Syntheses of Novel Exo and Endo Isomers of Ansa-Substituted Fluorophosphazenes and Their Facile Transformations into Spiro Isomers in the Presence of Fluoride Ions†

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Reactions of the dilithiated diols $RCH_2P(S)(CH_2OLi)_2$ [R = Fc (**1**), Ph (**2**) (Fc = ferrocenyl)] with $N_3P_3F_6$ in equimolar ratios at −80 °C result exclusively in the formation of two structural isomers of ansa-substituted compounds, *endo*-$RCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ [R = Fc (**3a**), Ph (**4a**)] and *exo*-$RCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ [R = Fc (**3b**), Ph (**4b**)], which are separated by column chromatography. Increasing the reaction temperature to −40 °C results in more of the exo isomers **3b** and **4b** at the expense of the endo isomers. The formation of the ansa-substituted compounds is found to depend on the dilithiation of the diols, as a reaction of the silylated phosphine sulfide $FcCH_2P(S)(CH_2OSiMe_3)_2$ (**5**) with $N_3P_3F_6$ in the presence of CsF does not yield either **3a** or **3b** but instead gives the spiro isomer $[FcCH_2P(S)(CH_2O)_2\ PN](F_2PN)_2$ (**6**) as the disubstitution product of $N_3P_3F_6$. The ansa isomers **3a** and **3b** are transformed into the spiro compound **6** in the presence of catalytic amounts of CsF at room temperature in THF, while **4a** and **4b** are transformed into the spiro compound $[PhCH_2P(S)(CH_2O)_2PN](F_2PN)_2$ (**7**) under similar conditions. The novel conversions of ansa-substituted phosphazenes into spirocyclic phosphazenes were monitored by time-dependent ^{31}P NMR spectroscopy. The effect of temperature on a transformation was studied by carrying out reactions at various temperatures in the range from −60 to +33 °C for **3b**. In addition, compounds **3a**, **3b**, **4a**, and **6** were structurally characterized. In the case of the ansa compounds, the nitrogen atom flanked by the bridging phosphorus sites was found to deviate significantly from the plane defined by the five remaining atoms of the phosphazene ring.

Introduction

Among the various types of products that can result from the reactions of a difunctional reagent with perhalogenated cyclophosphazenes, the ansa- or transannular-substituted compounds still remain elusive from the synthetic perspective[1] and at the same time are interesting from the standpoint of their reaction chemistry.[2] A large majority of the reactions of difunctional reagents with chloro- and fluorophosphazenes have resulted only in the formation of spirocyclic compounds, which necessitated blocking four of the six reactive sites of cyclotriphosphazene rings to realize specifically ansa compounds.[3] Labarre and co-workers, in a series of papers beginning in 1982, addressed the ansa versus spiro dilemma by preparing and structurally characterizing a variety of ansa- and spiro-substituted chlorophosphazenes using a variety of difunctional reagents.[4] Recently, Brandt, Shaw, and others attempted to explain the ansa versus 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] By using diols which can invoke crown-related cation assistance, they explained the preferential formation of ansa compounds and proposed the thermodynamic stability of five-, six-, and seven-membered rings as the reason for spirocycle formation.[6] However, it is of interest to note that no clear experimental evidence exists in support of the higher thermodynamic stability of spiro isomers compared to ansa compounds.

The reactions of difunctional reagents with fluorophosphazenes also result in interesting differences in the nature of the products formed. Shreeve and co-workers, using fluoride ion catalyzed desilylation reactions of a variety of silylated diols, dithiols, and mercapto alcohols with $N_3P_3F_6$, prepared a variety of spiro, bridged, and dangling derivatives of $N_3P_3F_6$. Quite interestingly, no ansa compounds were reported as products of these reactions.[7] In contrast, by using structurally rigid difunctional reagents, such as dilithiated ferrocene, ruthenocene, and

† Dedicated to Prof. Herbert W. Roesky on the occasion of his 65th birthday.

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dibenzylchromium, Allcock and co-workers obtained exclusively ansa compounds that retained their vicinal bonding even after ring-opening polymerization or thermal ring expansion.[8]

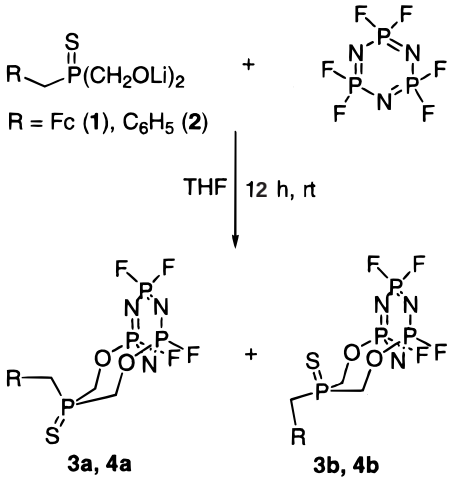
Herein, we report the syntheses, separations and structural characterizations of the first examples of exo and endo isomers of ansasubstituted fluorophosphazenes, which are exclusively obtained from the reactions of two different dilithiated bis(hydroxymethyl)phosphine sulfides with $N_3P_3F_6$. We also report the first observation of fluoride ion catalyzed transformation of these ansa fluorophosphazenes to their spirocyclic analogues, thereby providing experimental evidence for the stability of spiro- over ansa-substituted cyclophosphazenes. In addition, this study also compares the roles of delithiation with desilylation in deciding the preferential formation of ansa or spiro derivatives and provides reasons for the absence of ansa compounds in fluoride ion catalyzed desilylation reactions with $N_3P_3F_6$.

Results and Discussion

In the exploration of the chemistry of stable (hydroxymethyl)phosphines,[9] an interesting contrast was observed between the reactions of the bis(hydroxymethyl) phosphines $RCH_2P(CH_2OH)_2$ (R = Fc, Ph) with the corresponding phosphine sulfides. Although the hydroxymethyl groups of these phosphines behave like masked PH_2 groups, their reactivity becomes similar to that of a normal diol when the phosphines are converted to phosphine sulfides. With an eventual objective of preparing PN and PNC heterocycles and polymers having substituted phosphine moieties, we have begun an investigation of the reactions of stable bis(hydroxymethyl)phosphine sulfides with halogenated cyclophosphazenes and cyclocarbaphosphazenes. The reaction of $FcCH_2P(S)(CH_2OLi)_2$ with the substituted carbaphosphazene $(Me_2NCN)_2(Cl_2PN)$ results in the formation of the spirocyclic derivative which has been structurally characterized.[9b] However, quite surprisingly, similar 1:1 reactions of the dilithiated diols $RCH_2P(S)(CH_2OLi)_2$ [R = Fc (**1**),[9a] Ph (**2**)[10]] with $N_3P_3F_6$ do not yield the spiro derivatives but instead give exclusively two novel structural isomers of two ansa-substituted compounds, *endo*-$RCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ [R = Fc (**3a**), Ph (**4a**)], and *exo*-$RCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ [R = Fc (**3b**), Ph (**4b**)], which are separated by column chromatography (Scheme 1). The endo/exo nomenclature refers to the ferrocenylmethyl and benzyl groups.[11]

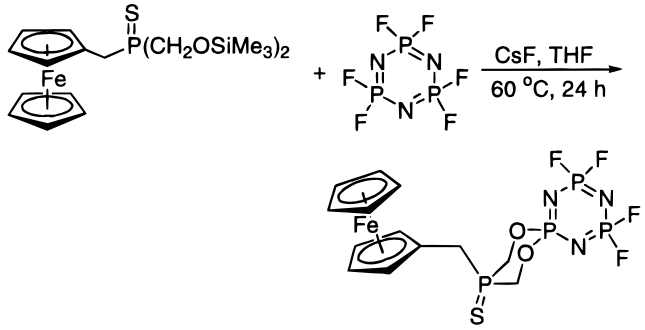
The yields of the exo/endo isomers of the ansa compounds are found to depend on the temperature of addition of $N_3P_3F_6$ to a large extent. When $N_3P_3F_6$ is added to **1** at −80 °C followed by slow warming to room temperature, 45% **3a** and 19% **3b** are obtained. A reaction under identical conditions with **2** gives 78% of **4a** and only traces of **4b**. However, when the addition of $N_3P_3F_6$ is carried out at −40 °C followed by slow warming to room temperature, traces of **3a** and 44% **3b** are obtained from the reaction of **1** and 61% **4a** and 8% **4b** are obtained in case of **2.** This indicates that the endo isomers, which are thermodynamically less stable than the exo isomers, are preferentially formed at low temperatures with a maximum yield of 78% in case of **4a**. When the temperature of the addition is increased further, the reactions become more complex, with decrease in the yields of the mono-ansa-substituted compounds.

Scheme 1



Desilylation reactions of silylated alcohols and mercaptans with $N_3P_3F_6$ in the presence of CsF, which are driven by the formation of Me_3SiF as a stable side product, have been performed at high temperatures and were observed to yield bridging and dangling derivatives of fluorophosphazenes in addition to spiro compounds.[7] With a view to comparing this method with delithiation reactions, we have prepared the silylated phosphine sulfide diol $FcCH_2P(S)(CH_2OSiMe_3)_2$ (**5**) and carried out its reaction with $N_3P_3F_6$ in the presence of CsF as catalyst (Scheme 2). We observed that, quite interestingly,

Scheme 2



this reaction yields only the spirocyclic compound **6** as the disubstitution product, without the formation of any ansa compounds. This result is in conformity with those of Shreeve and co-workers[7] and suggests that formation of ansa compounds is not favored in fluoride ion catalyzed desilylation reactions.

Spectral Properties. Multinuclear NMR spectra of the compounds prepared in this study exhibit interesting differences between the exo and endo ansa compounds as well as between the ansa and spirocyclic compounds. The most unique and useful differences are observed in the $^{31}P\{^1H\}$ NMR spectra. The endo isomers **3a** and **4a** show peaks for the P═S moiety at 44.67 and 46.59 ppm, while the corresponding peaks of the exo isomers **3b** and **4b** are found to be slightly deshielded and are observed at 45.48 and 48.17 ppm, respectively. However, for the spiro compounds **6** and **7**, these peaks are observed at 20.27 and 22.27 ppm, thus providing an easy way to differentiate between ansa and spiro isomers. Similar spirocyclic compounds of **1** with carbaphosphazenes show the P═S peak at 23.19−23.34 ppm.[9b] Although the PF_2 and PFO peaks are complex

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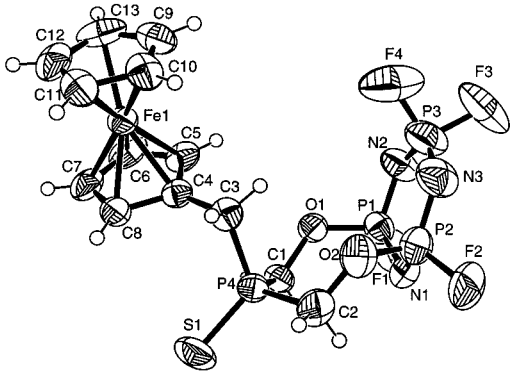

Figure 1. Crystal structure of compound **3a**.

multiplets, making their assignments difficult in these compounds, their peak patterns and chemical shifts are quite similar for the same kinds of isomers. Five sets of multiplets are observed in the range 19.97−3.13 ppm for the endo isomers **3a** and **4a**, while three sets of multiplets are observed in the range 18.93−5.33 ppm for the exo isomers **3b** and **4b**. For the spiro compounds **6** and **7**, three sets of multiplets are seen in the range 16.35−1.50 ppm. $^{19}F\{^{31}P\}$ NMR spectra show marked differences in chemical shifts for the ansa and spiro compounds. The PF_2 peaks appear in the range −75.11 to −78.95 ppm as complex multiplets for all of the ansa compounds, while the same are observed for **6** and **7** at −71.61 and −71. 59 ppm, which are closer to the PF_2 peak of $N_3P_3F_6$. The POF peaks for the ansa compounds appear in the range −68.91 to −73.42 ppm. Both the PF_2 and POF chemical shifts of the exo isomers are found to be more shielded than those of the endo isomers to the extent of 2−4 ppm. While the RCH_2P chemical shifts in the ^1H NMR spectra of ansa and spiro derivatives are quite similar to those of their parent diols, the chemical shifts of the PCH_2O groups show interesting differences. Their peaks are deshielded in comparison to those of their parent diols. A single multiplet is observed for the parent diols, while two sets of multiplets are observed for all of the ansa and spiro derivatives. The EI mass spectra of each set of ansa- and spiro-substituted compounds give the same molecular ion peak, and the fragmentation patterns of the ansa compounds differ only very slightly from those of the corresponding spiro compounds. The base peaks for the ferrocene-derived compounds correspond to that of $FcCH_2^+$, while, for the benzyl-substituted compounds, the base peaks correspond to that of $PhCH_2^+$. The intensities of the M^+ ion peaks are stronger for the spiro compounds **6** and **7** (86 and 99%) than for the ansa-substituted compounds (9−26% only).

X-ray Structural Studies. Figures 1 and 2 show the crystal structures of compounds **3a** and **3b**. The structure of **3b** reveals two crystallographically independent molecules in the unit cell. Figures 3 and 4 show the crystal structures of the endo ansa compound **4a** and the spirocycle **6**, respectively. Structure solution and refinement parameters are listed in Table 1, and

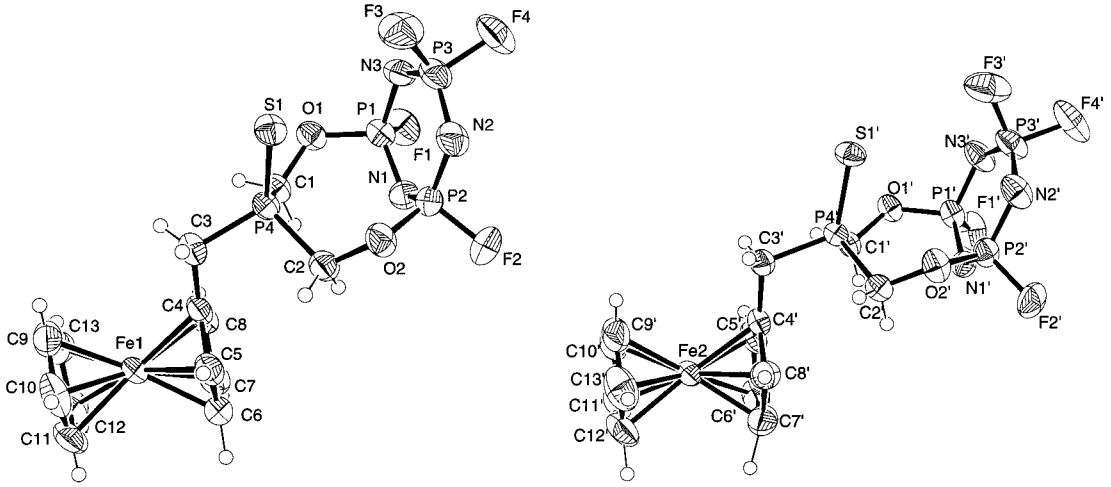

Figure 2. Crystal structure of compound **3b**, showing two crystallographically independent molecules: left, **3b**(1); right, **3b**(2).

Table 1. X-ray Crystallographic Parameters for **3a**, **4a**, **3b**, and **6**

	3a	**4a**	**3b**	**6**
empirical formula	$C_{13}H_{15}FeN_3P_4F_4O_2S$	$C_9H_{11}N_3P_4F_4O_2S$	$C_{13}H_{15}FeN_3P_4F_4O_2S$	$C_{13}H_{15}FeN_3P_4F_4O_2$
fw	533.07	425.15	533.07	533.07
cryst syst; space group	orthorhombic; *Pcab*	triclinic; $P\bar{1}$	triclinic; $P\bar{1}$	monoclinic; $2_1/c$
a (Å)	9.401(5)	8.006	11.2092(11)	13.247
b (Å)	14.712(2)	8.685	13.965(6)	10.747
c (Å)	29.956(6)	13.006	14.969(18)	13.995
α (deg)	90	86.39	109.55(6)	90
β (deg)	90	80.65	97.07(4)	100.21
γ (deg)	90	70.67	111.79(2)	90
V (Å^3)	4143(2)	842.0	1967(2)	1960.8
Z	8	2	4	4
D_{calc} (Mg m^{-3})	1.709	1.677	1.800	1.806
μ (cm^{-1})	0.1188	0.0620	0.1251	0.125
T (°C)	20(2)	20(2)	20(2)	20(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
final indices, 2σ data: R1 (wR2)[a]	0.0440 (0.1395)	0.0454 (0.1254)	0.0314 (0.0988)	0.0314 (0.0975)
final indices, all data: R1 (wR2)[a]	0.0961 (0.1861)	0.0559 (0.1290)	0.0395 (0.1080)	0.0507 (0.1145)

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound **3a**

Bond Distances			
P(1)−N(1)	1.567(5)	P(2)−N(1)	1.576(6)
P(1)−N(2)	1.563(5)	P(2)−N(3)	1.562(6)
P(1)−O(1)	1.555(4)	P(2)−O(2)	1.549(5)
P(1)−F(1)	1.525(4)	P(2)−F(2)	1.527(4)
P(4)−C(1)	1.819(6)	C(1)−O(1)	1.458(6)
P(4)−C(2)	1.820(6)	C(2)−O(2)	1.463(8)
P(4)−C(3)	1.807(6)	P(3)−N(2)	1.544(6)
P(4)−S(1)	1.934(2)	P(3)−N(3)	1.561(7)
Bond Angles			
P(1)−N(1)−P(2)	114.9(3)	C(1)−P(4)−C(2)	113.3(3)
N(1)−P(1)−N(2)	117.9(3)	P(4)−C(1)−O(1)	116.1(4)
N(1)−P(2)−N(3)	118.3(3)	P(4)−C(2)−O(2)	115.0(4)
O(1)−P(1)−N(2)	108.1(3)	C(1)−O(1)−P(1)	122.1(3)
O(2)−P(2)−N(3)	108.8(4)	C(2)−O(2)−P(2)	121.4(4)
O(1)−P(1)−N(1)	111.4(3)	O(2)−P(2)−N(1)	111.0(3)

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

Bond Distances			
P(1)−N(1)	1.572(3)	P(2)−N(1)	1.567(3)
P(1)−N(3)	1.575(3)	P(2)−N(2)	1.569(3)
P(1)−O(1)	1.565(2)	P(2)−O(2)	1.562(3)
P(1)−F(1)	1.533(2)	P(2)−F(2)	1.529(2)
P(4)−C(1)	1.857(3)	C(1)−O(1)	1.443(4)
P(4)−C(2)	1.851(4)	C(2)−O(2)	1.439(4)
P(4)−C(3)	1.824(3)	P(3)−N(3)	1.554(3)
P(4)−S(1)	1.9430(11)	P(3)−N(2)	1.554(3)
Bond Angles			
P(1)−N(1)−P(2)	120.33(18)	C(1)−P(4)−C(2)	109.33(18)
N(1)−P(1)−N(3)	117.79(15)	P(4)−C(1)−O(1)	112.6(2)
N(1)−P(2)−N(2)	118.25(16)	P(4)−C(2)−O(2)	113.3(2)
O(1)−P(1)−N(3)	111.04(15)	C(1)−O(1)−P(1)	121.6(2)
O(2)−P(2)−N(2)	111.05(16)	C(2)−O(2)−P(2)	122.4(2)
O(1)−P(1)−N(1)	110.38(14)	O(2)−P(2)−N(1)	110.14(14)

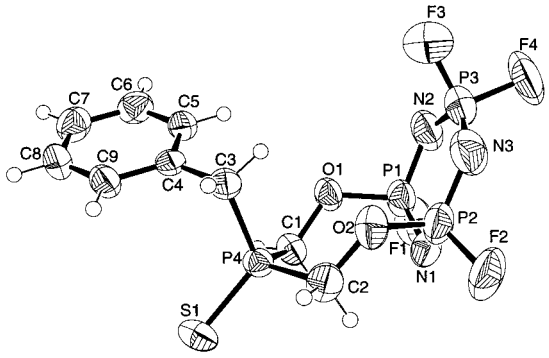

Figure 3. Crystal structure of compound **4a**.

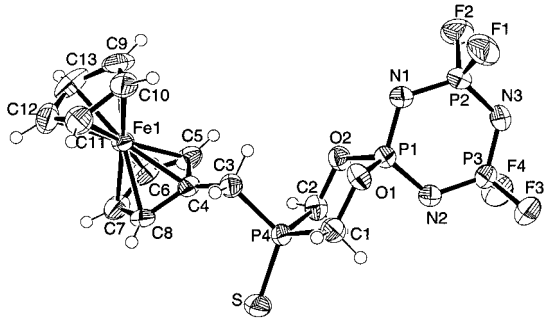

Figure 4. Crystal structure of compound **6**.

selected bond distances and angles are given in Tables 2−5. The structures of the ansa compounds **3a**, **3b**, and **4a** show interesting differences from as well as similarities to those of

Table 4. Selected Bond Distances (Å) and Angles (deg) for Compound **4a**

Bond Distances			
P(1)−N(1)	1.558(3)	P(2)−N(1)	1.570(4)
P(1)−N(2)	1.567(4)	P(2)−N(3)	1.554(4)
P(1)−O(1)	1.563(2)	P(2)−O(2)	1.562(3)
P(1)−F(1)	1.515(3)	P(2)−F(2)	1.520(3)
P(4)−C(1)	1.820(3)	C(1)−O(1)	1.439(4)
P(4)−C(2)	1.837(4)	C(2)−O(2)	1.438(5)
P(4)−C(3)	1.799(3)	P(2)−N(2)	1.554(4)
P(4)−S(1)	1.9326(12)	P(3)−N(3)	1.555(4)
Bond Angles			
P(1)−N(1)−P(2)	114.7(2)	C(1)−P(4)−C(2)	111.56(18)
N(1)−P(1)−N(2)	117.89(19)	P(4)−C(1)−O(1)	115.3(2)
N(1)−P(2)−N(3)	117.8(2)	P(4)−C(2)−O(2)	115.3(3)
O(1)−P(1)−N(2)	107.65(18)	C(1)−O(1)−P(1)	120.5(2)
O(2)−P(2)−N(3)	108.1(2)	C(2)−O(2)−P(2)	120.5(3)
O(1)−P(1)−N(1)	110.94(15)	O(2)−P(2)−N(1)	111.04(16)

Table 5. Selected Bond Distances (Å) and Angles (deg) for Compound **6**

Bond Distances			
P(1)−N(1)	1.585(3)	P(2)−N(1)	1.555(3)
P(1)−N(2)	1.586(3)	P(2)−N(3)	1.556(3)
P(1)−O(1)	1.565(2)	P(3)−N(2)	1.549(3)
P(1)−O(2)	1.575(2)	P(3)−N(3)	1.563(3)
P(4)−C(1)	1.830(3)	P(4)−C(2)	1.823(3)
C(1)−O(1)	1.462(4)	C(2)−O(2)	1.463(4)
Bond Angles			
O(1)−P(1)−O(2)	104.91(12)	O(2)−P(1)−N(1)	108.27(14)
C(1)−P(4)−C(2)	100.93(15)	O(1)−P(1)−N(1)	105.92(14)
C(2)−O(2)−P(2)	117.70(19)	O(1)−P(1)−N(2)	110.45(14)
C(1)−O(1)−P(1)	119.67(19)	O(2)−P(1)−N(2)	109.31(14)
N(1)−P(1)−N(2)	117.24(14)	N(1)−P(2)−N(3)	120.27(15)
N(2)−P(3)−N(3)	118.98(15)	P(2)−N(3)−P(3)	120.58(17)

the reported metallocene-derived ansa compounds $N_3P_3F_4(\eta$-$C_5H_4)$Fe (**A**),[12] $N_3P_3F_4(\eta$-$C_5H_4)$Ru (**B**),[13] and $N_3P_3F_4(\eta$-$C_6H_5)$-Cr (**C**).[14] Because of the strain induced by the transannular substitution of the metallocenes on the N_3P_3 ring, the phosphazene ring is distorted in compounds **A**−**C** and the nitrogen atom flanked by the bridging phosphorus sites is seen to be displaced 0.56−0.66 Å from the plane defined by the five remaining atoms of the phosphazene ring. A similar displacement of 0.56−0.67 Å is observed for the alkoxy- and aryl-substituted derivatives of **A**.[14] In **3a** and **4a**, the deviation of N(1) from the plane defined by the other five ring atoms is found to be 0.43 and 0.46 Å, respectively, and for the exo isomer **3b**, it is still less (0.23 Å).

The ring angles at N(1) in **3a** and **4a** are 114.9(3) and 114.7-(2)°, which are narrower than the angles at the other ring nitrogen atoms [119.1(4) and 118. 9(4)° for **3a** and 118. 8(2)° for **4a**]. Similar deviations of bond angles in the range 4.3−7.4° are observed for the metallocenyl-substituted ansa fluorophosphazenes, **A**−**C**. However, quite interestingly, the N(1) angles for the two crystallographically independent molecules of **3b** are 120.33(18)° [**3b**(1)] and 119.48(17)° [**3b**(2)] and are almost equal to the angles at the other two ring nitrogens, N(2) and N(3). These results indicate that, among the endo and exo isomers, the strain on the N_3P_3 ring is less for the latter than for the former. Angles at the bridging phosphorus sites are also

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(13) Lavin, K. D.; Riding, G. H.; Parvez, M.; Allcock, H. R. *J. Chem. Soc., Chem. Commun.* **1986**, *117*.
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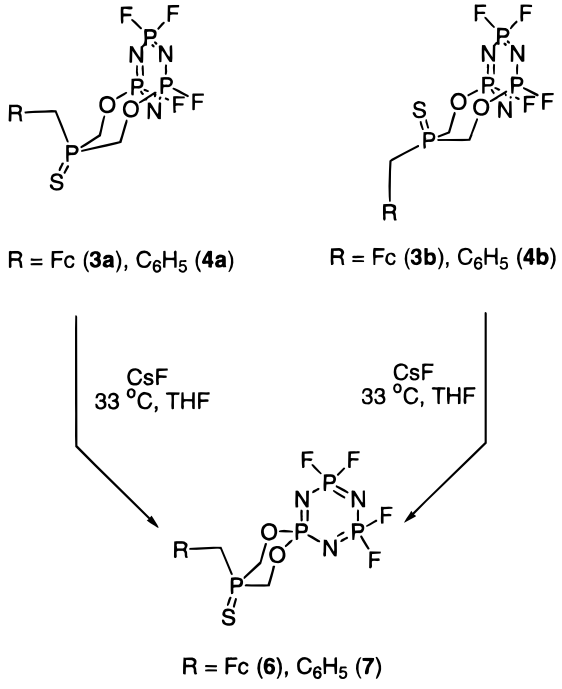
narrower than those at the PF_2 phosphorus sites for the ansa compounds **3a**, **3b**, and **4a** although the deviations are not pronounced to the same extent as seen in the cases of metallocenyl-substituted ansa fluorophosphazenes.[12−14] In contrast to the structures of **A**−**C** where the four ring P−N bonds near the metallocene linkage sites are longer than the other two, no noticeable differences in the P−N distances are observed for **3a**, **3b**, and **4a**. The structure of the spirocyclic compound **6** is similar to many other examples of six-membered spirocyclic compounds of fluorophosphazenes.[1a,7,15] The phosphazene ring is planar. In comparison to the CH_2−P−CH_2 angles of 110.0−111.6° for the ansa compounds, the same angle for spirocycle **6** is observed at 100.9°.

Ansa to Spiro Transformations of Substituted Fluorophosphazenes. Impure samples of ansa compounds prepared in this study on storage for long periods exhibited in their ^{31}P NMR spectra a strong peak in the range 20−22 ppm, suggesting the formation of spirocycles. This, supported by the observation that fluoride ion catalyzed desilylation reactions yield no ansa compounds, prompted us to consider the possible transformations of the ansa compounds into the spiro isomers in the presence of fluoride ions. ^{31}P NMR spectra of the reaction mixtures of both **3a** and **3b** with traces of CsF after refluxing in THF for 12 h indicated the formation of the spirocycle **6** along with quite a few other impurities, which could not be easily separated. However, when the same reactions were carried out at room temperature (33 °C), exclusive formation of the spirocycle **6** was observed. After purification by flash chromatography, **6** was obtained in 38.4 and 37.5% yields in the cases of **3a** and **3b**, respectively. The ^{31}P NMR study of these transformations also indicated that the spiro compounds were exclusively formed from the ansa compounds. **3a**, **3b**, and **4a**, and 1 h for **4a** at 33 °C (Scheme 3). A similar transformation was also observed for **4b**, but yields could not be quantified owing to the poor yields of **4b** obtained in this study. The time-dependent ^{31}P NMR spectra of **4a** at 20 °C clearly show the peak for the ansa compound at 46.59 ppm decreasing in intensity and the peak for the spiro compound at 22.28 ppm increasing in intensity with time as the transformation proceeds (Figure 5). To study the effect of temperature, the transformation of **3b** into **6** was investigated at various temperatures ranging from −60 to +33 °C. Quite interestingly, it was observed that, at −60 °C, the transformation did not occur, even on stirring for 10 h. The time for complete transformation of **3b** into **6** at 33, 20, 0, and −20 °C were 1.5 (38%), 2.2 (41%), 3.5 (50%), and 5 h (63%), respectively.

Scheme 3



when stirred in THF at room temperature with traces of CsF, were found to yield the spirocycles **6** and **7**, and the transformations were observed to be complete in 4 h for **3a**, 2 h for **3b**,

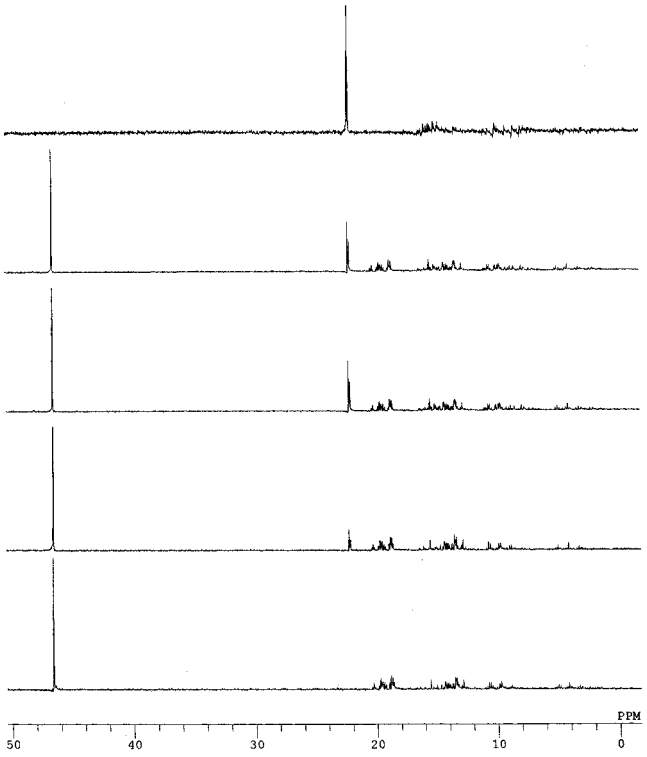


Figure 5. Time-dependent ^{31}P NMR spectra monitoring the transformation of **4a** into **7**.

Conclusions

The first examples of exo and endo isomers of ansa-substituted fluorophosphazenes have been synthesized and structurally characterized. Structural studies show that, as a result of the strain induced by the ansa formation, the N_3P_3 ring deviates from planarity in both the exo and endo isomers. However, the strain on the ring is less pronounced in the exo isomers than in the endo isomers. Exclusively ansa compounds are obtained from the reactions of the dilithiated phosphine sulfide diols with $N_3P_3F_6$, while desilylation reactions of the silylated diols give only the spiro isomers. The first ansa to spiro transformation reaction of substituted fluorophosphazenes have been carried out and monitored by time-dependent ^{31}P NMR spectroscopy. The effect of temperature on a transformation was studied, and it was found that this transformation occurred at temperatures in the range from −20 to +33 °C. Our study also shows why ansa compounds are not formed in fluoride ion catalyzed desilylation reactions of silylated diols and mercaptans with $N_3P_3F_6$.

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Experimental Section

Materials. $N_3P_3F_6$ is prepared from $N_3P_3Cl_6$ (Fluka) according to the literature method[16] and is purified by fractional distillation. The diol $FcCH_2P(S)(CH_2OH)_2$ (**1**) is also prepared as reported in the literature.[9a] The diol $PhCH_2P(S)(CH_2OH)_2$ (**2**) is prepared by reacting $P(CH_2OH)_3$ with $C_6H_5CH_2Br$ in methanol, followed by addition of $(C_2H_5)_3N$ and S, and is purified by column chromatography.[10] Hexane, ethyl acetate, toluene, and tetrahydrofuran (THF) are distilled and dried by standard procedures.

General Procedures. A conventional vacuum line equipped with a dry nitrogen apparatus and Schlenk glassware is used for all reactions. Reactions and workup procedures are carried out under an atmosphere of dry nitrogen. Infrared spectra are recorded on a Perkin-Elmer 1320 spectrometer for samples in KBr pellets. ^1H, $^{31}P\{^1H\}$, $^{19}F\{^{31}P\}$, and $^{13}C\{^1H\}$ NMR spectra are recorded using a JEOL JNM-LA 400 FT NMR spectrometer with $CDCl_3$ as the solvent and TMS, 85% H_3PO_4, and $CFCl_3$ as references. Mass spectra are obtained on a JEOL D-300 spectrometer in the EI mode, elemental analyses are performed on a Carlo Erba CHNSO 1108 elemental analyzer, and low-temperature reactions are carried out using a Julabo FT 901 low-temperature apparatus with ethanol as the medium.

X-ray Diffraction Studies. The X- ray diffraction data for compounds, **3a**, **3b**, **4a**, and **6** are collected on an Enraf-Nonius CAD-4 diffractometer. The data are reduced[17] and structures solved by using the WinGX program[18] and incorporating SHELX-97[19] for refinement by least-squares methods on F^2. All non-hydrogen atoms are refined anisotropically. The hydrogen atoms are located from difference electron density maps and are included isotropically in the refinement process

Preparations of 3a and 3b. The compound $FcCH_2P(S)(CH_2OH)_2$ (0.90 g, 2.78 mmol) is treated with *n*-BuLi (3.47 mL, 5.54 mmol) in dry THF (20 mL) at − 80 °C, and the mixture is stirred for 4 h before $N_3P_3F_6$ (0.69 g, 2.78 mmol) dissolved in dry THF (20 mL) is added at −80 °C under a nitrogen atmosphere. The mixture is brought to room temperature, and after 12 h of stirring, the solvent is removed in vacuo, the residue is dissolved in toluene, and LiF formed is filtered off using a frit. The reaction mixture is analyzed by TLC, and upon separation by column chromatography using ethyl acetate/hexane over silica gel, two products are isolated. The first fraction is identified as *endo*-$FcCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ **3a**. Yield: 0.66 g, 44.5%. Mp: 118 °C. IR (cm^{-1}) (KBr): 3070 vw, 2970 w, 2920 w, 1410 m, 1380 w, 1250 vs, 1160 m, 1100 w, 1060 vs, 1000 vs, 980 w, 970 s, 925 m, 910 m, 880 vs, 840 w, 810 vs, 770 s, 675 m, 630 m. NMR: ^1H, δ 3.23 [d (J = 11 Hz), 2 H, $FcCH_2P$], 4.15 [s, 5 H, C(9)H−C(13)H], 4.20 [m, 2 H, C(6)H and C(7)H], 4.35 [m, 2 H, C(5)H and C(8)H], 4.37 (qd, 2 H, PCH_2O), 4.72 (m, 2 H, PCH_2O); $^{31}P\{^1H\}$, δ 44.67 (s, P═S), 19.97−18.32 (set of three multiplets), 16.27−14.49 (multiplet), 14.20−12.55 (multiplet), 10.56−8.67 (set of three multiplets), 4.86−3.13 (set of three multiplets); $^{19}F\{^{31}P\}$, δ −75.11 [m (J_{P-F} = 935 Hz), PF_2], −68.91 [m (J_{P-F} = 900 Hz), OPF]; $^{13}C\{^1H\}$, δ 28.25 [d (J = 45 Hz), $FcCH_2P$], 66.86 [d (J = 47 Hz), PCH_2O], 68.92 [s, C(5) and C(7)], 69.06 [s, C(9)−C(13)], 69.71 [s, C(6)−C(7)], 73.51 [s, C(4)]. MS (EI) [*m*/*e* (species) intensity]: 533 (M^+) 7; 244 ($FcCH_2PCH_2$) 36; 211 ($N_3P_3F_4$) 5; 199 ($FcCH_2$) 100; 135 (N_3P_3) 5; 121 (C_5H_5Fe) 40. Anal. Calcd for $C_{13}H_{15}F_4FeN_3O_2P_4S$: C, 29.29; H, 2.84; N, 7.88. Found: C, 29.23; H, 2.90; N, 7.92; The second fraction is identified as *exo*-$FcCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ (**3b**). Yield: 0.28 g, 18.9%. Mp: 152 °C. IR (cm^{-1}) (KBr): 3060 vw, 2970 w, 2920 w, 1410 m, 1315 w, 1300 w, 1265 vs, 1190 vw, 1170 vs, 990 m, 975 w, 960 s, 920 s, 890 m, 870 m, 800 vs, 750 vs, 660 w. NMR: ^1H, δ 3.48 [d (J = 12 Hz), 2 H, $FcCH_2P$], 4.19 [s, 5 H, C(9)H−C(7)H], 4.22 [m, 2 H, C(6)H and C(7)H], 4.36 [m, 2 H, C(5)H and C(8)H], 4.38 (m, 2 H, PCH_2O), 4.60 (qd, 2 H, PCH_2O); $^{31}P\{^1H\}$, δ 45.48 (s, P═S), 18.93−17.17 (complex multiplet), 13.42−11.17 (complex multiplet), 6.99−5.33 (set of three multiplets); $^{19}F\{^{31}P\}$, δ −77.76 [m (J_{P-F} = 897 Hz), PF_2], −74 [m (J_{P-F} = 919 Hz), OPF], −70.85 [m (J_{P-F} = 868 Hz), OPF]; $^{13}C\{^1H\}$, δ 29.80 [d (J = 43 Hz), $FcCH_2P$], 67.07 [d (J = 40 Hz), PCH_2O], 68.87 [s, C(5) and C(8)], 69.12 [s, C(9)−C(13)], 69.57 [s, C(6) and C(7)], 74.19 [s, C(4)]. MS (EI) [*m*/*e* (species) intensity]: 533 (M^+) 16; 322 [$FcCH_2P(S)(CH_2O)_2$] 4; 290 [$FcCH_2P(S)(CH_2)_2$] 4; 244 ($FcCH_2PCH_2$) 63; 243 [$N_3P_3F_4(O)_2$] 5; 241 ($N_3P_3F_4CH_2O$) 11; 199 ($FcCH_2$) 100; 135 (N_3P_3) 10; 121 (C_5H_5Fe) 50. Anal. Calcd for $C_{13}H_{15}F_4FeN_3O_2P_4S$: C, 29.29; H, 2.84; N, 7.88. Found: C, 29.30; H, 2.81; N, 7.90. The compounds **3a** and **3b** are recrystallized from an ethyl acetate/hexane mixture.

Preparations of 4a and 4b. $C_6H_5CH_2P(S)(CH_2OH)_2$ (0.19 g, 0.92 mmol) is treated with *n*-BuLi (1.15 mL, 1.84 mmol) in dry THF (15 mL) at − 80 °C, and the mixture is stirred for 4 h before $N_3P_3F_6$ (0.23 g, 0.92 mmol) dissolved in dry THF (15 mL) is added at −40 °C under nitrogen atmosphere. After 12 h of stirring at room temperature, the residue is worked up as described for **3a** and **3b**. The first fraction is identified as *endo*-$C_6H_5CH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ **4a**. Yield: 0.24 g, 61.2%. Mp: 120 °C. IR (cm^{-1}) (KBr): 2900 w, 1580 vw, 1480 w, 1440 vw, 1400 m, 1380 w, 1230 vs, 1150 m, 1030 vs, 1000 s, 960 w, 920 m, 890 s, 790 vs, 685 w, 665 w. NMR: ^1H, δ 3.38 [d (J = 13 Hz), 2 H, $PhCH_2P$], 4.32 (q, 2 H, PCH_2O), 4.72 (m, 2 H, PCH_2O), 7.30 (m, 5 H, C_6H_5); $^{31}P\{^1H\}$, δ 46.59 (s, P═S), 19.74−18.78 (set of three multiplets), 15.62−14.08 (multiplet), 13.66−12.89 (multiplet), 10.77−9.11 (set of three multiplets), 4.90−3.55 (set of three multiplets); $^{19}F\{^{31}P\}$, δ −75.23 [m (J_{P-F} = 939 Hz), PF_2], −68.80 [m (J_{P-F} = 926 Hz), OPF]; $^{13}C\{^1H\}$, δ 32.14 [d (J = 45 Hz), $C_6H_5CH_2P$], 66.66 [d (J = 50 Hz), PCH_2O], 127.02 [d (J = 8 Hz), C(4)], 128.21 [d (J = 4 Hz), C(7)], 128.92 [d (J = 3 Hz), C(5) and C(9)], 130.40 [d (J = 6 Hz), C(6) and C(9)]. MS (EI) [*m*/*e* (species) intensity)]: 425 (M^+) 26; 334 [$P(S)(CH_2O)_2N_3P_3F_4$] 100; 304 [$P(S)CH_2O(P_3N_3F_4)$] 7; 302 [$P(CH_2O)_2P_3N_3F_4$] 2; 288 [$PCH_2O(P_3N_3F_4)O$] 6; 213 [$C_6H_5C^+HP(S)(CH_2O)_2$] 3; 211 ($N_3P_3F_4$) 2; 135 (N_3P_3) 9; 91 ($C_6H_5CH_2$) 74; 77 (C_6H_5) 11; 65 [$P(CH_2)_2$] 17. Anal. Calcd for $C_9H_{11}N_3P_4O_2F_4S$: C, 25.43; H, 2.61; N, 9.89. Found: C, 25.38; H, 2.58; N, 9.96. The second fraction is identified as *exo*-$C_6H_5CH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ (**4b**). Yield: 0.03 g, 7.6%. Mp: 105 °C. IR (cm^{-1}) (KBr): 2900 w, 1580 vw, 1480 w, 1440 w, 1400 m, 1300 vw, 1240 vs, 1110 vw, 1030 vs, 960 w, 920 w, 880 m, 860 s, 800 s, 760 s, 720 w, 690 m, 620 m. NMR: ^1H, δ 3.67 [d (J = 14 Hz), 2 H, $PhCH_2O$], 4.36 (m, 2 H, PCH_2O), 4.55 (qd, 2 H, PCH_2O), 7.30 (m, 5 H, C_6H_5); $^{31}P\{^1H\}$, δ 48.17 (s, P═S), 18.77−17.23 (multiplet), 13.00−11.74 (multiplet), 7.38−5.58 (multiplet); $^{19}F\{^{31}P\}$, δ −78.96 [m (J_{P-F} = 924 Hz), PF_2], −73.56 [m (J_{P-F} = 928 Hz), OPF], −70.82 [m (J_{P-F} = 835), OPF]; $^{13}C\{^1H\}$, δ 33.39 [d (J = 43 Hz), $C_6H_5CH_2P$], 66.91 [d (J = 44 Hz), PCH_2O], 127.08 [d (J = 8 Hz), C(4)], 128.21 [d (J = 4 Hz), C(7)], 128.95 [d (J = 4 Hz), C(5) and C(9)], 130.43 [d (J = 6 Hz), C(6) and (8)]. MS (EI) [*m*/*e* (species) intensity]: 425 (M^+) 17; 334 [$P(S)(CH_2O)_2N_3P_3F_4$] 100; 304 [$P(S)CH_2O(P_3N_3F_4)$] 6; 302 [$P(CH_2O)_2P_3N_3F_4$] 6; 288 [$PCH_2O(P_3N_3F_4)O$] 11; 213 [$C_6H_5C^+HP(S)(CH_2O)_2$] 5; 211 ($N_3P_3F_4$) 4; 135 (N_3P_3) 4; 91 ($C_6H_5CH_2$) 100; 77 (C_6H_5) 13; 65 [$P(CH_2)_2$] 41. Anal. Calcd for $C_9H_{11}N_3P_4O_2F_4S$: C, 25.43; H, 2.61; N, 9.89. Found: C, 25.35; H, 2.62; N, 9.80.

Preparation of 5. To $FcCH_2P(S)(CH_2OH)_2$ (1.07 g, 3.30 mmol) in toluene (50 mL) is added Me_3SiCl (1.08 g, 9.90 mmol) dropwise in the presence of Et_3N (1.33 g, 13.14) under a nitrogen atmosphere. After 12 h of stirring at room temperature, the solvent is removed in vacuo. The residue is dissolved in hexane, the unreacted diol is filtered off, and the unreacted Et_3N and Me_3SiCl are extracted with water. The organic portion is dried to give a crystalline compound which is identified as $FcCH_2P(S)(CH_2OSiMe_3)_2$ (**5**). Yield: (1.45 g, 94%). Mp: 84 °C. NMR: ^1H, δ 0.01 (s, 18 H, $OSiMe_3$), 2.93 [d (J = 12 Hz), 2 H, $FcCH_2P$], 3.73 (m, 4 H, PCH_2O), 3.96 [s, 5 H, Fe(η-C_5H_5)], 3.99 [m, 2 H, Fe(η-C_5H_4)], 4.10 [s, 2 H, Fe(η-C_5H_4)]; $^{31}P\{^1H\}$, δ 46.34 (s, P═S); $^{13}C\{^1H\}$, δ 28.78 [d (J = 45 Hz), $FcCH_2$], 61.53 [d (J = 65 Hz), PCH_2], 68.76 [s, C(5) and C(7)], 69.44 [s, C(9)−C(13)], 70.20 [s, C(6) and C(8)]. MS (EI) [*m*/*e* (species) intensity]: 469 (M^+) 26; 436 [$FcCH_2P(CH_2OSiMe_3)_2$] 5; 199 ($FcCH_2$) 5; 121 (C_5H_5Fe) 30. Anal. Calcd for $C_{19}H_{33}O_2Si_2PS$: C, 48.76; H, 7.11. Found: C, 48.60; H, 7.15.

Preparation of 6. Into an oven-dried, evacuated 25 mL flask fitted with a Teflon stopcock is sublimed $N_3P_3F_6$ (0.47 g, 1.88 mmol). After

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(17) Harms, K.; Wocadlo, S. *XCAD4-CAD4: Data reduction*; University of Marburg, Marburg, Germany, 1995.
(18) Farrugia, L. J. *WinGX: A windows program for crystal structure analysis*; University of Glasgow: Glasgow, Scotland, 1998.
(19) Sheldrick, G. M. *SHELX-97*: *Program for crystal structure analysis*, release 97-2; University of Göttingen: Göttingen, Germany, 1997.

addition of a pinch of CsF, $FcCH_2P(S)(CH_2OSiMe_3)_2$ (0.69 g, 1.47 mmol) dissolved in dry THF (15 mL) is introduced into the flask by syringe. The flask is then filled with nitrogen. After 12 h of stirring at 60 °C, solvent is removed and the product is purified by column chromatography using ethyl acetate/hexane and characterized as $[FcCH_2P(S)(CH_2O)PN](F_2PN)_2$ (**6**). Yield: 0.41 g, 52%. Mp: 178 °C. IR (cm^{-1}) (KBr): 2900 w, 1720 w, 1410 m, 1380 w, 1300 w, 1260 vs, 1220 w, 1190 vw, 1100 vw, 1060 m, 1050 s, 1000 w, 980 w, 970 w, 930 vs, 840 m, 830 s, 790 m, 760 m, 740 w, 700 w, 630 s. NMR: ^1H, δ 3.38 [d (J = 11 Hz), 2 H, $FcCH_2P$], 4.11 [s, 5 H, C(9)H−C(13)H], 4.14 [m, 2 H, C(6)H and C(7) H], 4.27 [m, 2 H, C(5)H and C(8)H], 4.28−4.38 (m, 2 H, PCH_2O), 4.72−4.77 (dd, 2 H, PCH_2O); $^{31}P\{^1H\}$, δ 20.26 (d, P═S), 16.32−12.80 (multiplet), 11.10−7.00 (multiplet), 5.50−1.40 (multiplet); $^{19}F\{^{31}P\}$, δ −71.61 [m (J_{P-F} = 930 Hz), PF_2]; $^{13}C\{^1H\}$, δ 29.29 [d (J = 46 Hz), $FcCH_2P$], 66.55 [dd (J = 49 Hz), PCH_2], 68.83 [s, C(5) and C(8)], 69.05 [s, C(9)−C(13)], 69.44 [s, C(6) and C(7)], 75.00 [s, C(4)]. MS (EI) [*m*/*e* (species) intensity]: 533 (M^+) 86; 501 $[FcCH_2P(CH_2O)_2(N_3P_3F_4)]$ 2; 211 ($N_3P_3F_4$) 5; 199 ($FcCH_2$) 100; 122 $[P(CH_2O)P]$ 6; 121 (C_5H_5Fe) 62. Anal. Calcd for $C_{13}H_{15}F_4FeN_3O_2P_4S$: C, 29.29; H, 2.84; N, 7.88. Found: C, 29.31; H, 2.92; N, 7.85.

Transformations of 3a and 3b into Spiro Isomer 6. The transformation reactions are carried out in a reaction flask kept at 33 °C where **3a** or **3b** with traces of CsF in THF are each stirred vigorously under nitrogen. The reactions are monitored by TLC as well as by ^{31}P NMR spectroscopy and found to be complete within 4 h in the case of **3a** and within 2 h in the case of **3b**. Purifications of the reaction residues on a silica gel column using ethyl acetate/hexane (2:98) give 38.46 and 37.5% yields of spiro isomer **6** in the cases of **3a** and **3b**, respectively. Spectral data for this compound agree with those for the compound prepared by the desilylation reaction. Recrystallization of **6** is carried out by dissolving it in toluene and cooling the solution at 15 °C.

Transformation of 4a into Spiro Isomer 7. Compound **4a** (0.09 g, 0.21 mmol) is placed in a reaction flask with traces of CsF in THF, and the mixture is stirred vigorously at 33 °C under nitrogen atmosphere. The reaction is monitored by TLC and ^{31}P NMR spectroscopy, and during a period of 1 h, all of **4a** is found to react. The product formed is purified on a silica gel column using ethyl acetate/hexane (2:98) and is identified as $[C_6H_5CH_2P(CH_2O)_2PN](F_2PN)_2$ (**7**). Yield: (0.04 g, 0.09 mmol. Mp: 125 °C. IR (cm^{-1})(KBr): 2900 m, 1410 vw, 1250 vs, 1210 vw, 1040 s, 1000 w, 920 m, 820 s, 770 m, 690 w, 610 w. NMR: ^1H, δ 3.61 [d (J = 13 Hz), $C_6H_5CH_2P$], 4.36 (m, 2 H, PCH_2O), 4.81 (d, 2 H, PCH_2O), 7.31 (s, 5 H, C_6H_5); $^{31}P\{^1H\}$, δ 22.28 (d, P═S), 16.35−14.41 (multiplet), 11.00−7.10 (multiplet), 4.41−1.50 (multiplet); $^{19}F\{^{31}P\}$, δ −71.60 (m, PF_2); $^{13}C\{^1H\}$, δ 33.57 [d (J = 44 Hz), $FcCH_2P$], 66.53 [dd (J = 50 Hz), PCH_2O], 128.22 [d (J = 3 Hz), C(7)], 129.02 [d (J = 3 Hz), C(5) and C(9)], 130.17 [d (J = 6 Hz), C(6) and C(8)]. MS (EI) [*m*/*e* (species) intensity]: 425 (M^+) 99; 334 $[P(S)(CH_2O)_2N_3P_3F_4]$ 18; 304 $[P(S)CH_2O(P_3N_3F_4)]$ 6; 302 $[P(CH_2O)_2P_3N_3F_4]$ 15; 288 $[PCH_2O(P_3N_3F_4)O]$ 8; 272 $[CH_2P(S)(CH_2O)_2N_3P_3]$ 4; 228 $[(N_3P_3)OCH_2P(S)]$ 11; 211 ($N_3P_3F_4$) 5; 135 (N_3P_3) 9; 91 ($C_6H_5CH_2$) 100; 77 (C_6H_5) 32; 65 $[P(CH_2)_2]$ 28. Anal. Calcd for $C_9H_{11}N_3P_4O_2F_4S$: C, 25.43; H, 2.61; N, 9.89. Found: C, 25.48; H, 2.63; N, 9.87.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for **3a**, **3b**, **4a**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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