Syntheses and Experimental Studies on the Relative Stabilities of Spiro, Ansa, and Bridged Derivatives of Cyclic Tetrameric Fluorophosphazene

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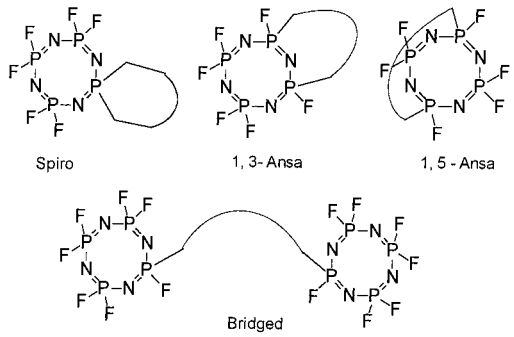
Reactions of $(CF_2CH_2OSiMe_3)_2$ and $CF_2(CF_2CH_2OSiMe_3)_2$ with $N_4P_4F_8$ (**1**) in a 1:2.5 molar ratio resulted in the formation of monospiro compounds $[(CF_2CH_2O)_2PN](F_2PN)_3$ (**2**) and $[CF_2(CF_2CH_2O)_2PN](F_2PN)_3$ (**4**) as well as the intermolecular bridged compounds $F_7N_4P_4OCH_2CF_2CF_2CH_2OP_4N_4F_7$ (**3**) and $F_7N_4P_4OCH_2CF_2CF_2CF_2CH_2OP_4N_4F_7$ (**5**). An equimolar reaction of dilithiated 1,3-propanediol with **1** resulted in the 1,3-ansa-substituted compound $CH_2(CH_2O)_2[P(F)N]_2(F_2PN)_2$ (**6**) as the major product in good yield. However, an analogous reaction of the dilithiated 1,3-propanedithiol with **1** gave only the spirocyclic compound $CH_2(CH_2S)_2(PN)(F_2PN)_3$ (**8**). The molecular structures of **2** and **6** were determined by single-crystal X-ray diffraction. In the presence of catalytic amounts of CsF in THF, the bridged compound **3** was converted to the spirocyclic compound **2** while the 1,3-ansa compound **6** under similar conditions transformed into the monospiro-substituted compound $CH_2(CH_2O)_2(PN)(F_2PN)_3$ (**7**). These transformations were monitored by time-dependent ^{19}F and ^{31}P NMR studies.

Introduction

Among inorganic heterocycles, cyclophosphazenes have continued to attract increased attention in recent years not only as precursors for phosphazene-based polymers[1] but also as a versatile core for building molecules with potential applications such as dendrimers having chiral ligands for asymmetric catalysis,[2] and mesomorphic compounds useful as liquid crystalline materials.[3] Reactions of difunctional reagents with cyclic halogenated phosphazenes have been of significant interest especially from the perspective of observing regioisomerism in substitution reactions. On the basis of the relevant literature, the spirocyclic compounds dominate among the possible products from such reactions with only relatively few examples of ansa and intermolecular bridged compounds having been prepared and fully characterized.[4−6,9−11] Brandt and others have tried to explain ansa vs spiro regioisomerism in terms of contributions of the respective thermodynamic and supramolecular effects to the regiocontrol of substitution in the $N_3P_3Cl_6$ ring.[5] It was also recently demonstrated that ansa-substituted trimeric fluorophosphazenes can be catalytically converted to spirocyclic isomers under mild reaction conditions.[6]

The chemistry of perfluorinated cyclophosphazenes differs significantly when compared to that of chloro and bromo analogues. The comparatively higher volatility, higher hydrolytic and thermal stabilities, and lower basicity of the ring nitrogens of fluorophosphazenes make them ideal precursors for phosphazene pendant polymers and for reactions with organometallic reagents.[7,8] Substitution of P−F bonds in the heterocycle by CsF-catalyzed desilylation of silylated alcohols, by mercaptans, and by CF_3SiMe_3 has been a typical reaction of fluorophosphatriazenes.[9−11] Among perfluorinated phosphazenes, the behavior toward nucleophiles has also been found to vary. Reaction of $[(CH_3)_2N]_3S[(CH_3)_3SiF_2]$ (TASF) with $N_3P_3F_6$ has been reported to cleave the six-membered ring, while with $N_4P_4F_8$ and $N_5P_5F_{10}$ the same reaction results in the formation of stable perfluorinated cyclophosphazenate anions.[12,13]



The impetus for the present study arose from the fact that reactions of difunctional reagents with tetrameric cyclophosphazenes are poorly understood. The relatively larger ring flexibility and the larger number of reactive phosphorus−

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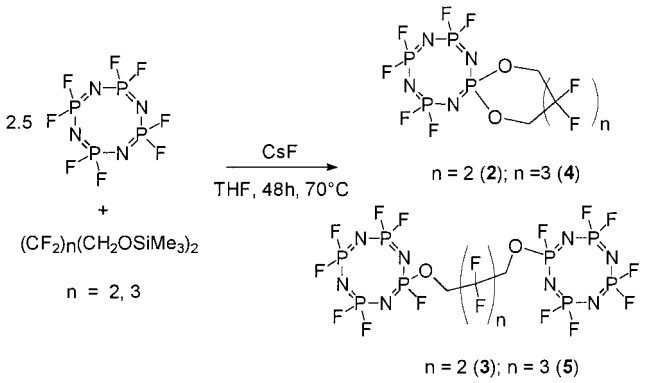
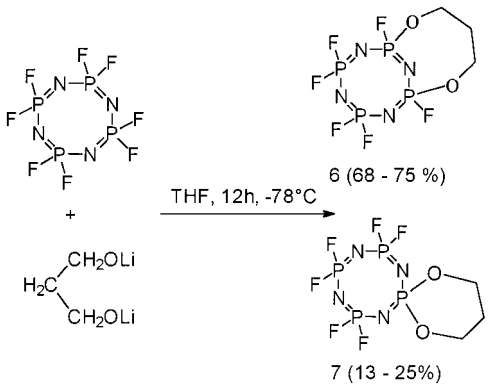
Scheme 1



Scheme 2



halogen bonds provide more versatility for the type of products possible from reactions of difunctional reagents with perhalogenated tetrameric phosphazenes. The scanty nature of such studies is indicated by the fact that the first structurally characterized examples of spiro as well as 1,3-ansa derivatives of $N_4P_4Cl_8$ have been reported only recently.[14,15] Studies on the reactions of $N_4P_4F_8$ with difunctional reagents have also been restricted primarily to dilithiated metallocenes and to a few diamines.[16−18]

In this paper we describe the preparation of spiro, ansa, and bridged derivatives of the tetrameric fluorophosphazene, $N_4P_4F_8$, by two different synthetic routes. We also report the first experimental studies comparing the relative stabilities of spiro, ansa, and bridged derivatives of tetrameric cyclophosphazenes.

Results and Discussion

Desilylation reactions of $(CF_2CH_2OSiMe_3)_2$ and $CF_2(CF_2CH_2OSiMe_3)_2$ with $N_4P_4F_8$ (**1**) in 1:2.5 molar ratio in the presence of catalytic amounts of CsF at 70 °C over a period of 48 h resulted in the formation of monospiro compounds $[(CF_2CH_2O)_2PN](F_2PN)_3$ (**2**) and $[CF_2(CF_2CH_2O)_2PN](F_2PN)_3$ (**4**) as well as the intermolecularly bridged compounds $F_7N_4P_4OCH_2CF_2CF_2CH_2OP_4N_4F_7$ (**3**) and $F_7N_4P_4OCH_2CF_2CF_2CF_2CH_2OP_4N_4F_7$ (**5**) (Scheme 1). The compounds were separated carefully by vacuum sublimation or distillation and, in contrast to spirocyclic chloro analogues,[14,19] were handled easily without decomposition in moist air. To the best of our knowledge, **3** and **5** are the first examples of bridged tetrameric fluorophosphazenes. The method offers easy access to perfluorinated spiro and bridged tetrameric phosphazenes. There is no generality in the reported attempts to fluorinate monospirocyclic chlorophosphazenes with fluorinating reagents.[14]

Since ansa compounds could not be isolated from desilylation reactions of polyfluoro diols, an alternative method of using dilithiated reagents was attempted with $N_4P_4F_8$.[6] Although equimolar reactions of a variety of dilithiated diols with $N_4P_4F_8$ at −78 °C were carried out, it was observed from GCMS and ^{31}P NMR spectral analysis that in many cases a mixture of three isomers with very close retention times on the GC column (possibly spiro, 1,3-, and 1,5-ansa) were obtained with the spiro isomer dominating. This makes separation and characterization very difficult. However, an interesting deviation from this trend was observed in the case of the reaction of dilithiated 1,3-propanediol with $N_4P_4F_8$ (Scheme 2).

An equimolar reaction of dilithiated 1,3-propanediol with **1** resulted in the formation of three isomeric products with *m*/*e* 368, which were identified by GCMS. From different reactions it was observed that the GC-based yield of the major product varied from 68% to 76% while the yield of the next major isomer was in the range of 13−25%. The major isomer was identified and characterized as 1,3-ansa $CH_2(CH_2O)_2[P(F)N]_2(F_2PN)_2$ (**6**) and the minor isomer as the monospiro $CH_2(CH_2O)_2(PN)(F_2PN)_3$ (**7**) based on spectral and analytical data as well as X-ray structural characterization of **6**. The third isomer, which was formed in very small amounts, could not be separated and purified but showed similarities to the ansa compound **6** in its mass spectral fragmentation pattern, indicating the possibility of it being a 1,5-ansa isomer. Compound **6** was found to crystallize readily from a hexane solution, while **7** remained in solution. Both compounds were reasonably stable in air, which is in contrast to the hexachloro analogue of **7**, which, because of its high hydrolytic sensitivity, could be prepared "in situ" only.[19]

It is of interest to note that the chain length of the diol in this case is the same as that of the diols that, after dilithiation, yielded ansa-substituted compounds with $N_3P_3F_6$.[6] However, an analogous reaction of the dilithiated 1,3-propanedithiol with **1** resulted only in the spirocyclic compound $CH_2(CH_2S)_2(PN)(F_2PN)_3$ (**8**). NMR and GC analyses of the reaction mixture showed only traces of the other possible products that were not isolable. This observation is similar to that of Herberhold and others, where, in a comparison of the reactions of a ferrocene-based diol, dithiol, and diselenol, only the diol was found to yield ansa-substituted products with cyclophosphazenes.[15]

Spectral Studies. The complex nature of P−F and P−P coupling in fluorinated cyclophosphazenes normally makes the task of ^{31}P and ^{19}F NMR spectral assignments difficult. However, by using a high-field NMR (500 MHz) spectrometer, better separation of the peaks was achieved. The gross spectral

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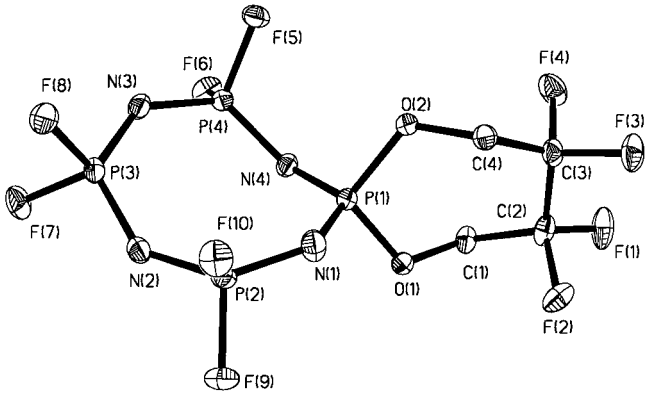

Figure 1. X-ray crystal structure of spiro $[(CF_2CH_2O)_2PN](F_2PN)_2$, **2**.

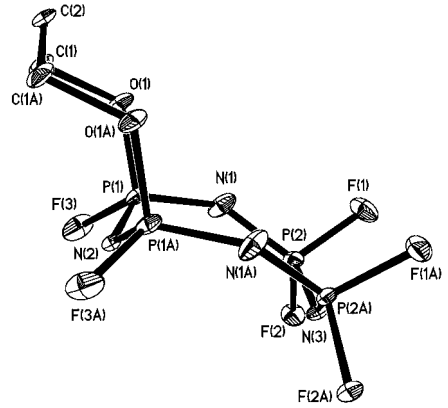

Figure 2. X-ray crystal structure of 1,3-ansa $CH_2(CH_2O)_2[P(F)N]_2$-$(F_2PN)_2$, **6**.

features of the P−F region in the three different types of products prepared in this study are unique and easily assignable. The ^{31}P NMR spectra of the monospiro compounds **2**, **4**, **7**, and **8** show that the resonance peaks assigned to the P_{spiro} moiety consist of a multiplet in the range −0.68 to + 21.83 ppm, indicating the influence of the substituent on the phosphorus chemical shift. In contrast, the PF_2 group appears as a triplet of multiplets in the narrow region −14.52 to −15.33 ppm ($^1J_{P-F}$ = 870−893 Hz). The ^{19}F NMR spectra for all the spirocylic compounds show a doublet of multiplets in the range −68.58 to −69.14 ppm for the PF_2 group. The ^{31}P NMR spectra of the 1,3-ansa (**6**) and bridged compounds (**3**, **5**) show a doublet of a multiplets for the PF(OR) moiety in the range − 0.23 to −8.46 ppm. As expected, one observes a triplet of a multiplets for PF_2 groups of these compounds in the range −13.04 to −15.45 ppm. The ^{19}F NMR spectra for the bridged compounds show doublets of multiplets for the PF_2 (−69.45, −69.79 ppm) as well as PF(OR) (−64.31, −64.39 ppm) groups. The ^{19}F NMR spectra for 1,3-ansa compound **6** were quite different with three sets of doublets of multiplets appearing at −74. 65 [PF(OR)], −69.18, and −70.05 (PF_2) ppm, indicating the loss of symmetry of the fluorine atoms belonging to the PF_2 group upon ansa formation. The assignments are further confirmed by decoupling studies of fluorine in the ^{31}P NMR spectra and vice versa.

X-ray Structural Studies. Single crystals of compounds **2** and **6** were grown from hexane solutions, and structures were determined (Figures 1 and 2). Selected data collection and structure solution parameters are given in Table 1, and selected bond distances and angles of **2** and **6** are given in Tables 2 and 3, respectively. A search of the Cambridge Crystallographic Database indicates that **2** represents the first structurally

Table 1. X-ray Crystallographic Parameters for **2** and **6**

	2	**6**
empirical formula	$C_4H_4F_{10}N_4O_2P_4$	$C_3H_6F_6N_4O_2P_4$
fw	453.99	368.00
cryst syst	orthorhombic	orthorhombic
space group	*Pbca*	*Pnma*
a (Å)	12.8938(2)	9.40730(10)
b (Å)	10.2999(2)	13.5890(2)
c (Å)	20.96840(10)	9.38060(10)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
V (Å^3)	2784.71(7)	1199.18(3)
Z	8	4
D_{calcd} (Mg m^{-3})	2.166	2.038
μ (mm^{-1})	0.674	0.711
T (°C)	−120(2)	−70(2)
λ (Å)	0.710 73	0.710 73
final R^a (2σ data)	R = 0.0613, wR2 = 0.1125	R = 0.0656, wR2 = 0.1702
R,[a] all data	R = 0.0758, wR2 = 0.1185	R = 0.0731, wR2 = 0.1764

[a] $R = \sum|F_o| - |F_c|/\sum|F_o|$. wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound **2**

	Bond Lengths		
P(1)−N(1)	1.561(3)	P(2)−N(1)	1.537(3)
P(1)−N(4)	1.564(3)	P(2)−N(2)	1.548(3)
P(1)−O(1)	1.575(2)	P(1)−O(2)	1.580(2)
P(4)−F(5)	1.532(2)	P (4)−F(6)	1.528(2)
P(4)−N(4)	1.547(3)	P(4)−N(3)	1.548(3)
P(3)−N(2)	1.543(3)	P(3)−N(3)	1.546(3)
	Bond Angles		
P(1)−N(1)−P(2)	137.2(2)	N(1)−P(2)−N(2)	123.63(17)
P(1)−N(4)−P(4)	135.1(2)	N(1)−P(1)−O(1)	104.34(16)
P(2)−N(2)−P(3)	140.3(2)	N(1)−P(1)−O(2)	110.04(16)
P(3)−N(3)−P(4)	135.4(3)	N(4)−P(1)−O(1)	109.72(15)
N(1)−P(1)−N(4)	120.17(17)	N(4)−P(1)−O(2)	106.46(15)
N(4)−P(4)−N(3)	122.50(17)	P(1)−O(1)−C(1)	122.3(2)
N(2)−P(3)−N(3)	124.11(16)	P(1)−O(2)−C(4)	120.6(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound **6**

	Bond Lengths		
P(1)−N(1)	1.557(4)	P(2)−N(1)	1.520(4)
P(2)−N(3)	1.541(2)	P(2A)−N(3)	1.541(2)
P(1)−O(1)	1.554(3)	P(1)−N(2)	1.558(2)
P(1)−F(3)	1.529(3)	P(2)−F(2)	1.519(3)
O(1)−C(1)	1.462(6)	C(1)−C(2)	1.502(6)
	Bond Angles		
P(1)−N(1)−P(2)	136.6(3)	N(1)−P(1)−O(1)	105.0(2)
P(2)−N(3)−P(2A)	135.6(3)	P(1)−N(2)−P(1A)	126.1(3)
N(1)−P(2)−N(3)	123.0(2)	N(1)−P(1)−F(3)	108.2(2)
N(1)−P(1)−N(2)	120.4(2)	O(1)−P(1)−N(2)	113.65(19)

characterized spirocyclic fluorinated tetrameric phosphazene. In the category of ansa-substituted derivatives of $N_4P_4F_8$, crystal structures of three examples of metallocene-derived 1,5-ansa-substituted compounds[16,17] and one example of a 1,3-ansa-substituted compound have been determined.[20] The structure of **6** provides an interesting comparison to that of 1,3-ansa $FcO_2(P_4N_4Cl_6)$[15] as well as 1,3-ansa $SN_2(P_4N_4F_6)$.[20] The angle P(1)−N(2)−P(1A) of the phosphazene ring of **6** between the two phosphorus centers forming the eight-membered ansa bridge is 126.1°. This is smaller than the other P−N−P angles of the

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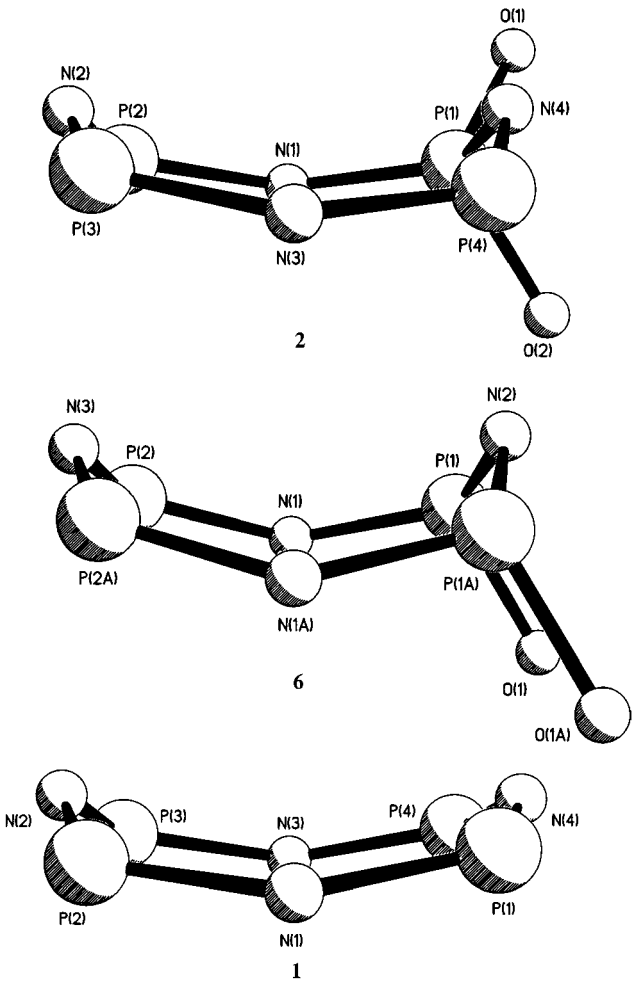
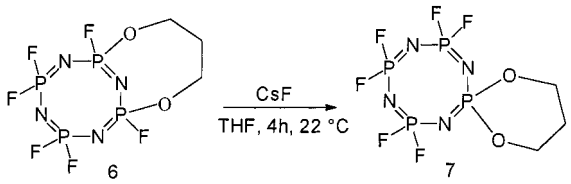


Figure 3. Comparison of the cyclophosphazene ring orientations of **2**, **6**, and **1**.

ring framework and indicates the extent of ring strain induced upon ansa formation. In the case of $SN_2(P_4N_4F_6)$, where the ansa bridge is shorter by two atoms than in **6**, this angle is 123.1°. However, for this structure, the opposite P−N−P angle in the ring is considerably larger (154. 9°). In contrast to these examples, all the P−N−P angles of 1,3-ansa $FcO_2(P_4N_4Cl_6)$ fall in the range 130.1−135.6°. The P−N−P bond angles of the monospirocyclic compound **2** are in the range 135.1−140.3°. The P−N bond lengths of **6** range from 1.520 to 1.558 Å, while for **2** the analogous bonds are in the range 1.537−1.564 Å.

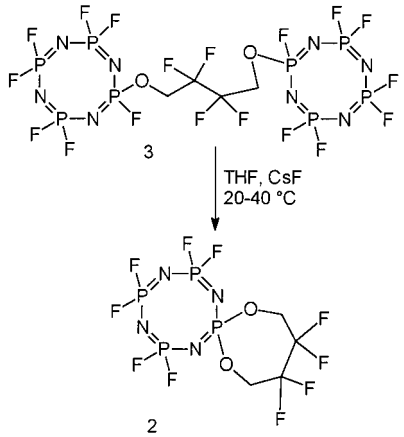
Recently, we as well as others have observed that in contrast to the previous belief, the $N_4P_4F_8$ ring is not planar. Above the phase-transition temperature of −74 °C, the ring appears pseudoplanar, but with appropriate modeling, the ring is really puckered as in the low-temperature case.[21] In Figure 3, the phosphazene ring frameworks of **6**, **2**, and **1** at low temperatures are compared, and quite interestingly, the tub conformation (similar to the K form of $N_4P_4Cl_8$) is observed in the substituted species as well.

Ansa to Spiro Transformation. On stirring a solution of **6** with traces of CsF in THF at 22 °C, a transformation was found to occur where **6** was converted to the spiro compound **7**. This transformation was followed by time-dependent GCMS and ^{19}F and ^{31}P NMR studies. The results from the GCMS study



indicate that over a period of 10 min around 40% of **6** had transformed to **7** and at the end of 2 h the ratio of **6** to **7** in the solution was 30:70. Continued stirring with larger amounts of CsF resulted in a viscous insoluble residue. The ^{19}F NMR study of the transformation (Figure 4) shows the gradual disappearance of the doublet at −74.65 ($P-F_{ansa}$) and the increase in the intensity of the doublet at −68.99 ppm (PF_{2spiro}). In the ^{31}P NMR study (Figure 5) the most striking feature is the appearance of a new multiplet centered at −4.57, characteristic of the P_{spiro} group of **7**, that grows in intensity at the expense of the doublet of multiplets of PF(OR) moiety at −0.23 ppm. Although all spectral and analytical data were obtained for **7**, it could not be completely separated from traces of the ansa compound **6**. This study indicates that higher ring flexibility does not preclude the ansa to spiro transformation of tetrameric fluorophosphazenes in comparison to the trimers[6] and also confirms the generality of this transformation being possible with both six- and eight-membered fluorophosphazenes.

Bridged to Spiro Transformation. We have reported previously that some intermolecular bridged trimeric fluorophosphazenes convert to the spiro isomers in the presence of nucleophiles.[9,10] It was therefore of interest to see if this transformation was influenced by the ring size of the fluorophosphazene. Figure 6 shows the time-dependent ^{19}F NMR spectra of the transformation of the bridged phosphazene **3** to the spirocyclic compound **2**. The transformation was performed by stirring a solution of **3** with traces of CsF in THF and warming the solution from 20 to 40 °C over a period of 8 h. The time-dependent ^{19}F NMR spectra show the slow disappearance of the minor doublet due to the PF(OR) group of **3** at −64.39 ppm. More noteworthy are the changes observed for the spectra of the CF_2 groups. The slow disappearance of the peak at −121.90 ppm of **3** and the appearance and intensification of the peak at −127.62, which is characteristic of **2** at the expense of the former, provide adequate evidence for this transformation. Mass spectral analysis of the reaction mixture



after 8 h also gave the molecular ion for **2**, further confirming its formation. Although $N_4P_4F_8$ is a possible side product of this transformation, it was not isolable from the viscous residue formed during this transformation. The possibility of $N_4P_4F_8$ forming phosphazenate anions also exists.[13] It should be noted

(21) Elias, A. J.; Twamley, B.; Haist, R.; Oberhammer, H.; Henkel, G.; Krebs, B.; Lork, E.; Mews, R.; Shreeve, J. M Manuscript in preparation.

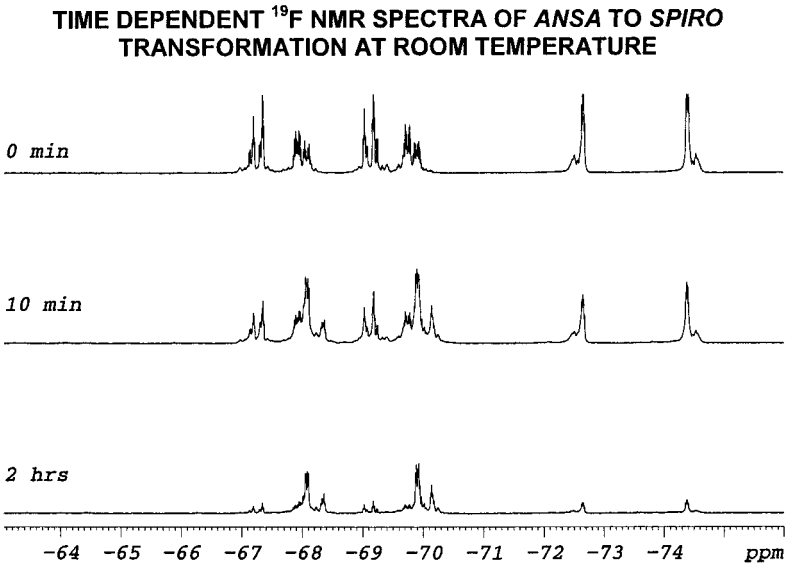


Figure 4. Time-dependent ^{19}F NMR spectra showing transformation of **6** to **7**.

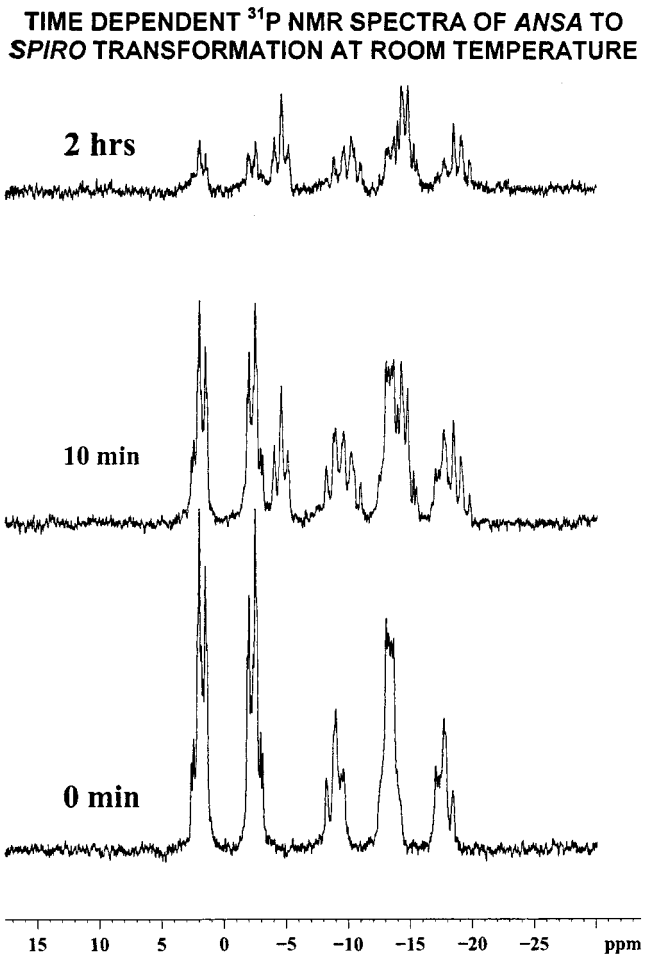


Figure 5. Time-dependent ^{31}P NMR spectra showing transformation of **6** to **7**.

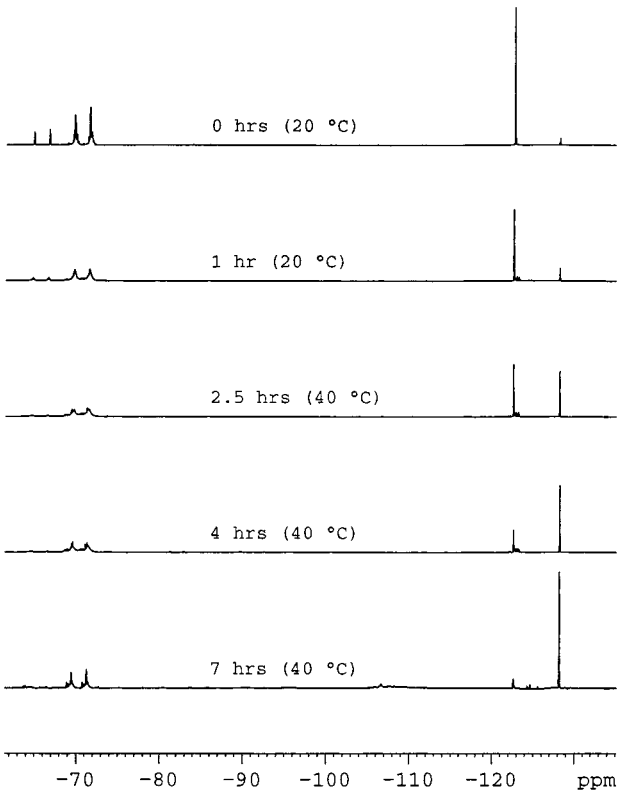


Figure 6. Time-dependent ^{19}F NMR spectra showing transformation of **3** to **2**.

that the bridged to spiro transformation does not proceed in chloroform or toluene.

Conclusions

We carried out the first reactions of silylated diols with $N_4P_4F_8$ and prepared the first examples of intermolecular-bridged tetrameric fluorophosphazenes, in addition to monospirocyclic compounds. The crystal structure of **2** is the first of its kind involving tetrameric fluorophosphazenes. The transformation of the bridged compound to the spirocyclic derivative was observed to occur in the presence of CsF under mild conditions similar to those of trimeric phosphazenes.

Delithiation reactions of dilithiated diols were necessary to prepare ansa-substituted tetrameric fluorophosphazenes. Best yields of the 1,3-monoansa derivatives were obtained using dilithiated 1,3-propanediol. Despite the ring flexibility associated with tetrameric fluorophosphazenes, the 1,3-ansa isomer was found to transform to the spiro analogue at room temperature in the presence of CsF in THF. The study therefore indicates the generality of ansa to spiro transformation and further

supports the higher thermodynamic stability of spirocyclic cyclophosphazenes over the ansa derivatives as was proposed previously by Brandt, Shaw, and others on trimeric chlorophosphazenes.[5a]

Experimental Section

Reagents. Literature methods were used to prepare $N_4P_4F_8$ (**1**).[22] Silylation of the diols was carried out by reactions with hexamethyldisilazane as described previously.[9] 1,3-Propanediol, 1,3-propanedithiol, *n*-BuLi (1.6 M in hexanes) (Aldrich), 2,2,3,3-tetrafluorobutanediol, and 2,2,3,3,4,4-hexafluoropentanediol (Lancaster) were used as received.

General Procedures. A conventional vacuum line equipped with dry nitrogen facility and Schlenk glassware were used for all reactions. Reactions were carried out and worked up under an atmosphere of dry nitrogen. Infrared spectra were recorded on a BioRad Merlin spectrometer as KBr pellets. The ^{1}H, ^{31}P{^{1}H}, ^{19}F{^{31}P}, and ^{13}C{^{1}H} NMR spectra were recorded using Bruker AC 200, AMX 300, and AVANCE 500 spectrometers with $CDCl_3$ as a solvent and with TMS, 85% H_3PO_4, and $CFCl_3$ as references. Mass spectra were obtained on a Shimadzu GCMS QP 5050A in the EI mode. Elemental analyses were carried out by Desert Analytics, Tuscon, Arizona.

X-ray Crystallographic Studies. The structure of compounds **2** and **6** were determined using a Siemens SMART 1000 X-ray diffractometer (Mo Kα radiation, $\lambda = 0.710\ 73$ Å) equipped with a Siemens LT-2A low-temperature device. The SHELXTL, version 5.10, program package was used for structure solution and refinement.[23] An empirical absorption correction was applied to **6** using SADABS.[24] The structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. Some details of the data collection and refinement are given in Table 1. Further details are provided as Supporting Information.

Reaction of $(CF_2CH_2OSiMe_3)_2$ with $N_4P_4F_8$ in 1:2.5 Molar Ratio. In an oven-dried 25 mL round-bottomed flask fitted with a Kontes Teflon stopcock was sublimed $N_4P_4F_8$ (1.33 g, 4.0 mmol). After addition of CsF (0.08 g), $(CF_2CH_2OSiMe_3)_2$ (0.49 g, 1.6 mmol) was introduced by a syringe. The contents of the flask were frozen and degassed, and 10 mL of dry THF was introduced. The mixture was brought to 25 °C, and the flask was filled with nitrogen at 1 atm. The mixture was then heated in an oil bath at 70 °C for 48 h. Analysis of the reaction mixture by ^{19}F NMR showed a complete reaction of the siloxane with the formation of two new products in addition to Me_3SiF. The reaction flask was held at 10 °C, and all volatile materials were pumped off. The residue was vacuum (0.035 Torr) sublimed at 50 °C into a U tube held in liquid nitrogen for 8 h in order to collect a crystalline solid. It was identified as the monospiro tetrameric hexafluoro phosphazene, $[(CF_2CH_2O)_2PN](F_2PN)_3$ (**2**) (0.36 g, 50%). Mp: 48−49 °C. IR (KBr): 2975 w, 1389 vs, 1289 m, 1231 vw, 1208 w, 1139 vs, 1117 vs, 1096 vs, 979 s, 944 vs, 918 s, 879 s, 836 m, 738 vs, 644 m, 615 w, 563 w, 491 vs cm^{-1}. ^{1}H NMR: δ 4.36 (m, CH_2). ^{31}P{^{1}H} NMR: δ P_{spiro}, −0.68 (m $^2J_{P-P} = 140$ Hz); PF_2, −14.77 (tm, $^1J_{P-F} = 893$ Hz). ^{19}F NMR: δ −127.62 (m, CF_2, 4F), −69.14 (dm, PF_2, 6F), $^1J_{P-F} = 894$ Hz. MS (EI) [*m*/*e* (species) intensity]: 454 (M^+) 28; 434 (M^+ − HF) 72; 311 ($N_4P_4F_6OH^+$) 100; 291 ($N_4P_4F_5O^+$) 17; 230 ($N_3P_3F_5^+$) 43; 126 ($C_4H_5F_3O^+$) 36; 95 (50). Elemental Anal. Calcd for $C_4H_4F_{10}N_4O_2P_4$: C, 10.58; H, 0.89; N, 12.34. Found: C, 10.63; H, 0.83; N, 12.07. After removal of **2**, a fresh U tube was placed between the reaction flask and the vacuum line and the flask was heated with a heating gun. A white solid was found to sublime onto the cool parts of the U tube. It was identified as $F_7N_4P_4OCH_2CF_2CF_2CH_2OP_4N_4F_7$ (**3**) (0.38 g, 30%). Mp: 49−50 °C. IR (KBr): 2970 w, 1420 vs, 1300 w, 1199 m, 1152 m, 1095 s, 978 vs, 948 vs, 753 vs, 483 s cm^{-1}. ^{1}H NMR: δ 4.51 (m, CH_2). ^{31}P{^{1}H} NMR: δ PF(OR) −0.23 (dm, $^1J_{P-F} = 868$ Hz); PF_2, −13.04 (tm, $^1J_{P-F} = 865$ Hz). ^{19}F NMR: δ −121.88 (m, CF_2, 4F) − 64.39 (dm, PF, 2 F), $^1J_{P-F} = 870$ Hz, −69.45 (dm, PF_2, 12F), $^1J_{P-F} = 865$ Hz. MS (EI) [*m*/*e* (species) intensity]: 787 ($M^+ + 1$) 4; 766 (M^+ − HF) 100; 736 (12); 423 (17); 313 ($N_4P_4F_7$) 52; 291 ($N_4P_4F_5O$) 17; 230 ($N_3P_3F_5$) 23. Elemental Anal. Calcd for $C_4H_4F_{18}N_8O_2P_8$: C, 6.11; H, 0.51; N,14.30: Found: C, 6.67; H,0.61; N,14.35.

Reaction of $CF_2(CF_2CH_2OSiMe_3)_2$ with $N_4P_4F_8$ in 1:2.5 Molar Ratio. The reaction of $N_4P_4F_8$ (1.16 g, 3.50 mmol) with $CF_2(CF_2CH_2OSiMe_3)_2$ (0.50 g, 1.4 mmol) was performed in the presence of CsF (0.10 g) and worked up as described above to yield two new products. The first one was separated by vacuum sublimation and was identified as the spirocyclic compound $[CF_2(CF_2CH_2O)_2PN](F_2PN)_3$ (**4**) (0.23 g, 33%). Mp: 43−44 °C. IR (KBr): 2970 vw, 1412 vs, 1260 w, 1230 w, 1210 w, 163 s, 1135 m, 1098 vs, 972 s, 945 s, 864 w, 751 vs, 623 vw, 518 m, 484 s cm^{-1}. ^{1}H NMR: δ 4.43 (m, CH_2). ^{31}P{^{1}H} NMR: δ P_{spiro}, −2.16 (m $^2J_{P-P} = 120$ Hz); PF_2, −14.94 (m, $^1J_{P-F} = 875$ Hz). ^{19}F NMR: δ −116.19 (t, CF_2, 4F), −125.12 (t, CF_2, 2 F), −68.94 (dm, PF_2, 6F), $^1J_{P-F} = 874$ Hz. MS (EI) [*m*/*e* (species) intensity]: 504 (M^+) 100; 485 (M^+ − F) 26; 343 (35); 313 ($N_4P_4F_7$) 92; 230 ($N_3P_3F_5$) 43. After removal of **4**, the residue was subjected to vacuum distillation and yielded a viscous liquid. It was identified as $F_7N_4P_4OCH_2CF_2CF_2CF_2CH_2OP_4N_4F_7$ (**5**) (0.60 g, 51%). IR (KBr): 2978 w, 1412 vs, 1290 m, 1205m, 1168 m, 1104 s, 1060 m, 1000 s,980 vs, 954 vs, 910 m, 758 vs, 613 w, 480 vs cm $^{-1}$. ^{1}H NMR: δ 4.50 (m, CH_2). ^{31}P{^{1}H} NMR: δ PF(OR), −8.46 (dm), $^1J_{P-F} = 868$ Hz; PF_2, −15.45 (tm, $^1J_{P-F} = 915$ Hz). ^{19}F NMR: δ −121.14 (s, CF_2, 4F), −125.63 (t, CF_2, 2F), − 64.31 (dm, PF, 2F), $^1J_{P-F} = 879$ Hz, −69.79 (dm, PF_2, 12F), $^1J_{P-F} = 881$ Hz. ^{13}C{^{1}H} NMR: δ 64.14 (m, OCH_2, 2C), 113.58 (CH_2CF_2, ttd), $^1J_{C-F} = 259$ Hz, $^2J_{C-F} = 31$ Hz, $^3J_{C-P} = 8.4$ Hz, 110.80 ($CF_2CF_2CF_2$, tt), $^1J_{C-F} = 264$ Hz, $^2J_{C-F} = 32$ Hz. MS (EI) [*m*/*e* (species) intensity]: 836 (M^+) 27; 814 (100); 751 (21); 314 ($N_4P_4F_7H$) 60; 231 ($N_3P_3F_5$) 18. Elemental Anal. Calcd for $C_5H_4F_{20}N_8O_2P_8$: C, 7.17; H, 0.48; N,13.40. Found: C, 7.61; H, 0.42; N, 13.16.

Reactions of Dilithiated 1,3-Propanediol with $N_4P_4F_8$ in 1:1 Molar Ratio. 1,3-Propanediol (0.52 g, 6.83 mmol) was treated with *n*-BuLi (8.55 mL, 13.68 mmol) in dry THF (20 mL) at −80 °C and stirred for 4 h before $N_4P_4F_8$ (2.27 g, 6.84 mmol) dissolved in dry THF (20 mL) was added at −80 °C under nitrogen atmosphere. The mixture was brought to room temperature and after 12 h of stirring, the solvent was removed in vacuo, the residue was dissolved in *n*-hexane, and the LiF that had formed was filtered off using a frit. Analysis of the hexane solution by GCMS indicated three products with *m*/*e* 368 with distinctly different fragmentation patterns in the percentage ratio 73:13:14. When the hexane solution was cooled, colorless platelike crystals were obtained and were identified as the major product 1,3-ansa $CH_2(CH_2O)_2[P(F)N]_2(F_2PN)_2$ (**6**) (1.37 g, 55%). Mp: 63 °C. IR (cm $^{-1}$) (KBr): 2968 vw, 1390 vs, 1305 s, 1254 m, 1143 m, 1056 vs, 980 vs, 936 vs, 915 s, 900 s, 890 m, 810 w, 792 s, 752 s, 709 s, 635 w, 575 w, 496 vs. ^{1}H NMR: δ 2.18−2.35 (m, 2H, CH_2), 4.20−4.42 [m, 4H, OCH_2). ^{31}P-{^{1}H} NMR: δ −0.23 (dm, PF(O), $^1J_{P-F} = 896$ Hz), −13.35 (tm, PF_2, $^1J_{P-F} = 892$ Hz). ^{19}F NMR: δ −74.65 [dm, $^1J_{P-F} = 894$ Hz, PF(O)], −70.05 (dm $^1J_{P-F} = 875$ Hz), −69.18 (dm, $^1J_{P-F} = 908$ Hz, PF_2). ^{13}C{^{1}H} NMR: δ 65.68 (OCH_2), 30.60 (CCH_2). MS (EI) [*m*/*e* (species) intensity]: 368 (M^+) 73; 341 (7); 329 ($N_4P_4F_7O$) 24; 312 ($N_4P_4F_6OH_2^+$) 100; 291 ($N_4P_4F_5O$) 21; 248 ($N_3P_3F_5OH_2^+$) 40; 230 ($N_3P_3F_5$) 80. Elemental Anal. Calcd for $C_3H_6F_6N_4O_2P_4$: C, 9.79; H, 1.64; N, 15.23. Found: C, 9.78; H, 1.75; N,14.29.

Transformation of 1,3-Ansa $CH_2(CH_2O)_2[P(F)N]_2(F_2PN)_2$ (6) into Spiro $CH_2(CH_2O)_2$ $(PN)(F_2PN)_3$ (7). Into a 25 mL round-bottomed flask, dry THF (10 mL) was distilled and 0.20 g of **6** was dissolved. CsF (0.05 g) was added, and the solution was stirred at room temperature. Aliquots were removed at regular intervals and analyzed by GCMS. It was observed that a new peak whose mass spectrum agreed with that of one of the minor products in the reaction of dilithiated 1,3-propanediol with $N_4P_4F_8$ began to grow in the gas chromatogram. This was identifed as the monospiro compound $CH_2(CH_2O)_2$ $(PN)(F_2PN)_3$ (**7**). Over a period of 3 h, the peak of the new product was found to grow in intensity and reach a ratio of 70:30 (**6**/**7**). Spectral data obtained for **7**. ^{1}H NMR: δ 1.97−2.28 (m, 2H, CH_2), 4.30−4.40 [m, 4H, OCH_2). ^{31}P{^{1}H} NMR: δ − 4.57 (m, $^2J_{P-P} = 114$ Hz P_{spiro}), −14.52 (tm, $^1J_{P-F} = 870$ Hz, PF_2). ^{19}F NMR: δ −68.99 (dm, $^1J_{P-F} = 850$ Hz, PF_2). ^{13}C{^{1}H} NMR: δ 67.93 (OCH_2), 26.04

(22) Schmutzler, R. *Inorg. Synth.* **1967**, *9*, 75.
(23) *SHELXTL*, version 5.10; PCNT Bruker AXS: Madison, WI, 1998.
(24) SADABS (Siemens Area Detector ABSorption correction program), an empirical absorption program by G. M. Sheldrick using the method described in the following reference. Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(CCH_2). MS (EI) [*m*/*e* (species) intensity]: 368 (M^+) 57; 329 ($N_4P_4F_7O$) 30; 311 ($N_4P_4F_6OH^+$) 100; 296 ($N_4P_4F_6H_2$) 18; 291 ($N_4P_4F_5O$) 40; 230 ($N_3P_3F_5$) 65; 211 (35). The transformation was followed by time-dependent ^{19}F and ^{31}P NMR studies wherein the peaks corresponding to the spiro compound were found to grow in intensity at the expense of the peaks of the ansa compound. The spiro−ansa mixture was filtered, the solvent evaporated, and the residue redissolved in chloroform. In the absence of CsF, further transformation and degradation are prevented. When a hexane solution of the two was cooled, only compound **6** crystallized out, leaving **7** in solution.

Reactions of Dilithiated 1,3-Propanedithiol with $N_4P_4F_8$ in 1:1 Molar Ratio. 1,3-Propanedithiol (0.15 g, 1.38 mmol) was added to a round-bottomed flask, dry THF (20 mL) was condensed in, and the solution was cooled to −78 °C. *n*-BuLi solution in hexanes (1.75 mL, 2.80 mmol) was added dropwise to this solution. The mixture was brought to room temperature over a period of 1 h and then stirred further for 2 h. Afterward the solution was cooled again to −78 °C and $N_4P_4F_8$ (0.46 g, 1.39 mmol) dissolved in dry THF was added dropwise over a period of 15 min. The solution was allowed to come to room temperature over a period of 2 h and was further stirred at that temperature for 12 h. Afterward the volatiles were removed in vacuo and the viscous residue was extracted with dry hexane. The hexane soluble part was separated by filtration and cooled at 0 °C to obtain a white solid. This was characterized as spiro $[CH_2(CH_2S)_2PN](F_2PN)_3$ (**8**) (0.38 g, 69%). Mp: 64−66 °C. IR (cm^{-1}) (KBr): 2965 vw, 2364 m, 1388 vs, 1267 m, 970 s, 937 vs, 845 w, 789 m, 725 s, 613 m, 591 s, 555 w, 483 vs. ^1H NMR: δ 2.07−2.19 (m, 2H, CH_2), 3.19−3.35 (d of m, 4H SCH_2). $^{31}P\{^1H\}$ NMR: δ 21.83 (m, P_{spiro}), −15.33 (tm, $^1J_{P-F}$ = 893 Hz, PF_2). ^{19}F NMR: δ, −68.58 (dm, $^1J_{P-F}$ = 887 Hz, PF_2). ^{13}C NMR: δ 31.89 (d, SCH_2), 25.37 (d, CH_2). MS (EI) [*m*/*e* (species) intensity]: 400 (M^+) 54; 367 (17); 295 ($N_4P_4F_6H$) 17; 230 ($N_3P_3F_5$) 13; 106 ($C_3H_6S_2$) 100. Elemental Anal. Calcd for $C_3H_6F_6N_4P_4S_2$: C, 8.91; H, 1.48; N, 13.86. Found: C, 9.49; H, 1.47; N, 12.77.

Transformation of $F_7N_4P_4OCH_2CF_2CF_2CH_2OP_4N_4F_7$ (3) to $[(CF_2CH_2O)_2PN](F_2PN)_3$ (2). About 0.75 g of **3** was placed in a 50 mL round-bottomed flask and dry THF (15 mL) was freshly distilled in. Cesium fluoride (0.15 g) was added to the solution and the mixture was stirred vigorously over a period of 8 h with slow warming from 20 to 40 °C. Aliquots were removed at regular intervals, volatile compounds removed under vacuum, and the residue was extracted in minimum amount of $CDCl_3$ for NMR spectral analysis. The transformation was found not to proceed in this medium and was used for obtaining time dependent ^{19}F NMR spectra. (Figure 6).

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Supporting Information Available: X-ray crystallographic files, in CIF format, for **2**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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