Reaction of the Cyclic Thionylphosphazene $NSOCl[NPCl_2]_2$ with Halide Abstraction Agents: An Ambient Temperature Ring-Opening Polymerization (ROP) Route to Poly(thionylphosphazenes)

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Abstract: The thionylphosphazene cation $[NSO(NPCl_2)_2]^+$ is a proposed intermediate in the thermal ring-opening polymerization of the cyclic thionylphosphazene $NSOCl(NPCl_2)_2$ (**1**) at 165 °C. The attempted generation of $[NSO(NPCl_2)_2]^+$ via halide abstraction from **1** with a variety of Lewis acids has been studied and the possible intermediacy of this species in the subsequent reactions is suggested by the products isolated. The thermal reaction of **1** with 2 equivalents of $AlCl_3$ at 80 °C in 1,2-dichloroethane led to the quantitative formation of $NSO(CH_2CHCl_2)(NPCl_2)_2$; reaction of **1** with $Ag[BF_4]$ at 25 °C afforded the sulfur(VI)-fluorinated species $NSOF(NPCl_2)_2$ and the treatment of **1** with $Ag[OSO_2CF_3]$ resulted in the quantitative formation of $NSO(OSO_2CF_3)(NPCl_2)_2$; the latter species was found to cleave diethyl ether and generate $NSO(OCH_2CH_3)(NPCl_2)_2$. Ambient temperature reaction of **1** with $GaCl_3$, $AlCl_3$ or $SbCl_5$ (10:1), produced the high molecular weight poly(thionylphosphazene) $[NSOCl(NPCl_2)_2]_n$ and, in addition 12-, 18-, 24- and higher-membered macrocycles. Studies showed $GaCl_3$ as the most effective ROP initiator, and $AlCl_3$ the least. Subsequent reaction of $[NSOCl(NPCl_2)_2]_n$ with n-$BuNH_2$ yielded the hydrolytically stable poly(aminothionylphosphazene) $[NSO(NHBu)\{NP(NHBu)_2\}_2]_n$, which possessed molecular weights in the range, $M_n = 25\,000-60\,000$; PDI $= 1.26-2.88$. The polymerization reaction studied represents the first example of the ambient temperature ROP of any phosphazene or heterophosphazene ring induced by the deliberate addition of an initiator. Interestingly, the concentration of monomer **1** in solution was found to have a dramatic influence on the extent of reaction and the product distribution. Concentrated solutions of **1** and $GaCl_3$ (10:1) afforded only $[NSOCl(NPCl_2)_2]_n$ and larger macrocycles, whereas more dilute solutions afforded $[NSOCl(NPCl_2)_2]_n$ together with smaller macrocyclic products with lower conversions. Remarkably, dilute solutions of **1** were found to be unreactive toward $GaCl_3$. This existence of a critical equilibrium concentration (∼0.15 M) below which the monomer does not polymerize has only rarely been observed for inorganic systems and is indicative of a polymerization with a small ΔH value which implies that heterocycle **1** is not very strained.

Introduction

The synthesis of inorganic macromolecules is motivated by the possibility of accessing new materials with interesting and useful properties.[1] Ring-opening polymerization (ROP) potentially offers an attractive route to new classes of inorganic polymers because of the prevalence of cyclic species in inorganic chemistry,[2] as well as the operation of a chain-growth mechanism which generally leads to high molecular weights.[1,3] However, in very few cases are the thermodynamic or mechanistic factors underlying the ROP process clearly understood. Studies directed at understanding how inorganic heterocycles polymerize are therefore clearly very desirable as they may allow improved or new ROP routes to be developed.

Over the last 25 years, six-membered cyclic thionylphosphazenes such as **1** and **2** have been well-studied, and the ring skeleton present in these compounds, consisting of four-coordinate sulfur(VI), nitrogen, and phosphorus atoms, has been shown to be robust and stable.[4] We have previously shown that heterocycles **1** and **2** undergo thermal ROP at 165 and 180 °C, respectively, to yield novel, substitutionally labile high molecular weight sulfur(VI)−nitrogen−phosphorus polymers, poly(thionylphosphazenes) **3** and **4**.[5−7] In addition to polymer, small quantities of macrocyclic products have been detected via mass spectrometry and the 12- and 24- membered rings (**5** and **6**) have been isolated and structurally characterized using X-ray

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(1) (a) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602. (b) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: New Jersey, 1992.

(2) Haiduc, I.; Sowerby, D. B. *The Chemistry of Inorganic Homo- and Heterocycles*; Academic Press: London, 1987; Vols. 1 and 2.

(3) Odian, G. *Principles Of Polymerization,* 3rd ed.; Wiley-Interscience: New York, 1991.

(4) (a) van de Grampel, J. C. *Rev. Inorg. Chem.* **1981**, *3*, 1. (b) van de Grampel, J. C. *Coord. Chem. Rev.* **1992**, *112* 247.

(5) Liang, M.; Manners, I. *J. Am. Chem. Soc.* **1991**, *113,* 4044.

(6) Review: Gates, D. P.; Manners, I. *J. Chem. Soc., Dalton Trans.* **1997**, 2525.

(7) Polymers with backbones of alternating S(O)=N and P=N units have recently been prepared via a condensation route see: Chunechom, V.; Vidal, T. E.; Adams, H.; Turner, M. L. *Angew. Chem., Int. Ed.* **1998** *37*, 1928.

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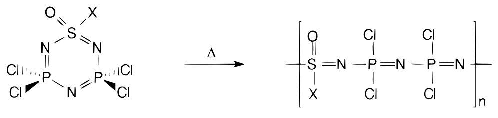
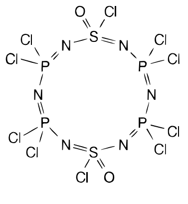


1 X = Cl (Δ = 165°C)
2 X = F (Δ = 180°C)

3 X = Cl
4 X = F



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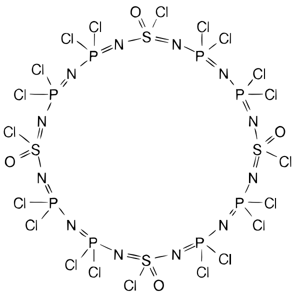

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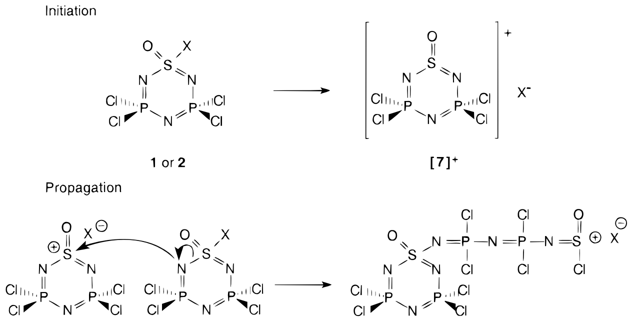
crystallography.[8] These new sulfur(VI)−nitrogen−phosphorus polymers represent a further class of poly(heterophosphazenes),[9] which in this case are hybrids of the well-studied poly(phosphazenes), $[N{=}PR_2]_n$,[10] and poly(oxothiazenes) $[N{=}S(O)R]_n$.[11] The high gas permeability of poly(aminothionylphosphazenes) has led to interest in their use as matrixes for phosphorescent oxygen sensors.[12]

Scheme 1

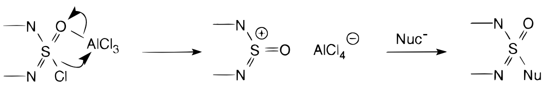


It has been speculated that the thermal ROP of both **1** and **2** involves a heterolytic dissociation of the sulfur−halogen bond as the initiation step (see Scheme 1) forming the highly reactive thionylphosphazene cation **[7]**$^+$.[13] A similar polymerization mechanism, involving ionization of a phosphorus−halogen bond, has also been proposed for the cyclic phosphazene $[NPCl_2]_3$ above 250 °C.[14] The mechanism for the formation of macrocyclic byproducts may involve cycloaddition reactions or backbiting reactions of cyclolinear intermediates, or alternatively, thermally induced depolymerization processes may occur.[10,14−16]

To our knowledge, no examples of cations of either phosphazenes or thionylphosphazenes have been isolated and characterized as stable species.[17] In this paper, as a means of probing the ROP mechanism, we describe our attempted generation of **[7]**$^+$ via halide abstraction from **1**.[18] In particular, we report full details on the resulting discovery of an ambient temperature ROP route to poly(thionylphosphazenes).

Results and Discussion

Although oxo-derivatives, including $[S(O)F_3][AsF_6]$[19] and $[S(O)F_2Cl][AsF_6]$,[20] have been characterized by X-ray diffraction, cations formally containing a sulfur(VI) moiety remain rare. More recently, the first sulfur(VI) dication, $[S(NPMe_3)_4]Cl_2$ has been structurally characterized.[21] Inorganic heterocycles containing a cationic sulfur(VI) center have proven more difficult to isolate. The cation $[(NSO)(NSOCl)(NPCl_2)]^+$ has been proposed by van de Grampel as an intermediate in the *cis/trans* isomerization of $(NSOCl)_2NPCl_2$ with catalytic quantities of $SbCl_5$ (5%).[22] Studies of the mechanism of the sulfonylation of aromatic rings in Friedel−Crafts-type reactions have suggested the involvement of S(VI) cations, $[RSO_2][AlCl_4]$, as the sulfonylation agent.[23] However, studies by Gillespie et al. and Olah et al. have suggested that SbX_5 forms a coordination complex with the oxygen atom in RSO_2Cl, rather than an ion pair.[24] Van de Grampel also proposed that phenylation and fluorination of **1** at sulfur occur by the initial coordination of the metal atom in AgF_2 or $AlCl_3$ to the exocyclic oxygen atom.[25] In the case of AgF_2, complex formation is believed to be followed by a concerted reaction mechanism, while $AlCl_3$ was proposed to form a cationic sulfur center that undergoes subsequent nucleophilic attack.



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(8) Ni, Y.; Lough, A. J.; Rheingold, A. L.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 998.

(9) Poly(heterophosphazenes) are known with carbon and sulfur(IV) as heteroelements: (a) Manners, I.; Allcock, H. R.; Renner, G.; Nuyken, O. *J. Am. Chem. Soc.* **1989**, *111*, 5478. (b) Dodge J. A.; Manners, I.; Allcock, H. R.; Renner, G.; Nuyken, O. *J. Am. Chem. Soc.* **1990**, *112*, 1268. Polymers with two-coordinate sulfur in the main chain have also been reported as insoluble materials; see, Chivers, T.; Doxsee, D. D.; Edwards, M.; Hilts R. W. in *The Chemistry of Inorganic Ring Systems*; Streudel, R., Ed.; *Studies in Chemistry*, Vol. 14; Elsevier: 1992; p 291. For reports of analogous polymers with metals in the main chain see Roesky, H. W.; Lücke M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 493.

(10) See, for example: Allcock, H. R. *Chem. Eng. News*, **1985**, *63*(11), 22; Allcock, H. R. *Angew. Chem.* **1977**, *16*, 147; *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; American Chemical Society: Washington, 1988; Chapters 19−25; Allcock, H. R. *Adv. Mater.* **1994**, *6*, 106; Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541; Montague, R. A.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1990**, *112*, 6721.

(11) Roy, A. K.; Burns, G. T.; Lie, G. C.; Grigoras, S. *J. Am. Chem. Soc.* **1993**, *115*, 2604.

(12) (a) Pang, Z.; Gu, X.; Yekta, A.; Masoumi, Z.; Coll, J. B.; Winnik, M. A.; Manners, I. *Adv. Mater.* **1996**, *8*, 768. (b) Ruffolo, R.; Evans, C. E. B.; Liu, X.; Ni, Y.; Pang, Z.; Park, P.; McWilliams, A. R.; Gu, X.; Lu, X.; Yekta, A.; Winnik, M. A.; Manners, I. *Anal. Chem.* **2000**, *72*, 1894.

(13) Manners, I. *Coord. Chem. Rev.* **1994**, *137*, 109.

(14) (a) Allcock, H. R. *Chem. Rev.* **1972**, *72*, 315. (b) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: New Jersey, 1992; Chapter 3.

(15) Hasselbring, R.; Roesky, H. W.; Noltemeyer, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 601.

(16) Roesky, H. W.; Katti, K. V.; Seseke, U.; Schmidt, H.; Egert, E.; Herbst, R.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1987**, 847.

(17) A crystal structure of the S(IV) thiophosphazene cation, $[SN(NPCl_2)_2]^+[SbCl_6]^-$, has been reported. Pohl, S.; Petersen, O.; Roesky, H, W. *Chem. Ber.* **1979**, *112*, 1545.

(18) Communication: Gates, D. P.; Edwards, M.; Liable-Sands, L. M.; Rheingold, A. L.; Manners, I. *J. Am. Chem. Soc.* **1998**, *120*, 3249.

(19) Lau, C.; Lynton, H.; Passmore, J.; Siew, P. *J. Chem. Soc., Dalton Trans.* **1973**, 2535.

(20) Lau, C.; Passmore, J. *Chem. Commun.* **1971**, 951.

(21) Folkerts, H.; Hiller, W.; Herker, M.; Vyboishchikov, S. F.; Frenking, G.; Dehnicke, K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1362.

(22) de Ruiter, B.; van de Grampel, J. C. *J. Chem. Soc., Dalton Trans.* **1982**, 1773.

(23) See: Jensen, F. R.; Goldman, G. In *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley-Interscience: New York, 1963−64; Vol. 3, Chapter 40.

(24) See, for example: Dean, P. A. W.; Gillespie, R. J. *J. Am. Chem. Soc.* **1969**, *91*, 7260; Olah, G. A.; Ku, A. T.; Olah, J. A. *J. Org. Chem.* **1970**, *35*, 3925; Olah, G. A.; Lin, H. C. *Synth. Commun.* **1973**, 343.

(25) van de Grampel, J. C.; van der Huizen, A. A.; Jekel, A. P.; Wiedijik, D.; Labarre, J. F.; Sourine, F. *Inorg. Chim. Acta* **1981**, *53*, L169.

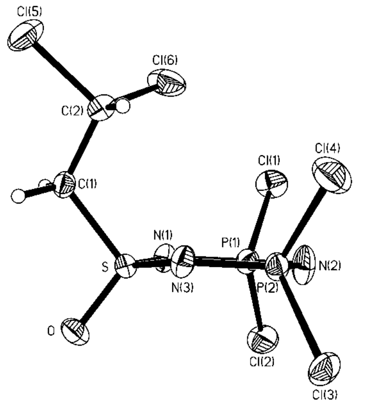
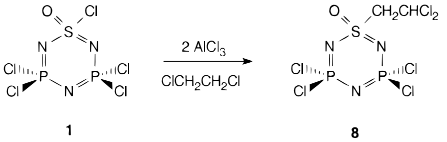


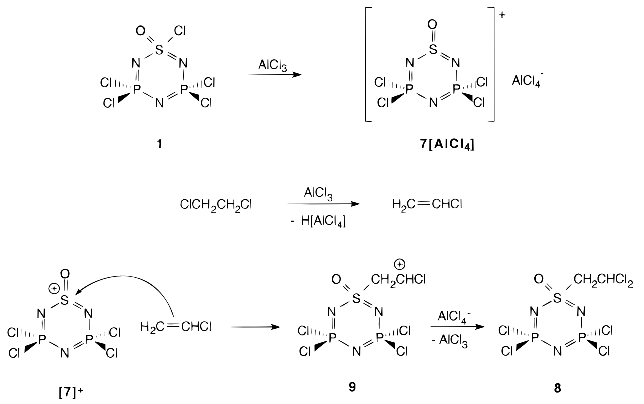
Figure 1. Molecular structure of **8** with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [deg]: S−N(1) 1.567(3), N(1)−P(1) 1.583(3), P(1)−N(2) 1.567(3), N(2)−P(2) 1.571(3), P(2)−N(3) 1.582(3), N(3)−S 1.563(3), S−O 1.434(3), S−C(1) 1.784(3); N(1)−S−N(3) 114.5(1), S−N(3)−P(2) 124.4(2), N(3)−P(2)−N(2) 117.2(1), P(2)−N(2)−P(1) 121.2(2), N(2)−P(1)−N(1) 117.9(1), P(1)−N(1)−S 123.5(2).

1. Attempted Synthesis of $[7]^+$ with $[AlCl_4]^-$ as Counterion; Synthesis and Characterization of $NSO(CH_2CHCl_2)(NPCl_2)_2$ (8). Halide abstraction from **1** was initially attempted in CH_2Cl_2 with $AlCl_3$ as the Lewis acid, but no reaction was observed by ^{31}P NMR after 24 h. Therefore, the thermal reaction of **1** with excess (two equiv.) $AlCl_3$ was attempted in 1,2-dichloroethane solution at reflux (80 °C) and analysis of the product by ^{31}P NMR spectroscopy in $CDCl_3$ showed a single new resonance at $\delta = 21.2$ ppm. Analysis of the crystalline product by ^1H NMR spectroscopy showed only two resonances, a doublet of triplets at $\delta = 4.00$ ppm and a downfield triplet at 6.06 ppm. The coupling pattern and integration suggested that one proton at 6.06 ppm ($^3J_{HH} = 6.2$ Hz) was coupled to two protons at 4.0 ppm which were also coupled to phosphorus ($^3J_{HH} = 6.2$ Hz, $^4J_{HP} = 2.1$ Hz). The ^{13}C NMR spectrum exhibited two resonances, a singlet at 64.2 ppm and a triplet at 67.9 ppm, and suggested coupling to phosphorus. The only structure which reasonably fit with the observed NMR data was **8**, in which a migration of one chlorine atom in 1,2-dichloroethane had occurred.

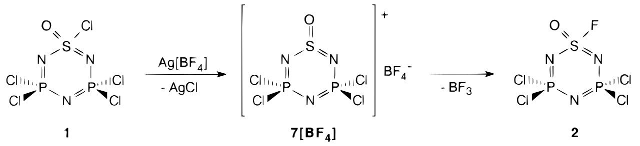


Further confirmation of the formation of **8** was provided by an X-ray diffraction study on crystals grown by vacuum sublimation. The molecular structure of **8** is shown in Figure 1 and the six-membered P_2N_3S ring has similar features to that observed for **1**.[26] The ring is essentially planar with the sulfur atom being slightly out of the plane of the other five ring atoms by 0.14(1) Å. Interestingly, unlike the situation in other thionylphosphazene rings, the S(O)R group does not adopt an equatorial/axial conformation. The angle between the S═O bond and the N(2)−S vector is 52(1)° and the similar angle for the S−C(1) bond is 53(1)°.

It is likely that **8** is formed via an ionic mechanism analogous to that proposed by van de Grampel for Friedel−Crafts reactions of **1**.[25] The reactive nucleophile derived from 1,2-dichloroethane is possibly vinyl chloride.[27] The first step may involve chloride abstraction from the sulfur atom in **1** by $AlCl_3$ yielding the sulfur(VI) cation complex **7[AlCl₄]**[28] which then selectively attacks the more electron rich carbon atom of vinyl chloride (i.e., the CH_2 site) to form a carbocation **9**. This species might then react with the $[AlCl_4]^-$ anion to yield the 2,2-dichloroethyl-substituted thionylphosphazene **8**.



2. Attempted Synthesis of $[7]^+$ with $[BF_4]^-$ as a Counterion; Synthesis of $NSOF(NPCl_2)_2$ (2). An attempt to generate the thionylphosphazene cation $[7]^+$ by the addition of **1** to a slurry of $Ag[BF_4]$ in dichloromethane solution resulted in the immediate formation of a white precipitate and the release of a volatile gas which fumed on exposure to air. Analysis of the reaction mixture by NMR spectroscopy showed a single ^{31}P NMR resonance at 26.8 ppm, and a single ^{19}F NMR resonance at 75.5 ppm. This was consistent with the spectra observed for **2**. Thus, it seems likely that the initial step in the reaction involves the abstraction of chlorine from sulfur, generating the thionylphosphazene cation as **7[BF₄]** which then abstracts fluoride from the $[BF_4]^-$ anion generating **2** and BF_3, which is eliminated as a gas. These results provide further evidence for the possible existence of this cation as a fleeting intermediate.



It is interesting to point out that, whereas the cyclic chlorinated thionylphosphazene **1** can be prepared quite readily using a procedure developed by Suzuki and co-workers,[29] the only reported route to the fluorinated cyclic thionylphosphazene, **2**, involves the regioselective fluorination of **1** with a large (10-fold) excess of the expensive reagent AgF_2 under conditions of reflux.[25] Obviously, this is an undesirable method for the large scale synthesis of **2**, because of the high cost of using a large excess of the silver(I) salt. Therefore, the use of $Ag[BF_4]$ provides a significantly more cost-effective (but still expensive) route to **2**, and also provides convenient ambient temperature

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[26] van Bolhuis, F.; van de Grampel, J. C. *Acta Crystallogr.* **1976**, *B32*, 1192.

[27] For an example of the dehydrochlorination of 1,2-dichloroethane to form vinyl chloride in the presence of $AlCl_3$: Rothan, P. N.; Sims, E. W. *Chem. Ind.* **1970**, *25*, 830; U.S. Patent 3,304,336, 1967; U.S. Patent 2,593,451, 1952.

[28] Additional support for the possible formation of a sulfur(VI) cation as an intermediate is provided by the observation that the reaction of excess (2 equiv) of HgF_2 and exactly 1 equiv of $AlCl_3$, in 1,2-dichloroethane at 70−80 °C, resulted in the quantitative production of **2**. A similar experiment with HgF_2 in the absence of $AlCl_3$ resulted in no reaction.

[29] Suzuki, D.; Akagi, H.; Matsumura, K. *Synthesis* **1983**, 369.

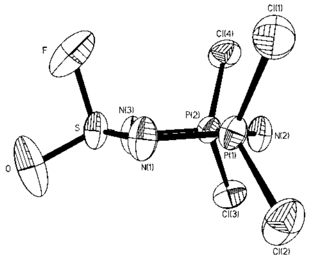


Figure 2. Molecular structure of **2** (molecule 1) with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [deg]: Molecule 1: S−N(1) 1.536(4), N(1)−P(1) 1.597(5), P(1)−N(2) 1.560(4), N(2)−P(2) 1.568(4), P(2)−N(3) 1.584(5), N(3)−S 1.520(5), S−O 1.387(6), S−F 1.511(6); N(1)−S−N(3) 116.9(2), S−N(3)−P(2) 123.3(3), N(3)−P(2)−N(2) 116.6(1), P(2)−N(2)−P(1) 121.5(3), N(2)−P(1)−N(1) 116.8(2), P(1)−N(1)−S 122.5(3); Molecule 2: S′−N(1′) 1.523(5), N(1′)−P(1′) 1.589(5), P(1′)−N(2′) 1.557(4), N(2′)−P(2′) 1.570(4), P(2′)−N(3′) 1.577(5), N(3′)−S′ 1.516(5); N(1′)−S′−N(3′) 116.7(3), N(1′)−S′−N(3′)−P(2′) 124.8(4), N(3′)−P(2′)−N(2′) 116.2(2), P(2′)−N(2′)−P(1′) 121.5(2), N(2′)−P(1′)−N(1′) 117.0(2), P(1′)−N(1′)−S′ 123.6(3).

access to significant quantities of this monomer which are required for the synthesis of the fluoropolymer **4**.

To fully characterize **2**, and because very few structural studies of thionylphosphazene rings have been reported, an X-ray crystallographic analysis of **2** was undertaken. The molecular structure of **2** is shown in Figure 2, and interestingly, the asymmetric unit contains two unique, but structurally similar, molecules. The SN_3P_2 ring is essentially planar, with the maximum deviation from planarity being at S which is removed by 0.14(1) Å from the plane of the other five ring atoms. One striking difference between the molecular structures of **1** and **2** is that the S−N bonds are significantly contracted in the latter. For example, the average S−N bond length is 1.521(6) Å for **2** which is significantly shorter than for the analogous bonds in **1** (1.557(3) Å).[26] A similar S−N bond contraction, although not as pronounced, was observed for *cis*-$[(NSOF)_2NPCl_2]$ (S−N(P) avg. 1.527(7) Å) compared with *cis*-$[(NSOCl)_2NPCl_2]$ (S−N(P) avg. 1.540(9) Å). The differences at the phosphazene end of the ring are, as expected, much less dramatic. For example, P−N(P) bond lengths (avg. 1.564(5) Å in **2** vs 1.574(3) Å in **1**) are considerably shorter than the P−N(S) bond lengths (avg. 1.588(5) Å in **2** vs 1.606(3) Å in **1**).

Interestingly, the S=O group is oriented in an equatorial environment and the S−F moiety is in a more axial environment with respect to the plane of the sulfur−nitrogen−phosphorus ring. This conformation is apparent from the side view of the molecular structure in Figure 2, and the angles between the S=O bond and the vector joining N(2) and S in the ring is 30(1)°, whereas the analogous angle for the S−F group is 72(1)°. Similar structural characteristics were noted by van de Grampel for the structure of **1**, in which the S=O group was in an equatorial position and the S−Cl is in an axial position.

3. Attempted Synthesis of $[7]^+$ with $[OSO_2CF_3]^-$ as a Counterion; Synthesis of $NSO(OSO_2CF_3)(NPCl_2)_2$ (10) and $NSO(OCH_2CH_3)(NPCl_2)_2$ (11). Due to the apparent reaction of fluorinated counterions with the thionylphosphazene cation **[7]**$^+$ generated by chloride abstraction with Ag^+, the triflate anion was chosen as a potentially less reactive anion. Thus, addition of a solution of **1** in CH_2Cl_2 to a slurry of $Ag[OSO_2CF_3]$ in CH_2Cl_2 resulted in the formation of a fine white precipitate of AgCl. Analysis of the reaction mixture by ^{31}P NMR spectroscopy showed the quantitative formation of product with a new singlet resonance at 27.2 ppm shifted slightly downfield from that for **1** (δ = 27.1 ppm), and a single peak in the ^{19}F NMR spectrum at −72.0 ppm (Figure 3). This is consistent with the formation of **10**, where the triflate anion is probably coordinated to the sulfur(VI) cation. It is unlikely that this is the fully ionic species **7**$[OSO_2CF_3]$; however, it is interesting to note that the ^{19}F NMR spectrum shows a single resonance at −72.0 ppm, whereas covalent triflates generally resonate at ∼−78 ppm.[30]

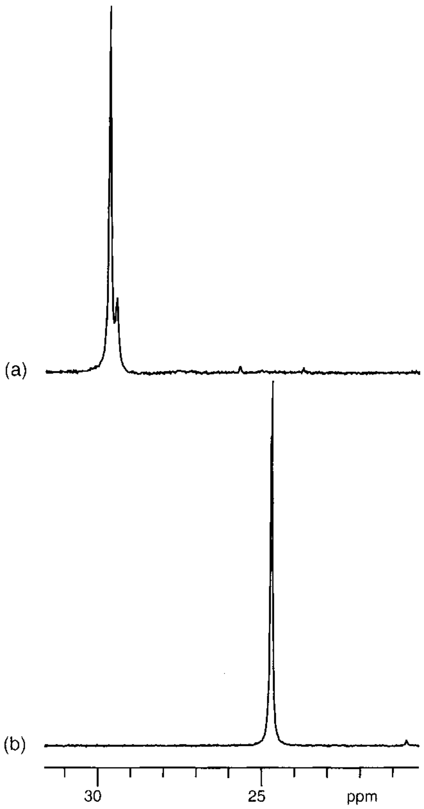
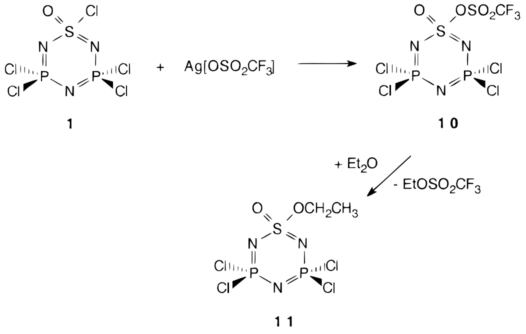


Figure 3. ^{31}P NMR spectra in CH_2Cl_2 of: (a) the initial reaction mixture containing **1** + $Ag[OSO_2CF_3]$, showing the formation of **10** along with a small amount of unreacted **1**; (b) the product, **11**, after the addition of Et_2O to **10**.



After solvent removal, an uncrystallizable elastomeric material was isolated, the soluble fraction of which exhibited very broad ^{31}P NMR resonances between 0 and −15 ppm, in addition to a resonance for **10** at 27.2 ppm. Diethyl ether was therefore chosen as a potential coordinating species with which to stabilize the cation and facilitate isolation as a stable crystalline solid. However, when a slight (∼25%) excess of diethyl ether was added to **10** in CH_2Cl_2 a new singlet resonance in the ^{31}P NMR

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[30] For example, $Me_3SiOSO_2CF_3$ (δ = −78 ppm in CH_2Cl_2) and $HOSO_2CF_3$ (δ = −78.5 ppm). Jones, V. A.; Thornton-Pett, M.; Kee, T. P. *J. Chem. Soc., Chem. Commun.* **1997**, 1317; Emsley, J. W.; Phillips, L. In *Progress in Nuclear Magnetic Resonance Spectroscopy*; Emsley, J. W., Feeney, J., Sutcliffe, L. H., Eds.; Pergamon Press: Toronto, 1971; Vol. 7.

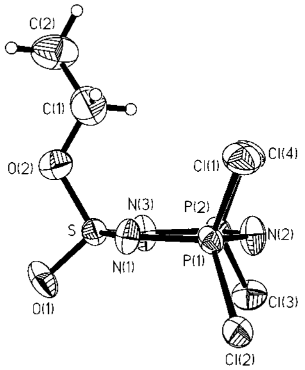
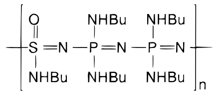


Figure 4. Molecular structure of **11** with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [deg]: S−N(1) 1.551(10), N(1)−P(1) 1.572(9), P(1)−N(2) 1.566(10), N(2)−P(2) 1.542(11), P(2)−N(3) 1.572(10), N(3)−S 1.575(10), S−O(1) 1.420(8), S−O(2) 1.557(10); N(1)−S−N(3) 114.5(1), S−N(3)−P(2) 123.9(7), N(3)−P(2)−N(2) 117.3(5), P(2)−N(2)−P(1) 122.5(6), N(2)−P(1)−N(1) 116.6(5), P(1)−N(1)−S 124.8(6).

spectrum was observed at 24.7 ppm. Solvent removal in vacuo, resulted in a colorless air-stable crystalline solid, and after sublimation and recrystallization, no resonances were observed in the ^{19}F NMR spectrum, and ^{1}H and ^{13}C NMR spectroscopy showed resonances attributed to an ethoxy group. Mass spectrometry was consistent with the formation of **11** and showed the molecular ion at $m/z = 339$ with the correct isotope pattern.

Confirmation of the structure of the product was provided by an X-ray crystallographic study of crystals grown from a hexanes solution. The structure (Figure 4) confirms that diethyl ether had been cleaved and an ethoxy group had been transferred to sulfur, presumably leading to the elimination of $EtOSO_2CF_3$. The structure of **11** is quite similar to that of **2**, with a planar ring and the maximum deviation from planarity is at N(3), which is removed from the plane of the other five ring atoms by 0.09(1) Å. The S−N bond lengths (avg. 1.563(11) Å) are slightly longer than in **2** (avg. 1.521(6) Å) and are similar to those in **1** (1.557(3) Å).[26] Also of particular note, and similar to the situation in **1** and **2**, is that the S═O bond is in an equatorial environment, and the angle to the vector joining S and N(2) is 44(1)°. In contrast, the S−O bond is in a more axial environment with an analogous angle of 58(1)°.

4. Ambient Temperature Polymerization and Oligomerization of 1. (a) Using $GaCl_3$ as an Initiator. The high electrophilicity of the sulfur(VI) center in **10**, demonstrated by the formation of **11**, and the evidence for intermolecular reactions during the attempted isolation of this species suggested that the cation **[7]**$^+$ might act as an initiator for the cationic ROP of **1** in solution at ambient temperature. Preliminary studies of the reaction of **1** with substoichiometric quantities of $GaCl_3$ (5 and 10%) at 25 °C indeed showed the formation of cyclic oligomers and polymer **3**.[18] As polymer **3** is hydrolytically sensitive, the material was reacted with $BuNH_2$ at 0 °C, and subsequent precipitation from THF into H_2O gave poly[(butylamino)thionylphosphazene], **12**. This material possessed molecular weight data comparable to that for **12** derived from the thermal ROP of **1** ($M_n = 24\,500$, PDI = 2.0). The success of the preliminary studies on the room-temperature ROP of **1** prompted us to investigate these reactions in detail.


$$\left[\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle NHBu}{\underset{|}{S}}}}=N-\overset{\displaystyle NHBu}{\overset{|}{\underset{\displaystyle NHBu}{\underset{|}{P}}}}=N-\overset{\displaystyle NHBu}{\overset{|}{\underset{\displaystyle NHBu}{\underset{|}{P}}}}=N\right]_n$$

12

Table 1. Conversion of **1** to Polymer **3** Using $GaCl_3$ as an Initiator in ~1 mL of CH_2Cl_2 after 4 Days[a]

amount of $GaCl_3$ used (mol %)	**1** (%)	**5** (%)	**3** (%)[b]	yield **12** (%)[c]	M_n **12**	PDI **12**
5.0	3	2	95	55	25 000	1.66
10.0	3	2	95	69	27 000	1.79
15.0	3	2	95	71	26 000	1.66

[a] 0.76 mmol of **1** were used. The composition of the reaction mixture was determined using ^{31}P NMR integration. [b] Estimate also includes higher-membered rings (>12-membered). [c] Isolated yield based on 252 mg of **1**.

Table 2. Conversion of **1** to Polymer **3** Using 10% $GaCl_3$ as an Initiator in Different Volumes of CH_2Cl_2 upon Equilibration[a]

volume CH_2Cl_2 used (mL)	**1** (%)	**5** (%)	**3** (%)[b]	yield **12** (%)[c]	M_n **12**	PDI **12**
0.25	0	0	100	68[d]	43 250[d]	1.86[d]
0.50	4	12	84	83	42 000	2.18
1	15	20	65	62	52 000	1.72
2	33	32	35	34	34 000	1.78
3	52	23	25	25	45 000	1.32
4	61	23	16	5	46 000	1.26
5	77	23	0	0	−	−
10	88	12	0	0	−	−
20	100	0	0	0	−	−

[a] 0.76 mmol of **1** were used. The composition of the reaction mixture was determined using ^{31}P NMR integration. [b] Estimate also includes higher-membered rings (>12-membered). [c] Isolated yield based on 252 mg of **1**. [d] Average of 4 experiments: Yield of **12**: 51−89%; M_n: 31 000−58 000; PDI: 1.63−2.52.

The polymerization mixture obtained from heating **1** at 165 °C for several hours contains, in addition to **1** and **3**, macrocycles identified at the 12 (**5**)-, 18-, 24 (**6**)-, and 6x (x = 5−11)-membered rings.[8] A typical ^{31}P NMR spectrum of the reaction mixture contains resonances for **1** ($\delta = 27.1$ ppm), the *cis*- and *trans*- isomers of **5** ($\delta = -7.77$ and -8.00 ppm) and for the polymer **3** ($\delta = -9.78$ ppm). After the removal of **1** and **3**, higher-membered macrocycles can be detected at −9.8 ppm. The reaction of **1** (0.76 mmol) with 5, 10, and 15% $GaCl_3$ at 25 °C was attempted in approximately 1 mL of CH_2Cl_2. After stirring for 4 days, the ^{31}P NMR spectrum for each sample showed a singlet resonance at −9.7 ppm, (for polymer **3**) with very small signals at −7.7 ppm, −7.9 ppm (*cis*- and *trans*-**5**) and a very small resonance at 27.1 ppm (for unreacted **1**). There was 2% conversion to the *cis*- and *trans*-12-membered rings **5** ($\delta = -7.7$ and -7.9 ppm). The singlet at −9.7 ppm indicated a 95% conversion of **1** to poly(thionylphosphazene) **3** and higher oligomers in each case (see Table 1).

Following aminolysis of **3**, analysis of **12** from each reaction by gel permeation chromatography (GPC) gave molecular weights and polydispersities which were remarkably similar (see Table 1), suggesting that the exact percentage of $GaCl_3$ used as initiator does not play an important role in determining the molecular weight of the product in the experiments performed. In addition, the yield of polymer **12** also appears to be fairly independent of the percentage of initiator used.

To investigate dependency of the extent of reaction and product distribution on reaction concentration a further series of experiments were performed. The reactions of equal quantities of **1** (0.76 mmol) with 10 mol % $GaCl_3$ were performed using varying, but accurately measured amounts of CH_2Cl_2 (between 0.25 and 20 mL) as a solvent (see Table 2). During the course of these investigations it became apparent by ^{31}P NMR that the reaction equilibria were reached in ~24 h. Analysis of the reaction mixture from the most concentrated sample (in 0.25 mL solvent) by ^{31}P NMR showed only a single peak at −9.7

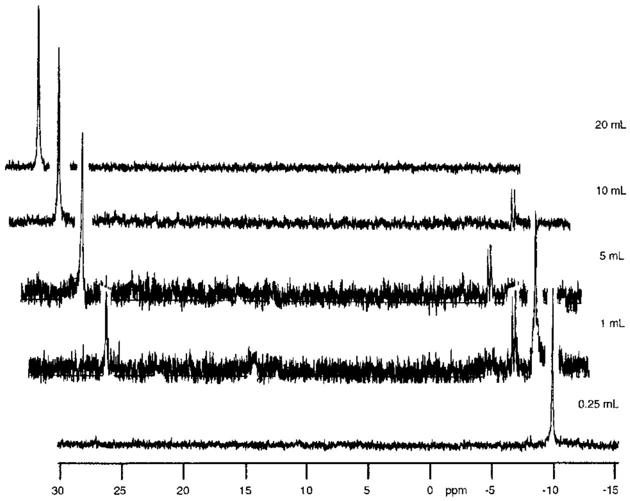


Figure 5. ^{31}P NMR spectra for ambient temperature reaction of **1** and 10 mol % $GaCl_3$ as an initiator for selected volumes of CH_2Cl_2.

ppm, indicative of full conversion to polymer **3**. As the amount of solvent increased, ^{31}P NMR resonances corresponding to the *cis*- and *trans*-12-membered rings and the starting material became more prominent as the conversion to the polymer **3** decreased (see Figure 5). It is interesting to note that only macrocycles were produced when 5 or 10 mL of CH_2Cl_2 were used and, remarkably, only a single peak at 27.1 ppm from unreacted **1** was detected when 20 mL of solvent were used. However, when the volume of the latter reaction mixture was reduced from 20 to 1 mL and the reaction allowed to reach equilibrium, ^{31}P NMR showed only a single resonance at −9.7 ppm, assigned to polymer **3** and corresponding (>12-membered) macrocycles.

Samples run in <5 mL of solvent showed appreciable conversion to polymer **3**, which was subsequently converted to **12** and analyzed by GPC (Table 2). To test reproducibility, three more samples of **1** (0.76 mmol) were reacted with 10% $GaCl_3$ in 0.25 mL of CH_2Cl_2. Analysis by ^{31}P NMR for each of the three samples showed 100% conversion to **3**. The samples were also subsequently converted to **12**. Although the overall yield of isolated **12** varied from 51 to 89% for these three samples, the GPC results showed were in fairly close agreement with each other (average results from the four runs are reported in Table 2).

(b) Using $AlCl_3$ and $SbCl_5$ as an Initiator. We described above (section 1) the absence of a reaction between **1** and $AlCl_3$ in a dilute CH_2Cl_2 solution over 24 h. However, on the basis of the results obtained with $GaCl_3$ we reinvestigated the potential reaction of **1** with $AlCl_3$ in more detail and, in particular, as a function of concentration. Reactions were performed to test the effectiveness of $AlCl_3$ as an initiator by reacting **1** (0.76 mmol) with 10 mol % $AlCl_3$ in 0.25−5 mL of 1,2-dichloroethane. After 9 days, ^{31}P NMR analysis of samples run in 1 mL of solvent or greater showed only a single resonance for unreacted **1** at 27.1 ppm. However, after 1 day, ^{31}P NMR analysis of the reaction mixture for the most concentrated solution (in 0.25 mL of solvent) also showed the development of a singlet resonance at −9.7 ppm, corresponding to a 20% conversion of **1** to higher membered macrocycles and polymer **3**. The sample was subsequently converted to polymer **12** ($M_n = 60\,000$ and PDI $= 2.88$) through the methods previously described. Under these reaction conditions, $AlCl_3$ is clearly much less effective as an initiator for the ROP of **1** than $GaCl_3$.

To investigate a third example of a halide acceptor, we explored the reaction of **1** with $SbCl_5$. Roesky and co-workers previously showed that antimony(V) chloride is an effective halide acceptor for the synthesis of the thiophosphazene cation, $[NS(NPCl_2)_2]^+$.[17] It has been reported that $SbCl_5$ also promotes the *cis/trans* isomerization of $(NSOCl)_2NPCl_2$.[22] In a series of experiments cyclic **1** was reacted with 10 mol % $SbCl_5$ in 1−5 mL of 1,2-dichloroethane. After the reaction mixtures had been stirred for 9 days, analysis of the ^{31}P NMR spectra for each sample revealed the presence of peaks at 27.1 ppm, −7.7 and −7.9 ppm, and −9.7 ppm in various ratios (see Table 3). Each sample showed evidence for the presence of the *cis*- and *trans*-12-membered ring **5** ($\delta = -7.7$ ppm, −7.9 ppm). Samples run in 1 and 2 mL of solvent each possessed a peak at −9.7 ppm, corresponding to formation of poly(thionylphosphazene) **3** and higher-membered rings (>12-membered).

Table 3. Conversion of **1** to Polymer **3** Using $SbCl_5$ as an Initiator in Varying Amounts of 1,2-Dichloroethane after 9 Days[a]

volume $(CH_2Cl)_2$ used (mL)	**1** (%)	**5** (%)	**3** (%)[b]	yield **12** (%)[c]	M_n **12**	PDI **12**
1	23	32	45	41	37 000	1.35
2	41	39	20	10	42 000	1.53
3	61	39	0	0	−	−
4	67	33	0	0	−	−
5	77	23	0	0	−	−

[a] 0.76 mmol of **1** were used. The composition of the reaction mixture was determined using ^{31}P NMR integration. [b] Estimate also includes higher-membered rings (>12-membered). [c] Isolated yield based on 252 mg of **1**.

The samples were precipitated into hexanes to remove any unreacted **1** and macrocycles. The samples were subsequently reacted with $BuNH_2$ and the product, **12**, precipitated from THF into H_2O. Only the samples run in 1 and 2 mL of solvent showed the presence of any poly[(butylamino)thionylphosphazene] **12**, and in each case the yield was relatively low. GPC analysis of the reactions which produced polymers are summarized in Table 3.

(c) Discussion of Results. Lewis acids such as BCl_3 have been shown to promote the ROP of cyclic phosphazene $[NPCl_2]_3$ allowing the temperature to be lowered from 250 °C to ca. 200 °C.[10,31] We have also found that Ag(I) salts (e.g., $Ag[BF_4]$) permit temperatures as low as 135 °C to be used for the thermal ROP of cyclic thionylphosphazene **1**.[32] Previously, it has been shown that the thiophosphazene $NSCl(NPCl_2)_2$ will slowly polymerize at ambient temperature, particularly if impure.[33] However, the observation that $GaCl_3$ (and, less effectively, $AlCl_3$ and $SbCl_5$) promotes the ambient temperature ROP of **1** represents the first example of ambient temperature ROP of a heterophosphazene or phosphazene ring induced by the addition of an initiating reagent. Equilibration was observed in 24 h when $GaCl_3$ was used. However, comparative inspections of Tables 2 and 3 indicate that in the case of $SbCl_5$ equilibrium is not reached even after 9 days as judged by the conversion to **3**. In the case of $AlCl_3$ the conversion to polymer was only detected at the highest monomer concentration used. Intriguingly, the formation of polymer **3** appears to be very sensitive to monomer concentration. This points to the existence of a critical concentration at room temperature (∼ 0.15 M) below which polymerization will not take place. Such observations have well-established precedent in the polymerization of organic monomers such as α-methylstyrene and tetrahydrofuran with relatively

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(31) See: Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York, 1972; Chapter 15.

(32) Liang, M.; Manners, I. Unpublished results.

(33) Allcock, H. R.; Dodge, J. A.; Manners, I. *Macromolecules* **1993**, *26*, 11.

small polymerization enthalpies.[34] However, very few examples have been established for inorganic systems[35] and the result suggests that ΔH_{ROP} is fairly low which implies a low degree of ring strain for **1**.[36] Further analysis of the ambient temperature ROP of **1**, such as variable temperature measurements, is therefore very desirable and will be the subject of future work.

Summary and Future Work

Attempts to generate **[7]**$^+$, the proposed cationic initiator in the ROP of **1**, via the reaction of the latter with halide acceptors has led to the discovery of novel chemistry and, most significantly, the ambient temperature ROP of **1**. The reaction of **1** with $AlCl_3$ in refluxing 1,2-dichloroethane resulted in the unexpected synthesis of the sulfur-2,2-dichloroethyl derivative **8**, which indicated that an unusual 1,2-chlorine migration reaction had taken place. Treatment of **1** with Ag[BF_4] resulted in an improved route to the sulfur-fluorinated thionylphosphazene **2**. The reaction of Ag[OSO_2CF_3] with **1** generated a highly electrophilic species **10** which cleaves diethyl ether to form the sulfur-ethoxy-substituted derivative, **11**. The formation of **8**, **2**, and **11** can be explained by mechanisms which involve **[7]**$^+$ as a reactive intermediate. Reaction of **1** with $GaCl_3$ led to ambient temperature ROP. To our knowledge, this represents the first example of the ROP of any cyclic phosphazene or heterophosphazene at room temperature via the deliberate addition of an initiator. Detailed studies of the polymerization revealed a remarkable sensitivity to reaction concentration which suggests that **1** is not very strained. The ambient temperature polymerization was also promoted by the addition of $SbCl_5$ and $AlCl_3$ with the order of efficiency $GaCl_3 > SbCl_5 > AlCl_3$. Further work will focus on an additional, detailed exploration of the novel ambient temperature ROP reaction including the effect of temperature, which will allow detailed thermodynamic insight, and on the attempted isolation of **[7]**$^+$ with counterions that are less coordinating than triflate.

Experimental Section

General Procedures. Reagents: PCl_5 (Aldrich), $SbCl_5$ (Aldrich), SO_2Cl_2 (Aldrich), NH_3 (Liquid Carbonic), $SO_2(NH_2)_2$ (Acros) were used as received. Reagents: $GaCl_3$ (Aldrich) and $AlCl_3$ (Aldrich) were sublimed before use. Silver(I) salts: Ag[BF_4] (Strem or Aldrich), Ag[OSO_2CF_3] (Aldrich) were dried in vacuo (~120 °C, 1×10^{-3} mmHg) for ~24 h before use. The cyclic thionylphosphazene $(NSOCl)(NPCl_2)_2$ was prepared following literature procedures,[29] and was purified by successive recrystallizations from hexanes and high vacuum sublimation (40−90 °C, 0.05 mmHg) prior to use. Authentic samples of the polymers $[NSOCl(NPCl_2)_2]_n$ and $[NSO(NHBu)\{NP(NHBu)_2\}_2]_n$ were prepared and purified following literature procedures.[37]

^{31}P NMR spectra (121.4 MHz) were referenced externally to 85% H_3PO_4, ^{13}C NMR spectra (75.4 MHz) were referenced to deuterated solvent, ^{1}H NMR spectra (300.0 MHz) were referenced to residual protonated solvent, ^{19}F NMR spectra (282.3 MHz) were referenced externally to $CFCl_3/CDCl_3$ and all were recorded on a Varian Gemini 300 spectrometer. Elemental analysis was performed by Canadian Microanalytical, Delta, BC. All manipulations were performed under nitrogen in an Innovative Technology glovebox or using standard Schlenk techniques. Molecular weight distributions were analyzed by gel permeation chromatography using a Waters Associates 2690 separations unit. Ultrastyragel columns with a pore between 500, 10^3, and 10^5 Å, and a Waters 410 differential refractometer were used. A flow rate of 1 mL min^{-1} was used and samples were dissolved in a THF solution of 0.1% tetra-*n*-butylammonium bromide. Polystyrene standards purchased from Aldrich were used for calibration purposes.

Preparation of 8. A slurry of **1** (1.00 g, 3.0 mmol) and $AlCl_3$ (0.40 g, 3.0 mmol) in 50 mL of CH_2Cl_2 was stirred for 24 h. Analysis of the reaction mixture by ^{31}P NMR showed only unreacted starting material. ^{31}P NMR ($CDCl_3$) $\delta = 27.1$ (s) ppm.

A slurry of **1** (2.00 g, 6.1 mmol) and $AlCl_3$ (1.62 g, 12.1 mmol) in 40 mL of 1,2-dichloroethane was heated at reflux for 17 h. The resulting purple slurry was filtered and the solvent removed under vacuum. The residue was dissolved in $CHCl_3$ (50 mL), poured onto 50 mL of ice−water, and stirred with a glass rod for 5 min. The water layer was extracted three times with $CHCl_3$ (3 × 20 mL). The combined $CHCl_3$ extracts were washed once with H_2O, dried over $MgSO_4$, filtered, and pumped to dryness under vacuum. Recrystallization of the pale yellow residue from 10 mL of hexanes (at −40 °C) followed by sublimation under vacuum (90 °C, 0.05 mmHg) gave **8** as colorless crystals. Yield = 1.65 g (69%).

For **8**: ^{31}P NMR ($CDCl_3$) $\delta = 21.2$ (s) ppm; ^{1}H NMR ($CDCl_3$) $\delta = 6.06$ (t, $^3J_{HH} = 6.2$ Hz, CH_2CHCl_2), 4.00 ppm (d of t, $^3J_{HH} = 6.2$ Hz, $^4J_{HP} = 2.1$ Hz, CH_2CHCl_2); ^{13}C NMR $\delta = 67.9$ (t, $^3J_{CP} = 5.3$ Hz, CH_2CHCl_2), 64.2 ppm (s, CH_2CHCl_2); MS (EI, 70 eV): *m*/*z*[%] = 392 [M$^+$], 355 [M$^+$ − HCl − H], 294 [M$^+$ − CH_2CHCl_2], 278 [$(NPCl_2)_2NS^+$], 101 [PCl_2^+], 61 [$C_2H_2Cl^+$].

Preparation of 2. A solution of **1** (2.10 g, 6.4 mmol) in 20 mL of CH_2Cl_2 was added to a slurry of Ag[BF_4] (1.46 g, 7.5 mmol) in ~20 mL of CH_2Cl_2 in a dark environment. An immediate copious white precipitate was observed accompanied by a buildup of pressure in the vessel. The reaction mixture was then allowed to stir overnight and filtered, and the solvent was removed under vacuum yielding a yellow oil, which was sublimed (×2) under vacuum (1×10^{-3} mmHg) yielding **2** as a white crystalline solid. Yield = 1.58 g (79%**)**. **2** was identified by comparison of the ^{31}P and ^{19}F NMR spectra with those of an authentic sample. For **2**: ^{31}P NMR (CH_2Cl_2) $\delta = 26.8$ ppm; ^{19}F NMR (CH_2Cl_2) $\delta = 75.5$ ppm; MS (EI, 70 eV): *m*/*z*[%] 313 [M$^+$], 294 [M$^+$ − F], 278 [M$^+$ − Cl].

Preparation of 10 and 11. A solution of **1** (0.48 g, 1.5 mmol) in CH_2Cl_2 (~15 mL) was added to a stirred suspension of Ag[OSO_2CF_3] (0.42 g, 1.6 mmol) in CH_2Cl_2 (~10 mL). The reaction mixture was stirred for 6−12 h, and the soluble fraction was decanted from a white precipitate.

For **10**, ^{31}P NMR (CH_2Cl_2) $\delta = 27.2$ ppm, ^{19}F NMR (CH_2Cl_2) $\delta = -72.0$ ppm.

To the solution of **10** in CH_2Cl_2 was added diethyl ether (0.20 mL, 1.9 mmol) via syringe. The reaction solution was then stirred overnight and the solvent removed in vacuo. The resulting colorless crystalline solid was sublimed (90 °C, 1×10^{-3} mmHg). Crystals suitable for X-ray analysis were grown by cooling a solution of the product **11** in hexanes (~10 mL) to −40 °C. Yield = 0.22 g (44%)

For **11**: ^{31}P ($CDCl_3$) $\delta = 24.7$ ppm; ^{1}H NMR ($CDCl_3$) $\delta = 1.41$ (t, CH_3, $^3J_{HH} = 7.1$ Hz, 3 H), 4.29 ppm (q, CH_2, $^3J_{HH} = 7.1$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) $\delta = 14.5$ (CH_3), 68.3 ppm (CH_2); MS (EI, 70 eV): *m*/*z*[%] 340 [M$^+$ + H], 339 [M$^+$], 324 [M$^+$ − CH_3], 311 [M$^+$ − C_2H_4], 294 [M$^+$ − OCH_2CH_3]. Elemental Analysis: calcd for $C_2H_5O_2Cl_4N_3P_2S$: C 7.09, H 1.49, N 12.40, found: C 7.24, H 1.43, N 11.87.

Ambient Temperature Polymerization of 1. Solution Polymerization of 1 using $GaCl_3$ as an Initiator. In a typical reaction, $GaCl_3$ (13 mg, 0.074 mmol) was added to a stirred solution of **1** (0.25 g, 0.76 mmol) in CH_2Cl_2 (0.25 mL). The reaction was stirred for 1 day, and an increase in viscosity was observed in the amber- colored solution. A further 2 mL of CH_2Cl_2 was added and an aliquot taken for ^{31}P NMR analysis which showed an almost quantitative conversion to polymer ($\delta = -9.7$ ppm).

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[34] The polymerization of α-methylstyrene is only possible above concentrations of 2.2 M at 25 °C. See, Odian, G. *Principles Of Polymerization*, 3rd ed.; Wiley-Interscience: New York, 1991; Chapter 3.

[35] The measured value of ΔH_{ROP} for the chlorinated phosphazene ring $(NPCl_2)_3$ is −5.81 ± 0.50 kJ/mol, Jacques, J. K.; Mole, M. L.; Paddock, N. L. *J. Chem. Soc., London* **1965**, 2112. For further discussion of ΔH_{ROP} for the chlorinated phosphazene rings $(NPCl_2)_x$ ($x = 3-7$) and their implications in polymerization/depolymerization equilibria, see: Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York, 1972; Chapter 15 and references therein.

[36] For an example of a system that is a ring in solution and a polymer in the solid-state see: Beckmann, J.; Jurkschat, K.; Schollmeyer, D.; Schürmann, M. *J. Organomet. Chem.* **1997**, *543*, 229.

[37] Ni, Y.; Park, P.; Liang, M.; Massey, J.; Waddling, C.; Manners, I. *Macromolecules* **1996**, *29*, 3401.

The solvent was removed almost to dryness in vacuo, and the polymer (**3**) was separated from macrocycles by precipitation with hexanes (10 mL). The polymer was then redissolved in CH_2Cl_2 (20 mL), and $BuNH_2$ (1.4 mL, 13.6 mmol) was added to the mixture (0 °C) to substitute the chlorine atoms. The solvent was removed in vacuo, and the yellow elastomeric material was redissolved in a minimum of THF (<1 mL) and precipitated into H_2O (50 mL). This process was repeated twice. The formation of substituted polymer **12** was confirmed by comparison of the ^{31}P NMR with that of the authentic sample.[37] Yield = 0.27 g (69%).

Similar reactions were performed using 5 and 15% $GaCl_3$, which produced similar results in both conversion and yield (see Table 1).

Attempted Solution Polymerization of 1 using 10 mol % $GaCl_3$ as an Initiator at Varying Concentrations. Similar reactions were attempted using 10% $GaCl_3$ using 0.25, 0.50, 1, 2, 3, 4, 5, 10, and 20 mL of CH_2Cl_2. After 1 day, ^{31}P NMR showed there was only 84% conversion to polymer **3** and higher membered macrocycles, and 12% conversion to *cis*- and *trans*-**5** in 0.50 mL of CH_2Cl_2. At lower concentrations than 4 mL, only small amounts of macrocycles could be detected after reaching equilibrium.

Solution Polymerization of 1 using 10 mol % $AlCl_3$ as an Initiator at Varying Concentrations. Similar reactions were attempted using **1** (0.25 g, 0.76 mol) and 10% $AlCl_3$ (10 mg, 0.075 mmol) using 0.25−5 mL of 1,2-dichloroethane. After 1 day, ^{31}P NMR showed there was only 20% conversion to polymer **3** and higher macrocycles ($>$12-membered) and no conversion to *cis*- and *trans*-**5** in 0.25 mL of solvent. The polymer was purified as described above and subsequently reacted with $BuNH_2$ to form **12**.[37] Yield = 0.06 g (15%); M_n = 60 000; PDI = 2.88.

At lower concentrations, only unreacted **1** could be detected after 9 days.

Solution Polymerization of 1 using $SbCl_5$ as an Initiator. Similar reactions were attempted using **1** (0.25 g, 0.76 mmol) with 10% $SbCl_5$ (24 mg, 0.08 mmol) as in initiator in 1−5 mL of 1,2-dichloroethane. After 9 days, ^{31}P NMR there was 45% conversion to polymer and 32% conversion to macrocycle **5** in 1 mL of solvent. The polymer was purified as described above and subsequently reacted with $BuNH_2$ to form **12**. Yield = 0.16 g (41%); M_n = 37 000; PDI = 1.35. With solvent quantities greater than 3 mL, only low conversion to macrocycles ($<$35%) and no polymer was detected.

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Supporting Information Available: Experimental details and spectroscopic data for **2**, **8**, and **11**; X-ray crystallographic files for structure **2**, **8**, and **11** (PDF). Supporting Information for structures **8** and **11** containing an X-ray crystallographic file, in CIF format, previously available via the Internet (JA9740475).[18] Details of X-ray structural determinations for **8** and **11** have been deposited in the Cambridge Database. This material is available free of charge via the Internet at http://pubs.acs.org.

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