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Preparation of the First Examples of Ansa–Spiro Substituted Fluorophosphazenes and Their Structural Studies: Analysis of C–H···F–P Weak Interactions in Substituted Fluorophosphazenes

K. Muralidharan[†] and Anil J. Elias*[,‡]

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India, and Department of Chemistry, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi 110 016, India

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The reactions of fluorophosphazenes, endo ansa $FcCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ (**1**) (Fc = ferrocenyl) and spiro $[RCH_2P(S)(CH_2O)_2PN](F_2PN)_2$ (R = Fc (**2**), C_6H_5 (**3**)], with dilithiated diols have been explored. The study resulted in the formation of the first examples of ansa–spiro substituted fluorinated cyclophosphazenes as well as a bisansa substituted fluorophosphazene. The bisansa compound $\{1,3\text{-}[FcCH_2P(S)(CH_2O)_2]\}\{1,5\text{-}[CH_2(CH_2O)_2]\}N_3P_3F_2$ (**4**) was found to be nongeminaly substituted with both the ansa rings in cis configuration, which is in stark contrast to the observations on cyclic chlorophosphazenes where geminal bisansa formation has been observed. The ansa–spiro compounds (**5**–**7**) underwent the ansa to spiro transformation leading to dispiro compounds in the presence of catalytic amounts of CsF at room temperature. Two of the ansa–spiro compounds, *endo*-$\{3,5\text{-}[FcCH_2P(S)(CH_2O)_2]\}\{1,1\text{-}[CH_2(CH_2O)_2]\}N_3P_3F_2$ (**5**) and *endo*-$\{3,5\text{-}[FcCH_2P(S)(CH_2O)_2]\}\{1,1\text{-}[FcCH_2P(S)(CH_2O)_2]\}N_3P_3F_2$ (**6**), were structurally characterized, and the crystal structures indicate boat–chair conformation as well as crown conformation for the eight-membered ansa rings. Weak C–H···F–P interactions observed in the crystal structures of the ansa–spiro substituted fluorophosphazene derivatives have been analyzed and compared with C–H···F–P interactions of other fluorinated phosphazenes and thionyl phosphazenes.

Introduction

Reactions of difunctional reagents with perhalogenated cyclophosphazenes have been of considerable interest recently from the perspective of observing regioisomerism in substitution reactions,[1] in synthesizing phosphazene based macrocycles and air stable inclusion adducts,[2,3] as well as in the preparation of stable trispiro compounds which show novel shape selective host−guest interaction phenomena.[4]

Among the various products which can result from the reactions of bifunctional reagents with cyclophosphazenes, obtaining ansa or transannular substituted cyclophosphazenes has been quite difficult, since they are found to be thermodynamically less stable compared to the more frequently observed spiro substituted cyclophosphazenes.[5] Recent studies indicate the requirement of cation assisted supramolecular effects to prepare ansa substituted chlorophosphazenes while low-temperature reactions involving dilithiated reagents were required to prepare ansa substituted fluorophosphazenes.[6] Unlike monoansa substituted fluorophosphazenes, there are no examples of ansa−spiro and bisansa substituted trimeric fluorophosphazenes known in the literature (Figure 1). It may be noted that the only known example of a bisansa fluorophosphazene is the nongem "double transannular" bisruthenocenyl cyclotetraphosphazene having substitution on

* To whom correspondence should be addressed. E-mail: elias@chemistry.iitd.ac.in.
[†] Indian Institute of Technology, Kanpur.
[‡] Indian Institute of Technology, Delhi.

(1) (a) Allen, C. W. *Chem. Rev.* **1991**, *91*, 119−135. (b) Chandrasekhar, V.; Justin Thomas, K. R. *Struct Bonding* **1993**, *81*, 41. (c) Chandrasekhar, V.; Krishnan, V. *Adv. Inorg. Chem.* **2002**, *53*, 159.
(2) (a) Schneider, R.; Köllner, C.; Weber, I.; Togni, A. *Chem. Commun.* **1999**, 2415−2416. (b) Moriya, K.; Kawanishi, Y.; Yano, S.; Kajiwara, M. *Chem. Commun.* **2000**, 1111−1112.
(3) (a) Allcock, H. R.; Primrose, A. P.; Silverberg, E. N.; Visscher, K. B.; Rheingold, A. L.; Guzei, I. A.; Parvez, M. *Chem. Mater.* **2000**, *12*, 2530−2536. (b) Allcock, H. R.; Primrose, A. P.; Sunderland, N. J.; Rheingold, A. L.; Guzei, I. A.; Parvez, M. *Chem. Mater.* **1999**, *11*, 1243−1252.
(4) Hertzsch, T.; Budde, F.; Weber, E.; Hulliger, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2281−2284.
(5) (a) Elias, A. J.; Shreeve, J. M. *Adv. Inorg. Chem.* **2001**, *52*, 335−358. (b) Muralidharan, K.; Reddy, N. D.; Elias, A. J. *Inorg. Chem.* **2000**, *39*, 3988−3994.
(6) (a) Brandt, K.; Siwy, M.; Porwolik-Czomperlik, I.; Silbering, J. J. *Org. Chem.* **2001**, *66*, 5701−5712. (b) Muralidharan, K.; Venugopalan, P.; Elias, A. J. *Inorg. Chem.* **2003**, *42*, 3176−3182.

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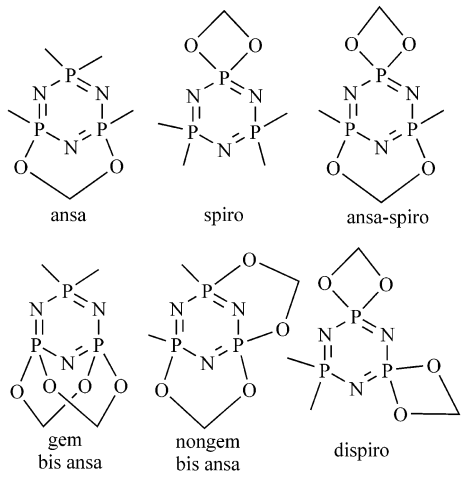


Figure 1. Possible structural isomers during the secondary stage of substitution on phosphazene ring by difunctional reagents.

different P atoms of the N_4P_4 ring.[7] The sensitivity of ansa substituted fluorophosphazenes to undergo ansa to spiro transformation has also been explored in detail recently.[5b,6b,8]

To understand the mode of substitution on the fluorophosphazene ring during the secondary stage of substitution, we have performed reactions of bifunctional reagents with monoansa and monospiro substituted trimeric fluorophosphazenes. We report herein the first examples of bisansa and ansa−spiro substituted fluorinated cyclotriphosphazenes, the latter being obtained as two different structural isomers. Involvement of C−H···F−C hydrogen bonding as a motif in supramolecular self-assembly has been of considerable interest recently.[9] While recent reports describe C−H···Cl−P[6b,10] and C−H···N[11] weak interactions involved in substituted chlorophosphazenes, to the best of our knowledge there are no reports on the C−H···F−P weak interactions in fluorophosphazenes. In this paper, we report the first detailed analysis of C−H···F−P weak interactions shown by substituted fluorinated cyclophosphazenes.

Results and Discussion

A reaction of the dilithiated propanediol, $LiO(CH_2)_3OLi$, at −80 °C, with *endo*-monoansa substituted fluorophosphazene $FcCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ (**1**),[5b] yielded the first example of a nongeminal, bisansa substituted trimeric fluorophosphazene {1,3-[$FcCH_2P(S)(CH_2O)_2$]}{1,5-[$CH_2(CH_2O)_2$]}$N_3P_3F_2$ (**4**) as well as an ansa−spiro substituted fluorophosphazene {1,1-[$CH_2(CH_2O)_2$]}{3,5-[$FcCH_2P(S)(CH_2O)_2$]}$N_3P_3F_2$ (**5**) (Scheme 1). Compounds **4** and **5** were separated by column chromatography over silica gel and were characterized by $^{31}P\{^1H\}$ and ^{19}F NMR spectral studies and mass spectral analysis. The structure of compound **5** was also determined by X-ray crystallography.

Unlike the reactions of chlorophosphazenes, where cation involved macromolecular assistance was required to prepare ansa−spiro as well as bisansa substitution on the N_3P_3 ring,[12] this reaction of dilithiated diol at −80 °C afforded a straightforward method to realize ansa−spiro and bisansa substitution on the N_3P_3 ring. For the bisansa compound, the substitution was found to be nongeminal, which is in stark contrast to the observations with cyclic chlorophosphazenes, where geminal bisansa compounds were found to be the major or exclusive products. For such a geminal ansa substitution, the presence of an ansa ring, which also constituted a macrocycle having a cation, was reported to be a requirement.[12]

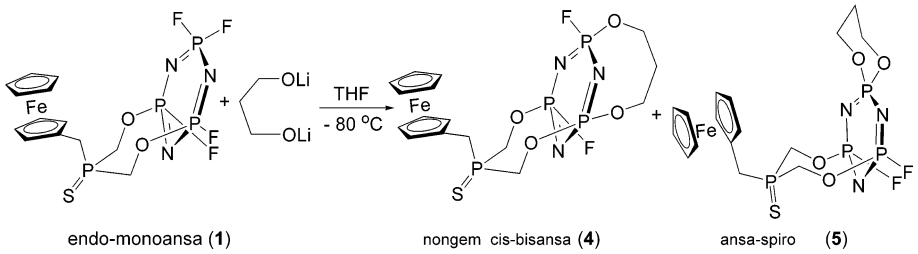
The reaction of the disodium salt of propanediol with **1** was also initially found to yield the bisansa and the ansa−spiro substituted products **4** and **5**, but with passage of time these compounds transformed to dispiro substituted fluorophosphazenes. A similar reaction of the dilithiated diol, $FcCH_2P(S)(CH_2OLi)_2$, with **1** resulted in a complex reaction mixture, and no pure compounds could be isolated by column chromatography or by crystallization methods. The complexity of the reaction mixture was possibly due to the presence of a number of structural isomers, such as the endo−endo, exo−exo, or endo−exo of the bisansa and the ansa−spiro substituted products, which are obtainable from the reaction of this diol with $N_3P_3F_6$ during multiple stages of substitution.

In contrast, reactions of the dilithiated diols, $RCH_2P(S)(CH_2OLi)_2$ (R = Fc, C_6H_5), with the corresponding monospiro substituted fluorophosphazenes,[5b] [$RCH_2P(S)(CH_2O)_2PN$](F_2PN)$_2$ [R = Fc (**2**), C_6H_5 (**3**)], at −80 °C resulted in the formation of novel isomers of ansa−spiro substituted fluorophosphazenes, *endo*-{3,5-[$RCH_2P(S)(CH_2O)_2$]}{1,1-[$RCH_2P(S)(CH_2O)_2$]}$N_3P_3F_2$ [R = Fc (**6**), C_6H_5 (**7**)] and *exo*-{3,5-[$RCH_2P(S)(CH_2O)_2$]}{1,1-[$RCH_2P(S)(CH_2O)_2$]}$N_3P_3F_2$ [R = Fc (**8**), C_6H_5 (**9**)] (Scheme 2). Compounds **6**−**9** were separated by column chromatography over silica gel and characterized by $^{31}P\{^1H\}$ and ^{19}F NMR spectral studies and mass spectral analysis. In addition, compound **6** was also structurally characterized by X-ray crystallography.

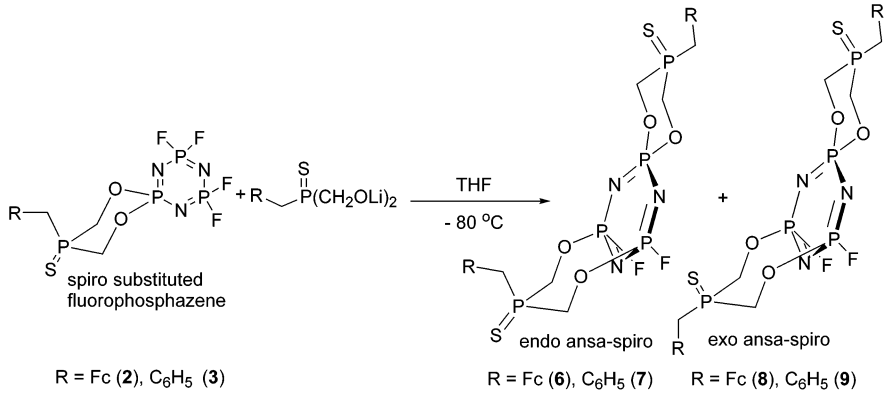
Interestingly, the reactions of the dilithiated diols, $RCH_2P(S)(CH_2OLi)_2$ (R= Fc, C_6H_5), with $N_3P_3F_6$ at 0 °C, were found to result in the formation of the ansa−spiro substituted fluorophosphazenes **6**−**9**, along with the endo $RCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ (R = Fc, C_6H_5) and exo $RCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ (R = Fc, C_6H_5) monoansa substituted fluorophosphazenes, which we had reported earlier.[5b] No bisansa substituted products were isolable from this reaction mixture. These studies indicate that the formation of ansa−spiro substituted derivatives is the preferred pathway at the secondary stage of substitution of trimeric fluorophosphazenes irrespective of the nature of the precursor

(7) Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Whittle, R. R.; Parvez, M. *Organometallics* **1986**, *5*, 1626.
(8) Elias, A. J.; Twamley, B.; Shreeve, J. M. *Inorg. Chem.* **2001**, *40*, 2120−2126.
(9) (a) Desiraju, G. R. *Acc. Chem. Res.* **2002**, *35*, 565. (b) Thalladi, V. R.; Weiss, H. C.; Bläser, D.; Boese, R.; Nangia, A.; Desiraju, G. R. *J. Am. Chem. Soc.* **1998**, *120*, 8702−8710. (c) Desiraju, G. R.; Steiner, T. *The weak hydrogen bond*; Oxford University Press: Oxford, 1999; p 20.
(10) Chandrasekhar, V.; Athimoolam, A.; Dastagiri Reddy, N.; Nagendran, S.; Steiner, A.; Zacchini, S.; Butcher, R. *Inorg. Chem.* **2003**, *42*, 51−59.
(11) Bickley, J. F.; Law, R. B.; Lawson, G. T.; Richards, P. I.; Rivals, F. Steiner, A.; Zacchini, S. *J. Chem. Soc., Dalton Trans.* **2003**, 1235−1244.
(12) Brandt, K.; Porwolik-Czomperlik, I.; Siwy, M.; Kupka, T.; Shaw, R. A.; Davies, D. B.; Hursthouse, M. B.; Sykara, G. A. *J. Am. Chem. Soc.* **1997**, *119*, 12432−12440.

Scheme 1



Scheme 2



being ansa or spiro, and bisansa substitution is less favored in these reactions.

Characterization of Bis−Ansa Fluorophosphazene (4). In the $^{31}P\{^1H\}$ NMR spectrum of the bisansa compound **4**, the peak corresponding to the P═S moiety appeared as a singlet at 48.61 ppm, which is the typical region for ansa substituted fluorophosphazenes. The OPF phosphorus was observed as two different sets of a doublet of multiplets, at 24.64 and 21.01 ppm, with $^1J_{PF}$ coupling constants of 890 and 886 Hz, respectively, indicating the difference in the two OPF groups that are present in the bisansa compound **4**. The same difference was also observed in the ^{19}F NMR spectrum, in which the fluorines of the OPF groups were observed as two different sets of doublet of multiplets, which appeared at −75.46 and −72.79 ppm, with $^1J_{PF}$ coupling constants of 891 and 885 Hz, respectively.

The first ansa−spiro substituted chlorophosphazenes was reported in 1984,[13] and the first examples of bisansa substituted chlorophosphazenes were reported only recently with geminal bisansa substitution seen as the preferred substitution route.[14] For the bisansa compound prepared in the present study, one can expect four possible structures as shown in the Figure 2.

For structure a, the presence of the PF_2 group would have shown a triplet in the ^{31}P NMR spectrum with a $^1J_{PF}$ coupling constant around 900 Hz. The absence of any such triplets in the $^{31}P\{^1H\}$ NMR spectrum and the presence of only doublets rules out this structure. In the two non gem ansa structures, b and c, one or both of the diols have formed trans-ansa substitution. This kind of trans-ansa substitution is not possible with short chain diols such as the ones what we have chosen for this study, as they are not of sufficient length to span over the two sides of the phosphazene plane. The structures b and c can therefore be ruled out. Thus, the only possible structure for bisansa compound **4** is the nongeminal cis-bisansa configuration d, which is also in conformity with the presence of two types of phosphorus and fluorine signals for the OPF moiety that are observed in the $^{31}P\{^1H\}$ and ^{19}F NMR spectra of this compound. It was of interest to note that the only other example of a nongem bisansa compound of chlorophosphazenes reported in the literature belongs to the nongem cis−trans-ansa configuration b. The trans-ansa configuration in this case was made possible by the use of the diol $H(OCH_2CH_2)_5OH$ which formed a large macrocyclic ring.[12]

In the $^{31}P\{^1H\}$ NMR spectrum of the compounds, **5**−**9**, the peaks corresponding to the P═S moiety appeared in the range 45.31−49.14 ppm, which was the expected range for ansa substitution in these compounds. The positions of the peaks corresponding to the P═S moiety in the spirocyclic portion of the ansa−spiro compounds **6**−**9** differ only slightly from that of the monospiro compound. The fluorine chemical shifts of the OPF groups in compounds **8** and **9** appeared at −78.90 and −79.33 ppm, respectively, while that of compound **5** appeared at −71.61 ppm.

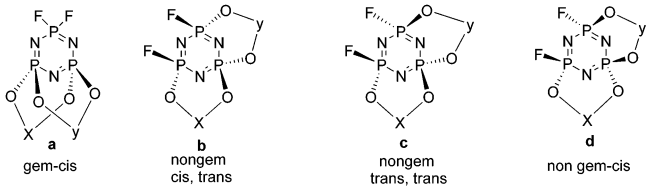


Figure 2. Possible structural isomers for the bisansa substituted compound **4**.

(13) Contractor, S. R.; Hursthouse, M. B.; Parkes, H. G.; Shaw, L. S.; Shaw, R. A.; Yilmaz, H. *J. Chem. Soc., Chem. Commun*. **1984**, 675−676.

(14) (a) Brandt, K.; Porwolik, I.; Olejnik, A.; Shaw, R. A.; Davies, D. B.; Hursthouse, M. B.; Sykara, G. A. *J. Am. Chem. Soc*. **1996**, *118*, 4496−4497. (b) Brandt, K.; Porwolik, I.; Siwy, M.; Kupka, T.; Shaw, R. A.; Davies, D. B.; Hursthouse, M. B.; Sykara, G. A. *J. Am. Chem. Soc*. **1997**, *119*, 1143−1144.

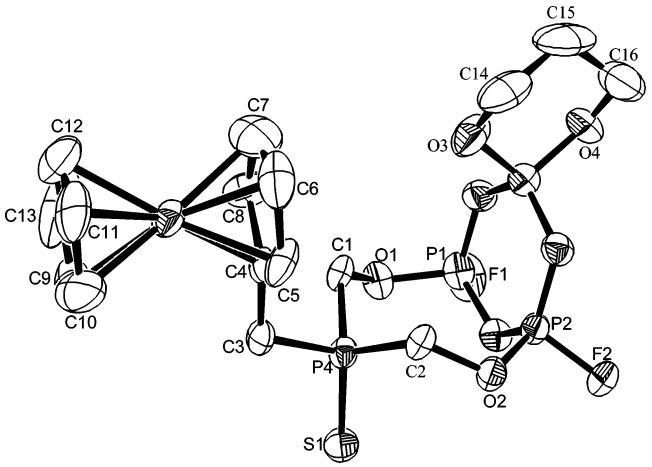


Figure 3. ORTEP diagram (50% probability ellipsoids) showing the molecular structure of the compound **5**.

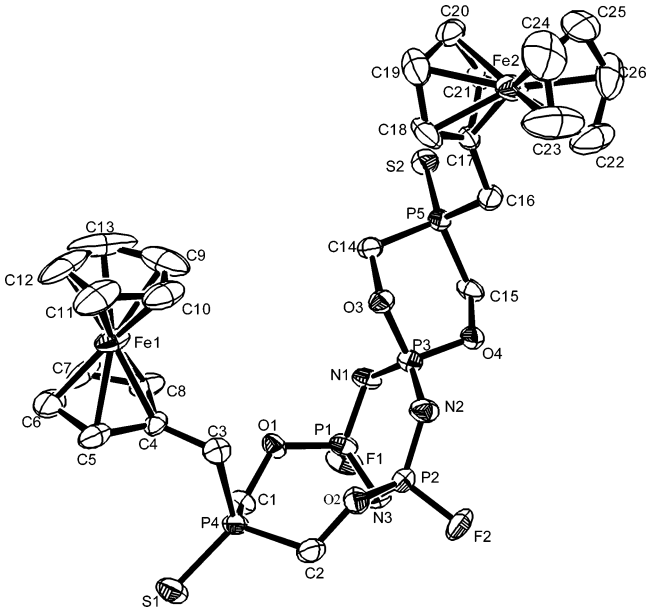


Figure 4. ORTEP diagram (30% probability ellipsoids) showing the molecular structure of the compound **6**.

Structures of Ansa−Spiro Substituted Compounds. The molecular structures of compounds **5** and **6** are depicted in Figures 3 and 4, respectively.

In the crystal structure of compound **6**, the eight-membered ring, formed by the ansa substitution, indicates a boat−chair conformation, which is the conformation normally observed by almost all eight-membered rings that are formed by ansa substitution on the N_3P_3 ring.[5b,6b] The N_3 nitrogen, which is between the two phosphorus atoms involved in the ansa substitution, is flanked away from the plane defined by the other five atoms of the N_3P_3 ring to a distance of 0.432(5) Å. This deviation, which indicates a strain on the phosphazene ring, was also observed in the endo-monoansa (0.43 Å) and exo-monoansa (0.23 Å) compounds that were reported earlier.[5b] In contrast, the eight-membered ansa ring of compound **5** depicts a crown conformation, which is unusual when compared with the boar−chair conformation of known examples of ansa substituted fluorophosphazenes.

Theoretical calculations on the energy of the eight-membered C−C rings have shown that the boat−chair conformation was lowest in energy among the 10 possible conformers.[15] The crown conformation is also a stable conformation but has slightly higher energy compared to that of the boat−chair conformation. During the reaction with dianion of the propanediol, the boat−chair conformation of the monoansa compound **1** has flipped resulting in a crown conformation in compound **5**. One of the possible reasons for this change of conformation from boat−chair to crown is that, in compound **5**, the N_3 nitrogen of the N_3P_3 ring flanked between the two ansa forming phosphorus atoms is at a distance of 0.213(5) Å away from the plane defined by the rest of the atoms of the phosphazene ring. This nitrogen was originally deviating at a distance of 0.433(5) Å in the starting endo-monoansa compound **1**.[5b] This indicates that changing the conformation of the eight-membered ring from boat−chair to crown relieves to some extent the strain on the phosphazene ring. The possibility for the other conformation to form is not ruled out, as the $^{31}P\{^1H\}$ spectral analysis of the reaction mixture indicated the presence of two more minor compounds with peaks in the region 45.1−48.5 ppm in very poor yields, which could not be isolated.

Weak Hydrogen Bonding Interactions in Substituted Fluorophosphazenes. Unlike the fluoride ion, which forms significant hydrogen bonds even with C−H groups, the so-called "organic fluorines" of the C−F group form relatively very weak and often elusive C−H···F−C bonding interactions which often get masked in the presence of hydrogen bonds involving other elements. Desiraju and co-workers[9] as well as others[16,17] have recently designed molecules which elegantly demonstrate weak C−H···F−C interactions in fluorinated aromatic compounds in the absence of other hydrogen bonding interactions. Although C−H···F−P[18] and C−H···F−B[19] interactions have been observed in ionic molecules involving moieties such as PF_6^- and BF_4^-, no systematic study on weak interactions has been performed on molecules having purely covalent P−F bonds. In many ways, fluorophosphazenes resemble organofluorine compounds as they are covalent molecules, many of which are volatile, and the presence of the electronegative fluorines on these heterocycles reduces drastically the basicity of the ring nitrogens compared to those of chlorophosphazene derivatives. Therefore, it was of interest to search for weak C−H···F−P interactions on fluorophosphazene derivatives.

A detailed analysis of the crystal structures of compounds **5** and **6** reveals the existence of interesting C−H···F−P weak hydrogen bonding interactions. This prompted us to study C−H···F−P interactions in other crystal structures of cyclic fluorophosphazenes, fluorinated thionyl phosphazenes, and fluorophosphazenate anions as well. Considering the sum of the van der Waals radii of fluorine and hydrogen atoms

(15) Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of organic compounds*; John Wiley: New York, 1994; p 765.
(16) Chandrasekhar, V.; Nagendran, S.; Gopal, K.; Steiner, A.; Zacchani, S. *Chem. Commun*. **2003**, 862−863.
(17) Lee, H.; Knobler, C. B.; Hawthorne, M. F. *Chem. Commun*. **2000**, 2485−2486.
(18) Grepioni, F.; Cojazzi, G.; Draper, S. M.; Scully, N.; Brago, D. *Organometallics* **1998**, *17*, 296−307.
(19) Brammer, L.; Klooster, W. T.; Lemke, F. R. *Organometallics* **1996**, *15*, 1721.

Table 1. C−H···F−P Weak Hydrogen Bonding Parameters for Substituted Fluorinated Phosphazenes, Thionyl Phosphazenes, and Phosphazenate Anions

compd	C···H···F (Å)	H···F (Å)	C−H···F (deg)	ref
5	3.34(1)	2.61(1)	135.3(4)	this work
	3.40(1)	2.63(1)	136.6(6)	
6	3.15(1)	2.58(1)	117.0(3)	this work
endo-1,3-[$FcCH_2P(S)(CH_2O)_2$]$N_3P_3F_4$ (**1**)	3.14(1)	2.66(6)	111.3(4)	5b
exo-1,3-[$FcCH_2P(S)(CH_2O)_2$]$N_3P_3F_4$	3.51(1)	2.58(5)	146.7(4)	5b
	3.48(1)	2.66(5)	136.7(4)	
	3.30(1)	2.67(6)	133.1(5)	
	3.40(1)	2.60(7)	151.9(5)	
endo-1,3-[$C_6H_5CH_2P(S)(CH_2O)_2$]$N_3P_3F_4$	3.36(1)	2.49(6)	145.6(4)	5b
1,1-[$OCH_2(CF_2)_2CH_2O$]$N_4P_4F_6$	3.41(1)	2.58(1)	140.4(2)	8
	3.02(1)	2.56(1)	108.1(2)	
1,1-[$S(CH_2)_2O$]$N_3P_3F_4$	3.31(2)	2.57(3)	128.5(2)	21
1,1-[$S(CH_2)_3O$]$N_3P_3F_4$	3.35(1)	2.69(5)	127.8(4)	21
1,1-[$S(CH_2)_2S$]$N_3P_3F_4$	3.36(1)	2.70(4)	125.0(3)	21
1,1-[$S(CH_2)_3S$]$N_3P_3F_4$	3.65(1)	2.60(12)	161.9(9)	21
	3.52(1)	2.64(12)	138.4(9)	
$N_3P_3F_4$[1,2-$C_6H_4O_2$]	3.19(1)	2.61(3)	119.0(1)	21
$N_3P_3F_4$[1,2-$C_6H_4O_2$]$_2$	3.49(6)	2.68(5)	148.9(4)	21
$N_3P_3F_4$[2,3-$C_{10}H_6O_2$]	3.40(1)	2.61(1)	138.3(3)	21
$N_3P_3F_4$[2,2′-$C_{12}H_8O_2$]	3.27(1)	2.60(6)	129.0(5)	21
$N_4P_4F_9^-$ [a]	3.28(2)	2.44(2)	142.7(8)	22
	3.47(1)	2.59(1)	149.6(5)	
	3.51(5)	2.64(4)	147.5(7)	
	3.41(1)	2.51(1)	153.5(4)	
	3.49(1)	2.57(1)	157.4(5)	
	3.39(2)	2.69(1)	128.1(6)	
$N_6P_6F_{13}^-$ [a]	3.55(1)	2.65(3)	152.0(1)	22
	3.31(1)	2.44(2)	147.5(1)	
	3.48(1)	2.70(3)	137.4(2)	
	3.30(1)	2.48(4)	140.5(3)	
	3.24(1)	2.58(4)	125.6(3)	
	3.46(2)	2.59(3)	147.7(2)	
NSO(4-^{t}BuC_6H_4)[NPF_2]$_2$	3.16(1)	2.49(1)	128.2(4)	23
	3.61(1)	2.65(1)	173.8(5)	

[a] The C−H bonds belong to the NMe_2 groups of the cation $(Me_2N)_3S^+$.

as per Bondi,[20] we restricted the maximum distance between the H and F atoms to 2.70 Å and studied the C−H···F−P hydrogen bonding interactions.[9c] The C−H···F−P hydrogen bonding parameters of substituted fluorinated phosphazenes, thionyl phosphazenes, and phosphazenate anions are listed in Table 1.

As expected, the C−H···F−P interactions for the phosphazenate anions $N_4P_4F_9^-$ and $N_6P_6F_{13}^-$ were found to be the strongest as indicated by an H···F distance of 2.44(2) Å. Among the neutral compounds, the thionylphosphazene NSO(4-^{t}BuC_6H_4)[NPF_2]$_2$ [2.49(1) Å] and the substituted fluorophosphazene *endo*-1,3-[$C_6H_5CH_2P(S)(CH_2O)_2$]$N_3P_3F_4$ [2.49(6) Å] showed relatively significant interactions. The ansa−spiro compounds **5** and **6** showed C−H···F−P interactions in the range 2.58−2.62 Å which is well with in the accepted range of C−H···F interactions. The two-dimensional structure developed by C−H···F−P interactions in compound **5** is shown in Figure 5. [The metric parameters involved in C(15)−H(15B)···F(2) interactions are C(15)−H(15B) = 0.97(1) Å, H(15B)−F(2) = 2.63(1) Å, C(15)−F(2) = 3.40(1) Å, C(15)−H(15B)−F(2) = 136.6(6)°, and symmetry code = $1 + x, y, z$. In C(5)−H(5)···F(1), interactions are C(5)−H(5) = 0.93(1) Å, H(5)−F(1) = 2.61(1) Å, C(5)−F(1) = 3.34(1) Å, C(5)−H(5)−F(1) = 135.3(4)°, and symmetry code = $x, -1 + y, z$.] It can be seen from the figure that one of two nongeminal fluorine atoms interacts with the hydrogen atom of the cyclopentadienyl ring to form a linear chain of molecules. These chains are linked further in parallel by H···F interactions between a second fluorine and hydrogen atom in the propanediol moiety to form a two-dimensional network of the molecules. In compound **6**, the fluorine atoms interact with hydrogen atoms in the $FcCH_2$ group to form a dimer as shown in Figure 6. [The metric parameters involved in C(16)−H(16B)···F(2) are C(16)−H(16B) = 0.97(1) Å, H(16B)−F(2) = 2.58(1) Å, C(16)−F(2) = 3.14(1) Å, C(16)−H(16B)−F(2) = 117.0(3)°, and symmetry code is $-x, -y, 1 - z$.]

Transformations of Ansa−Spiro Substituted Compounds to Dispiro Substituted Compounds. The ansa−spiro substituted compounds **6** and **8** were treated separately with catalytic amounts of CsF in THF, and the course of the reaction was monitored by time-dependent $^{31}P\{^1H\}$ NMR spectroscopy. After the entire amount of compound **6** or **8** disappeared, the analysis of the reaction mixture by $^{31}P\{^1H\}$, ^{19}F, and ^1H NMR spectra indicated the formation of three isomers of dispiro compounds. Extremely close mobility for the three compounds precluded separation of these compounds by column chromatography over silica gel or alumina. An attempted sublimation also failed to separate this mixture. However, one of the compounds crystallized out from the solution of a mixture in ethyl acetate/hexane. This compound was characterized as *dispiro*-{1,1,3,3-[$FcCH_2P(S)(CH_2O)_2]_2$}$N_3P_3F_2$ (**10**) by NMR and mass spectral studies.

As desilylation reactions of silylated diols exclusively give spirocyclic compounds, we reacted 2 mol of the disilylated diol, $FcCH_2P(S)(CH_2OSiMe_3)_2$, with 1 mol of $N_3P_3F_6$ in the presence of catalytic amount of CsF in THF. The spectral data obtained for this reaction mixture were compared with that of the mixture obtained from the transformation study and found that this reaction also yielded the same mixture of three dispiro compounds. Analysis of the crystal structures of spirocyclic compounds resulting from the reactions of the phosphine sulfide diol $RCH_2P(S)(CH_2OH)_2$ (R = Fc, C_6H_5) indicates that, as part of a rigid six-membered chair conformation, the S atom of the P═S group always occupies the equatorial position.[5b,6b] This observation was also applicable to the spiro substituted compounds of carbaphosphazene[24] and thionylphosphazene[25] as well. Considering this factor, one can propose possible isomeric structures for the three dispiro compounds as given in Figure 7. However

(20) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(21) Vij, A.; Geib, S. J.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1996**, *35*, 2915−2929.

(22) Lork, E.; Böhler, D.; Mews, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2696−2698.

(23) Elias, A. J.; Twamley, B.; Shreeve, J. M. *Inorg. Chem.* **2001**, *40*, 2120−2126.

(24) Reddy, N. D.; Elias, A. J.; Vij, A. *Inorg. Chem. Commun.* **2000**, *3*, 29−31.

(25) (a) Ramakrishna, T. V. V.; Elias, A. J. *J. Organomet. Chem.* **2001**, *637−639*, 382−389. (b) Ramakrishna, T. V. V.; Elias, A. J.; Vij, A. *J. Organomet. Chem.* **2000**, *602*, 125−132.

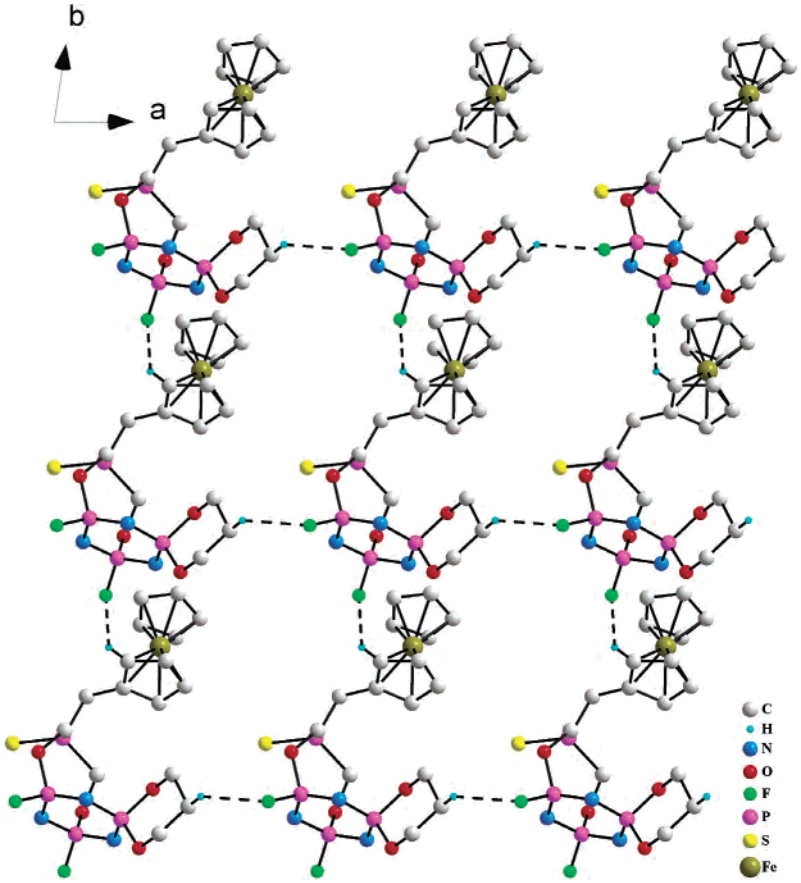


Figure 5. Two-dimensional network of the molecules developed by C−H···F−P interactions in the crystal structure of the ansa−spiro compound **5** (viewed through *c* axis).

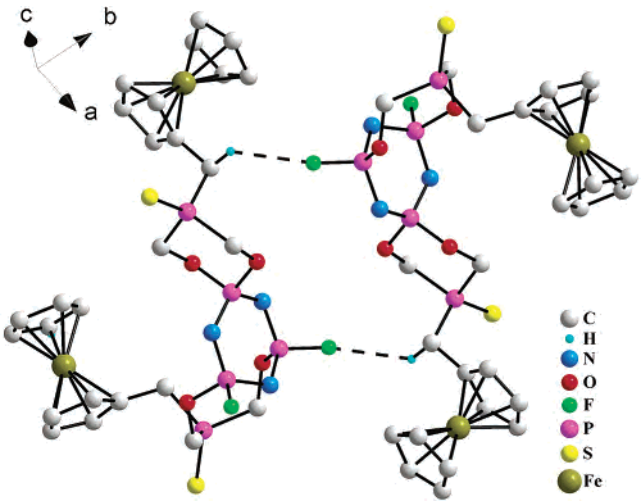


Figure 6. Dimer formed by the C−H···F−P interactions in the crystal structure of the ansa−spiro compound **6**.

assignment of the spectral data to each isomeric structure separately proved quite difficult.

The transformations of ansa−spiro substituted compounds to the dispiro isomers were slower than transformation of monoansa compounds to their spiro isomers. Time-dependent NMR studies indicate that, to complete the transformation from ansa−spiro to dispiro isomers, compounds **6** and **8** take 14 h, while the corresponding monoansa compounds take only 3−4 h for complete transformation to their spiro isomer. An attempted transformation study of the bisansa compound **4** was inconclusive as the study led to a complex mixture of products.

We have also attempted ansa to spiro transformation of the ansa−spiro substituted compound **5** in the presence of CsF in THF and monitored the reaction by $^{31}P\{^{1}H\}$ NMR spectroscopy. As expected, there was only one peak corresponding to the P═S moiety in the spiro region at 20.11 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum. A triplet of multiplets corresponding to the PF_2 group also started appearing after 16 h at 7.76 ppm with a coupling constant of 906 Hz. Purification of this reaction mixture by column chromatography yielded the dispiro compound {1,1-[$FcCH_2P(S)(CH_2O)_2$]}{3,3-[$OCH_2CH_2CH_2O$]}$N_3P_3F_2$ (**11**) (Scheme 3). The transformation of ansa−spiro compound **5** to dispiro compound **11** was relatively slower with only partial transformation observed even after 11 days of stirring at room temperature.

Conclusions

In conclusion, we have carried out the first systematic study on the reactions of monoansa and monospiro substituted fluorophosphazenes with difunctional reagents. The study indicates that the formation of ansa−spiro substituted derivatives is the preferred pathway at the secondary stage of substitution of trimeric fluorophosphazenes irrespective of the nature of the precursor being ansa or spiro. The study has resulted in the synthesis of five novel examples of ansa−

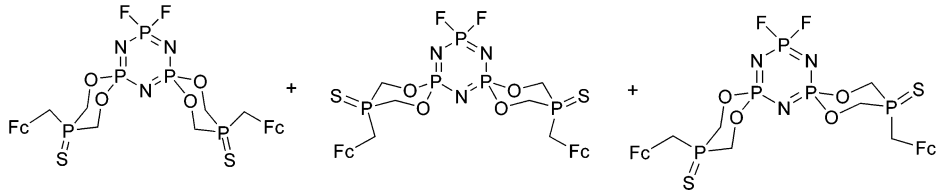
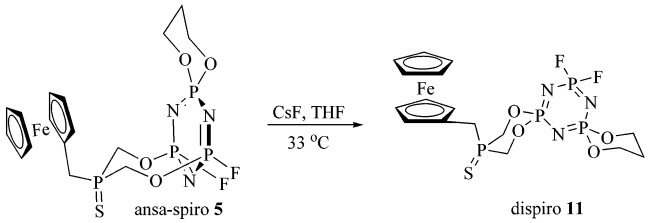


Figure 7. Possible structural isomers of the dispiro compound -{1,1,3,3-[$FcCH_2P(S)(CH_2O)_2]_2$}$N_3P_3F_2$.

Scheme 3



spiro substituted fluorophosphazenes and nogem cis-bisansa substituted fluorophosphazenes, which are all the first examples of their kind. All the ansa−spiro compounds were found to transform to their dispiro isomer in the presence of CsF as catalyst, which further confirms the higher thermodynamic stability of spirocylic isomers over the ansa analogues. The crystal structures of the ansa−spiro compounds show typical boat−chair conformations as well as rare crown conformations for eight-membered ansa rings. The C−H···F−P weak interactions observed in the ansa−spiro substituted fluorophosphazenes were determined and compared with similar weak C−H···F−P interactions in substituted fluorinated phosphazenes, thionylphosphazenes, and fluorophosphazenate anions. The C−H···F−P distances were found as low as 2.44(2) Å for phosphazenate anions $N_4P_4F_9^-$ and $N_6P_6F_{13}^-$ and 2.49(6) Å for ansa substituted fluorophosphazene 1,3-$[C_6H_5CH_2P(S)(CH_2O)_2]N_3P_3F_4$.

Experimental Section

General Procedures. A conventional vacuum line equipped with a dry nitrogen apparatus and Schlenk glassware was used for all reactions. Reactions and workup procedures were carried out under an atmosphere of dry nitrogen. $N_3P_3F_6$ was prepared from $N_3P_3Cl_6$ (Fluka) according to the literature method[26] and was purified by fractional distillation (caution: $N_3P_3F_6$ is a potentially toxic compound and has high vapor pressure at room temperature). The synthesis of the diol, $RCH_2P(S)(CH_2OH)_2$ (R = Fc, C_6H_5), disilylated diol $FcCH_2P(S)(CH_2OSiMe_3)_2$, the monoansa compound *endo*-{$FcCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$}, and the monospiro compound $RCH_2P(S)(CH_2O)_2PN](F_2PN)_2$ (R = Fc, C_6H_5) were carried out as given in the literature.[5b,27] 1,3-Propanediol was used as obtained from Lancaster. Hexane, ethyl acetate, dichloromethane, and tetrahydrofuran were distilled and dried by standard procedures.

Instrumentation. ^1H, $^{31}P\{^1H\}$, ^{19}F, and $^{13}C\{^1H\}$ NMR spectra were recorded using a JEOL JNM-LA 400 FT NMR spectrometer with $CDCl_3$, as solvent. The chemical shifts are reported with respect to the internal standards, TMS (for ^1H), 85% H_3PO_4 [for $^{31}P\{^1H\}$], and $CFCl_3$ (for ^{19}F). Mass spectra were obtained on a JEOL D-300 spectrometer. Elemental analyses were carried out Carlo-Erba CHNO 1108 elemental analyzer. IR spectra were recorded as KBr pellets on a Bruker vector 22 FTIR spectrometer operating at 400−4000 cm^{-1}.

X-ray Diffraction Studies. The X-ray diffraction data for compounds **5** and **6** were collected on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by using WINGX version 1.64.04, a crystallographic collective package.[28] The structures were solved initially by SIR-97[29] and refined with SHELX-97[30] which are incorporated in the WINGX program. The structures were refined against F^2 with a full-matrix least-squares algorithm. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated by HFIX command and refined isotropically. The X-ray data pertaining to data collection, crystal systems, and structure solution as well the selected bond distances and angles for the compounds **5** and **6** are given in the Supporting Information.

Reaction of 1 with 1,3-Propanediol. The diol $CH_2(CH_2OH)_2$ (0.11 g, 1.5 mmol) was treated with *n*-BuLi (1.87 mL, 3.0 mmol) in dry THF (10 mL) at −80 °C, and the mixture was stirred for 4 h before the endo-monoansa compound $FcCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ (0.80 g, 1.5 mmol) dissolved in dry THF (20 mL) was added at −80 °C under nitrogen atmosphere. After 12 h of stirring at room temperature, the solvent was removed under vacuum, the residue dissolved in minimum amount of dichloromethane and the LiF formed filtered off using a frit. After analysis by TLC, the reaction mixture was separated by column chromatography, and two products were isolated. The first compound which came out of the column was identified as the ansa−spiro compound, {1,1-$[CH_2(CH_2O)_2]$}{3,5-$[FcCH_2P(S)(CH_2O)_2]$}$N_3P_3F_2$ (**5**). Yield: 0.26 g, 30.4%. Mp: 141 °C. IR (KBr) (cm^{-1}): 2924 s, 1467 w, 1413 w, 1254 vs, 1142 w, 1042 vs, 968 s, 919 w, 879 s, 841 s, 809 w, 761 s, 460 vs. NMR: ^1H, δ 4.44−4.63 (m, 8H, CH_2O), 4.31−4.34 [m, 2H, (ηC_5H_4)], 4.12−4.14 [m, 2H, (ηC_5H_4)], 4.11 [s, 5H, (ηC_5H_5)], 3.15 [d (J = 11 Hz), 2H, $FcCH_2P$], 2.02 [quintet, 2H, $CH_2CH_2CH_2$]; $^{31}P\{^1H\}$, δ 48.61 (s, P═S ansa) 13.19 [dd ($^2J_{PNP}$ = 106.7 Hz), OPO], 16.09 [md ($^1J_{PF}$═916.0 Hz), OPF]; ^{19}F, δ −71.61 [md ($^1J_{PF}$ = 931.2 Hz), OPF]; $^{13}C\{^1H\}$, δ 25.96 (s, $CH_2CH_2CH_2$), 28.07 ($FcCH_2$), 66.68 [d (J = 45 Hz), CH_2O], 67.93 [d (J = 42 Hz), CH_2O], 68.89 [s, C(5) and C(8)], 69.07 [s, C(9)−C(13)], 70.01 [s, C(6)−C(7)]. MS (FAB) [*m*/*e* (species) intensity]: 569 (M^+) 100, 307 [$FcCH_2P(S)(CH_2O)(CH_2)^-H^+$] 18, 199 ($FcCH_2$) 36, 154 ($N_3P_3F_1$) 78, 135 ($N_3P_3$) 68. Anal. Calcd for $C_{16}H_{21}O_4P_4N_3F_2S_1Fe$ (%): C, 33.76; H, 3.72; N, 7.38. Found: C, 33.58; H, 3.54; N, 7.52.

The second compound was identified as the bisansaphosphazene {1,3-$[FcCH_2P(S)(CH_2O)_2]$}{1,5-$[CH_2(CH_2O)_2]$}$N_3P_3F_2$ (**4**). Yield: 0.19 g, 22.2%. Mp: 138 °C. IR (KBr)(cm^{-1}): 2920 w, 1460 s, 1264 vs, 1147 w, 1051 vs, 962 w, 875 s, 851 s, 822 s, 761 s, 465

(26) Schmutzler, R. *Inorg. Synth.* **1967**, *9*, 75.
(27) Goodwin, N. J.; Henderson, W.; Nicholson, B. K.; Sarfo, J. K.; Fawcett, J.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1997**, 4377.
(28) Farrugia, L. J. *WinGX−A windows program for crystal structure analysis*; University of Glasgow: Glasgow, 1998. Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.
(29) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.
(30) Sheldrick, G. M. *SHELX97, Programs for Crystal Structure Analysis (Release 97-2)*; Institüt für Anorganische Chemie der Universität: Göttingen, Germany, 1998.

s. NMR: ^{1}H, δ 4.77−4.67 and 4.52−4.34 (two set of multiplets, 8H, CH_2O), 4.26−4.29 [m, 2H, (ηC_5H_4)], 4.12−4.16 [m, 2H, (ηC_5H_4)], 4.09 [s, (ηC_5H_5)], 3.40 to 3.17 (m, 2H, $FcCH_2P$), 2.24−2.02 (m, $CH_2CH_2CH_2$); ^{31}P{^{1}H}, δ 46.10 (s, P═S ansa), 18.46 [dd ($^2J_{PNP}$ = 94.1 Hz), OPO], 24.64 [md ($^1J_{PF}$ = 891.0 Hz), OPF] 21.01 [md ($^1J_{PF}$ = 886.1 Hz), OPF]; ^{19}F, δ −75.46 [md ($^1J_{PF}$ = 891.1 Hz), OPF], −72.79 [md ($^1J_{PF}$ = 885.5 Hz), OPF];^{13}C{^{1}H}, δ 30.01 (s, $CH_2CH_2CH_2$), 29.15 (s, $FcCH_2$), 67.91 [d (J = 45 Hz), CH_2O], 68.87 [d (J = 42 Hz), CH_2O], 69.12 [s, β-C], 69.37 [s, η-C_5H_5], 71.01 [s, γ-C]. MS (FAB) [*m*/*e* (species) intensity]: 569 (M^+) 100, 307 [$FcCH_2P(S)(CH_2O)(CH_2)^-H^+$] 18, 199 ($FcCH_2$) 16, 154 ($N_3P_3F_1$) 40, 135 ($N_3P_3$) 26. Anal. Calcd for $C_{16}H_{21}O_4P_4N_3F_2S_1Fe$ (%): C, 33.76; H, 3.72; N, 7.38. Found: C, 33.66; H, 3.47; N, 7.42.

Reaction of Compound 2 with $FcCH_2P(S)(CH_2OLi)_2$. The diol $FcCH_2P(S)(CH_2OH)_2$ was treated with *n*-BuLi (0.37 mL, 6.0 mmol) in dry THF (10 mL) at −80 °C, and the mixture was stirred for 4 h before the spiro compound $FcCH_2P(S)(CH_2O)_2PN](F_2PN)_2$ (0.16 g, 3.0 mmol) dissolved in dry THF (10 mL) was added at −80 °C under nitrogen atmosphere. The reaction was worked up as described for compounds **4** and **5**. The first compound which came out of the column was identified as *endo*-{3,5-[$FcCH_2P(S)(CH_2O)_2$]}{1,1-[$FcCH_2P(S)(CH_2O)_2$]}$N_3P_3F_2$ (**6**). Yield: 0.09 g, 36.8%. Mp: 166 °C. IR (KBr)(cm^{-1}): 3430 w, 3143 w, 3082 s, 1738 s, 1639 w, 1463 s, 1411 vs, 1263 vs, 1219 s, 1165 s, 1035 vs, 971 w, 938 s, 891 s, 872 vs, 826 s, 771 vs, 716 w, 641 s, 590 w, 533 s, 480 vs. NMR: ^{1}H, δ 4.91−4.40 (m, 8H, CH_2O), 4.30−4.15 [m, 8H, (ηC_5H_4)], 4.12 [s, 5H, (ηC_5H_5)], 4.06 [s, 5H, (ηC_5H_5)], 3.44−3.40 [m, 2H, $FcCH_2P$ (spiro)], 3.14 [d (J = 11 Hz), 2H, $FcCH_2P$ (ansa)]; ^{31}P{^{1}H}, δ 45.31 (s, P═S ansa), 20.23 [d ($^3J_{PP}$ = 16.17 Hz), P═S spiro] 14.72−16.95 (m, OPO), 15.55 [md ($^1J_{PF}$ = 911.2 Hz), OPF]; ^{19}F, δ −74.60 [md ($^1J_{PF}$ = 937.0 Hz), OPF], −73.99 [md ($^1J_{PF}$ = 937.9 Hz), OPF]; ^{13}C{^{1}H}, δ 73.40 (s, α-C of ηC_5H_4, spiro), 74.20 (s, α-C of ηC_5H_4, ansa), 69.71, 69.55, 68.98, 68.79 (all singlets, β and γ C of ηC_5H_4), 69.15 (s, ηC_5H_5), 66.82 [d (J = 41 Hz), PCH_2O ansa], 66.54 [d (J = 41 Hz), PCH_2O spiro], 28.21 [d (J = 42 Hz), $FcCH_2P$ ansa], 28.80 [d (J = 43 Hz), $FcCH_2P$ ansa]. MS (FAB) [*m*/*e* (species) intensity]: 817 (M^+) 32, 307 [$FcCH_2P(S)(CH_2O)(CH_2)^-H^+$] 100, 199 ($FcCH_2$) 58. Anal. Calcd for $C_{26}H_{30}O_4P_5N_3F_2S_2Fe_2$ (%): C, 38.21; H, 3.70; N, 5.14. Found: C, 38.16, H, 3.57, N, 5.30.

The second compound obtained was identified as *exo*-{3,5-[$FcCH_2P(S)(CH_2O)_2$]}{1,1-[$FcCH_2P(S)(CH_2O)_2$]}$N_3P_3F_2$ (**8**). Yield: 0.06 g, 24.6%. Mp: 129 °C. IR (KBr)(cm^{-1}): 2852 s, 2738 w, 1414 w, 1248 vs, 1042 s, 979 vs, 872 s, 808 s, 773 s, 725 vs, 642 w, 501 vs. NMR: ^{1}H, δ 4.84−4.77 and 4.48−4.35 (two set of multiplets, 8H, CH_2O), 43.31−4.18 [m, 8H, (ηC_5H_4)], 4.16 [s, 5H, (ηC_5H_5)], 4.15 [s, 5H, (ηC_5H_5)], 3.50 [d (J = 12 Hz), 2H, $FcCH_2O$ (ansa)], 3.45−3.42 [m, 2H, $FcCH_2O$ (spiro)]; ^{31}P{^{1}H}, δ 47.45 (s, P═S ansa), 22.32 [d ($^3J_{PP}$ = 14.5 Hz), P═S spiro], 18.84−17.93 (m, OPO), 15.90 [md ($^1J_{PF}$ = 939.5 Hz), OPF]; ^{19}F{^{31}P}, δ −78.90 [md ($^1J_{PF}$ = 878 Hz), OPF]; ^{13}C{^{1}H}, δ 75.07 (s, α-C of ηC_5H_4, spiro), 74.29 (s, α-C of ηC_5H_4 ansa), 69.76, 69.51, 68.91, 68.70 (all singlets, ηC_5H_4), 69.06 (s, ηC_5H_5), 67.07 [d, (J = 41 Hz), PCH_2O ansa], 66.24 [d, (J = 41 Hz), PCH_2O spiro], 29.54 [d (J = 42 Hz), $FcCH_2P$ ansa], 28.88 [d (J = 43 Hz), $FcCH_2P$ ansa]. MS (FAB) [*m*/*e* (species) intensity]: 817 (M^+) 100, 307 [$FcCH_2P(S)(CH_2O)(CH_2)^-H^+$] 31, 199 ($FcCH_2$) 22.

Reaction of Compound 3 with $C_6H_5CH_2P(S)(CH_2OLi)_2$. The diol $C_6H_5CH_2P(S)(CH_2OH)_2$ was treated with *n*-BuLi (0.17 mL, 2.8 mmol) in dry THF (10 mL) at −80 °C, and the mixture was stirred for 4 h before the compound $C_6H_5CH_2P(S)(CH_2O)_2PN](F_2PN)_2$ (0.06 g, 1.4 mmol) dissolved in dry THF (10 mL) was added at −80 °C under nitrogen atmosphere. The reaction was worked up as described for compounds **4** and **5**. The compound which came out first from the column was identified as *endo*-{3,5-[$C_6H_5CH_2P(S)(CH_2O)_2$]}{1,1-[$C_6H_5CH_2P(S)(CH_2O)_2$]}$N_3P_3F_2$ (**7**). Yield: 0.026 g, 30.7%. Mp: 108 °C. IR (KBr)(cm^{-1}): 2924 s, 1492 w, 1453 w, 1413 s, 1261 vs, 1178 w, 1049 vs, 978 vs, 930 w, 901 s, 871 vs, 773 vs, 735 w, 699 s, 628 s, 571 w, 527 w, 508 vs, 459 w. NMR: ^{1}H, δ 7.34−7.28 (m, 10H, C_6H_5), 4.88−4.80 and 4.52−4.28 (two set of multiplets, 8H, CH_2O), 3.71 [d (J = 14 Hz), 2H, $C_6H_5CH_2$, (ansa)], 3.64−3.61 [m, 2H, $C_6H_5CH_2$ (spiro)]; ^{31}P{^{1}H}, δ 47.45 (s, P═S ansa), 22.32 [d ($^3J_{PF}$ = 14.55 Hz), P═S spiro], 16.75−15.25 (m, OPO), 15.90 [md ($^1J_{PF}$ = 939.5 Hz), OPF]; ^{19}F, δ −74.90 [md ($^1J_{PF}$ = 938.1) OPF], −74.47 [md ($^1J_{PF}$ = 934.9), OPF]. MS (FAB) [*m*/*e* (species) intensity]: 601 (M^+) 90, 404 [$C_6H_5CH_2P(S)(CH_2O)_2P_3N_3OH$] 100, 154 ($N_3P_3F_1$) 62, 135 ($N_3P_3$) 72. Anal. Calcd for $C_{18}H_{22}P_5N_3O_4F_2S_2$ (%): C, 35.95; H, 3.69; N, 6.99. Found: C, 35.90; H, 3.60, N, 6.81.

The second compound was identified as *exo*-{3,5-[$C_6H_5CH_2P(S)(CH_2O)_2$]}{1,1-[$C_6H_5CH_2P(S)(CH_2O)_2$]}$N_3P_3F_2$ (**9**). Yield: 0.023 g, 27.1%. Mp: 135 °C. IR (KBr)(cm^{-1}): 2920 w, 1463 w, 1415 s, 1265 vs, 1168 w, 1052 vs, 970 vs, 901 s, 773 s, 735 w, 690 s, 638 s, 576 w, 527 w, 508 vs. NMR: ^{1}H, δ 7.34−7.29 (m, 10H, C_6H_5), 4.86−4.78 and 4.58−4.34 (two set of multiplets, 8H, CH_2O), 3.69−3.67 [m, 2H, $C_6H_5CH_2$ (spiro)], 3.53 [d (J = 14 Hz), 2H, $C_6H_5CH_2$, (ansa)]; ^{31}P{^{1}H}, δ 49.14 (s, P═S ansa), 22.41 [d ($^3J_{PF}$ = 14.55 Hz), P═S spiro], 18.46 [md ($^2J_{PNP}$ = 101.9), OPO], 14.89 [md ($^1J_{PF}$ = 854.6 Hz), OPF]; ^{19}F, δ −79.33 [md ($^1J_{PF}$ = 879.0 Hz), OPF]. MS (FAB) [*m*/*e* (species) intensity]: 601 (M^+) 100, 404 [$PhCH_2P(S)(CH_2O)_2P_3N_3OH$] 15, 154 ($N_3P_3F$) 91, 135 ($N_3P_3$) 61.

Reaction of $FcCH_2P(S)(CH_2OLi)_2$ with $N_3P_3F_6$ at 0 °C. The compound $FcCH_2P(S)(CH_2OH)_2$ (0.62 g, 1.9 mmol) was treated with *n*-BuLi (2.40 mL, 3.84 mmol) in dry THF (30 mL) at −80 °C, and the mixture was stirred for 4 h before $N_3P_3F_6$ (0.48 g, 1.9 mmol) dissolved in dry THF (30 mL) was added at 0 °C under a nitrogen atmosphere. The mixture was brought to room temperature, and after 12 h of stirring, the solvent was removed under vacuum, the residue was dissolved in minimum amount of dichloromethane, and the LiF that formed was filtered off using a frit. The reaction mixture was analyzed by TLC. Upon separation by column chromatography using ethyl acetate/hexane over silica gel, three products were isolated. The first two fractions were identified as endo-monoansa $FcCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ (**1**) (0.31 g, 30%) and exo-monoansa $FcCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ (0.12 g, 11.7%), respectively. The spectral data of these compounds were compared to those of the authentic sample.[5b] The analysis of the ^{31}P{^{1}H} NMR spectrum of the third fraction showed it as mixture (0.23 g) of endo ansa−spiro **6** and exo ansa−spiro **8**. Separation of this mixture again by column chromatography yielded compound **6** (0.11 g) and compound **8** (0.09 g). The spectral data of these compounds were compared to those of the compounds obtained in the reaction of the monospiro-[$FcCH_2P(S)(CH_2O)_2PN](F_2PN)_2$ with the corresponding dilithiated diol.

Reaction of $C_6H_5CH_2P(S)(CH_2OLi)_2$ with $N_3P_3F_6$ at 0 °C. The compound $C_6H_5CH_2P(S)(CH_2OH)_2$ (0.17 g, 0.8 mmol) was treated with *n*-BuLi (1 mL, 1.6 mmol) in dry THF (30 mL) at −80 °C, and the mixture was stirred for 4 h before $N_3P_3F_6$ (0.20 g, 0.8 mmol) dissolved in dry THF (30 mL) was added at 0 °C under a nitrogen atmosphere. After 12 h of stirring at room temperature, the residue was worked up as described for the previous reaction. After separation by column chromatography, the first two fractions were identified as endo-monoansa $C_6H_5CH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ (0.05 g, 14.6%) and exo-monoansa $C_6H_5CH_2P(S)(CH_2O)_2[P(F)N]_2$-$(F_2PN)$ (0.01 g, 2.9%), respectively. The spectral data of these

compounds were compared to those of authentic samples.[5b] The analysis of $^{31}P\{^1H\}$ NMR spectrum of third fraction showed it as mixture (0.06 g) of endo ansa−spiro (**7**) and exo ansa−spiro (**9**). Separation of this mixture again by column chromatography yielded compound **7** (0.027 g) and compound **9** (0.029 g). The spectral data of these compounds were found to agree with those of authentic samples.[5b]

General Procedure for the Transformation of Ansa−Spiro Substituted Compounds into Dispiro Compounds. The ansa−spiro compounds were dissolved separately in THF, and catalytic amounts of CsF (5−10 mol %) were added to them. The mixtures were stirred at room temperature, and the reaction was monitored by $^{31}P\{^1H\}$ NMR spectra till the peaks corresponding to the P═S in the ansa region disappeared. Afterward, the THF was evaporated, and the mixture was dissolved in ethyl acetate and passed through a column packed with silica gel to filter off the CsF and insoluble materials. The filtrate was further purified by column chromatography and by crystallization to get dispiro compounds.

Spectral Data for Dispiro Compounds. Dispiro 1,1,3,3-[FcCH$_2$P(S)(CH$_2$O)$_2$]$_2$N$_3$P$_3$F$_2$ (10). Mp: 121 °C. NMR: ^1H, δ 4.80−4.77 and 4.41−4.32 (two set of multiplets, 8H, CH_2O), 4.28−4.14 [two set of multiplets, 8H, (ηC_5H_4)], 4.11 [s, (ηC_5H_4)], 3.40 [d (J = 11 Hz), 4H, $FcCH_2P$]; $^{31}P\{^1H\}$, δ 19.6 [d (J_{PP} = 10 Hz), P═S], 16.20 [dd (J_{PNP} = 90 Hz, 14 Hz), OPO], 5.86 [tt ($^2J_{PNP}$ = 96 H, $^1J_{PF}$ = 913 Hz), PF_2]; ^{19}F, δ −68.35 [td (J_{PF} = 913 and 14 Hz), PF_2]. MS (FAB) [*m*/*e* (species) intensity]: 817 (M^+) 90, 307 [$FcCH_2P(S)(CH_2O)(CH_2)^-H^+$] 60, 199 ($FcCH_2$) 100. Anal. Calcd for $C_{26}H_{30}O_4P_5N_3F_2S_2Fe_2$ (%): C, 38.21; H, 3.70; N, 5.14. Found: C, 38.32, H, 3.85, N, 5.06. $^{31}P\{^1H\}$ and ^{19}F NMR spectral data for other two isomers are as follows.$^{31}P\{^1H\}$ 20.87 [d, P═S (J = 16 Hz)], 17.20−15.90 (m, OPO), 8.36 [mt, PF_2, (J = 906 Hz)]; ^{19}F, δ −68.29 [td, (J = 920 Hz); and $^{31}P\{^1H\}$, δ 22.28 [d, P═S, (J = 18 Hz)], a multiplet merged with triplet of PF_2 for OPO, 9.01 [mt, PF_2, (J = 906 Hz)]; ^{19}F, δ −68.17 [td, PF_2, (J = 935 Hz)].

Dispiro {1,1-[FcCH$_2$P(S)(CH$_2$O)$_2$]}{3,3-[OCH$_2$CH$_2$CH$_2$O]}-N$_3$P$_3$F$_2$ (11). Mp: charring at 160 °C. NMR: ^1H, δ 4.73−4.30 (m, 8H, CH_2O), 4.26−4.06 (m, 9H, Fc), 3.34 [d (J = 12 Hz), $FcCH_2P$], 1.90 (quintet, 2H, $CH_2CH_2CH_2$); $^{31}P\{^1H\}$, δ 22.11 [d ($^3J_{PP}$ = 15 Hz), P═S], 15.88 [mt ($^2J_{PNP}$ = 101 Hz), OPO], 12.88 (m, OPO), 7.76 [mt ($^1J_{PF}$ = 906 Hz), PF_2]; ^{19}F, δ −68.12 [md ($^1J_{PF}$ = 902 Hz), PF_2]; $^{13}C\{^1H\}$, δ 75.33 (s, α-C of ηC_5H_4), 69.61 and 68.78 (s, ηC_5H_4), 69.04 (s, ηC_5H_5), 67.62 (s, CH_2O), 66.09 [d (J = 53 Hz), PCH_2O], 29.91 [d (J = 71 Hz), $FcCH_2P$], 25.74 (s, $CH_2CH_2CH_2$). MS(FAB) [*m*/*e* (species) intensity]: 567 (M^+) 100, 307 ($FcCH_2P(S)(CH_2O)(CH_2)^-H^+$ 20, 199 ($FcCH_2$) 20, 135 (N_3P_3) 38. Anal. Calcd for $C_{16}H_{21}O_4P_4N_3F_2S_1Fe$ (%): C, 33.76; H, 3.72; N, 7.38. Found: C, 33.60; H, 3.52; N, 7.20.

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Supporting Information Available: Crystallographic information file (CIF) as well as X-ray data pertaining to data collection, crystal systems, and structure solution. Selected bond distances and angles and conformations of eight-membered ansa rings of compounds **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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