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Ansa versus Spiro Substitution of Cyclophosphazenes: Is Fluorination Essential for Ansa to Spiro Transformation of Cyclophosphazenes?

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Fluorinated ansa substituted cyclophosphazenes *endo*-$FcCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ [Fc = ferrocenyl] (**1**) and *exo*-$FcCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ (**2**) readily transform to the spirocyclic compound $[FcCH_2P(S)(CH_2O)_2PN](F_2PN)_2$ (**3**) not only in the presence of CsF but also with non-fluorinated bases such as Cs_2CO_3, K_2CO_3, $KOBu^t$, Et_3N, DABCO, DBN, and DBU. The analogous tetrachloro ansa compound *exo*-$FcCH_2P(S)(CH_2O)_2[P(Cl)N]_2(Cl_2PN)$ (**5**), however, did not transform to the chlorinated spiro compound (**6**) in the presence of these bases. With excess of CsF, P–Cl bonds of **5** were found to undergo fluorination leading to the formation of **2**, which transformed to spirocyclic compound **3**. Time dependent ^{31}P NMR spectroscopy was used to monitor this transformation. Crystal structure studies on the ansa substituted compounds **4** and **5** have shown weak bonding interactions involving C–H···Cl, C–H···O, and C–H···S interactions.

Introduction

Cyclic phosphazenes have shown potential for a host of applications. These include their use as precursors for the well-known phosphazene polymers,[1] as stable multidirectional cores on which convergent as well as divergent synthesis of dendrimers can be readily performed,[2] and as precursors for multianionic phosphazenates[3] and for realizing rigid trispirocycles which are novel examples of organic zeolites.[4] The unique substitution reactions possible on the phosphorus−halogen bonds of these heterocycles continues to be the subject of detailed investigations from different perspectives.[5,6]

Reactions of difunctional alcohols and amines with perhalogenated cyclophosphazenes have been of considerable interest as these reactions lead to the formation of regioisomers.[7] Lately, the preference of spiro substitution over the other possible products, especially the ansa or transannular substitution in the reactions of diols with a cyclophosphazene, has been explained from the viewpoint of thermodynamic stability versus cation assisted supramolecular effect in the substitution reactions of chlorophosphazenes.[8] The first experimental evidence for the higher thermodynamic stability of spiro substituted phosphazenes over the ansa isomers was shown by transforming ansa substituted trimeric as well as tetrameric fluorophosphazenes to the spiro isomer in the presence of catalytic amounts of CsF.[9,10]

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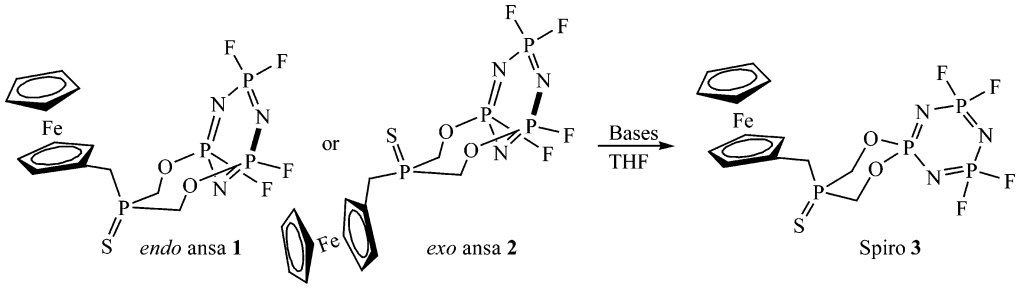
Scheme 1



One of the very essential issues which has not been addressed so far is the generality of the ansa to spiro transformation especially with respect to chlorinated cyclophosphazenes whose derivatives largely outnumber those of the fluorinated cyclophosphazenes. Given the fact that the chemistry and reactivity preferences of fluorophosphazenes differ considerably with that of the chloro analogues, it was of significant interest to explore this factor.[11,12] In this context, it was also of importance to see if CsF, which was the only catalyst used for this study so far, is a specific requirement for this transformation. The response to these queries as well as the synthesis and characterization of the first examples of exo and endo substituted chloro ansa compounds are reported in this paper. Details of unique supramolecular interactions in compounds **4** and **5** are also discussed.[13−17]

Results and Discussion

Reactions of Ansa Substituted Fluorophosphazenes with Bases. To study the effect of the nature of catalyst on the ansa to spiro transformation reactions, we have chosen the endo and exo ansa substituted compounds $FcCH_2P(S)(CH_2O)_2[P(F)N]_2(F_2PN)$ (Fc = ferrocenyl) [endo (**1**) and exo (**2**)] which we had reported earlier.[9] Compound **1** or **2** was treated separately with catalytic amounts of a variety of bases in THF, and the reaction was monitored by TLC as well as $^{31}P\{^1H\}$ NMR spectroscopy till the entire amount of the ansa compound reacted. In the presence of catalytic amounts of NEt_3, CsF, TBAF, Cs_2CO_3, K_2CO_3, KOBu^t, DABCO, DBN, DBU, and TMEDA, the ansa substituted fluorophosphazenes **1** and **2** transformed to the spiro isomer $[FcCH_2P(S)(CH_2O)_2PN](F_2PN)_2$ (**3**)[9] at temperatures ranging from −20 to +33 °C (Scheme 1).

However, in the presence of LiF, Me_3SnF, ^{t}BuNH$_2$, $HN(SiMe_3)_2$, pyridine, KSCN, CH_3CN, NaCl, Et_3NHCl, NaH, and Ph_3P, ansa isomers remained as such even after 12 h of stirring at 33 °C followed by 12 h reflux in THF. This suggests that bulky and weak bases as well as side products of substitution reactions of halogenated cyclophosphazenes do not induce the ansa to spiro transformation. The catalyst and ansa isomer used in the study, reaction conditions employed, and yield of spiro isomer obtained are given in Table 1.

Table 1. Transformation of Ansa Substituted Compounds **1** and **2** into Spiro Isomer **3** in the Presence of Various Catalysts[a]

catalyst	compd used and reaction conditions	isolated yield of **3** (%)
CsF	**1**, 33 °C (4 h)	38.4
	2, 33 °C (2 h)	37.5
	2, −20 °C (5 h)	63.0
TBAF	**1**, 33 °C (15 min)	45.5
NEt_3	**2**, 33 °C (12 h)	33.3
KOBu^t	**2**, 33 °C (6 h)	64.2
	2, −20 °C (2.5 h)	73.1
Cs_2CO_3	**2**, 33 °C (2.5 h)	51.9
	2, −20 °C (14 h)	71.3
K_2CO_3	**2**, 33 °C (16 days)	traces
	2, 33 °C, DMF (13 h)	44.4
DABCO	**2**, 33 °C (18 h)	44.0
DBU	**1**, 33 °C (10 min)	75.0
	2, 33 °C (20 min)	41.2
DBN	**2**, 33 °C (15 min)	51.9
TMEDA	**1**, 33 °C (48 h)	36.7

[a] All the reactions were carried out using THF as solvent unless otherwise specified.

The data suggest that lower reaction temperatures lead to increased yields of the spirocyclic product. For example, in the presence of Cs_2CO_3, the transformation of exo ansa compound **2** at +33 and −20 °C yielded 51.9% and 71.3% of compound **3**, respectively. A similar result was also obtained in the case of KOBu^t. This is in conformity with our previous study of CsF catalyzed transformation where the reactions were carried out in the temperature range −60 to +33 °C.[9] Apart from the temperature, the amount of catalyst used also had an impact on the transformation reactions. For example, in the presence of 0.83 and 0.15 equiv of the base DBN, spiro isomer **3** was obtained in yields of 27% and 52%, respectively.

This study revealed that the fluoride ions are not the only catalysts that can bring about the ansa to spiro transformation. Both exo and endo ansa isomers of the fluorinated cyclotriphosphazene undergo this transformation with equal propensity with trace amounts of a variety of bases. It is of interest to note that, among these catalysts, NEt_3, DBU, Cs_2CO_3, and K_2CO_3 are used as hydrogen halide scavengers in the substitution reactions of halogenated cyclophosphazenes

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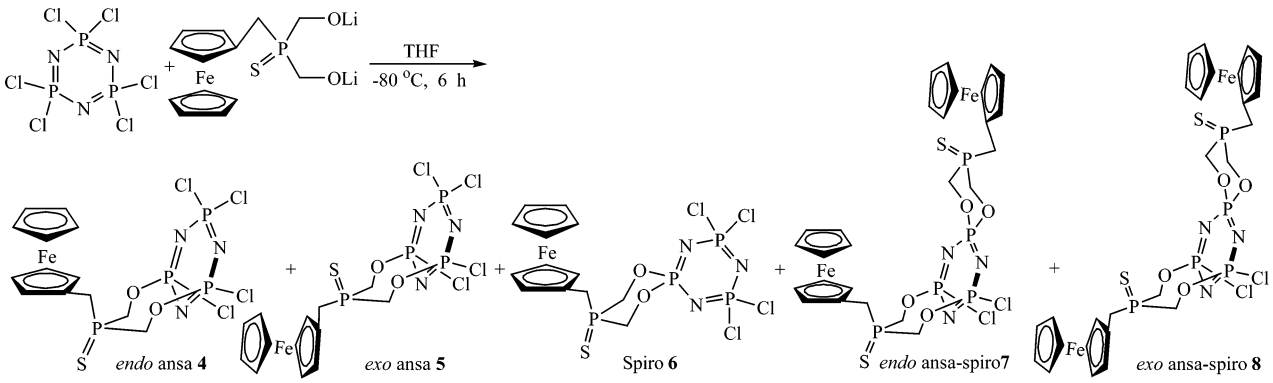
Scheme 2



with diols and diamines. Cesium fluoride and potassium *tert*-butoxide are used as catalysts for desilylation reactions of silanediols with fluorophosphazenes which had resulted exclusively in spirocyclic compounds.[9,18,19] We have also tried reactions of disodium salts of 1,3-propanediol with **1**. The analysis of the ^{31}P NMR spectrum of the reaction mixture indicates partial conversion of the ferrocene diol moiety to the spiro configuration. These observations indicate that bases such as the ones used in this study, if used in reactions of bifunctional reagents with perfluorinated cyclophosphazenes, can possibly preclude the formation of ansa substituted products in such reactions.

Formation of Ansa Substituted Chlorophosphazenes. A reaction of the dilithiated diol $FcCH_2P(S)(CH_2OLi)_2$ with $N_3P_3Cl_6$ at −80 °C for 6 h followed by immediate workup yielded two isomers of the ansa substituted chlorophosphazene *endo*-$FcCH_2P(S)(CH_2O)_2[P(Cl)N]_2(Cl_2PN)$ (**4**) and *exo*-$FcCH_2P(S)(CH_2O)_2[P(Cl)N]_2(Cl_2PN)$ (**5**) along with the chloro spiro isomer $[FcCH_2P(S)(CH_2O)_2PN](Cl_2PN)_2$ (**6**) (Scheme 2).

Similar to that of $N_3P_3F_6$, the reaction of this diol with $N_3P_3Cl_6$ yielded the two isomers of ansa substituted compounds, but in contrast to $N_3P_3F_6$, this reaction also yielded the spiro isomer **6** (12%). Compounds **4** (18%) and **5** (34%) are the first examples of exo and endo isomers of ansa substituted chlorophosphazenes. The endo and exo ansa substituted chlorophosphazenes **4** and **5** were structurally characterized by X-ray crystallography. These ansa substituted compounds were stable to air and moisture and can be handled in an open atmosphere. Unlike spirocyclic compound **3** of fluorophosphazene, spirocyclic compound **6** of chlorophosphazene is highly sensitive and decomposes immediately on exposure to air and moisture, which is similar to the observation of Brandt et al. with ansa and spiro isomers of $N_3P_3Cl_4[O(CH_2CH_2O)_4]$.[8b]

Apart from these three isomers, this reaction also yielded two isomers of ansa−spiro substituted compounds **7** and **8** (total yield 2.7%). Between these two compounds, the exo ansa−spiro compound **8** was more in yield, while the endo ansa−spiro compound **7** was obtained only in trace amounts. This reaction yielded five compounds **4**−**8** with an overall yield of approximately 73%. When the reaction was carried out at 0 °C rather than at −80 °C, and the reaction temperature maintained at 0 °C for 6 h, it yielded the same five products **4**−**8** with an overall yield of 41%.

Spectral Properties of Ansa Substituted Chlorophosphazenes. The $^{31}P\{^1H\}$ NMR spectra of these ansa and spiro compounds are less complex when compared to ansa and spiro compounds of fluorophosphazene. In $^{31}P\{^1H\}$ NMR, the P═S chemical shift of the endo and exo ansa compounds **4** and **5** appeared at 43.12 and 45.10 ppm, respectively, while for the spiro compound **6**, it appeared at 20.33 ppm. In the $^{31}P\{^1H\}$ NMR spectrum of the exo ansa compound **5**, the ring phosphorus atoms of OPCl and PCl_2 groups was observed as a simple A_2X pattern at 22.53 and 27.59 ppm, respectively. In the $^{31}P\{^1H\}$ NMR spectrum of endo ansa compound **4**, the chemical shift difference between the OPCl and PCl_2 groups was less compared to that of compound **5**. This changes the A_2X pattern observed for compound **5** to an A_2B pattern for compound **4**. Hence, the overall spectrum was complex for compound **4**. In the $^{31}P\{^1H\}$ NMR spectrum of exo ansa−spiro compound **8**, the two OPCl groups were observed as a doublet of doublets at 28.05 ppm and as a triplet at 25.52 ppm, respectively. The OPO moiety was observed as a multiplet at 13.05 ppm. The ansa P═S was observed as a singlet at 45.72 ppm while the spiro P═S was observed as doublet at 20.39 ppm. A similar spectrum was observed for compound **7** also.

Structure of Ansa Substituted Chlorophosphazenes. The crystal structures of endo and exo ansa substituted compounds **4** and **5** are depicted in Figures 1 and 2. The structure solution and refinement parameters and selected bond lengths and angles for compounds **4** and **5** are given in Tables 2−4, respectively. There are two independent molecules present in the crystal lattice of endo ansa compound **4**. The basic structure of these endo and exo ansa compounds **4** and **5** of chlorophosphazene are almost similar to those of fluorophosphazene **1** and **2**.[9] In these ansa compounds, the eight-membered ansa ring depicts a boat−chair conformation. Similar to the ansa compounds of fluorophosphazene **1** and **2**, in ansa compounds **4** and **5**, the N atom flanked by the P atoms that are bearing the ansa substitution on the phosphazene ring were found to be displaced from the plane defined by the other five atoms of

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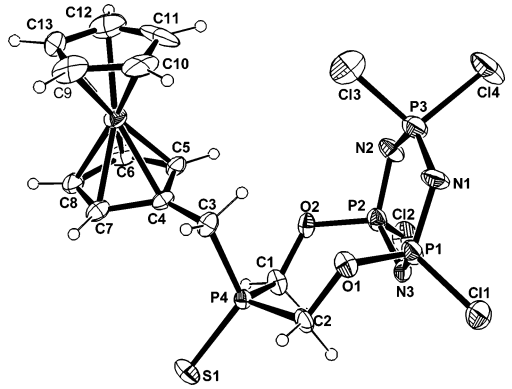

Figure 1. Crystal structure of endo ansa compound **4**.

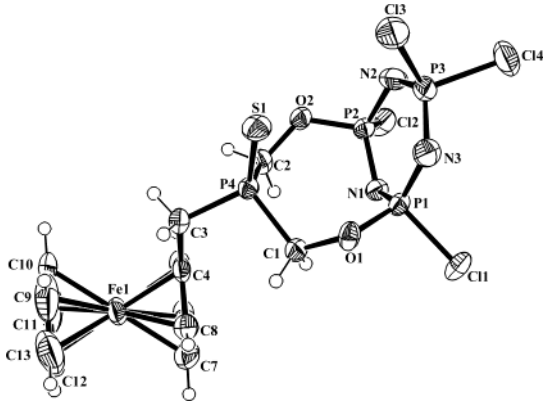

Figure 2. Crystal structure of exo ansa compound **5**.

Table 2. Structure Solution and Refinement Parameters for Endo and Exo Ansa Substituted Chlorophosphazenes **4** and **5**

	endo ansa (**4**)	exo ansa (**5**)
emprical formula	$C_{13}H_{15}Cl_4FeN_3O_2P_4S$	$C_{13}H_{15}Cl_4FeN_3O_2P_4S$
fw	598.87	598.87
cryst syst, space group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$
a (Å)	20.941(5)	8.427(1)
b (Å)	9.434(5)	9.61(1)
c (Å)	23.663	14.201(1)
α (deg)	90.000(5)	98.49(1)
β (deg)	102.894(5)	97.27(1)
γ (deg)	90.000(5)	95.89(1)
Z	4	2
D (Mg m^{-3})	1.746	1.776
T (°C)	20 (2)	20 (2)
λ (Å)	0.71069	0.71073
GOF	0.974	1.057
final indices, 2σ data R1 (wR2)[a]	0.0610 (0.0753)	0.0279 (0.0750)
final indices, all data R1 (wR2)[a]	0.2490 (0.0937)	0.0299 (0.0763)

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

the ring to a distance of 0.34 and 0.25 Å for compounds **4** and **5**, respectively. In the structure of compound **4**, another nitrogen atom N1 also was found to deviate from the phosphazene plane to a distance of 0.15 Å.

A detailed analysis of the X-ray crystal structure of exo ansa compound **5** shows the presence of weak hydrogen bonding interactions[13] leading to a supramolecular network mediated through C−H···Cl[14] and C−H···O[15] interactions. The two nongeminal chlorines [Cl(1) and Cl(2)] in the phosphazene ring interact with hydrogens [H(1B) and H(2A)] of the PCH_2O groups of the neighboring molecule. The Cl-

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for Compound 4

Bond Lengths			
P(1)−N(1)	1.584(6)	P(1)−N(3)	1.564(7)
P(1)−Cl(1)	1.969(3)	P(1)−O(1)	1.561(6)
P(2)−N(2)	1.584(7)	P(2)−N(3)	1.577(6)
P(2)−Cl(2)	1.974(4)	P(2)−O(2)	1.574(5)
P(3)−N(1)	1.571(7)	P(3)−N(2)	1.557(8)
P(3)−Cl(3)	1.993(4)	P(3)−Cl(4)	1.977(3)
P(4)−C(1)	1.823(8)	P(4)−C(2)	1.816(7)
P(4)−S(1)	1.938(3)	P(4)−C(3)	1.800(8)
Bond Angles			
P(1)−N(3)−P(2)	116.2(4)	N(3)−P(2)−N(2)	118.4(4)
P(2)−N(2)−P(3)	120.0(5)	N(2)−P(3)−N(1)	119.1(4)
P(3)−N(1)−P(1)	118.4(4)	N(1)−P(1)−N(3)	117.9(4)
O(1)−P(1)−N(3)	109.4(3)	O(2)−P(2)−N(3)	110.3(3)
C(1)−P(4)−C(2)	112.5(4)	S(1)−P(4)−C(3)	117.2(3)
C(3)−P(4)−C(1)	105.1(4)	C(3)−P(4)−C(2)	105.9(4)

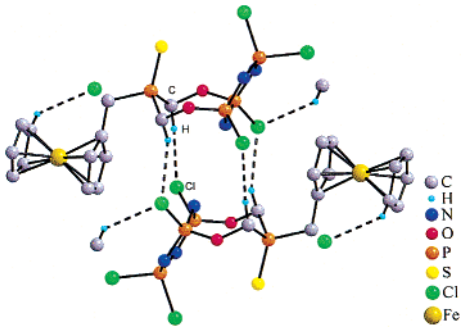

Figure 3. The weak C−H···Cl hydrogen bonding interactions in compound **5** leading to the formation of a dimer. The hydrogen atoms, which are not involved in hydrogen bonding interactions, are removed for clarity.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for Compound **5**

Bond Lengths			
P(1)−N(1)	1.579(2)	P(1)−N(3)	1.586(2)
P(1)−Cl(1)	1.9937(9)	P(1)−O(1)	1.5774(18)
P(2)−N(2)	1.577(2)	P(2)−N(3)	1.580(2)
P(2)−Cl(2)	2.0004(10)	P(2)−O(2)	1.5775(18)
P(3)−N(1)	1.573(2)	P(3)−N(2)	1.580(3)
P(3)−Cl(3)	1.9844(11)	P(3)−Cl(4)	1.9975(10)
P(4)−S(1)	1.9356(9)	P(4)−C(1)	1.844(2)
P(4)−C(2)	1.850(2)	P(4)−C(3)	1.822(2)
Bond Angles			
P(1)−N(3)−P(2)	118.90(12)	N(3)−P(2)−N(2)	118.94(12)
P(2)−N(2)−P(3)	119.92(15)	N(2)−P(3)−N(1)	118.89(12)
P(3)−N(1)−P(1)	121.51(14)	N(1)−P(1)−N(3)	118.06(12)
O(1)−P(1)−N(3)	109.09(10)	O(2)−P(2)−N(3)	110.64(10)
C(1)−P(4)−C(2)	106.97(12)	S(1)−P(4)−C(3)	117.53(8)
C(3)−P(4)−C(1)	102.68(11)	C(3)−P(4)−C(2)	102.11(11)

(1) and Cl(2) chlorines of the neighboring molecule also interact in a similar way with the first molecule. Thus, these interactions result in the formation of a dimer as shown in Figure 3. The metric parameters involved in C(1)−H(1B)···Cl(2) interactions are C(1)−H(1B) = 0.97 Å, H(1B)−Cl(2) = 2.91 Å, C(1)−Cl(2) = 3.58 Å, C(1)−H(1B)−Cl(2) = 126.7°, and symmetry code = $-x$, $1 - y$, $-z$. In C(2)−H(2A)···Cl(1) interactions are C(2)−H(2A) = 0.91 Å, H(2A)−Cl(1) = 2.97 Å, C(2)−Cl(1) = 3.78 Å, C(2)−H(2A)−Cl(1) = 141.5°, and symmetry code = $-x$, $1 - y$, $-z$. Similar C−H···Cl interactions were reported in substituted carbaphosphazenes as well.[16]

These dimers are linked parallel in both directions by the interactions of chlorines of the OPCl group with one of the

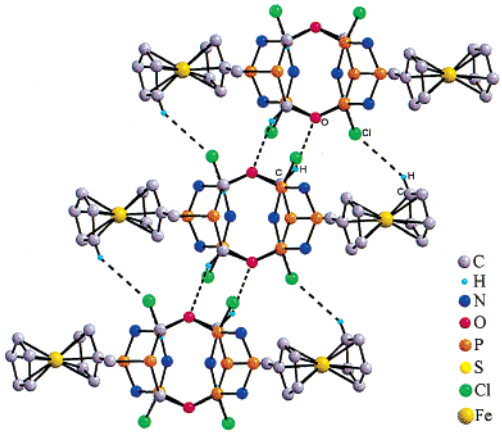

Figure 4. Two-dimensional layer of compound **5** formed by the weak bonding interactions involving C−H···Cl and C−H···O showing an array of ferrocenes. The sulfur, chlorines of PCl_2 group, and hydrogen atoms, which are not involved in weak bonding interactions, are omitted for clarity.

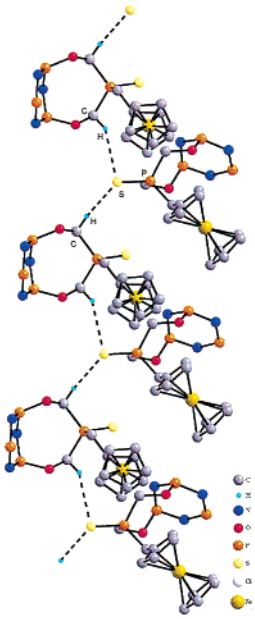

Figure 5. The C−H···S weak hydrogen bonding interactions in compound **4** leading to a linear chain arrangement of the molecules. The chlorines and hydrogen atoms, which are not involved in weak bonding interactions, are omitted for clarity.

hydrogens of the free cyclopentadienyl group of the ferrocene through C−H···Cl interaction and also through the C−H···O interactions of PCH_2O groups leading to the formation of an interesting two-dimensional layer which has a symmetrical array of ferrocene units as shown in Figure 4. The metric parameters involved in C(10)−H(10B)−Cl(2) interactions are C(10)−H(10B) = 0.97 Å, H(10B)−Cl(2) = 2.96 Å, C(10)−Cl(2) = 3.80 Å, C(10)−H(10B)−Cl(2) = 141.5°, and symmetry code = $-x$, $1 - y$, $-z$, and those involved in C(2)−H(2B)···O(2) interaction are C(2)−H(2B) = 0.97 Å, H(2B)−O(2) = 2.73 Å, C(2)−O(2) = 3.49 Å, C(2)−H(2B)−O(2) = 135.7°, H(10)−O(2) = 2.734 Å, and symmetry code = $1 - x$, $1 - y$, $-z$.

Apart from these interactions, the molecule also shows C(1)−H(1A)···O(1) [metric parameters: C(1)−H(1A) = 0.97 Å, H(1A)−O(1) = 2.73 Å, C(1)−O(1) = 3.46 Å, C(1)−H(1A)−O(1) = 133.0°, symmetry code = $-x$, $-y$, $-z$] and C(3)−H(3A)···O(1) [metric parameters: C(3)−H(3A) = 0.97 Å, H(3A)−O(1) = 2.61 Å, C(3)−O(1) = 3.40 Å, C(3)−H(3A)−O(1) = 139.4°, symmetry code = $-x$, $-y$, $-z$] interactions leading to a complex three-dimensional arrangement of molecules. Owing to the complexity, it is not shown in the figures.

Quite interestingly, a closer look at the structure of endo ansa compound **4** did not show any weak hydrogen bonding interactions involving C−H···Cl or C−H···O. However, this molecule does show C−H···S interactions, which were not observed in the exo ansa compound **5**. The two independent molecules in the crystal lattice of this compound were linked together alternatively by C−H···S weak interactions,[17] which involve the interaction of sulfur of the P═S group with hydrogen of the PCH_2O group of the neighboring independent molecule. These interactions lead to a linear chainlike arrangement of molecules in which the ferrocene moieties are embedded almost perpendicular to each other in the chain as shown in Figure 5. The metric parameters in C(15)−H(15B)−S(1) interactions are C(15)−H(15B) = 0.97 Å, H(15B)−S(1) = 2.91 Å, C(15)−S(1) = 3.78 Å, C(15)−H(15B)−S(1) = 149.4°, and symmetry code = x, y, z, and those in C(14)−H(14A)−S(1) interactions are C(14)−H(14A) = 0.97 Å, H(14A)−S(1) = 2.83 Å, C(14)−S(1) = 3.66 Å, C(14)−H(14A)−S(1) = 143.8°, and symmetry = x, $-1 + y$, z.

Ansa to Spiro Transformation Study on Chlorophosphazenes. Ansa substituted chlorophosphazene **5** was treated with all the non-fluorinated bases given in Table 1, under the same reaction conditions which facilitated ansa to spiro transformation of **1** and **2**. However, none of the reaction mixtures on analysis by ^{31}P NMR showed formation of the spiro isomer of chlorophosphazene. Extending the reaction time further or heating the reaction mixture to reflux conditions, however, resulted in the degradation of ansa compound **5** but did not show any indication of the formation of the spiro isomer.

The ferrocene derived phosphine sulfide diol used in this study has a P═S moiety, which shows specific and highly structure sensitive chemical shift variations in its ^{31}P NMR spectra with respect to the ansa and spiro derivatives of the fluorophosphazene. The exact chemical shift of the P═S group of both ansa and spiro compounds were also found to vary slightly but uniquely when one goes from chloro to fluoro phosphazenes and when there is more than one diol reacting to form products. This sensitivity of the chemical shift of the P═S group was utilized in monitoring the transformations.

When compound **5** was treated with CsF (from trace amounts up to 1:1 molar equivalent), no spirocyclic product formation was observed. When the reaction was carried out with 4 mol of CsF and was monitored by time dependent ^{31}P NMR (Figure 6), two additional peaks corresponding to P═S around 45 ppm started appearing. After 3 h, a triplet of multiplets with a coupling constant of 923 Hz appeared at 5.57 ppm corresponding to the formation of PF_2. This shows that the reaction proceeded with fluorination of the PCl_2 leading to the formation of the partially fluorinated exo

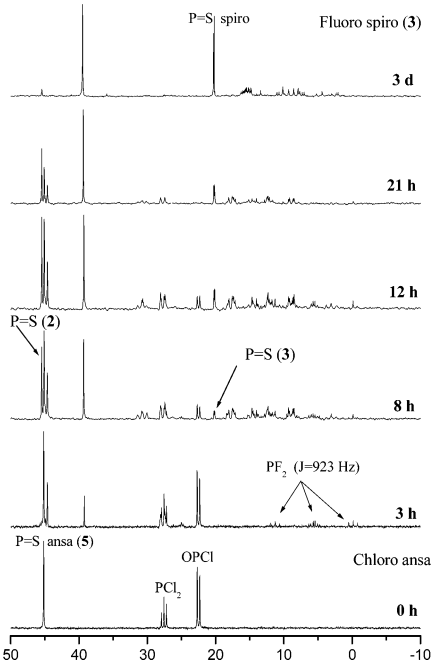

Figure 6. Time dependent ^{31}P NMR showing the transformation of ansa substituted chlorophosphazene **5** to spiro substituted fluorophosphazene **3**.

ansa compound $FcCH_2P(S)(CH_2O)_2[P(Cl)N]_2(F_2PN)$ (δ P═S, 44.62 ppm). This compound on further fluorination yielded the perfluorinated exo ansa compound **2** (δ P═S, 45.43 ppm).

Immediately after the formation of **2**, a new peak corresponding to the P═S moiety of fluorospiro compound **3** appeared at 20.25 ppm indicating that OPF formation is vital for the ansa to spiro transformation to occur (Scheme 3). Apart from the peaks around 45 ppm, a peak around 39 ppm was also observed in all the transformation studies of chloro ansa compound **5**. Attempts to separate, purify, and completely characterize the compound corresponding to this peak proved difficult. However, NMR and mass spectral studies indicate a possible degradation product with the $FcCH_2P(S)$ moiety intact. Analysis of reaction mixtures from repeated transformation studies by ^{1}H NMR and mass spectra showed the presence of degradation product with peaks around 39−41 ppm in their $^{31}P\{^1H\}$ NMR spectra.

In summary, we have established that the ansa substituted fluorophosphazenes can be transformed to their spiro isomers not only in the presence of fluoride ion sources but also in the presence of a host of other nonfluorinated bases. The reaction of dilithiated ferrocene derived diol with $N_3P_3Cl_6$ was found to yield the first examples of endo and exo isomers of chlorinated ansa phosphazenes along with the spiro isomer. This reaction also yielded two isomers of ansa−spiro substituted chlorophosphazenes. The ansa substituted chlorophosphazene compounds do not transform to the chlorinated spirocyclic isomers in the presence of bases, which is in sharp contrast to the behavior of fluoro ansa compounds. In the presence of sufficient excess of fluoride ions, they first convert to the corresponding fluoroansa compounds which further transform to the fluorospirocyclic compounds indicating that the ansa to spiro transformation is unique to fluorinated cyclophosphazenes. The chloro ansa compounds show weak hydrogen bonding interactions involving C−H···Cl and C−H···O interactions in the case of the exo ansa compound and C−H···S interactions in the case of the endo ansa compound.

Experimental Section

Materials and General Procedures. A conventional vacuum line equipped with dry nitrogen facility and Schlenk glassware was used for all reactions. Reactions were carried out and worked up under an atmosphere of dry nitrogen. The solvents tetrahydrofuran, ethyl acetate, and hexane were purified and dried as per standard procedures. The compounds $N_3P_3Cl_6$, CsF, NEt_3, Cs_2CO_3, K_2CO_3, $KOBu^t$, TBAF (tetrabutylammonium fluoride), DABCO (diazabicyclo[2.2.2]octane), DBN (1,5-diazabicyclo[4.3.0]non-5-ene), DBU (1,8-diazabicyclo[5.4.0]undecane-7-ene), and TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) were used as such. The diol $FcCH_2P(S)(CH_2OH)_2$ was prepared as reported in the literature.[20] Infrared spectra were recorded on Perkin-Elmer 1320 spectrometer as KBr pellets. The ^{1}H, $^{31}P\{^1H\}$, $^{19}F\{^{31}P\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded using a JEOL JNM-LA 400 FT NMR spectrometer using $CDCl_3$ as a solvent and TMS, 85% H_3PO_4, and $CFCl_3$ as references. Mass spectra were obtained on a JEOL D-300 spectrometer in the EI mode. Elemental analyses were carried out on a Carlo Erba CHNSO 1108 elemental analyzer. Low temperature reactions were carried out using a Julabo FT 901 low temperature apparatus with ethanol as medium.

X-ray Diffraction Studies. The X- ray diffraction data on compounds **4** and **5** were collected on an Enraf-Nonius CAD-4 diffractometer. The data were reduced and structure solved by using WINGX program[21] incorporating SHELX 97[22] for refinement by least-squares methods on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference electron density maps and were included in the refinement process in an isotropic manner.

Transformation Reactions of Compounds 1 and 2. Compounds **1** or **2** was dissolved in THF, and calculated quantities (3 to 10 mol %) of catalyst were added to it. The reaction was monitored by TLC and $^{31}P\{^1H\}$ NMR till the entire ansa compound reacted. Afterward, products were purified by column chromatography over silica gel using ethyl acetate/hexane mixture as eluent to give compound **3**, if formed, in the reactions.

Preparation of Compounds 4−8. The compound $FcCH_2P(S)(CH_2OH)_2$ (0.47 g, 1.5 mmol) was dilithiated in THF (20 mL) by reaction with *n*-BuLi (1.8 mL, 2.9 mmol) at −80 °C in an oven dried 100 mL round-bottomed flask. The $N_3P_3Cl_6$ (0.50 g, 1.5 mmol) was dissolved in THF (20 mL) separately in a 100 mL flask and was cooled to −80 °C. It was then mixed with the dilithiated diol at −80 °C, with constant stirring under nitrogen atmosphere using a cannula. The temperature was maintained at −80 °C for 6 h after which it was allowed to reach 0 °C within 3 h. Then, the THF was evaporated under vacuum, and the residue was dissolved in dry dichloromethane. The LiCl formed was filtered off. After TLC analysis, the mixture was made into a slurry with silica gel, placed on a silica gel (100−200 mesh) column, and eluted with dry hexane to remove the unreacted $N_3P_3Cl_6$. It was then gradually

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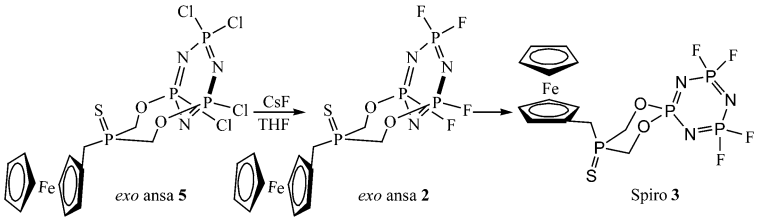
(22) Sheldrick, G. M. *SHELX97, Programs for Crystal Structure Analysis (Release 97-2)*; Institüt für Anorganische Chemie der Universität: Göttingen, Germany, 1998.

Scheme 3



eluted with a mixture of dry ethyl acetate/hexane under nitrogen atmosphere. The fractions (0.51 g, 69.9%) which came out of the column with 4−7% of ethyl acetate in hexane were collected and analyzed by $^{31}P\{^1H\}$ NMR, and these samples showed the presence of three compounds. This mixture was then dissolved in the minimum quantity of ethyl acetate, and a large excess of hexane was added to precipitate out a compound which was characterized as *spiro*-[$FcCH_2P(S)(CH_2O)_2PN$][Cl_2PN]$_2$ (**6**).Yield: 0.09 g, 12%. Mp: 174 °C. IR (cm^{-1}) (KBr): 2922 w, 1412 w, 1249 w, 1206 vs, 1048 vs, 893 w, 815 s, 744 w, 681 w, 639 w, 570 vs. NMR: ^1H, δ 3.36 [d (J = 10 Hz), $FcCH_2P$], 4.22 [s, 5H, η^5-C_5H_5], 4.29−4.31 [m, 2H, η^5-C_5H_4], 4.37−4.41 [m, 2H, η^5-C_5H_4], 4.80−4.84 [m, 4H, PCH_2O]; $^{31}P\{^1H\}$, δ 25.16 [dd ($^2J_{PP}$ = 85 Hz, 58.21 Hz), PCl_2], 21.83 [t ($^2J_{PP}$ = 57 Hz), PCl_2], 20.35 [d ($^3J_{PP}$ = 15 Hz), P═S], 4.71 [ddd ($^2J_{PP}$ = 83 Hz, 57 Hz, $^3J_{PP}$ = 15 Hz), $P(O)_2$]; $^{13}C\{^1H\}$, δ 29.43 [d (J_{PC} = 46 Hz), $FcCH_2P$], 66.55 [d (J_{PC} = 50 Hz), PCH_2O], 68.88 [s, β-C of η^5-C_5H_4], 69.01 [s, η^5-C_5H_5], 69.60 (s, γ-C of η^5-C_5H_4), 75.12 (s, α-C of η^5-C_5H_4). MS (FAB): 599-(M^+), 306 ($FcP(S)(CH_2O)(CH_2)$, 199 ($FcCH_2^+$), 121 (CpFe).

The remaining filtrate was reduced in volume and cooled to 4 °C to crystallize out the compound *exo*-$FcCH_2P(S)(CH_2O)_2$-[P(Cl)N]$_2$(Cl_2PN) (**5**). Yield: 0.13 g, 18%. Mp: 149 °C. IR (cm^{-1}) (KBr): 2929 w, 1209 vs, 1063 vs, 891 s, 844w, 766 w, 729 s, 666 s, 569 vs, 544 s. NMR: ^1H, δ 3.53 [d (J = 12 Hz), 2H, $FcCH_2P$], 4.19 [s, 5H, C(1)H−C(5)H], 4.20−4.23 [m, 2H, C(8)H and C(10)H], 4.32−4.35 [m, 2H, C(6)H and C(7)H], 4.45−4.52 [m, 4H, PCH_2O]; $^{31}P\{^1H\}$, δ 45.12 (s, P═S), 27.59 [t ($^2J_{PP}$ = 61 Hz), PCl_2], 22.53 [dd ($^2J_{PP}$ = 59 Hz and $^3J_{PP}$ = 6 Hz), OPCl]; $^{13}C\{^1H\}$, δ 29.25 [d (J_{PC} = 43 Hz), $FcCH_2P$], 66.17 [d (J_{PP} = 39 Hz), PCH_2O], 68.74 (s, C5 and C8), 69.09 (s, C9−C13), 69.75 (s, C6 and C7), 74.32 (s, C4). MS (FAB): 599(M^+), 306 ($FcP(S)(CH_2O)$-(CH_2), 274 ($N_3P_3Cl_4$), 199 ($FcCH_2^+$), 135 N_3P_3, 121 (CpFe). Anal. Calcd for $C_{13}H_{15}Cl_4FeN_3O_2P_4S$ (%): C, 26.07; H, 2.52; N, 7.02. Found: C, 26.18; H, 2.66; N, 6.91.

After repeated crystallization of compound **5**, the remaining solution was kept at 0 °C. It yielded a crop of crystals after 15 days, which were characterized as *endo*-$FcCH_2P(S)(CH_2O)_2$-[P(Cl)N]$_2$(Cl_2PN) (**4**). Yield: 0.25 g, 34.2%. Mp: 138 °C. IR (cm^{-1}) (KBr): 2921 w, 1411 w, 1207 vs, 1041 vs, 891 w, 846 w, 743 s, 678 s, 569 vs, 498 w. NMR: ^1H, δ 3.25 [d ($^2J_{PH}$ = 11 Hz), $FcCH_2P$], 4.05 (s, 5H, η^5-C_5H_5), 4.11−4.13 (m, β−H of η^5-C_5H_5), 4.37−4.39 (m, γ−H of η^5-C_5H_5), 4.64−4.67 (m, PCH_2O); ^{31}P-$\{^1H\}$, δ 43.12 (s, P═S), 24.70, 23.99, 23.82, 23.53, 23.03, 23.00, 22.69, and 22.56 (eight peaks corresponding to phosphazene ring); $^{13}C\{^1H\}$, δ 28.08 [d (J_{PC} = 45 Hz), $FcCH_2P$], 65.34 [d (J_{PC} = 46 Hz), PCH_2O], 68.85 (s, β-C of η^5-C_5H_4), 68.98 (s, η^5-C_5H_5), 69.79 (s, γ-C of η^5-C_5H_4), 73.87 (s, α-C of X_PCH_2). MS (FAB): 599-(M^+), 306 ($FcP(S)(CH_2O)(CH_2)$, 199 ($FcCH_2^+$), 121 (CpFe). Anal. Calcd for $C_{13}H_{15}Cl_4FeN_3O_2P_4S$ (%): C, 26.07; H, 2.52; N, 7.02. Found: C, 26.18; H, 2.40; N, 7.10.

The second fraction which came out of column with 10−12% of ethyl acetate/hexane was collected and analyzed by $^{31}P\{^1H\}$ NMR, and it showed the presence of two compounds (0.02 g, 2.7%). Upon dissolving this mixture in ethyl acetate/hexane and cooling, it yielded a crystalline compound, which was characterized as ansa−spiro *exo*-$FcCH_2P(S)(CH_2O)_2$[P(Cl)N]$_2$[$FcCH_2P(S)(CH_2O)_2PN$] (**7**). Mp: chars above 220 °C. NMR: ^1H, δ 3.46−3.49 (m, 4H, $FcCH_2P$), 4.16 (s, 10H, η^5-C_5H_5), 4.42−4.45 (m, 8H, η^5-C_5H_4), 4.80 to 4.91 (m, 8H, PCH_2O); $^{31}P\{^1H\}$, δ 45.72 (s, P═S ansa), 28.05 [dd ($^2J_{PP}$ = 89 Hz, 68 Hz), OPCl], 25.52 [t ($^2J_{PP}$ = 68 Hz), OPCl], 20.39 [d ($^3J_{PP}$ = 18 Hz), P═S spiro], 13.47−12.54 (m, OPO); $^{13}C\{^1H\}$, δ 29.35 [d (J_{PC} = 43 Hz), $FcCH_2P$ ansa], 31.10 [d (J_{PC} = 46 Hz), $FcCH_2P$ spiro], 65.84 [d (J_{PC} = 48 Hz), CH_2O spiro], 67.17 [d (J_{PC} = 42 HZ), CH_2O ansa], 68.72 (s, β-C ansa), 68.92 (s, β-C spiro), 69.08 (s, η^5-C_5H_5), 69.12 (s, η^5-C_5H_5), 69.53 (s, γ-C spiro), 69.81 (s, γ-C ansa), 74.48 (s, α-C ansa), 75.09 (s, α-C spiro). MS (FAB): 849 (M^+), 199 ($FcCH_2^+$). Anal. Calcd for $C_{26}H_{30}Cl_2Fe_2N_3O_4P_5S_2$ (%): C, 36.73; H, 3.56; N, 4.94. Found: C, 36.63; H, 3.50; N, 5.10. The compound (**8**) was identified by the $^{31}P\{^1H\}$ NMR spectrum of this mixture of compounds. NMR: $^{31}P\{^1H\}$, δ 45.64 (s, P═S), 28.0 (m, OPCl), 25.70 (m, OPCl), 9.65 (m, OPO).

Transformation Reactions of 5. The transformation reactions of exo ansa compound **5** in the presence of catalytic amounts of bases NEt_3, DABCO, DBU, DBN, Cs_2CO_3, and $KOBu^t$ were carried out similarly to one discussed for compounds **1** and **2**. In the case of CsF, the reactions were carried out with catalytic amounts of CsF as well as in 4:1 mole ratio (CsF: **5**) separately. Spirocyclic compound **3** formed in this reaction was purified by column chromatography over silica gel using ethyl acetate/hexane mixture as eluent. The spectral data were compared with an authentic sample.[9]

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Supporting Information Available: Crystallographic information file (CIF) for compounds **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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