Syntheses and Reactions of the Fluorinated Cyclic Thionylphosphazene NSO(Ar)[NPF_2]$_2$ (Ar = 4-t-BuC_6H_4−) with Difunctional Reagents

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The S−aryl substituted thionylphosphazene ($Cl_2PN)_2$[4-t-BuC_6H_4(O)SN] (**1**) was prepared by Friedel−Craft's reaction of NSOCl($NPCl_2)_2$ with *tert*-butylbenzene. When it reacted with excess KSO_2F at 110 °C, the P−Cl bonds of **1** were fluorinated, yielding the tetrafluorothionylphosphazene, ($F_2PN)_2$[4-t-BuC_6H_4(O)SN] (**2**). An equimolar reaction of **2** with dilithiated 1,3-propanediol in THF at −78 °C resulted in the formation of the ansa-substituted compound $CH_2(CH_2O)_2$[FPN]$_2$[4-t-BuC_6H_4(O)SN] (**3**). The crystal structures of **2** and **3** were determined. In **3** the ansa ring is trans on the PNS heterocycle with respect to the aryl group. Reaction of **2** with the disiloxane ($CF_2CH_2OSiMe_3)_2$, in the presence of catalytic amounts of CsF in THF at 90 °C, resulted in the formation of the dispiro compound [($CF_2CH_2O)_2$PN]$_2$[4-t-BuC_6H_4(O)SN] (**4**). Compounds **1**−**4** were characterized by IR, NMR (^{1}H, ^{13}C, ^{19}F, ^{31}P), mass spectral, and elemental analyses.

Introduction

The chemistry of fluorinated cyclophosphazenes differs significantly when compared to that of the well-known and widely used chlorophosphazenes.[1−3] The comparatively higher volatility, higher hydrolytic and thermal stabilities, and lower basicity of the ring nitrogens of fluorophosphazenes make this unique difference. Because of the absence of complexity in the nature of products formed, fluorinated phosphazenes are preferred over the chloro analogues for reactions with organometallic reagents.[4] It was also recently demonstrated that ansa substitution is more facile with fluorinated phosphazenes.[5,6]

Thionylphosphazenes of the type NSOX($NPCl_2)_2$ (X = Cl, F) are considered as hybrid heterocycles of cyclophosphazenes and oxothiazenes and are well-known for their robustness and stability.[7] These properties of the heterocycle have been utilized to prepare stable macrocyclic compounds as well as novel, substitutionally labile, high molecular weight sulfur(VI)−nitrogen−phosphorus polymers by thermal ring-opening polymerization.[8,9] However, it is of interest to note that the syntheses and reactions of fluorinated thionylphosphazenes are still poorly understood. Surprisingly, attempts to fluorinate the perchlorinated heterocycle NSOCl($NPCl_2)_2$ indicated regiospecificity depending on the type of fluorinating reagents used. While reactions of NSOCl($NPCl_2)_2$ with AgF_2 or $AgBF_4$ yielded only the fluorinated sulfur compound,[8,10] reaction with KSO_2F was reported to selectively fluorinate the P−Cl bonds of the heterocycle.[11]

With the objective of exploring the chemistry of the PF_2 groups of the fluorinated thionylphosphazenes, we have carried out the syntheses and tetrafluorination of a new S−aryl, P−chloro substituted thionylphosphazene. Reactions of the tetrafluorinated thionylphosphazene were performed with dilithiated and disilylated diols to compare the mode of substitution and the nature of products formed. The first crystal structures of a tetrafluorinated thionylphosphazene and its ansa-substituted derivative are also reported.

Experimental Section

Materials. ($Cl_2PN)_2$[Cl(O)SN] was prepared on the basis of literature methods[12] and was purified by recrystallization. KSO_2F was prepared according to the method of Seele.[13] Reagents $AlCl_3$, *tert*-butylbenzene, 1,3-propane diol, *n*-BuLi (1.6 M in hexane), and 3,3,4,4-tetrafluorobutane diol were procured from Aldrich. *tert*-Butylbenzene, hexane, diethyl ether, and tetrahydrofuran (THF) were distilled and dried by standard procedures.

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. Infrared spectra were recorded on a BioRad Merlin spec-

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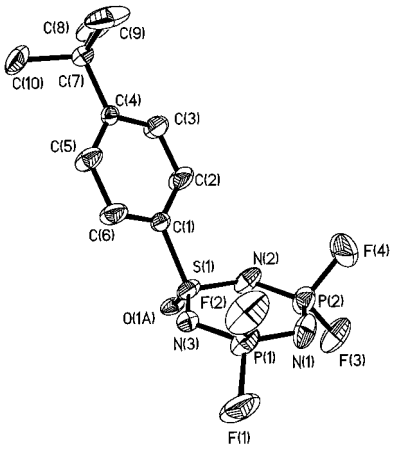

Figure 1. Thermal ellipsoid plot (30%) of **2**. H atoms are omitted for clarity.

trometer as KBr pellets. The ^{1}H, ^{31}P{^{1}H}, ^{19}F{^{31}P}, and ^{13}C{^{1}H} NMR spectra were recorded using Bruker AC 200, AMX 300, and AVANCE 500 spectrometers using $CDCl_3$ as a solvent and TMS, 85% H_3PO_4, and $CFCl_3$ as references. Mass spectra were obtained on a Shimadzu GCMS QP 5050A in the EI mode. Appropriate chlorine isotopic ratios were observed. Elemental analyses were carried out by Desert Analytics, Tuscon, Arizona.

X-ray Crystallographic Studies. The crystals of **2** and **3** were removed from the flasks and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream.[14] Data for **2** and **3** were collected at −70 °C using a Siemens SMART 1000 instrument (Mo Kα radiation, λ = 0.710 73 Å) equipped with a Siemens LT-2A low-temperature device. The SHELXTL, version 5.10, program package was used for structure solution and refinement.[15] An absorption correction was applied to **2** and **3** using SADABS.[16] The structures were solved by direct methods and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. The thionyl oxygen atom in **2** was disordered, and the occupancy was refined as 80% as shown in Figure 1. Some carbon atoms showed large librational movement around the axis defined by $C_1-C_4-C_7$. Attempts at refining a complete disordered carbon backbone or a disordered t-Bu group were unsatisfactory and led to unstable refinements. The model shown gave the best refinement. Compound **3** also displays disorder in the thionyl oxygen, fluorine, and ansa bridge oxygen atom sites with a refined occupancy of 50%. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

Preparation of (Cl$_2$PN)$_2$[4-t-BuC$_6$H$_4$(O)SN] (1). Aluminum trichloride (0.29 g, 2.17 mmol) was taken in a 50 mL round-bottomed flask fitted with a reflux condenser under an atmosphere of nitrogen. **(**Cl$_2$PN)$_2$[Cl(O)SN] (0.71 g, 2.17 mmol) was added as solid followed by *tert*-butylbenzene (15 mL). When the solution was stirred vigorously for 20 min, it turned dark yellow. It was slowly brought to 70 °C and maintained at that temperature for 48 h during which the solution turned dark brown. The solution was cooled and was poured into a mixture of 50 g of ice and 8 mL of concentrated HCl. The mixture was stirred for 30 min and the organic portion separated. The aqueous solution was extracted with dichloromethane (2 × 30 mL). The organic portions were again washed with water, dried over anhydrous sodium sulfate, and concentrated in a vacuum. GCMS of the mixture showed that in addition to the expected product, two major side products were present that were identified from a comparison of fragmentation patterns of standard compounds as 1,2- and 1,4-di(*tert*-butyl)benzenes. The mixture was evacuated with heating (70 °C, 40 mmHg) to remove the *tert*-butylbenzenes and the side products. The residue was recrystallized from hexane to yield **(**Cl$_2$PN)$_2$[4-t-BuC$_6$H$_4$(O)SN] (**1**) (0.60 g, 65%). Mp: 98 °C. IR (cm $^{-1}$) (KBr): 2963 s, 2869 w, 1593 w, 1472 w, 1470 w, 1397 m, 1365 w, 1255 vs, 1204 vs, 1186 vs, 1091 s, 1013 w, 839 s, 777 m, 721 vw, 613 vs, 600 s, 559 vs, 534 vs, 500 w. ^{1}H NMR: δ 1.32 (s, 9H, CH_3), 7.52 (d, 2H, ArH), 7.78 (d, 2H, ArH). ^{31}P{^{1}H} NMR: δ 20.64 (s). ^{13}C{^{1}H} NMR: δ 31.02 [s, CH_3], 35.22 [s, *C*-Me], 125.08 and 126.24 [s, Ar], 140.08 [s, *C*-S(O)Cl], 157.14 [s, *C*-C(Me)$_3$]. MS (EI) [*m*/*e* (species) intensity]: 427 (M^+) 8; 412 ($M^+ - CH_3$) 80; 294 ($N_3OSP_2Cl_4$) 7; 278 ($N_3SP_2Cl_4$) 13. Elemental Anal. Found: C, 28.60; H, 3.33; N, 9.55. Calcd for $C_{10}H_{13}Cl_4N_3OP_2S$: C, 28.1; H, 3.1; N, 9.8.

Table 1. Crystal Data and Structure Refinement for **2** and **3**

	2	**3**
empirical formula	$C_{10}H_{13}F_4N_3OP_2S$	$C_{13}H_{19}F_2N_3O_3P_2S$
fw	361.23	397.31
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
color	colorless	colorless
habit	block	block
cryst dimens (mm)	0.35 × 0.20 × 0.13	0.54 × 0.39 × 0.32
a (Å)	8.0392(15)	8.5112(10)
b (Å)	9.9467(18)	10.1847(12)
c (Å)	10.4353(19)	11.3687(13)
α (deg)	66.655(3)	111.302(2)
β (deg)	88.870(3)	98.453(2)
γ (deg)	83.702(3)	101.292(2)
V (Å^3)	761.3(2)	873.87(18)
Z	2	2
D_{calcd} (Mg m^{-3})	1.576	1.510
μ (mm^{-1})	0.466	0.406
T (°C)	−70(2)	−70(2)
λ (Å)	0.710 73	0.710 73
final *R* indices[a] [$I > 2\sigma(I)$]	R1 = 0.0687, wR2 = 0.1495	R1 = 0.0534, wR2 = 0.1216
R indices[a] (all data)	R1 = 0.1078, wR2 = 0.1693	R1 = 0.0680, wR2 = 0.1308

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

Preparation of (Cl$_2$PN)$_2$[4-t-BuC$_6$H$_4$(O)SN] (2). A mixture of **(**Cl$_2$PN)$_2$[4-t-BuC$_6$H$_4$(O)SN] (0.80 g, 1.87 mmol) and KSO_2F (1.00 g, 8.20 mmol) was taken in a 100 mL round-bottomed flask fitted with an air condenser and gas outlet bubbler. The mixture was stirred well and was warmed slowly. At around 70 °C, it was found to melt with evolution of SO_2. When the mixture was further heated at 110 °C for 1 h, the evolution of SO_2 ceased. White crystals were found to sublime onto the cooler portions of the flask and condenser. The residue was heated using a heating gun in a sublimation unit at a vacuum of 40 mmHg, and a white solid was found to sublime out of the mixture, which was characterized as **(**F$_2$PN)$_2$[4-t-BuC$_6$H$_4$(O)SN] (**2**) (0.58 g, 86%). Mp: 95−96 °C. IR (cm $^{-1}$) (KBr): 2970 w, 1595 w, 1476 w, 1400 w, 1281vs, 1232 vs, 1152 s, 1094 m, 1015 w, 943 vs, 895 s, 823 vs, 756 s, 710 w, 643 vs, 578 w, 551 m, 529 vs, 473 s. ^{1}H NMR: δ, 1.33 (s, 9H, CH_3), 7.54 (d, 2H, ArH), 7.77 (d, 2H, ArH). ^{31}P{^{1}H} NMR: δ 4.91 (tm, J_{P-F} = 913 Hz) PF_2. ^{19}F{^{31}P} NMR: δ −69.45 [dm (J_{P-F} = 910 Hz), PF], − 72.55 [dm (J_{P-F} = 915 Hz), PF]. ^{13}C-{^{1}H} NMR: δ 31.42 (s, CH_3), 35.67 (s, *C*-Me), 125.31 and 126.78 (s, Ar), 140.47 (s, *C*-S(O)Cl), 157.94 (s, *C*-C(Me)$_3$). MS (EI) [*m*/*e* (species) intensity]: 361 (M^+) 11; 346 ($M^+ - CH_3$) 100; 228 ($N_3OSP_2F_4$) 9; 212 ($N_3SP_2F_4$) 20. Elemental Anal. Found: C, 33.11; H, 3.71; N, 11.31. Calcd for $C_{10}H_{13}F_4N_3OP_2S$: C, 33.2; H, 3.6; N, 11.6.

Preparation of Ansa CH$_2$(CH$_2$O)$_2$(FPN)$_2$[4-t-BuC$_6$H$_4$(O)SN] (3). 1,3-Propanediol (0.10 g, 1.31 mmol) and freshly distilled THF (20 mL) were placed in a 50 mL round-bottomed flask. It was cooled to −78 °C, and *n*-BuLi (1.65 mL, 2.64 mmol) was added over a period of 5 min using a syringe. The solution was allowed to come to room temperature and was stirred further for 2 h. It was then cooled to −78 °C, and (F$_2$PN)$_2$[4-t-BuC$_6$H$_4$(O)SN] (**2**) (0.47 g, 1.30 mmol) dissolved in 10 mL of freshly distilled THF was slowly added over a period of 10 min. The mixture was allowed to come to room temperature slowly over 1 h and thereafter was stirred at room temperature for 12 h. All volatile materials were evaporated, and the residue was extracted with

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a mixture of chloroform/hexane. The insoluble LiF was filtered off, and the clear solution was cooled at 0 °C for 48 h to yield a microcrystalline compound that was characterized as ansa $CH_2(CH_2O)_2$-$(FPN)_2$[4-t-BuC_6H_4(O)SN] (**3**) (0.31 g, 60%). Mp: 149 °C. IR (cm^{-1}) (KBr): 3066 vw, 2964 m, 1595 w, 1466 m, 1386 w, 1267 vs, 1237 vs, 1200 s, 1116 s, 1100 m, 1080 m, 1058 vs, 964 s, 923 s, 875 s, 837 m, 778 vs, 705 w, 631 vs, 570 m, 547m, 530 m, 500 w, 450 s. $^{31}P\{^1H\}$ NMR: δ 13.51 (dm, $J_{P-F} = 917$ Hz) PFO. ^{19}F NMR: δ −80.66 [dm ($J_{P-F} = 917$ Hz), PFO]. ^1H NMR: δ 1.37 (s, 9H, CH_3), 2.25−2.45 (m, 2H, CH_2), 4.39−4.60 (m, 4H, OCH_2) 7.53 (d, 2H, ArH), 7.83 (d, 2H, ArH). $^{13}C\{^1H\}$ NMR: δ 31.48 (s, CH_3),31.66 (s, CCH_2C), 35.52 [s, *C*-Me], 68.92 (t, OCH_2), 125.37 and 126.47[s, Ar], 141.55 [s, *C*-S(O)-Cl], 156.74 [s, *C*-C($Me)_3$]. MS (EI) [*m/e* (species) intensity]: 397 (M^+) 35; 382 ($M^+ - CH_3$) 100; 248 10; 178 (15). Elemental Anal. Calcd for $C_{13}H_{19}F_2N_3O_3P_2S$: C, 39.3; H, 4.8; N, 10.6. Found: C, 38.12; H, 5.05; N, 9.94.

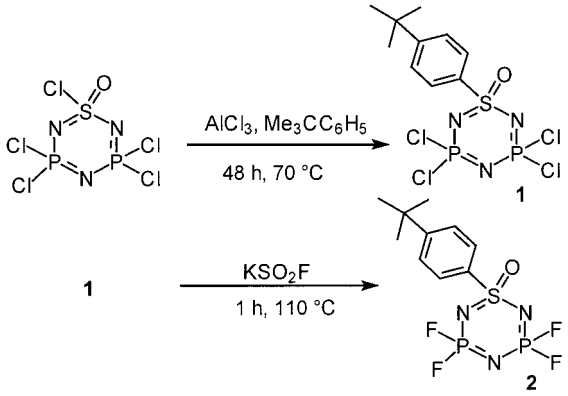
Preparation of Dispiro [$(CF_2CH_2O)_2PN]_2$[4-t-BuC_6H_4(O)SN] (4). To an oven-dried 25 mL round-bottomed flask fitted with a Kontes Teflon stopcock was added **2** (0.40 g, 1.11 mmol). After addition of CsF (0.08 g), $(CF_2CH_2OSiMe_3)_2$ (0.68 g, 2.22 mmol) was introduced by a syringe. The contents of the flask were frozen and degassed, and 10 mL of dry THF was introduced. The mixture was brought to 25 °C, and the flask was filled with nitrogen at 1 atm. The mixture was then heated in an oil bath at 90 °C for 48 h. The analysis of the reaction mixture by ^{19}F NMR showed complete reaction of the siloxane with the formation of a major product and a minor product in addition to Me_3SiF. All volatile materials were pumped off, and the residue was extracted with a mixture of $CHCl_3$ and hexane (1:1 v/v). It was filtered and cooled to obtain a white solid that was further purified by high-temperature vacuum sublimation. It was identified as the dispiro compound $[(CF_2CH_2O)_2PN]_2$[4-t-BuC_6H_4(O)SN] (**4**) (0.58 g, 86%). Mp: 222 °C. IR (cm^{-1}) (KBr): 2968 w, 1458 m, 1392 m, 1262 vs, 1238 s, 1205 vs, 1143 vs, 1106 m,1083 vs, 1056 s, 956 m, 947 m, 938 m, 851 s, 773 s, 752 m, 708 w, 671 vs, 646 s, 628 vw, 590 w, 575 w, 565 w, 552 w, 542 w, 532 w, 495 m. $^{31}P\{^1H\}$ NMR: δ 14.75 (s).^{19}F NMR: δ −128.74, 126.91 (AB, $J = 278$ Hz). ^1H NMR: δ 1.34 (s, 9H, CH_3), 4.29−4.48 (m, 4H, OCH_2) 7.48 (d, 2H, ArH), 7.75 (d, 2H, ArH). $^{13}C\{^1H\}$ NMR: δ 31.09 [s, CH_3], 35.11 [s, *C*-Me], 61.95 (tm, CH_2), 112.61 (ttm, CF_2; $^1J_{C-F} = 256$ Hz, $^2J_{C-F} = 27$ Hz), 124.92 and 126.09 [d, Ar], 142.13 [d, *C*-S(O)Cl], 156.11 [s, *C*-C($Me)_3$]. MS (EI) [*m/e* (species) intensity]: 605 (M^+) 24; 590 ($M^+ - CH_3$) 100; 472 ($M^+ - Me_3CC_6H_4$) 7; 456 ($M^+ - Me_3CC_6H_4O$) 19. Elemental Anal. Found: C, 35.60;H, 3.38; N, 6.90. Calcd for $C_{18}H_{21}F_8N_3O_5P_2S$: C, 35.7; H, 3.5; N, 6.9.

Results and Discussion

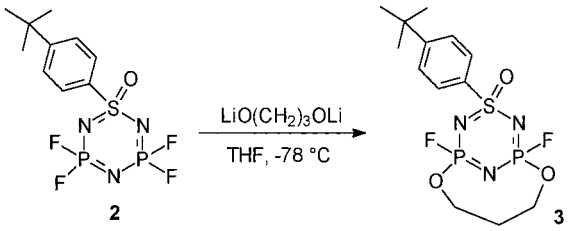
A Friedel−Crafts reaction of $NSOCl(NPCl_2)_2$ with *tert*-butylbenzene, carried out over a period of 48 h, yielded the S-aryl thionylphosphazene $(Cl_2PN)_2$[4-t-BuC_6H_4(O)SN] (**1**) in good yields. Analysis of the reaction mixture indicated the preferential formation of the para-substituted isomer. Two solid side products were also found to form in this reaction, namely, 1,2- and 1,4-di(*tert*-butyl)benzenes. These compounds as well as unreacted *tert*-butylbenzene were separated from **1** by high-temperature vacuum distillation (70 °C, 40 mmHg). Compound **1** was recrystallized from hexane as colorless crystals.

Heating **1** with KSO_2F in a 1:4 molar ratio with a slight excess of the fluorinating agent in the absence of any solvent resulted in the formation of $(F_2PN)_2$[4-t-BuC_6H_4(O)SN] (**2**). The reaction was performed at 110 °C. Progress was monitored by observing the evolution of SO_2 (Scheme 1). The compound was readily purified by vacuum sublimation. The use of dilithiated 1,3-propanediol in the preparation of ansa-substituted tetrameric fluorophosphazenes was recently reported from our laboratory.[6] When the former was reacted with **2**, the ansa-substituted thionylphosphazene **3** (Scheme 2) was the primary product. The GCMS analysis of the reaction mixture also showed the presence of small amounts of another isomer with a very similar MS

Scheme 1



Scheme 2



fragmentation pattern but with a slightly longer GC retention time. However, ^{19}F and ^{31}P NMR analyses of a mixture of both isomers only showed the gross features for the ansa-substituted compound. This compound may be the other structural isomer possible from this reaction.

The single-crystal X-ray structure of **3** was determined, and it was observed that the aryl group and the ansa bridge were trans to each other. To correlate the solid-state structure with the GCMS results, the crystal used for structural determination was demounted from the diffractometer and was analyzed by GCMS. This identified the crystal as the major product of the mixture that had the lesser GC retention time. A desilylation reaction of the silylated diol $(CF_2CH_2OSiMe_3)_2$, when carried out with **2** in the presence of CsF as catalyst, yielded the dispiro-substituted compound $[(CF_2CH_2O)_2PN]_2$[4-t-BuC_6H_4(O)SN] (**4**) (Scheme 3). Similar reactions of trimeric and tetrameric fluorophosphazenes have always resulted in spirocyclic compounds.[1a,b,6] This observation further helps to extend the generality of this reaction to thionylphosphazenes as well.

Spectral and Structural Studies. Single crystals of **2** and **3** were grown from hexane solutions at room temperature and their structures determined (Figures 1 and 2). Given in Table 1 are selected data collection and structure solution parameters for **2** and **3**. Selected bond distances and angles are given in Tables 2 and 3. A search of the Cambridge Crystallographic Database indicates that although the structures of two S−F substituted thionylphosphazenes have been reported,[17] **2** represents the first structural characterization of a tetrafluorothionylphosphazene. The six-membered PNS heterocycle is planar, as indicated by the sum of the angles of the ring (719.9 °) compared to the sum 720° for a planar hexagon. Calculation of the mean plane of the ring also confirms the ring planarity, with a deviation of only ±0.02 Å. The P−N (1.534−1.561 Å) and S−N (1.533, 1.555 Å) bond distances are comparable. Interestingly, the two six-membered rings face each other, and the angle between the plane of the phenyl ring and that of the PNS heterocycle is 122.7°.

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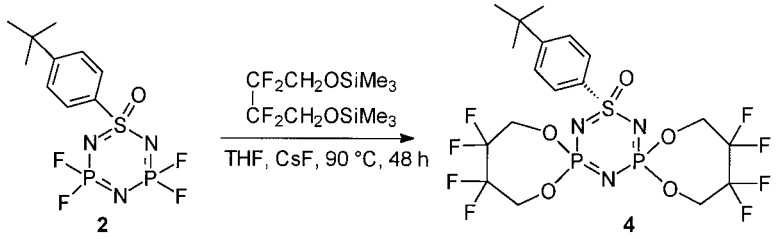
Scheme 3



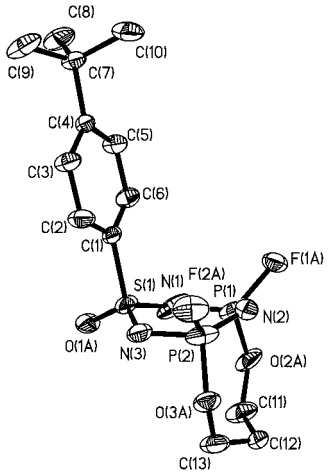


Figure 2. Thermal ellipsoid plot (30%) of **3**. H atoms are omitted for clarity.

Table 2. Selected Bond Lengths and Angles for **2**

Bond Lengths (Å)			
P(1)−F(1)	1.510(4)	P(2)−N(2)	1.539(5)
P(1)−N(1)	1.534(5)	P(2)−N(2)	1.557(5)
P(1)−F(2)	1.540(4)	N(2)−S(1)	1.553(5)
P(1)−N(3)	1.561(5)	N(3)−S(1)	1.555(5)
P(2)−F(4)	1.520(4)	S(1)−O(1B)	1.434(9)
P(2)−F(3)	1.521(4)	S(1)−O(1A)	1.49(3)
S(1)−C(1)	1.764(4)		

Bond Angles (deg)			
F(1)−P(1)−N(1)	109.5(3)	S(1)−N(3)−P(1)	124.8(3)
F(1)−P(1)−F(2)	97.8(3)	O(1B)−S(1)−O(1A)	33(2)
N(1)−P(1)−F(2)	108.9(3)	O(1B)−S(1)−N(2)	118.4(18)
F(1)−P(1)−N(3)	109.8(3)	O(1A)−S(1)−N(2)	88(4)
N(1)−P(1)−N(3)	118.8(3)	O(1B)−S(1)−N(3)	105.8(19)
F(2)−P(1)−N(3)	110.0(3)	O(1A)−S(1)−N(3)	133(3)
F(4)−P(2)−F(3)	96.9(3)	N(2)−S(1)−N(3)	113.0(2)
F(4)−P(2)−N(1)	110.5(3)	O(1B)−S(1)−C(1)	107.3(3)
F(4)−P(2)−N(2)	107.3(3)	N(2)−S(1)−C(1)	106.2(2)
F(3)−P(2)−N(2)	110.6(2)	N(3)−S(1)−C(1)	105.4(2)
N(1)−P(2)−N(2)	119.2(3)	P(1)−N(1)−P(2)	119.6(3)
S(1)−N(2)−P(2)	124.5(3)		

The structure of **3** gave evidence of the trans orientation of the ansa bridge with respect to the aryl group. In contrast to **2**, the P_2SN_3 ring is not planar but had a boat configuration with both the sulfur and the nitrogen flanked by the two phosphorus atoms positioned out of the mean plane. The deviation of the former was 0.22 Å and the latter was 0.24 Å out of the mean plane of the ring. The phenyl group also faces the PNS ring, and the angle extended by the phenyl group with respect to the mean plane of the PNS ring is 79.7°. A partial structural report of an ansa-substituted fluorinated thionylphosphazene has also been mentioned in a review article.[7] As mentioned in the Experimental Section, disorder of the thionyl oxygen sites was observed in both **2** and **3**. Compound **3** also displays disorder in the fluorine and oxygen sites.

Table 3. Selected Bond Lengths) and Angles for **3**

Bond Lengths (Å)			
S(1)−O(1A)	1.480(3)	S(1)−O(1B)	1.482(3)
S(1)−N(3)	1.543(3)	S(1)−N(1)	1.552(4)
S(1)−C(1)	1.766(3)	P(1)−F(1B)	1.507(7)
P(1)−O(2A)	1.593(3)	P(1)−N(2)	1.563(4)
P(1)−N(1)	1.572(4)	P(1)−F(1A)	1.623(7)
P(1)−O(2B)	1.593(3)	P(2)−N(2)	1.518(4)
P(2)−F(2A)	1.525(8)	P(2)−O(3A)	1.573(3)
P(2)−O(3B)	1.573(3)	P(2)−N(3)	1.556(3)
P(2)−F(2B)	1.581(9)		

Bond Angles (deg)			
N(3)−S(1)−N(1)	112.29(16)	N(3)−S(1)−C(1)	107.18(16)
N(1)−S(1)−C(1)	107.65(18)	O(2A)−P(1)−N(2)	121.5(6)
O(2A)−P(1)−N(1)	98.0(6)	N(2)−P(1)−N(1)	115.69(17)
N(2)−P(2)−O(3A)	120.2(5)	N(2)−P(2)−N(3)	116.97(18)
O(3A)−P(2)−N(3)	101.3(5)	S(1)−N(1)−P(1)	121.8(2)
P(2)−N(2)−P(1)	117.62(19)	S(1)−N(3)−P(2)	122.3(2)

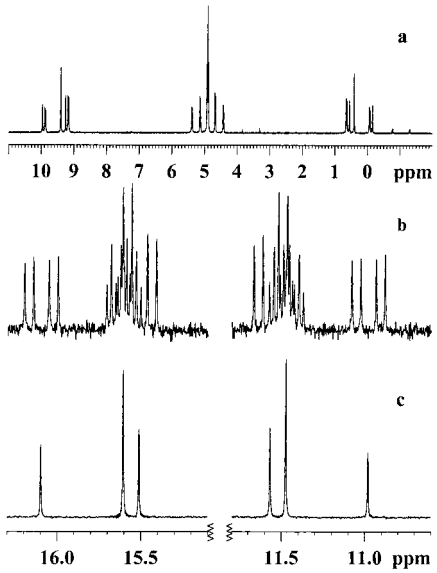


Figure 3. ^{31}P NMR spectra of (a) **2**, (b) **3**, and (c) proton-decoupled **3**.

Although ^{31}P chemical shifts of a few fluorinated thionylphosphazenes have been determined, it was reported that the direct analysis of ^{19}F NMR was not possible because of the complexity of the spectra.[11] By using a 500 MHz NMR spectrometer, we have been able to interpret the spectra more effectively. Figure 3 shows the comparison of the ^{31}P NMR spectra of **2** and **3** and proton decoupled **3** and **4**. Similar to the observation with trimeric and tetrameric fluorophosphazenes, one finds a triplet of multiplets for the PF_2 groups with a P−F coupling constant of 913 Hz. Although decoupling of protons was carried out for the ^{31}P NMR spectra of **2**, there was no difference vis-à-vis the undecoupled spectra, indicating that the complexity of splitting was only due to coupling with fluorine atoms that are in two different environments. The ^{31}P NMR spectra of the ansa-substituted compound contained a doublet

of multiplets ($J_{P-F} = 917$ Hz). For the 1,3-ansa-substituted derivative of $N_4P_4F_8$, $CH_2(CH_2O)_2[P(F)N]_2(F_2PN)_2$, a similar doublet of multiplets was observed with a P−F coupling constant of 896 Hz.[6] Interestingly, proton decoupling of **3** gave a much simpler spectrum. After ansa substitution, there is only one type of fluorine atom remaining in the molecule. As expected, the proton-decoupled ^{31}P NMR spectra of **4** gave a broad singlet.

The ^{19}F NMR spectra of **2** contained two doublets of multiplets at −69.45 ($J_{P-F} = 910$ Hz) and at − 72.55 ($J_{P-F} = 915$ Hz) rather than a single doublet of multiplets observed for $(NPF_2)_n$ ($n = 3, 4$), indicating the asymmetry of the molecule as a result of the two different substituents on the ring sulfur atom. When the phosphorus atoms were decoupled, these two doublets collapsed into two separate multiplets. The ansa-substituted compound also gave a doublet of multiplets with a chemical shift about 10 ppm further from the tetrafluoro compound. A similar shift was observed for the 1,3-ansa compoud $CH_2(CH_2O)_2[P(F)N]_2(F_2PN)_2$. The fluorine NMR of the dispiro compound shows only the CF_2 groups of the ligand, and this also was an AB spectrum as a result of the difference in the chemical environment. ^{13}C NMR also assisted greatly in the identification of the compounds. The electron impact mass spectra of all the compounds gave the molecular ion peak and $M^+ - CH_3$ as the base peak.

Conclusions

Tetrafluorination of the thionylphosphazene $(Cl_2PN)_2[4\text{-}t\text{-}BuC_6H_4(O)SN]$ has been effectively carried out using KSO_2F. The crystal structure of the compound shows a planar thionylphosphazene ring framework. Reaction of this compound with dilithiated 1,3-propanediol gave the ansa-substituted product. The X-ray structure of this compound showed that the PNS ring framework is in a boat form with both the sulfur and the opposite nitrogen positioned out of the mean plane of the ring. The structure also indicated a trans orientation of the ansa bridge with respect to the aryl group. Desilylation reaction of $(CF_2CH_2OSiMe_3)_2$, when carried out with **2** in the presence of CsF as catalyst, yielded the dispiro-substituted compound $[(CF_2CH_2O)_2PN]_2[4\text{-}t\text{-}BuC_6H_4(O)SN]$. Further studies are underway to explore the usefulness of these reactions in realizing novel derivatives of fluorinated thionylphosphazenes.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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