Regioselective Substitution Reactions of Sulfur(VI)−Nitrogen−Phosphorus Rings: Reactions of the Halogenated Cyclic Thionylphosphazenes [NSOX(NPCl$_2$)$_2$] (X = Cl or F) with Oxygen-Based Nucleophiles

Derek P. Gates,[†] Peter Park,[†] Mong Liang,[†] Mark Edwards,[†] Constantina Angelakos,[†] Louise M. Liable-Sands,[‡] Arnold L. Rheingold,[‡] and Ian Manners*,[†]

Departments of Chemistry, University of Toronto, 80 St. George Street, Toronto M5S 3H6, Ontario, Canada, and University of Delaware, Newark, Delaware 19716

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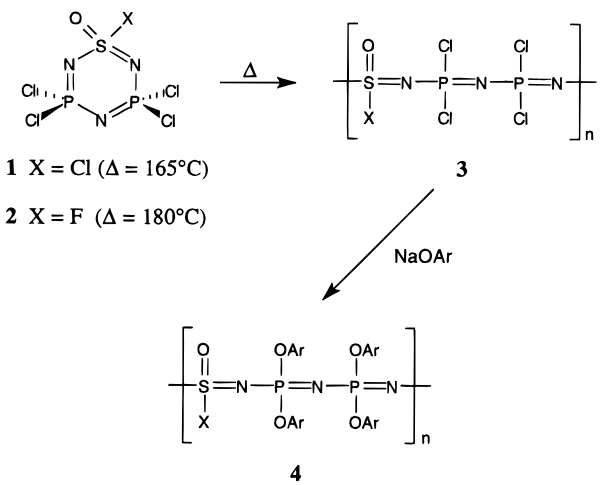
The reactions of the cyclic thionylphosphazenes [NSOX(NPCl$_2$)$_2$] (**1**, X = Cl; **2**, X = F) with three oxygen-based nucleophiles of increasing basicity, sodium phenoxide (NaOPh), sodium trifluoroethoxide (NaOCH$_2$CF$_3$), and sodium butoxide (NaOBu) have been studied. The reaction of **1** and **2** with 4 equiv of NaOPh at 25 °C yielded the regioselectively tetrasubstituted species [NSOX{NP(OPh)$_2$}$_2$] (**5d**, X = Cl; **6d**, X = F). Further reaction of **5d** with an additional 2 equiv of NaOPh over several days or at elevated temperatures gave the fully substituted compound [NSO(OPh){NP(OPh)$_2$}$_2$] (**5e**), whereas **6d** did not react further. The reaction of **1** and **2** with 5 equiv of NaOCH$_2$CF$_3$ yielded in both cases [NSO(OCH$_2$CF$_3$){NP(OCH$_2$CF$_3$)$_2$}$_2$] (**7e**), and similarly reaction with 5 equiv of NaOBu yielded [NSO(OBu){NP(OBu)$_2$}$_2$] (**9e**). In all cases, the reactions were monitored by ^{31}P NMR and (where applicable) ^{19}F NMR and were found to involve complete substitution at phosphorus via a predominantly vicinal pathway, followed by substitution at sulfur. Substitutional control of the reactions of NaOPh, NaOBu, with **1** and **2** was found to conform to the following general order of reactivity, PCl$_2$ > PCl(OR) > SOX (X = Cl, F). Although the reaction with NaOCH$_2$CF$_3$ followed the same order of reactivity, a significant enhancement of reaction rate was detected with each equivalent of trifluoroethoxide added. Reaction of **7e** with excess NaOCH$_2$CF$_3$ led to elimination of (CF$_3$CH$_2$)$_2$O and the formation of the salts Na[NSO(OCH$_2$CF$_3$)NP(OCH$_2$CF$_3$)$_2$NP(OCH$_2$CF$_3$)O] (**11**) and Na[NS(O)O{NP(OCH$_2$CF$_3$)$_2$}$_2$] (**12**). Crystals of **6d** are triclinic, space group $P\bar{1}$, with a = 9.789(3) Å, b = 11.393(4) Å, c = 12.079(5) Å, α = 107.40(3)°, β = 91.23(3)°, γ = 93.18(3), V = 1283.6(8) Å^3, and Z = 2. Crystals of **5e** are monoclinic, space group $C2/c$, with a = 32.457(3) Å, b = 10.747(1) Å, c = 18.294(2) Å, β = 110.37(1)°, V = 5982.4(9) Å^3, and Z = 8.

Introduction

Inorganic heterocycles have attracted considerable attention because of their interesting structures, bonding, and reactivity,[1−6] their applications as precursors to or components of solid state materials,[7,8] and their use as precursors to novel polymers via ring-opening polymerization (ROP).[9−15] Over the past two decades six-membered cyclic thionylphosphazenes such as **1** have been well-studied, and the skeleton present in these compounds, which consists of four-coordinate sulfur(VI), nitrogen, and phosphorus atoms, has been shown to be robust and stable.[16,17] We recently reported that **1** and the fluorinated analogue **2** undergo thermal ROP to yield high molecular weight sulfur(VI)−nitrogen−phosphorus polymers, poly(thionylphosphazenes) (**3**), and macrocycles.[12,13,18] Reaction of **3** with aryloxide nucleophiles was found to yield moisture stable poly(aryloxythionylphosphazenes) **4** in which the sulfur−halogen bonds remain intact.[19] In contrast, treatment of **3** with primary amines yielded poly(aminothionylphosphazenes) in which the halogen substituents at both phosphorus and at sulfur are replaced.[20] Consequently, these sulfur(VI)−nitrogen−phosphorus polymers show interesting differences from classical polyphosphazenes,[21] in terms of substitution patterns and the types of polymer structures that are accessible.[15,19,20,22]



[†] University of Toronto.
[‡] University of Delaware.
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Of particular interest is the possibility of utilizing regioselective nucleophilic substitution reactions on **3**, by exploiting differences in the reactivity of the sulfur−halogen and phosphorus−halogen bonds toward nucleophiles. The stereochemistry of substitution can also influence polymer tacticity since the S(VI) atoms are stereocenters.[20] At the macromolecular level these types of reactions should lead to novel control of microstructure and properties; however, it is difficult to monitor substitution patterns on the polymer. The study of small molecule model compounds can provide an alternative method to gain valuable information on macromolecular substitution reactions.[23]

The cyclic thionylphosphazene **1** would therefore be expected to provide an excellent model to study such substitution pathways. Previous studies by van de Grampel and co-workers have shown that there is some degree of regioselectivity in the reactions of **1** and **2** with amine nucleophiles.[24] Interestingly, the same research group has also reported that selective arylation at sulfur can be achieved by electrophilic aromatic substitution.[25] However, no systematic studies of the reactions of **1** and **2** with oxygen-based nucleophiles have been reported. In this paper we describe full details of our studies of the reactions of these species with several oxygen-based nucleophiles of different basicity which were initiated in order to elucidate the regiochemistry of substitution.

Experimental Section

Materials and Equipment. Starting materials, phosphorus pentachloride (98%), sulfamide (99%), hexamethyldisilazane (98%), silver difluoride (98%), sodium hydride (95%), and trifluoroethyl ether (99%) were obtained from Aldrich and were used as received. Reagents were purified as follows, *n*-butanol (ACP) was distilled from sodium, 2,2,2-trifluoroethanol (Aldrich) was distilled from $CaSO_4/NaHCO_3$, and phenol (Aldrich) was sublimed under high vacuum (ca. 0.05 mmHg).[26] The cyclic thionylphosphazenes $(NSOX)(NPCl_2)_2$ (X = Cl, F) were prepared following literature procedures[27,28] and were purified by high vacuum sublimation (40−90 °C, 0.05 mmHg). The sodium salts were prepared by reaction of alcohol with sodium hydride in THF.[29] All manipulation of materials and synthetic experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres glovebox or Innovative Technology glovebox, or by using standard Schlenk line techniques. Solvents were dried by standard methods.

The $^{31}P\{^1H\}$ and ^{19}F NMR spectra were recorded on a Varian XL-300 spectrometer operating at 121.4 and 282.3 MHz, respectively. The ^1H and ^{13}C NMR spectra were obtained with a Varian XR-200 spectrometer operating at 200.0 and 50.3 MHz, respectively, and the ^{13}C NMR spectrum of **5e** was obtained on a Varian XL-400 spectrometer operating at 100.6 MHz. Chemical shifts are reported relative to residual protonated solvent (^1H or ^{13}C), external H_3PO_4/D_2O (^{31}P), and external $CFCl_3$ (^{19}F). Mass spectra were obtained with the use of a VG 70-250S operating in electron impact (EI) mode. GC/MS was recorded on a HP5890 GC with a J&W Scientific DB-5 column (30 m, 0.250 mm i.d.), and a Fisons 70-250S (double focusing) mass spectrometer operating in electron impact (EI) mode. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, B.C., Canada.

Preparation of [NSOCl{NP(OPh)$_2$}$_2$] (5d). To a colorless solution of **1** (0.30 g, 0.91 mmol) in dioxane (ca. 20 mL) was added freshly prepared NaOPh (0.42 g, 3.6 mmol) in dioxane (ca. 10 mL), and an immediate white precipitate was formed. The mixture was stirred overnight, and the resulting pale yellow reaction mixture was filtered through Celite and solvent was removed from the filtrate leaving a pale yellow oil. The oil was redissolved in a mixture of diethyl ether and hexanes (ca. 4:1) and cooled (ca. 0 °C) giving an air stable white crystalline solid which was isolated and dried *in vacuo*. Yield: 0.29 g (57%).

For **5d**: ^{31}P NMR ($CDCl_3$) δ 2.6 ppm, ^1H NMR ($CDCl_3$) δ 7.25 ppm [mult. $P(OPh)_2$]; ^{13}C NMR ($CDCl_3$) δ 120.6, 121.2 (*o*-PhO−P), 126.1 (*p*-PhO−P), 129.8 (*m*-PhO−P), 149.5, 149.6 ppm (*i*-PhO−P); MS (EI, 70 eV) *m*/*z* (%) 561 [4, $M^+(^{37}Cl)$], 559 [11, $M^+(^{35}Cl)$], 524 (100, $M^+ - Cl$), 466 (5, $M^+ - OPh$). Anal. Calcd for $C_{24}H_{20}ClN_3O_5P_2S$: C, 51.48; H, 3.60; N, 7.50. Found: C, 51.70; H, 3.61; N, 7.46.

Preparation of [NSO(OPh){NP(OPh)$_2$}$_2$] (5e). The same experimental procedure was followed as above with the exception that an additional 2 equiv of NaOPh (1.8 mmol) were required and the mixture was stirred vigorously for 7 days. The crude product was isolated as a yellow oil, which was redissolved in a mixture of diethyl ether and hexanes (4:1) and cooled (ca. 0 °C) giving an air stable white crystalline solid. Yield: 0.24 g (43%). X-ray quality crystals were obtained by cooling (−55 °C) a solution of **5e** dissolved in a mixture of hexanes and dichloromethane (20:1).

For **5e**: ^{31}P NMR ($CDCl_3$) δ 4.0 ppm; ^1H NMR ($CDCl_3$) δ 7.3 ppm [mult. $P(OPh)_2$, S(O)−OPh]; ^{13}C NMR ($CDCl_3$) δ 120.7, 120.8 (*o*-PhO−P), 122.3 (*o*-PhO−S), 125.6 (*m*-PhO−P), 126.3 (*m*-PhO−S), 129.2 (*p*-PhO−S), 129.6 (*p*-PhO−P), 149.7, 150.0 (*i*-PhO−P), 150.2 ppm (*i*-PhO−S), MS (EI, 70 eV) *m*/*z* (%) 617 (1, M^+), 524 (100, $M^+ - OPh$). Anal. Calcd for $C_{30}H_{25}N_3O_6P_2S$: C, 58.35; H, 4.08; N, 6.81. Found: C, 58.26; H, 4.15; 6.83.

Preparation of [NSOF{NP(OPh)$_2$}$_2$] (6d). To a colorless solution of **2** (0.40 g, 1.3 mmol) in THF (ca. 25 mL) was added a stirred solution of NaOPh (0.75 g, 6.4 mmol) in THF (ca. 15 mL) dropwise, and the formation of a white precipitate was observed. After overnight stirring, the solution was turbid and possessed a slightly orange color. The mother liquor was evaporated to dryness, and the residue was redissolved in dichloromethane. The NaCl and excess NaOPh were removed by extraction into water, and the remaining dichloromethane solution was pumped to dryness leaving an oil, **6d**. Yield: 0.42 g (60%). Crystals suitable for X-ray analysis were obtained by cooling (ca. 0 °C) a solution of **6d** in a mixture of diethyl ether and hexanes (ca. 4:1) giving air stable white crystals.

For **6d**: ^{31}P NMR ($CDCl_3$) δ 4.0 ppm; ^{19}F NMR ($CDCl_3$) δ 77.2 ppm; ^1H NMR ($CDCl_3$) δ 7.2 ppm (mult. $P(OPh)_2$, S(O)-OPh); ^{13}C NMR ($CDCl_3$) δ 120.7, 120.9 (*o*-PhO−P), 126.0 (*p*-PhO−P), 129.8 (*m*-PhO−P), 149.3, 149.5 ppm (*i*-PhO−P), MS (EI, 70 eV) *m*/*z* (%) 543 (100, M^+), 524 (17, $M^+ - F$).

Monitoring Reactions of 1 and 2 with Nucleophiles. Reaction of NSOCl(NPCl$_2$)$_2$ (1) with NaOPh. To a stirred solution of **1** (0.40 g, 1.2 mmol) in THF (ca. 25 mL) was added via syringe a 0.30 M solution of NaOPh (4.0 mL, 1.2 mmol) in THF. Upon addition the solution immediately became cloudy. The reaction mixture was allowed to stir for approximately 20 min, and an aliquot was taken for ^{31}P NMR analysis.

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Table 1. NMR Spectral Data[a]

compound	^{31}P NMR, δ, ppm	$^{2}J_{PP}$, Hz	^{19}F NMR, δ, ppm[b]
5a	29.6, 16.2	87	
5b	18.1		
5c	20.4, 1.6	101	
5d	3.2		
5e	4.8		
6a	29.4, 16.1	88	77.7
6b	18.5		77.6
6c	20.4, 2.9	99	78.3
6d	4.6		79.3
7a	29.8, 20.3	90	
7b	22.5		
7c	24.7, 9.4	110	
7d	11.8		
7e	13.5		
8a	29.8, 20.5	93	76.8
8b	23.0		76.6
8c	25.2, 10.1	109	77.5
8d	12.9		78.8
7e	13.5		
9a	29.3, 18.1	90	
9b	20.7		
9c	23.0, 8.3	99	
9d	11.3		
9e	13.9		
10a	29.4, 18.5	89	76.0
10b	21.5		75.2
10c	23.9, 9.6	98	76.7
10d	12.7		78.7
9e	13.9		

[a] All chemical shifts are reported using THF as solvent. [b] The ^{19}F shifts in the S(O)F region are given.

Table 2. Composition of Reaction Mixture for Reaction of **1** with NaOPh[a]

amt of NaOPh, equiv	% composition					
	1	**5a**	**5b**	**5c**	**5d**	**5e**
1	28	47	24	1		
2	2	16	64	18		
3			2	88	10	
4					100	
6						100

[a] The composition of the reaction mixture was determined using the ^{31}P NMR integration for the major isomer.

Upon completion of the spectra, the sample was returned to the reaction vessel, and an additional equivalent of nucleophile was added to the reaction mixture. This was continued until the a total of 6 equiv were added to the reaction mixture. After refluxing for several hours **5e** was formed quantitatively by ^{31}P NMR. ^{31}P NMR data for the products are compiled in Tables 1 and 2, and the spectra are shown in Figure 5.

Reaction of $NSOF(NPCl_2)_2$ (2) with NaOPh. To a stirred solution of **2** (0.40 g, 1.3 mmol) in THF (ca. 25 mL) was added via syringe a 0.64 M solution of NaOPh (2.1 mL, 1.3 mmol) in THF. The mixture was allowed to stir for 20 min, and an aliquot was taken for ^{31}P and ^{19}F NMR analysis. The sample was returned to the reaction flask and the next equivalent of phenoxide was added. The procedure was repeated until a total of 6 equiv of nucleophile was added. With each subsequent addition the reaction mixture became increasingly cloudy with the formation of white precipitate of sodium chloride. After the addition of the sixth equivalent the reaction mixture was allowed to stir overnight, resulting in a slightly orange solution. After heating the reaction mixture for several hours no change was detected by ^{31}P NMR. ^{31}P and ^{19}F NMR data for the products are compiled in Tables 1 and 3.

Reaction of $NSOCl(NPCl_2)_2$ (1) with $NaOCH_2CF_3$. To a stirred solution of **1** (0.37 g, 1.1 mmol) in THF (ca. 25 mL) was added a 0.64 M solution of $NaOCH_2CF_3$ (1.8 mL, 1.1 mmol) in THF and the resulting mixture was allowed to stir for 20 min. A white precipitate formed immediately upon addition of the nucleophile. An aliquot was taken for NMR analysis, and subsequently the sample was returned to the reaction vessel, and the next equivalent of nucleophile was then added to the reaction mixture. The above procedure was repeated until a slight excess of 5 equiv of trifluoroethoxide were added. This yielded predominantly **7e** as a yellow oil, as well as traces of a second compound as the final products. ^{31}P NMR data for the products are compiled in Tables 1 and 4.

Table 3. Composition of Reaction Mixture for Reaction of **2** with NaOPh[a]

amt of NaOPh, equiv	% composition				
	2	**6a**	**6b**	**6c**	**6d**
1	51	20	23	6	
2	10	21	47	22	
3		5	15	76	4
4					100

[a] The composition of the reaction mixture was determined using the ^{31}P NMR integration for the major isomer.

Table 4. Composition of Reaction Mixture for Reaction of **1** with $NaOCH_2CF_3$[a]

amt of $NaOCH_2CF_3$, equiv	% composition					
	1	**7a**	**7b**	**7c**	**7d**	**7e**
1	48	9	5	15	16	6
2	26	8	8	18	30	12
3	8	6	6	18	43	20
4					71	29
5						100

[a] The composition of the reaction mixture was determined using the ^{31}P NMR integration for the major isomer.

Table 5. Composition of Reaction Mixture for Reaction of **2** with $NaOCH_2CF_3$[a]

amt of $NaOCH_2CF_3$, equiv	% composition					
	2	**8a**	**8b**	**8c**	**8d**	**7e**
1	62	8	6	13	11	
2	32	8	10	20	30	
3	8	8	8	24	52	
4				4	96	
5					35	65
6						100

[a] The composition of the reaction mixture was determined using the ^{31}P NMR integration for the major isomer.

For **7e**: ^{19}F NMR (THF) δ −74.0 (t, 6F, $POCH_2CF_3$, $^{3}J_{HF}$ = 8 Hz), −73.7 (t, 6F, $POCH_2CF_3$, $^{3}J_{HF}$ = 9 Hz), −72.7 ppm (t, 3F, $SOCH_2CF_3$, $^{3}J_{HF}$ = 9 Hz); ^{1}H NMR ($CDCl_3$) δ 4.3 ppm (mult. CH_2CF_3); ^{13}C NMR ($CDCl_3$) δ 64.0 (q of m, $P-OCH_2CF_3$, $^{2}J_{CF}$ = 39 Hz), 64.3 (q of m, $P-OCH_2CF_3$, $^{2}J_{CF}$ = 39 Hz), 65.2 (q, $S-OCH_2CF_3$, $^{2}J_{CF}$ = 38 Hz), 122.3 (q of m, $P-OCH_2CF_3$, $^{1}J_{CF}$ = 277 Hz), 122.5 ppm (q, $S-OCH_2CF_3$, $^{1}J_{CF}$ = 276 Hz); MS (EI, 70 eV) *m*/*z* (%) 647 (7, M^+), 628 (33, M − F), 548 (100, $M^+ - OCH_2CF_3$).

Reaction of $NSOF(NPCl_2)_2$ (2) with $NaOCH_2CF_3$. To a stirred solution of **2** (0.50 g, 1.5 mmol) in THF (ca. 15 mL) was added dropwise via syringe a 0.42 M solution of $NaOCH_2CF_3$ (3.6 mL, 1.5 mmol) in THF. The reaction mixture was allowed to stir for 20 min, and an aliquot was taken for NMR analysis. After ^{31}P and ^{19}F NMR spectra were recorded, the sample was returned to the reaction vessel. The next equivalent of $NaOCH_2CF_3$ was added and the volume of the reaction mixture was reduced *in vacuo*. The above procedure was repeated until a total of 6 equiv of $NaOCH_2CF_3$ was added and each addition monitored by ^{31}P and ^{19}F NMR spectroscopy. The pentasubstituted product **7e** was formed quantitatively 30 min after the addition of the sixth equivalent of $NaOCH_2CF_3$. Isolated as a pale yellow oil and characterized as **7e**. ^{31}P NMR data for the products are compiled in Tables 1 and 5 and shown in Figure 6. Yield of **7e**, 0.42 g (43%).

Reaction of $NSOCl(NPCl_2)_2$ (1) with NaOBu. To a stirred solution of **1** (0.40 g, 1.2 mmol) in THF was added a suspension of NaOBu (0.12 g, 1.2 mmol) in THF (ca. 10 mL). The reaction mixture was allowed to stir for 20 min after which an aliquot was taken for NMR

Table 6. Composition of Reaction Mixture for Reaction **1** with NaOBu[a]

amt of NaOBu equiv	% composition					
	1	**9a**	**9b**	**9c**	**9d**	**9e**
1	15	70	9	6		
2		22	51	24	3	
3				68	32	
4				20	60	20
5				8	2	90

[a] The composition of the reaction mixture was determined using the ^{31}P NMR integration for the major isomer.

Table 7. Composition of Reaction Mixture for Reaction of **2** with NaOBu[a]

amt of NaOBu, equiv	% composition					
	2	**10a**	**10b**	**10c**	**10d**	**9e**
1	17	76	7			
2		27	73			
3			22	73	5	
4				41	55	5
5				11	60	30

[a] The composition of the reaction mixture was determined using the ^{31}P NMR integration for the major isomer.

analysis. The NMR sample was returned to the stirred reaction mixture and a second equivalent of nucleophile was added. After a further 20 min, the volume reduced *in vacuo*. The above procedure was repeated until a total of 5 equiv of nucleophile had been added, with reduction in volume of the reaction mixture by solvent removal. After the addition of the fifth equivalent of nucleophile, quantitative formation of **9e** was observed and this species was isolated as a yellow oil. ^{31}P NMR data for the products are compiled in Tables 1 and 6 and shown in Figure 7.

For **9e**: ^{1}H NMR ($CDCl_3$) δ 0.86 (t, $OCH_2CH_2CH_2CH_3$, $^3J_{HH} = 7.2$ Hz), 1.34 (sextet, $OCH_2CH_2CH_2CH_3$, $^3J_{HH} = 7.6$ Hz), 1.61 (quintet, $OCH_2CH_2CH_2CH_3$, $^3J_{HH} = 7.3$ Hz), 3.94 (m, $P-OCH_2CH_2CH_2CH_3$), 4.03 (t, $S-OCH_2CH_2CH_2CH_3$, $^3J_{HH} = 7.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 14.0 ppm ($P-OCH_2CH_2CH_2CH_3$, $S-OCH_2CH_2CH_2CH_3$), 19.1 ($S-OCH_2CH_2CH_2CH_3$), 19.2 ($P-OCH_2CH_2CH_2CH_3$), 31.4 ($S-OCH_2CH_2CH_2CH_3$), 32.4 (m, $P-OCH_2CH_2CH_2CH_3$), 67.2 (m, $P-OCH_2CH_2CH_2CH_3$), 69.2 ($S-OCH_2CH_2CH_2CH_3$); MS (EI, 70 eV) *m*/*z* (%) 517 (22, M^+), 488 (9, $M^+ - C_2H_5$), 462 (43, $M^+ - C_4H_7$), 406 [37, (462) $- C_4H_8$], 350 [28, (406) $- C_4H_8$], 294 [32, (350) $- C_4H_8$], 238 [100, (294) $- C_4H_8$], 220 [48, (238) $- H_2O$].

Reaction of $NSOF(NPCl_2)_2$ (2) with NaOBu. To a stirred solution of **2** (0.50 g, 1.5 mmol) in THF (ca. 15 mL) was added a suspension of NaOBu (0.15 g, 1.5 mmol) THF (ca. 10 mL). The reaction was allowed to stir for 20 min, and the reaction mixture was examined by ^{31}P and ^{19}F NMR spectroscopy. The NMR sample was returned to the stirred reaction mixture and a second equivalent of nucleophile was added. After a further 20 min, the volume was reduced *in vacuo*. This process was repeated for every equivalent until a total of 6 equiv was added. Pentasubstituted product **9e** was not formed quantitatively due to the difficulty in transferring a stoichiometric amount of NaOBu. The product was isolated as a mixture of **10d** and **9e** which formed a yellow oil. ^{31}P and ^{19}F NMR data for the products are compiled in Tables 1 and 7.

Reaction of $NSOCl(NPCl_2)_2$ (1) with Excess $NaOCH_2CF_3$. To a stirred solution of **1** (0.40 g, 1.2 mmol) in THF (ca. 30 mL) was added a 0.18 M solution of $NaOCH_2CF_3$ (40 mL, 7.2 mmol) in THF. An immediate white precipitate was observed, and the reaction mixture was left to stir for 1 day and was then refluxed for 15 h. ^{31}P NMR analysis showed the presence of two new sets of two doublet resonances assigned to major and minor isomers of **11**, a new singlet resonance assigned to **12**, and unreacted **7e** (ratio ca. 58:5:37). The solvent was then removed *in vacuo* and analyzed by GC/MS. This showed the presence of the ether $(CF_3CH_2)_2O$.

For **11**: ^{31}P NMR (THF) δ major isomer, 2.7 [$P(OCH_2CF_3)O$, $^2J_{PP} = 90$ Hz], 15.1 [$P(OCH_2CF_3)_2$, $^2J_{PP} = 90$ Hz], minor isomer, 1.6 [$P(OCH_2CF_3)O$, $^2J_{PP} = 90$ Hz], 15.7 ppm [$P(OCH_2CF_3)_2$, $^2J_{PP} = 90$ Hz]; ^{19}F NMR (THF) δ −74.1 [t, 6F $P(OCH_2CF_3)_2$, $^3J_{HF} = 8$ Hz], −73.7 [t, 3F, $P(OCH_2CF_3)O$, $^3J_{HF} = 8$ Hz], −72.8 [t, 3F, $SOCH_2CF_3$, $^3J_{HF} = 8$ Hz].

For **12**: ^{31}P NMR (THF) δ 17.0 ppm.

For $(CF_3CH_2)_2O$: MS (EI, 70 eV) *m*/*z* (%) 163 (9, $M^+ - F$), 113 (100, $M^+ - CF_3$), 83 (90, $M^+ - OCH_2CF_3$), 69 (18, CF_3^+). This mass spectrum was found to be identical to that of an authentic sample of this compound.

Table 8. Crystallographic Data for $[NSO(OPh)\{NP(OPh)_2\}_2]$ (**5e**) and $[NSOF\{NP(OPh)_2\}_2]$ (**6d**)

	5e	**6d**
formula	$C_{30}H_{25}N_3O_6P_2S$	$C_{24}H_{20}FN_3O_5P_2S$
fw	617.53	543.4
space group	*C*2/*c*	*P*$\bar{1}$
a, Å	32.457(3)	9.789(3)
b, Å	10.747(1)	11.393(4)
c, Å	18.294(2)	12.079(5)
α, deg		107.40(3)
β, deg	110.37(1)	91.23(3)
γ, deg		93.18(3)
V, Å^3	5982.4(9)	1283.6(8)
Z	8	2
cryst color	colorless	colorless
D(calc), g cm^{-3}	1.371	1.370
μ(MoKα), cm^{-1}	2.63	2.85
temp, K	298	298
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)	
$R(F)$, %	5.71[a]	7.08[c]
$R_w(F)$, %	11.73[a,b]	8.43[c]

[a] Quantity minimized $= (R_w(F^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$. [b] $R_w(F^2)$, %. [c] Quantity minimized $= \sum w\delta^2$; $R = \sum\Delta/\sum(F_o)$; $R_w = \sum\Delta w^{1/2}/\sum(F_o w^{1/2})$, $\Delta = |(F_o - F_c)|$.

For $(CF_3CH_2)_2O$: MS (EI, 70 eV) *m*/*z* (%) 163 (9, $M^+ - F$), 113 (100, $M^+ - CF_3$), 83 (90, $M^+ - OCH_2CF_3$), 69 (18, CF_3^+). This mass spectrum was found to be identical to that of an authentic sample of this compound.

X-ray Structure Determination Technique. Crystal, data collection, and refinement parameters for **5e** and **6d** are given in Table 8. Suitable crystals for single-crystal X-ray diffraction were sectioned and mounted in thin-walled glass capillaries flushed with nitrogen. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20° \le 2\theta \le 25°$).

The unit-cell parameters, photographic data, systematic absences and occurrences of equivalent reflections for **5e** indicated a *C*-centered monoclinic crystal system. *E*-Statistics indicated that centrosymmetric space group, *C*2/*c*, and refinement gave chemically reasonable and computationally stable results. The unit-cell parameters and photographic data for **6d** revealed no symmetry higher than triclinic, and solution in the centrosymmetric space group provided chemically reasonable and computationally stable results.

The structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. No absorption corrections were applied due to low absorption coefficients.

All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in several versions of SHELXTL programs (G. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

Whereas the nucleophilic substitution behavior of the cyclic phosphazene $[NPCl_2]_3$ has been studied extensively,[30] similar studies of the reactivity of thionylphosphazenes are much more limited. The reactions of **1** and to a lesser extent **2** with nitrogen-based nucleophiles have been reported and were found to be characterized by the following general order of reactivity: PCl_2 > PCl(NHR) > SOCl for primary amines and PCl_2 > SOCl > $PCl(NR_2)$ for secondary amines.[16,17] In contrast, no reactions of thionylphosphazenes with oxygen-based nucleophiles have been reported.[31] We therefore examined the reaction of **1** and **2** with several oxygen-based nucleophiles of different basicity and nucleophilicity.

(30) Allen, C. W. *Chem. Rev.* **1991**, *91*, 119.

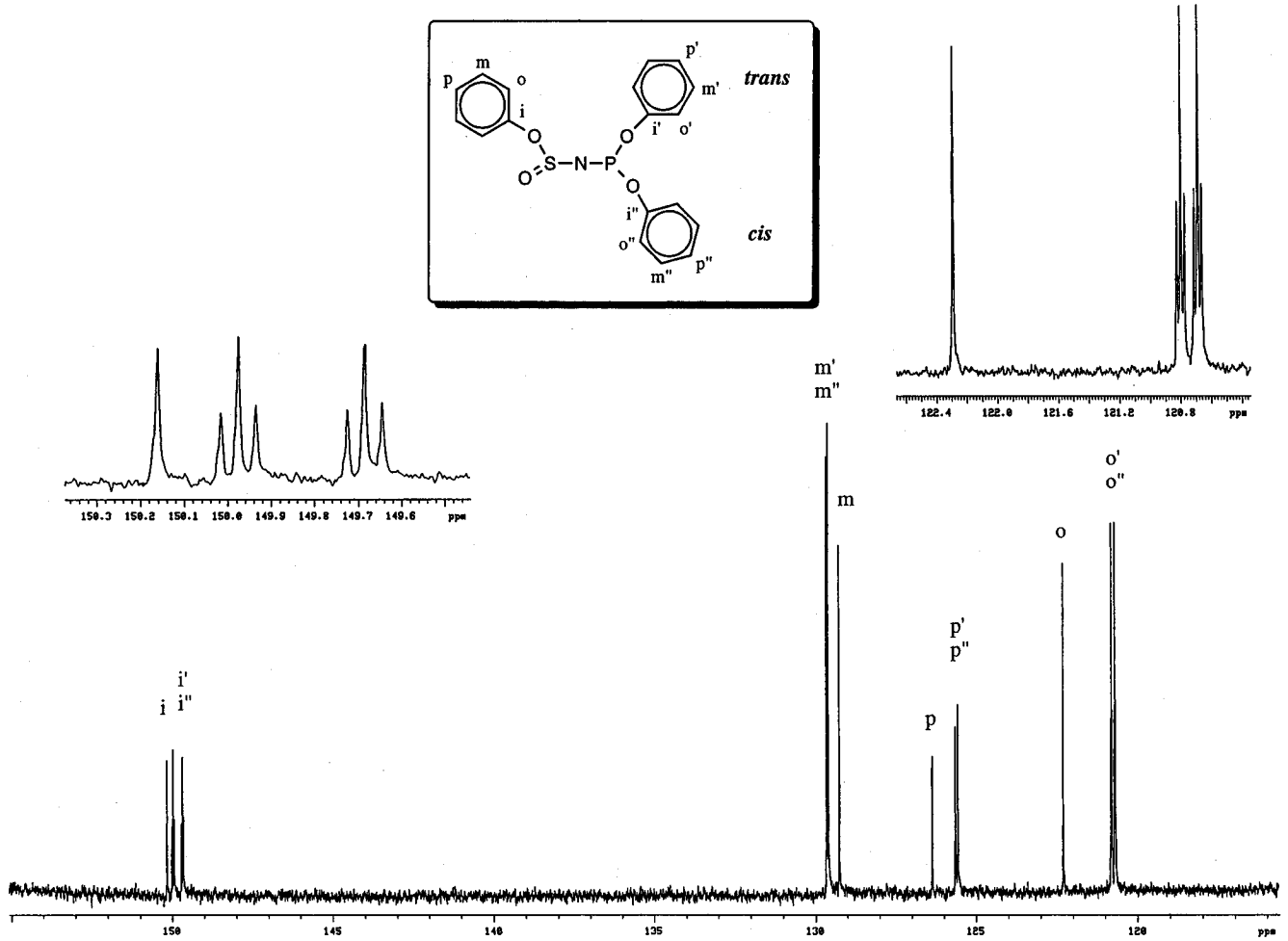


Figure 1. ^{13}C NMR (100.6 MHz) spectrum of **5e** in $CDCl_3$.

Reaction of $NSOX(NPCl_2)_2$ (1; X = Cl, 2; X = F) with NaOPh. The reaction of the chlorinated cyclic thionylphosphazene **1** with 4 equiv of sodium phenoxide in dioxane (25 °C, 12 h) yielded a single product by ^{31}P NMR, which exhibited a new singlet resonance at 3.4 ppm (in dioxane). After workup, a colorless crystalline product was isolated which was subsequently characterized by ^{13}C and ^{1}H NMR, mass spectrometry, and elemental analysis. The data obtained identified the product as the tetraphenoxy-substituted thionylphosphazene **5d** in which the phosphorus−chlorine bonds had been regioselectively substituted by phenoxide groups and the sulfur−chlorine bond was retained. Thus, an examination of the ^{13}C NMR spectrum revealed that there were only four types of carbon atoms present. However, the *ipso* and *ortho* carbon resonances appeared as two peaks because of the inequivalence of the carbon nuclei in the phenoxy groups *cis* and *trans* to the oxygen on sulfur. The mass spectrum of this species exhibited a molecular ion at *m*/*z* 559:561 with a 3:1 intensity ratio confirming the presence of one chlorine atom, and the base peak (*m*/*z* 524) corresponded to the molecular ion minus a chlorine substituent which is typical for cyclic thionylphosphazenes (such as **1**) with a halogen bound to sulfur.

The reaction of the fluorinated cyclic thionylphosphazene **2** with sodium phenoxide under similar conditions yielded **6d** which was similarly characterized and was also studied by single-crystal X-ray diffraction. In this case, the ^{19}F NMR spectrum of the product showed a strong singlet resonance at 79.3 ppm which confirmed that the fluorine substituent at sulfur had not been replaced (cf. for **2**: $\delta = 78.3$ ppm). The ^{31}P NMR spectrum of **6d** consisted of a singlet resonance at 4.6 ppm (in THF) and the ^{13}C NMR spectrum showed a single set of resonances for the phenoxy carbon atoms with a similar pattern as that found for **5d**. The mass spectrum exhibited a molecular ion at *m*/*z* 543 and the presence of a strong peak corresponding to the molecular ion minus fluorine. Interestingly, the molecular ion **6d** was much more intense than in **5d** with respect to the corresponding cation (*m*/*z* 524) which probably reflects the much stronger sulfur−fluorine bond in the former compound.

In order to investigate whether substitution of the chlorine atom at sulfur could be achieved, the reaction of **5d** with excess sodium phenoxide at elevated temperatures was studied. When **5d** was heated with 2 equiv of NaOPh at 65 °C for 4 h, ^{31}P NMR analysis showed the formation of a new product **5e** with a singlet resonance at 4.8 ppm. The same product was formed when **1** was reacted with 6 equiv of sodium phenoxide at 25 °C but in this case 7 days were required for the quantitative formation of **5e**. The colorless crystalline product was identified as the pentasubstituted species **5e** by NMR, mass spectrometry, elemental analysis, and single-crystal X-ray diffraction. In particular, the ^{13}C NMR spectrum of **5e** (Figure 1) showed the presence of three different sets of aryloxy resonances which is consistent with one group bonded to sulfur and two bonded to phosphorus in environments *cis* and *trans* to the oxygen of the S=O group. The four resonances for the sulfur-bonded phenoxy group are singlets. In contrast, the *ipso* carbons (i′ and i″) and *ortho* carbons (o′ and o″) of the phenoxy groups bonded to

(31) In a review in 1981 (see ref 16), it was reported that **1** can undergo substitution reactions with alkoxides and aryloxides, but no details were provided. This is referenced to Kok-Hettinga, M. G.; Kok, D. M.; van de Grampel, J. C. Unpublished results. The only subsequent report since that review involves the phenoxy substitution on the related $(NSOCl)_2NPCl_2$ system, which proceeded via complete substitution at phosphorus with no substitution at sulfur. See: Kok, D. M.; Kok-Hettinga, M. G.; van de Grampel, J. C. *Inorg. Chim. Acta* **1982**, *59*, 105.

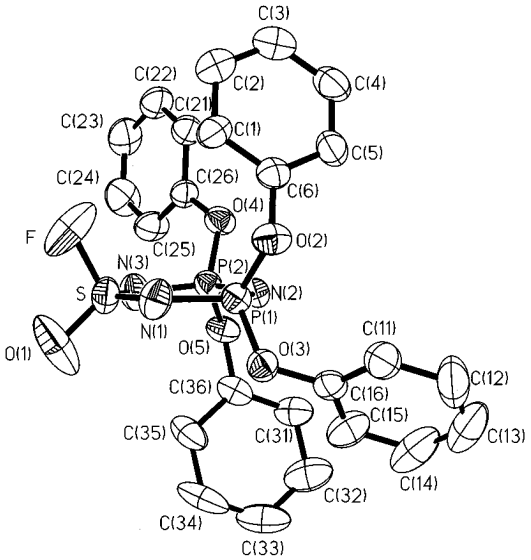


Figure 2. Molecular structure of **6d** with thermal ellipsoids at the 30% probability level.

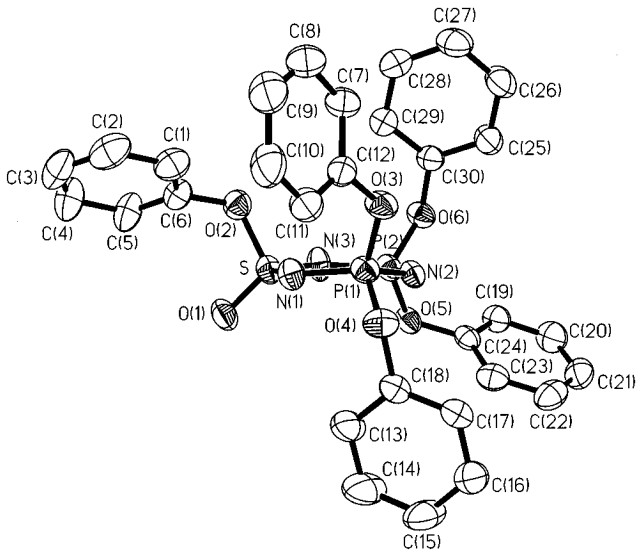


Figure 3. Molecular structure of **5e** with thermal ellipsoids at the 30% probability level.

phosphorus show coupling to two magnetically inequivalent phosphorus atoms, to give doublet of doublet patterns, which are observed as "pseudo" triplets. The *meta* (m′ and m″) and *para* (p′ and p″) carbon atoms are separated from phosphorus by four and five bonds respectively and are not coupled to this nucleus. The mass spectrum of **5e** exhibited a molecular ion at *m*/*z* 617 and a base peak at *m*/*z* 524 for the loss of phenoxide from the molecular ion.

Interestingly, substitution of the fluorine atom at sulfur in **6d** could not be achieved via reaction with aryloxide nucleophiles even at elevated temperatures. Thus, no new products were formed when **6d** was heated with excess sodium phenoxide at 102 °C in dioxane for 48 h. The lack of substitution of the fluorine atom at the sulfur(VI) center can be attributed to the relative strength of a typical S−F bond (327 kJ/mol) compared to a typical S−Cl bond (271 kJ/mol).[32]

X-ray Crystal Structures of 6d and 5e. In order to completely characterize an example of a regioselectively substituted and a completely aryloxy-substituted cyclic thionylphosphazene, single-crystal X-ray diffraction studies of **6d** and **5e** were undertaken. Suitable crystals of **6d** were grown from a mixture of ether and hexanes (4:1), whereas to obtain suitable crystals of **5e**, a mixture of hexanes and dichloromethane (20:1) was used. Molecular structures of **6d** and **5e** are shown in Figures 2 and 3. Their cell constants, data collection parameters, bond lengths and angles, and atomic coordinates are given in Tables 8−16 (see also Supporting Information). There are no significant deviations from planarity in either thionylphosphazene ring with the maximum deviation of 0.061 Å for **6d** and 0.085 Å for **5e**. The sum of the ring angles total 719(1)° for **6d** and 718.5(1)° for **5e**, which are both close to the expected value of 720° for a planar hexagon. In both **6d** and **5e** the S═O group is oriented in a more equatorial position relative to the plane of the sulfur-nitrogen-phosphorus ring skeleton than the other substituent on sulfur (i.e. F for **6d**, O(2) for **5e**). Thus the angles of the S═O groups with respect to the vector between N(2) and S in the thionylphosphazene ring are 44(1) and 46(1)° for **6d** and **5e**, respectively. In contrast, the analogous angles for the S−F group of **6d** and the S−O(Ph) group of **5e** are 62(1) and 61(1)°, respectively. This preference for an equatorial environment for the S═O group has been previously noted by van de Grampel and co-workers.[33]

Within the S−N−P fragments, the mean N−P bond length in **5e** is 1.586(2) Å which is slightly less than in **1** [1.606(4) Å][33] reflecting increased π character in the former compound. The analogous N−P bond length in **6d** [1.595(6) Å] lies inbetween these two values. Within the P(1)−N(2)−P(2) moiety, the mean N−P bond lengths in **5e** (1.569(2) Å], **1** [1.574(3) Å], and **6d** [1.560(4) Å] are comparable. For comparison, the N−P bond lengths in $[NP(OPh)_2]_3$ [average 1.575(2) Å] and $[NPCl_2]_3$ (average 1.581(3) Å) are also similar.[34,35] Interestingly, the mean S−N bond length in **5e** [1.549(2) Å] is slightly less than in **1** [1.557(3) Å] but is significantly greater than in **6d** [1.518(6) Å]. The smaller value in the latter compound is probably a consequence of the electron-withdrawing effect of the fluorine bonded to sulfur.

Substitution Reactions of 1 and 2 with NaOPh Monitored by ^{31}P and ^{19}F NMR. In an attempt to gain more insight into the pattern of substitution in the reactions of **1** and **2** with the different nucleophiles, the effects of the addition of each equivalent of nucleophile was monitored by ^{31}P NMR and (where appropriate) ^{19}F NMR spectroscopy. The products were characterized based on the observed coupling patterns and comparison of the chemical shifts of their NMR resonances with those of **1**, **2**, and the fully characterized phenoxy-substituted species **5d**, **6d**, and **5e**. There are five possible substitution sites on each molecule of **1** and **2**, and depending on whether substitution is vicinal (*vic*) or geminal (*gem*), there are many possible substitution isomers. The possible isomers for substitution at phosphorus followed by substitution at sulfur are shown in Figure 4. The substitution isomers were labeled as to whether the alkoxide or aryloxide is *cis* or *trans* to the S═O bond. In the case of the disubstituted ring, the first label indicates the relative conformation of the OR groups followed by the relation between the OR groups and the S═O bond. The determination of the stereochemistry of substitution is very difficult to elucidate based on ^{31}P NMR evidence alone and is beyond the scope of the work described in this paper.

Examination of the reaction of the chlorinated cyclic thionylphosphazene **1** with sodium phenoxide revealed controlled substitution occurring regioselectively at phosphorus, based on the estimated composition of products in the reaction mixture

(32) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, England, 1984, see p. 817.

(33) van Bolhuis, F.; van de Grampel, J. C. *Acta Crystallogr*. **1976**, *B32*, 1192.

(34) Bullen, G. J. *J. Chem. Soc. A* **1971**, 1450.

(35) Marsh, W. C.; Trotter, J. *J. Chem. Soc. A* **1971**, 169.

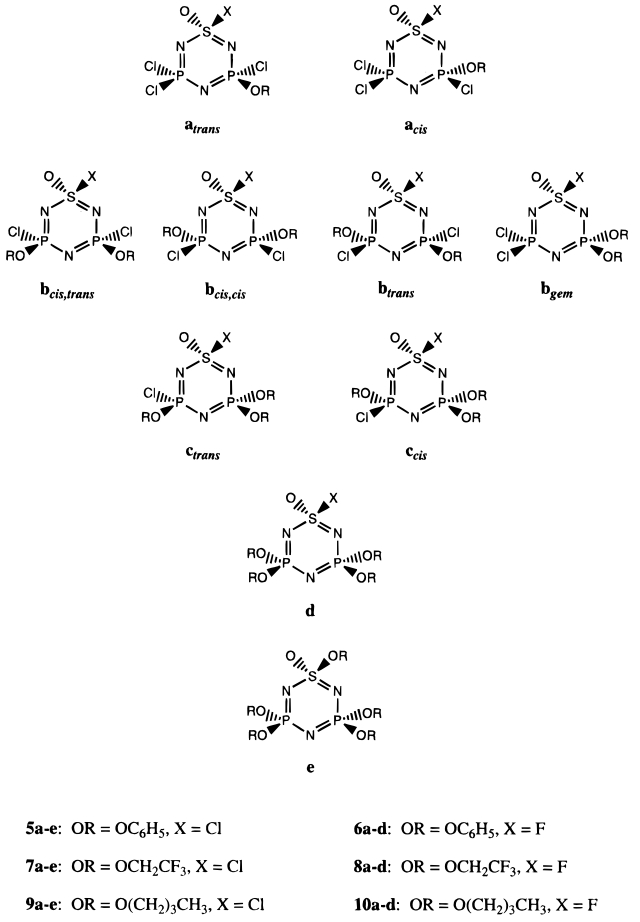


Figure 4. Possible substitution isomers for the reaction of **1** and **2** with the oxygen-based nucleophiles NaOPh, $NaOCH_2CF_3$, and NaOBu.

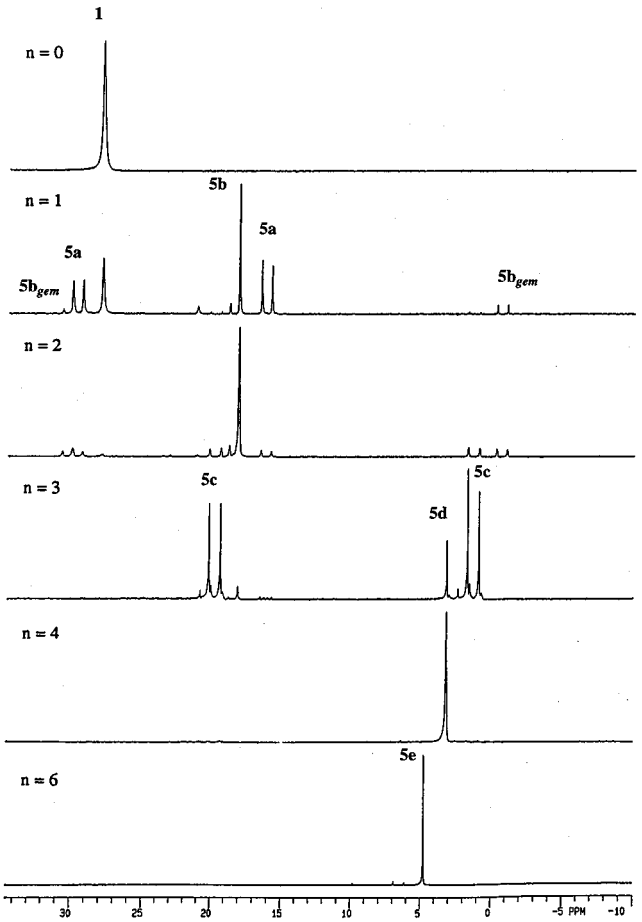


Figure 5. ^{31}P NMR spectra of the reaction of **1** with *n* equiv of NaOPh in THF ($n = 0$, 1, 2, 3, 4, and 6).

(Figure 5, Table 2). Upon addition of the first ($n = 1$) equivalent of phenoxide, the ^{31}P NMR shows several different products. Of particular note, there was still a significant amount of starting material (**1**) present (28%) and a similar amount of disubstituted product (**5b**) (24%). This indicates that the ring is not deactivated toward further substitution after the initial replacement of chlorine at phosphorus by an aryloxy group. There appeared to be only a single monosubstituted isomer present (**5a**) where two are possible. Studies by van de Grampel of reactions of **1** and **2** with amines suggest that the dominant monosubstituted isomer formed is most likely that with the aryloxy substituent *cis* to the oxygen of the S=O group (**5a**$_{cis}$).[36] After addition of the second equivalent, one major disubstituted product (**5b**) can be seen by ^{31}P NMR with a singlet resonance at 18.1 ppm. This is most likely **5b**$_{cis,cis}$ or **5b**$_{cis,trans}$[37] as the *trans*-substituted product **5b**$_{trans}$ would possess two chemically inequivalent phosphorus environments which would give rise to two doublets.[38] This revealed that substitution mainly occurs via a vicinal route and *cis* to the previously introduced aryloxy substituent. In addition, a small amount of geminal substitution occurs to give **5b**$_{gem}$, which can be identified by two doublets, one at 30.3 ppm, slightly downfield from that of **1**, and the other at −0.7 ppm, slightly upfield from the ^{31}P NMR resonance for the tetrasubstituted species **5d**. Upon addition of the third equivalent of phenoxide, the dominant product was the trisubstituted species **5c** (88%). After 4 equiv of phenoxide had been added, the tetrasubstituted ring (**5d**) was formed quantitatively. Then 6 equiv of phenoxide converted **5d** into the to pentasubstituted product **5e** at elevated temperatures or after 7 days at 25 °C.

During the reaction of **2** with NaOPh, the ^{31}P and ^{19}F NMR spectra suggested that the initial equivalent of phenoxide produced mainly the monosubstituted species **6a** but also small amounts of the di- (**6b**), and trisubstituted (**6c**) cyclothionylphosphazenes were detected (Table 3). The reaction with subsequent equivalents of NaOPh was also similar to the case of **1**, and with 4 equiv the tetrasubstituted species **6d** was formed quantitatively. No further reaction with excess NaOPh was detected over extended reaction periods.

Reaction of 1 and 2 with Sodium Alkoxides: Substitutions Monitored by ^{31}P and ^{19}F NMR. 1. Reaction of 1 and 2 with $NaOCH_2CF_3$. The reactions of **1** and **2** with trifluoroethoxide anion exhibited distinct differences to the analogous reactions with sodium phenoxide (Tables 4 and 5). Thus, after the addition of 1 equiv of nucleophile to a THF solution of **1**, the formation of mono- (**7a**), di- (**7b**), tri- (**7c**), tetra- (**7d**) and pentasubstituted (**7e**) products were all observed by ^{31}P NMR. This suggested that the presence of trifluoroethoxy substituents appreciably activates the ring to further halogen replacement. The subsequent reactions proceeded through stepwise vicinal substitution at the phosphorus centers with the formation of substituted rings analogous to those formed in the phenoxide reaction. However, in this case no geminal substitution was observed indicating increased regioselectivity with trifluoroethoxide as a nucleophile. Addition of the subsequent equivalents of nucleophile ($n = 2$ and 3) only increased the quantity of **7d** and **7e** in the reaction mixture, and the relative quantities of **7b** and **7c** remained fairly constant. Upon addition of the fourth equivalent of trifluoroethoxide, only tetrasubstituted **7d** and

(36) Baalmann, H. H.; van de Grampel, J. C. *Z. Naturforsch.* **1978**, *33B*, 964.
(37) If the assigned structure for the monosubstituted isomer is indeed **5a**$_{cis}$, then the disubstituted isomer is most likely to have the structure **5b**$_{cis,cis}$.
(38) de Ruiter, B.; Baalmann, H. H.; van de Grampel, J. C. *J. Chem. Soc., Dalton Trans.* **1982**, 2337.

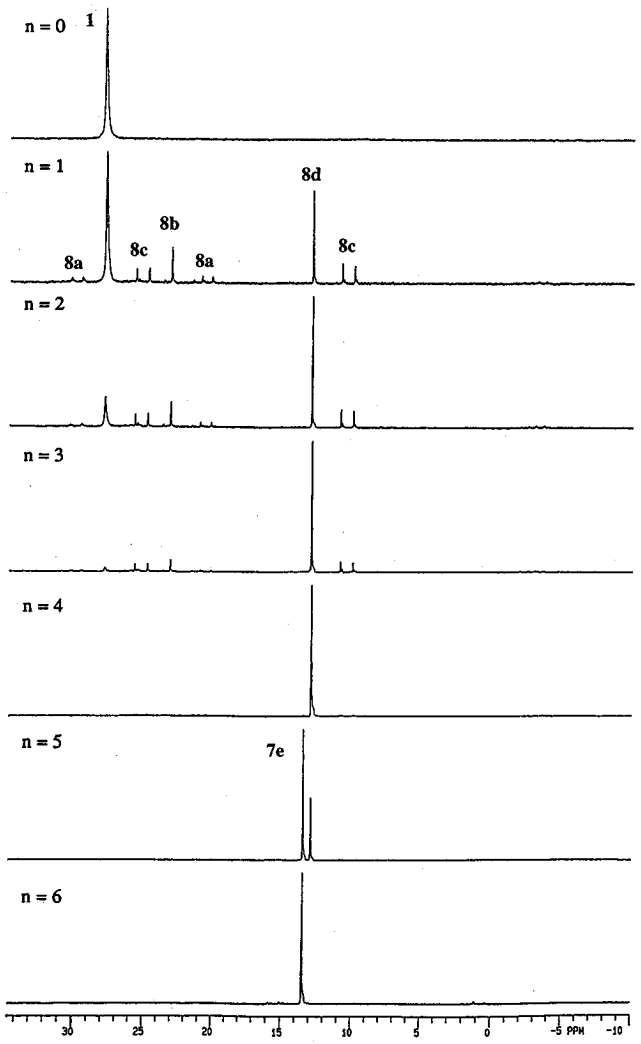


Figure 6. ^{31}P NMR spectra of the reaction of **2** with *n* equiv of $NaOCH_2CF_3$ in THF ($n = 0$, 1, 2, 3, 4, and 5).

pentasubstituted **7e** were present. With the addition of the fifth and sixth equivalent of nucleophile, a further reaction of **7e** was apparent after 12 h. This reaction is discussed further below.

The reaction of trifluoroethoxide with **2** (Figure 6) was similar to that with **1** except that substitution of the S−F bond was slower. Thus, in contrast to the reaction with **1**, the pentasubstituted compound **7e** was not formed after addition the first equivalent of trifluoroethoxide. Furthermore, after the addition of 4 equiv of nucleophile the tetrasubstituted species **8d** ($\delta(^{31}P) = 12.9$ ppm) was formed without the formation of **7e** as a side product. The singlet ^{31}P NMR resonance for **8d** was substantially downfield from that of phenoxy-substituted **6d** ($\delta(^{31}P) = 4.6$ ppm) which is consistent with the more electron withdrawing nature of the OCH_2CF_3 group. Upon addition of the fifth and sixth equivalents of trifluoroethoxide, the pentasubstituted product **7e** was formed initially in quantitative yield. Over extended reaction periods further products were also formed and the nature of this further reaction is discussed below.

2. Reaction of 1 and 2 with NaOBu. The reaction of **1** with butoxide (Figure 7) was analogous to the reaction of **1** with phenoxide (Table 6). The substitution was again regioselective with preferential substitution occurring at phosphorus. It is interesting to note that although sodium butoxide is more basic than sodium trifluoroethoxide, the formation of all possible products was not observed upon the addition of a single equivalent of this nucleophile; rather the major product detected was the expected monosubstituted product (**9a**). The ring did not appear to be activated toward further substitution as in the case of $NaOCH_2CF_3$, thus the dominant product in the reaction

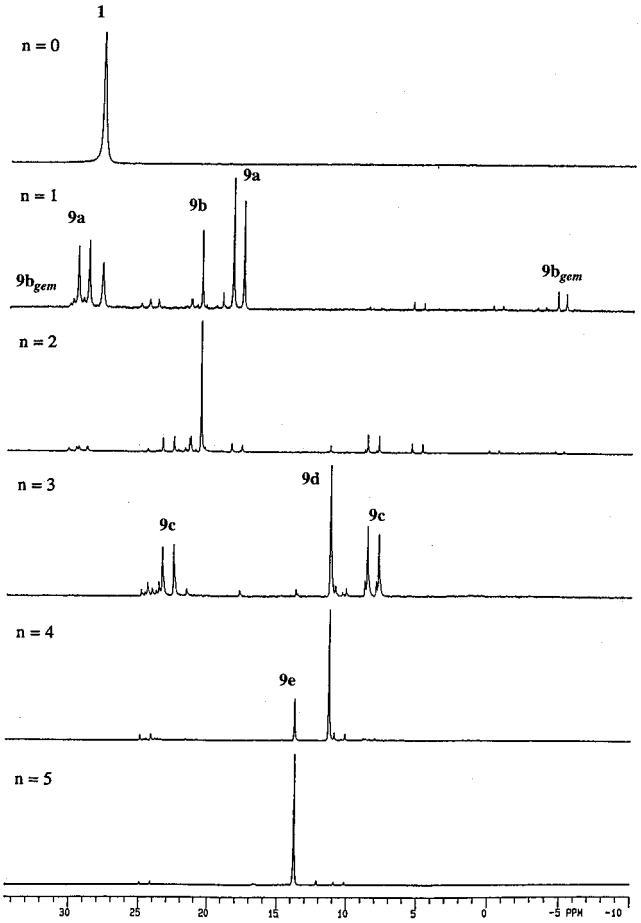


Figure 7. ^{31}P NMR spectra of the reaction of **1** with *n* equiv of NaOBu in THF ($n = 0$, 1, 2, 3, 4, and 5).

mixture was the expected product after each equivalent. Both the tetrasubstituted (**9d**) and pentasubstituted (**9e**) rings were formed after the addition of 4 equiv of nucleophile. Unlike the case of phenoxide but similar to the case of trifluoroethoxide, a further equivalent of butoxide resulted in the formation of the pentasubstituted ring under ambient conditions. Further addition of butoxide led to no further reaction with the fully substituted product (**9e**), in contrast to the situation with trifluoroethoxide.

The reactivity of **2** to nucleophilic substitution by sodium butoxide was similar to that of **1** (Table 7). However, because of the stronger S−F bond in **2**, complete substitution with butoxide occurred only with a 2-fold excess of the nucleophile.

Reaction of 1 and 2 with excess $NaOCH_2CF_3$. When **1** and **2** were reacted with an excess of $NaOCH_2CF_3$ (6 equiv) in THF over 24 h, the formation of **7e** together with several new products was detected by ^{31}P NMR. Thus after refluxing in THF for 15 h, only ca. 37% of the **7e** remained and two widely spaced sets of doublets ($\delta = 2.7$ and 15.1 ppm) were observed together with a minor set of two doublet resonances and a new singlet resonance (Figure 8). This is consistent with the formation of the anionic products *cis* and *trans* **11** and **12**, respectively, via the trifluoroethoxide-induced elimination of the ether $(CF_3CH_2)_2O$ which has previously been reported for cyclic and polymeric trifluoroethoxy-substituted phosphazenes by Ferrar, Marshall, and co-workers.[39] The formation of trifluoroethyl ether (bp 63 °C) was confirmed by GC/MS of the solvent (THF, bp 65 °C) removed from the reaction mixture. Thus, the mass spectrum was found to be identical to that of an authentic sample of $(CF_3CH_2)_2O$.

(39) Ferrar, W. T.; Marshall, A. S.; Whitefield, J. *Macromolecules* **1987**, *20*, 317.

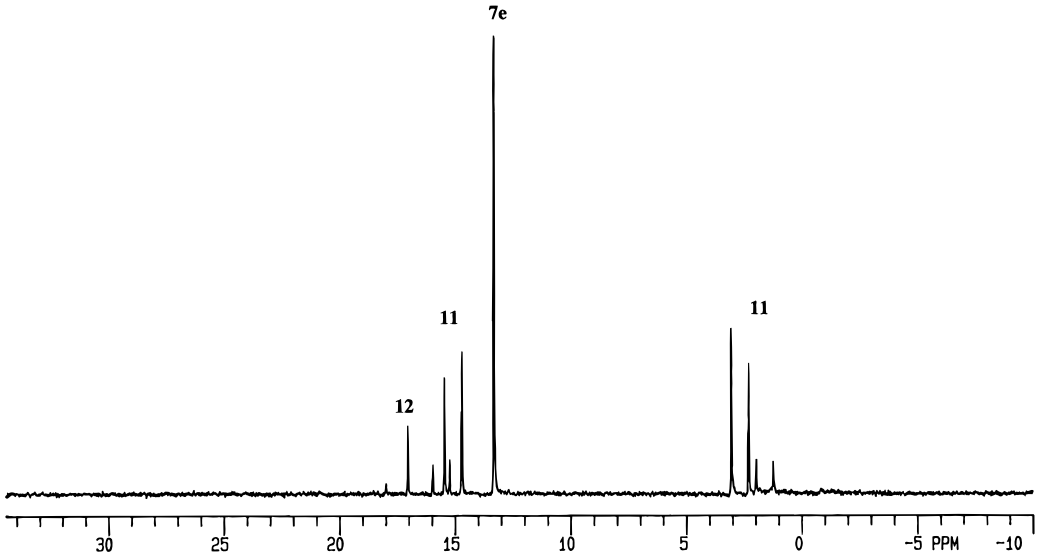
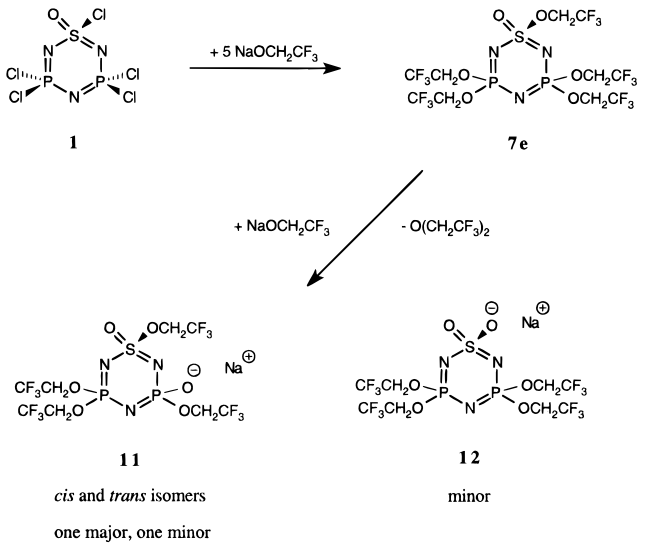


Figure 8. ^{31}P NMR spectrum of the reaction of **1** with 6 equiv of $NaOCH_2CF_3$ in THF after reflux.



Implications of the Results for Substitution Reactions on the High Polymeric Poly(thionylphosphazenes) 3 (X = Cl or F). The regioselective substitution pattern observed in the reactions of the cyclic thionylphosphazenes **1** and **2** with sodium phenoxide is in agreement with that found for the high polymeric poly(thionylphosphazene) **3**, $[NSOX(NPCl_2)_2]_n$ (X = Cl or F). Thus, at room temperature exclusive substitution at phosphorus was detected for **3** (X = Cl or F) leaving the sulfur−chlorine or sulfur−fluorine bond intact.[19] However, on addition of excess phenoxide to **1** and the use of elevated temperatures or extended reaction times, substitution at the sulfur(VI) center was also observed. A similar reaction has not yet been observed with the high polymer **3** (X = Cl). However, based on the small molecule work further investigations in this area are warranted.

The results of the substitution reactions of cyclic thionylphosphazenes **1** and **2** with sodium alkoxides suggest it should be possible to carry out analogous reactions on the high polymers **3** (X = Cl or F) to yield poly(alkoxythionylphosphazenes). Preliminary work has led to the synthesis of poly(thionylphosphazenes) with mixed alkoxy/aryloxy substitution.[15] Further work aimed at generating these completely alkoxy and aryloxy-substituted poly(thionylphosphazenes) is underway.

Summary

The substitution reactions of three representative oxygen-based nucleophiles (phenoxide, trifluoroethoxide, and butoxide) with cyclic thionylphosphazenes **1** and **2**, was found to proceed with regioselective substitution at the phosphorus centers, followed by subsequent substitution at sulfur. Although the formation of various regio- and stereoisomers can be envisaged for the substitution reactions, ^{31}P NMR and (where applicable) ^{19}F NMR spectroscopy indicated the preferential (but not exclusive) formation of single isomer for the mono-, di-, and trisubstituted cyclothionylphosphazene products. The replacement of chlorine by aryloxy and alkoxy groups occurred primarily through a vicinal substitution pathway, and the general order of reactivity was found to be PCl_2 > PCl(OR) > SOX (X = Cl, F). Some geminal substitution was observed in the reactions of **1** and **2** with phenoxide and butoxide; however, none was detected for the analogous reaction with trifluoroethoxide. Further reaction was observed with an excess of trifluoroethoxide nucleophile, resulting in the formation of the salts **11**, **12**, and $(CF_3CH_2)_2O$ as byproducts. The work described in this paper suggests that all of the three nucleophiles studied (phenoxide, trifluoroethoxide, and butoxide) offer the possibility of obtaining completely halogen-substituted poly(thionylphosphazenes) via their reaction with **3** (X = Cl). The difficulties concerning the replacement fluorine substituent at sulfur in **2** due to the higher strength of the S−F bond would be expected to lead to similar problems at the macromolecular level with **3** (X = F). In addition, trifluoroethoxy-substituted poly(thionylphosphazenes) are likely to react with excess trifluoroethoxide nucleophile to afford polymeric analogues of **11**: these species might prove to be synthetically useful intermediates, however.

Research aimed at exploring the applicability of these results to the reactions of the poly(thionylphosphazene) **3** (X = Cl or F) is in progress.

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Supporting Information Available: Tables 9−16, giving atomic coordinates, bond lengths and angles of anisotropic thermal parameters, and hydrogen atom coordinates (11 pages). Ordering information is given on any current masthead page.

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