reaction of Excess 4-$FC_6H_4OSiMe_3$ with 4. A 0.1 g (0.16 mmol) portion of **4** is placed into a reaction vessel with a catalytic amount of CsF and 0.42 g (2.28 mmol) of 4-$FC_6H_4OSiMe_3$. THF (5 mL) is condensed in and the mixture is stirred at 80 °C for 16 h. Analysis of the volatile materials shows Me_3SiF. A viscous residue remains after all volatile materials are removed in vacuo. The residue is washed with cold hexane to remove unreacted siloxane. It is then extracted with $CHCl_3$ and separated from the insoluble solids by filtration. On concentration and cooling of this solution, needlelike crystals of $(4\text{-}FC_6H_4O)_5N_3P_3OCH_2CF_2CF_2CH_2ON_3P_3(4\text{-}FC_6H_4O)_5$, **7**, are obtained (0.2 g, 80%), mp 122–123 °C. IR (Nujol): 3199 w, 3077 w, 1600 vw, 1505 vs, 1276 s, 1246 s, 1222 s, 1180 vs, 1152 vs, 1096 s, 1014 w, 988 s, 962 vs, 928 s, 897 s, 841 vs, 830 vs, 816 m, 776 w, 762 w, 750 w, 719 m, 691 m, 637 w, 562 w, 546 w, 528 w, 519 w, 504 s, 482 m, 463 w cm^{-1}. NMR: ^1H, δ 7.04–6.72 (m, Ph), 3.86–3.76 (m, CH_2); ^{19}F, δ −117.38 (s, 10 F), −122.13 (t, CF_2); ^{31}P, δ 14.57–8.97 (m). MS (EI) [*m/e* (species), intensity]: 1539 ($M^+ - 1$), 20. Anal. Calcd for $C_{64}H_{44}F_{14}O_{12}N_6P_6$: C, 49.89; H, 2.88; F, 17.26. Found: C, 47.27; H, 2.90; F, 19.00.

Reaction of Excess 3-$FC_6H_4OSiMe_3$ with 4. A 0.42 g (2.28 mmol) sample of 3-$FC_6H_4OSiMe_3$ is taken along with **4** (0.1 g, 0.16 mmol) under the conditions described for **7**. After workup and purification, an oily compound is obtained which is found to crystallize very slowly at 0 °C in $CHCl_3$. The compound is identified as $(3\text{-}FC_6H_4O)_5N_3P_3OCH_2CF_2CF_2CH_2ON_3P_3(3\text{-}FC_6H_4O)_5$, **8**, mp 36 °C. IR (neat): 3083 w, 2960 w, 1604 vs, 1527 m, 1489 vs, 1451 s, 1258 s, 1225 s, 1158 s, 1122 vs, 1072 s, 1039 m, 1012 s, 980 vs, 936 m, 896 s, 862 s, 834 s, 777 s, 735 m, 720 m, 680 m, 626 s, 551 m, 519 m, 459 w cm^{-1}. NMR: ^1H, δ 7.26–6.64 (m, Ph), 3.97–3.87 (m, CH_2); ^{19}F, δ −110.21 (s, 10 F), −122.10 (t, 4 F); ^{31}P, δ 14.03–8.00 (m). MS (laser desorption) [*m/e* (species), intensity]: 1543 ($M^+ + 2$), 100. Anal. Calcd for $C_{64}H_{44}F_{14}O_{12}N_6P_6$: C, 49.89; H, 2.88; F, 17.26. Found: C, 49.58; H, 2.83; F, 17.8.

Reaction of Excess $CF_3CH_2OSiMe_3$ with 4. Method a. At 54 °C with Potassium *tert*-Butoxide as Catalyst. A 0.1-g (0.16-mmol) sample of **4** is reacted with 0.39 g (2.27 mmol) of $CF_3CH_2OSiMe_3$ in the presence of potassium *tert*-butoxide (0.04 g) in THF (5 mL). A slow reaction is found to occur with the formation of Me_3SiF. After 24 h, ^{19}F NMR spectra of the reaction mixture show only two unreacted P–F groups. The mixture is stirred at 54 °C for 12 h with 0.02 g of fresh potassium *tert*-butoxide. All volatile materials are removed in vacuo, and the residue is extracted with $CHCl_3$ and filtered to give a viscous oil which is identified as $(CF_3CH_2O)_5N_3P_3OCH_2(CF_2)_2CH_2ON_3P_3(OCH_2CF_3)_5$, **9** (0.19 g, 83%). IR (neat): 2943 m, 2900 w, 1455 m, 1423 s, 1289 vs, 1251 vs, 1171 vs, 1083 vs, 965 s, 890 s, 848 s, 813 s, 660 s, 560 s, 527 m, 490 m cm^{-1}. NMR: ^1H, δ 4.24 (m); ^{19}F, δ −122.11 (q, 4 F), −75.69 (m, 30 F); ^{31}P, δ 17.07 (bs). MS (EI) [*m/e* (species), intensity]: 1337 ($M^+ - CF_3CH_2$), 92.

Method b. At 82 °C with CsF as Catalyst. The reaction using 0.1 g (0.16 mmol) of **4** and $CF_3CH_2OSiMe_3$ (0.39 g, 2.27 mmol) is carried out using CsF (0.1 g) as catalyst at 82 °C. Working up the reaction mixture as described above after 36 h yields a viscous oil whose ^{19}F NMR spectrum shows in addition to **9** the formation of the spiro derivative as well (δ-(CF_2) at −127.78 ppm). The mass spectrum confirms the formation of the spiro compound $(CF_2CH_2O)_2N_3P_3(OCH_2CF_3)_4$. MS (EI) [*m/e* (species), intensity]: 691 (M^+), 15; 671 ($M^+ - HF$), 55; 592 ($M^+ - CF_3CH_2O$), 25. The ratio of the bridged derivative **9** to this spiro compound is 14:86 based on the NMR data. The separation of these two products could not be achieved.

Reaction of 1 with 4 in 2:1 Molar Ratio. Into a 25-mL reaction flask, 0.13 g (4.77 mmol) of **4**, 0.13 g (2.35 mmol) of **1**, and CsF (0.04 g) are

placed, frozen, and degassed, and dry THF (5 mL) is added. The mixture is brought to 25 °C, and the flask is filled with nitrogen. Stirring on an oil bath at 54 °C is continued for 48 h. Analysis of the reaction mixture shows a complete reaction of **1** with the formation of a spiro-bridged derivative and Me_3SiF. All volatile materials are removed in vacuum, and the residue is extracted with $CHCl_3$. After the solvent is evaporated, a viscous oil is identified as spiro-$(CF_2CH_2O)_2F_3N_3P_3OCH_2CF_2CF_2$-$CH_2ON_3P_3F_3$-spiro-$(OCH_2CF_2)_2$ based on ^{19}F NMR data which shows appropriate chemical shift positions and relative intensities.

Reaction of $CF_3CH_2OSiMe_3$ with $N_3P_3F_6$ in the Presence of CsF. A 0.15-g (0.60-mmol) portion of $N_3P_3F_6$ and 1.0 g (5.81 mmol) of CF_3-CH_2OSiMe_3 are combined in a 50-mL round-bottomed flask fitted with a high-vacuum Teflon stopcock along with a catalytic amount of CsF (0.05 g). The reagents are frozen and degassed and then brought to room temperature. The reaction mixture is stirred at 85 °C for 24 h. ^{19}F NMR of the reaction mixture shows Me_3SiF and the disappearance of all P–F peaks. The flask is kept at 0 °C, and all volatile materials are removed. The residue is extracted with $CHCl_3$, and after distillation $(CF_3CH_2O)_6N_3P_3$ (0.37 g, 84%) is obtained. The physical and spectral characteristics of this compound are found to agree with the literature data.[15]

Reaction of $CF_3CH_2OSiMe_3$ with $N_3P_3Cl_6$ in the Presence of Excess KF. Samples of $N_3P_3Cl_6$ (0.25 g, 0.72 mmol) and $CF_3CH_2OSiMe_3$ (1.24 g, 7.19 mmol) are placed in a 50-mL reaction flask fitted with a Kontes Teflon stopcock and are stirred at 80 °C for 48 h. Subsequently, KF (0.45 g, 7.74 mmol) is added and the mixture is stirred at 85 °C. Periodic monitoring of the reaction mixture shows the formation of P–F bonds and later Me_3SiF. After 36 h, workup of the reaction filtrate yields $(CF_3CH_2O)_6N_3P_3$ (0.38 g, 72%), whose spectral and physical data agree with literature reports.[15]

Reaction of $Me_3SiO(CH_2)_3OSiMe_3$ with $N_3P_3F_6$. Method a. Reaction Time of 36 h. $Me_3SiO(CH_2)_3OSiMe_3$ (0.44 g, 1.99 mmol), $N_3P_3F_6$ (1.25 g, 5.02 mmol), 0.08 g of CsF, and 5 mL of dry THF are placed in a 25-mL reaction vessel. After stirring of the mixture at 54 °C for 36 h, it is kept in a −25 °C bath and evacuated (0.07 Torr) to remove Me_3SiF and unreacted $N_3P_3F_6$. The flask is brought to 20 °C and pumped off into a U tube kept in liquid nitrogen. The fraction collected is identified as the monospiro derivative $CH_2(CH_2O)_2N_3P_3F_4$ (0.21 g, 16%) whose physical and spectral data agree with the literature.[16] When the flask is held at 45 °C a fraction (0.20 g, 27%) is obtained after additional distillation which is identified as the dangling derivative $F_5N_3P_3OCH_2$-$CH_2CH_2OSiMe_3$ **11**, bp 45 °C (0.07 Torr). IR (neat): 2961 s, 2878 m, 2744 m, 1540 w, 1475 m, 1399 m, 1384 m, 1362 m, 1285 vs, 1206 m, 1113 vs, 1072 vs, 1011 s, 951 vs, 845 vs, 784 m, 749 s, 714 m, 584 w, 568 w, 523 s, 497 m, 485 m, 466 vs, 455 m cm^{-1}. NMR: ^1H, δ 4.28 (q, 2 H), 3.67 (t, 2 H), 1.90 (q, 2 H), 0.08 (s, 9 H); ^{19}F, δ 65.55 (m, PF, 1 F) $^1J_{P-F}$ = 960 Hz, 69.25 (4 F, PF_2) $^1J_{P-F}$ = 960 Hz, $^{31}P\{^{19}F\}$, δ PF_2 9.99, $^2J_{P-P}$ = 128 Hz, PF(OR) 13.37. MS (EI) [*m/e* (species), intensity]: 362 ($M^+ - CH_3$), 10; 304 ($M^+ - C_3H_9Si$), 100; 287 ($N_3P_3F_5OCH_2$-CH_2CH^+), 15; 248 ($N_3P_3F_5OH_2^+$), 30; 230 ($N_3P_3F_5^+$), 17. MS (CI) [*m/e* (species), intensity]: 377 (M^+), 12; 362 ($M^+ - CH_3$), 100. Anal. Calcd for $C_6H_{15}F_5O_2N_3P_3Si$: C, 19.1; F, 25.2; N, 11.1 Found: C, 20.62; F, 25.3; N, 10.88. Further increasing of the temperature to 100 °C yields a viscous oil. On sublimation this oil gives a white crystalline solid which is $F_5N_3P_3OCH_2CH_2CH_2ON_3P_3F_5$, **12**, mp 46 °C (0.18 g, 17%). IR (Nujol): 1468 m, 1419 w, 1267 vs, 1223 s, 1207 s, 1106 vs, 1081 vs, 1009 vs, 996 s, 973 s, 955 vs, 935 vs, 902 vs, 877 s, 843 vs, 810 nm, 749 s, 720 m, 578 w, 515 s, 498 s, 489 s, 465 s, 439 w, 424 w cm^{-1}. NMR: ^1H, δ 4.29 (q, 4 H), 2.15 (q, 2 H); ^{19}F, δ 65.50 (m, PF, 2 F), $^1J_{P-F}$ = 979 Hz, 69.10 (m, PF_2, 8 F), $^1J_{P-F}$ = 979 Hz; $^{31}P\{^{19}F\}$, δ PF_2, 9.76, $^2J_{P-P}$ = 132 Hz, PF(OR) 13.50, $^2J_{P-P}$ = 131 Hz. MS (EI) [*m/e* (species), intensity]: 533 ($M^+ - H$), 3; 515 ($M^+ - F$), 5; 288 ($F_5N_3P_3OCH_2CH_2CH_2^+$), 100; 248 ($F_5N_3P_3OH_2^+$), 65; 230 ($F_5N_3P_3^+$), 20. Anal. Calcd for C_3H_6-$O_2F_{10}N_6P_6$: C, 6.75; H, 1.13; F, 35.58; N, 15.74. Found: C, 6.79; H, 1.19; F, 35.2; N, 16.26.

Method b. Reaction Time of 68 h. An identical reaction using Me_3-$SiO(CH_2)_3OSiMe_3$ (0.41 g, 1.86 mmol) and $N_3P_3F_6$ (1.25 g, 4.70 mmol) in the presence of CsF is carried out for 68 h and gives preferentially $CH_2(CH_2O)_2N_3P_3F_4$, **16** (0.10 g, 19%), and **12** (0.39 g, 39%). Traces of **11** (0.02 g, 3%) are also obtained.

Method c. Reaction Time of 24 h in CH_3CN. A reaction in CH_3CN using 0.49 g (2.22 mmol) of $Me_3SiO(CH_2)_3OSiMe_3$ and $N_3P_3F_6$ (1.39 g, 5.58 mmol) for 24 h at 54 °C gives traces of spiro compound CH_2-$(CH_2O)_2N_3P_3F_4$ (0.03 g, 4.7%) and **12** (0.72 g, 61%). Compound **11** is not isolated from this reaction.

Transformation Studies on the Bridged Derivatives 4 and 6. Samples (0.05 g) of **4** and **6** are taken in NMR tubes along with C_6D_6 and THF (1:5 ratio v/v) and with CsF (0.05 g). Each tube is sealed under nitrogen at 1 atm. The temperature is raised from 27 °C to 82 °C during NMR spectral measurement and maintained at 82 °C for 3 d. The sample tube is occasionally retrieved and agitated vigorously during data acquisition. A separate thermolysis of **4** and **6** is carried out in a 25-mL flask under similar conditions and the products sublimed to isolate the spiro derivatives **3** and **5**, respectively.

Crystallography. Suitable crystals of **3** for diffraction studies are obtained on sublimation of the thermolysis product of **4**, and crystals of **7** are obtained by slow crystallization from a $CHCl_3$ solution of **7** over a period of 1 week at 4 °C. A Siemens P4/R diffractometer is used for data collection of **3** using Cu Kα (λ = 1.541 78 Å) radiation at 120 K, while data on **7** are collected at 295 K on a Siemens R3m/v diffractometer using Mo Kα (λ = 0.710 73 Å) radiation. The monochromator in the case of **3** is a Ni filter while a highly oriented graphite crystal is used for **7**. In both cases the structure is solved by direct methods using the Siemens SHELXTL PLUS (VMS)[17] program and refined by the full-matrix least-squares method. The quantity minimized is $\sum w(F_o - F_c)^2$. The hydrogen atoms are located by the riding model with a fixed isotropic *U*. Details of the data collection, solution and refinement for **3** and **7** are given in Table 2. Tables 3 and 4 list selected bond distances and angles for **3** and **7**.

Acknowledgment. Financial assistance of the Air Force Office of Scientific Research (Grant 91-0189) and the National Science Foundation (Grant CHE-9003509) is gratefully acknowledged. The authors thank Prof. H. Hope, UC Davis; Prof. R. Willett, Washington State University, and Dr. A. M. Arif, University of Utah, for structural data. Thanks are due to Dr. Gary Knerr for the NMR and mass spectral measurements. Dr. Jerry E. Hunt of the Chemical Division at Argonne National Laboratory is owed special thanks for the matrix-assisted laser desorption mass spectra data.

Supplementary Material Available: Listings of thermal and positional parameters, derived and rigid group positional and thermal parameters, and bond distances and angles (8 pages). Ordering information is given on any current masthead page.