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Attempted Generation of the Thionylphosphazene Cation [NSO(NPCl$_2$)$_2$]$^+$: Novel Reactivity and the Discovery of an Ambient Temperature Ring-Opening Polymerization Route to Poly(thionylphosphazenes)

Derek P. Gates,[†] Mark Edwards,[†] Louise M. Liable-Sands,[‡]
Arnold L. Rheingold,[‡] and Ian Manners*,[†]

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

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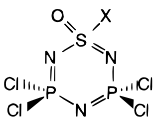
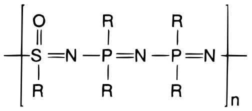
In addition to their considerable intrinsic interest,[1] cyclic compounds containing main-group or transition elements are increasingly important as precursors to new high molecular weight polymers via ring-opening polymerization (ROP) reactions.[2,3] However, in very few cases is the mechanism of polymerization clearly understood.[3] Recently, we reported that the cyclic thionylphosphazene **1**[4] and the regioselectively fluorinated analog **2** undergo thermal ROP in the melt at 165 and 180 °C, respectively, to yield the corresponding the poly(thionylphosphazenes) **3** (R = halogen) and macrocyclic byproducts.[5,6] In this paper, we report on our attempts to generate [**4**]$^+$, the proposed cationic initiator in the ROP of **1**, via the reaction of the latter with halide acceptors and the novel chemistry that ensued.[7−10]



1 X = Cl
2 X = F



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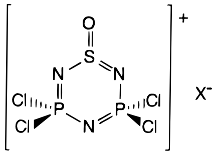
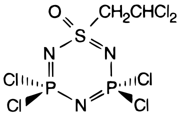


[**4**]$^+$

As part of this work, we also describe the discovery of the ambient temperature ROP of **1**.

Compound **1** undergoes Friedel−Crafts arylation at sulfur when heated in arene solvents in the presence of AlCl$_3$. Cation [**4**]$^+$ has been proposed as the key electrophilic intermediate in these reactions.[11] We found that treatment of a solution of **1** with 2 equiv of AlCl$_3$ in the non-arene solvent 1,2-dichloroethane (80 °C, 17 h) afforded a new product with a singlet ^{31}P NMR resonance at 21.2 ppm. After workup, ^{1}H and ^{13}C NMR, mass spectrometry, and elemental analysis surprisingly identified the white crystalline product as **5** (yield, 69%) invoking a formal migration of a chlorine atom in the 1,2-dichloroethane-derived C$_2$ unit.[12] Further characterization of **5** was provided by an X-ray diffraction study (Figure 1).[13]



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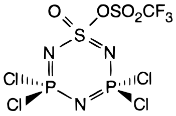

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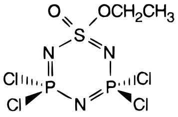

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The mechanism of formation for **5** is not clear but it may involve an ionic process similar to that proposed for Friedel−Crafts reactions of **1**.[14,15] The substrate that could be attacked by [**4**]$^+$ is clearly derived from 1,2-dichloroethane and is possibly vinyl chloride.[16] Selective attack of [**4**]$^+$ at the more electron-rich carbon atom of vinyl chloride followed by chloride abstraction from [AlCl$_4$]$^-$ by the resulting carbocation would provide a possible explanation for the formation of **5**.

An attempt to generate [**4**]$^+$ by the addition of **1** to a slurry of Ag[BF$_4$] (CH$_2$Cl$_2$, 25 °C) resulted in the immediate formation of a white precipitate (AgCl) and the release of a volatile, fuming gas. Analysis of the reaction mixture and the isolated white crystalline product by ^{31}P and ^{19}F NMR indicated that the fluorinated species **2** had been formed, presumably via the decomposition of [**4**][**BF$_4$**].[17]

[†] University of Toronto.

[‡] University of Delaware.

(1) See, for example: Chivers, T.; Gao, X.; Parvez, M. *J. Am. Chem. Soc.* **1995**, *117*, 2359. Dias, H. V. R.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 144. Brown, D. S.; Decken, A.; Cowley, A. H. *J. Am. Chem. Soc.* **1995**, *117*, 5421. Qiao, S.; Hoic, D. A.; Fu, G. *J. Am. Chem. Soc.* **1996**, *118*, 6329. Hasselbring, R.; Roesky, H. W.; Heine, A.; Stalke, D.; Sheldrick, G. M. *Z. Naturforsch.* **1993**, *48b*, 43. Bryan, C. D.; Cordes, A. W.; Fleming, R. M.; George, N. A.; Glarum, S. H.; Haddon, R. C.; MacKinnon, C. D.; Oakley, R. T.; Palstra, T. T. M.; Perel, A. S. *J. Am. Chem. Soc.* **1995**, *117*, 6880. Agocs, L.; Burford, N.; Cameron, T. S.; Curtis, J. M.; Richardson, J. F.; Robertson, K. N.; Yhard, G. B. *J. Am. Chem. Soc.* **1996**, *118*, 3225. Beswick, M. A.; Davies, M. K.; Paver, M. A.; Raithby, P. R.; Steiner, A.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1508. Li, X.; Pennington, W. T.; Robinson, G. H. *J. Am. Chem. Soc.* **1995**, *117*, 7578. Lork, E.; Mews, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1113. Gates, D. P.; Liable-Sands, L. M.; Yap, G. P. A.; Rheingold, A. L.; Manners, I. *J. Am. Chem. Soc.* **1997**, *119*, 1125.

(2) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602.

(3) See: Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: New Jersey, 1992.

(4) Baalmann, H. H.; Velvis, H. P.; van de Grampel, J. C. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 935. Klingebiel, U.; Glemser, O. *Z. Naturforsch.* **1972**, *27b*, 467. Suzuki, D.; Akagi, H.; Matsumura, K. *Synthesis* **1983**, 369.

(5) Liang, M.; Manners, I. *J. Am. Chem. Soc.* **1991**, *113*, 4044. Gates, D. P.; Manners, I. *J. Chem. Soc. Dalton Trans.* **1997**, 2525.

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

(7) A mechanism involving the initial formation of P(V) cations has been proposed for the thermal ROP of cyclic phosphazenes at >230 °C. For example, see: ref 3 pp 77−79. Allcock, H. R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 147. Allcock, H. R.; Best, R. J. *Can. J. Chem.* **1964**, *42*, 447. Allcock, H. R.; Kugel, R. L.; Stroh, E. G. *Inorg. Chem.* **1972**, *11*, 1120.

(8) For a discussion of the proposed cationic chain growth ROP mechanism for **1** and **2**, see: Manners, I. *Coord. Chem. Rev.* **1994**, *137*, 109.

(9) An X-ray 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.

(10) Isolated cations containing S(VI) centers are rare. For examples, see: [S(O)F$_3$][AsF$_6$] Lau, C.; Lynton, H.; Passmore, J.; Siew, P. *J. Chem. Soc. Dalton Trans.* **1973**, 2535. [S(O)F$_2$Cl][AsF$_6$] Lau, C.; Passmore, J. *J. Chem. Soc., Chem. Commun.* **1971**, 950. [S(NPMe$_3$)$_4$]Cl$_2$ Folkerts, H.; Hiller, W.; Herker, M.; Vyboishchikov, S. F.; Frenking, G.; Dehnicke, K. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1362.

(11) van de Grampel, J. C. *Rev. Inorg. Chem.* **1981**, *3*, 1.

(12) For **5**: ^{1}H NMR (CDCl$_3$) $\delta = 4.0$ (d of t, $^3J_{HH} = 6.2$ Hz, $^4J_{HP} = 2.1$ Hz, CH$_2$), 6.06 (t, $^3J_{HH} = 6.2$ Hz, CH); ^{13}C NMR $\delta = 64.2$ (s, CH), 67.9 (t, CH$_2$); MS (EI, 70 eV) $m/z = 392$ (M$^+$, 1%); satisfactory C, H, N analysis.

(13) Crystal data for C$_2$H$_3$Cl$_6$N$_3$OP$_2$S (**5**) (yield 69%): $P1$, $a = 6.392(2)$ Å, $b = 9.332(3)$ Å, $c = 10.983(3)$ Å, $\alpha = 86.14(3)°$, $\beta = 82.74(3)°$, $\gamma = 85.50(2)$, $V = 646.7(4)$ Å^3, $Z = 2$, $\mu = 17.12$ cm^{-1}, Mo Kα ($\lambda = 0.710\,73$ Å), $\delta_{calcd} = 2.012$ g cm^{-3}, 296 K, Siemans P4 diffractometer with graphite monochromator, colorless crystal (0.36 × 0.44 × 0.50 mm) mounted in a capillary. Of 3878 reflections collected ($4 \leq 2\theta \leq 60$), 2481 were observed with $F_o \geq 5\sigma(F_o)$. Solution by direct methods, non-hydrogen atoms were refined with anisotropic thermal parameters, hydrogen atoms fixed and idealized, $R = 0.0358$, wR2 = 0.0510, GOF = 1.18, $N_o/N_v = 18.2$.

(14) van den Berg, J. B.; de Ruiter, B.; van de Grampel, J. C. *Z. Naturforsch.* **1976**, *31b*, 1216.

(15) The intermediacy of S(VI) cations [RSO$_2$][AlCl$_4$] has been invoked in aromatic sulfonylation reactions (Jensen, F. R.; Goldman, G. In *Friedel−Crafts and Related Reactions, Vol. 3*; Olah, G. A., Ed.; Wiley-Interscience: New York, 1963−64; Chapter 40). However, other studies have suggested that SbX$_5$ forms a coordination complex with the oxygen atom in RSO$_2$Cl, rather than an ion pair. (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. *Synthesis* **1973**, 343). Similar mechanistic considerations exist for the initial reaction of **1** with halide acceptors.

(16) Reactions of AlCl$_3$ with 1,2-dichloroethane have been studied and suggest formation of vinyl chloride. See, for example: Rothan, R. N.; Sims, E. W. *Chem. Ind.* **1970**, *25*, 830.

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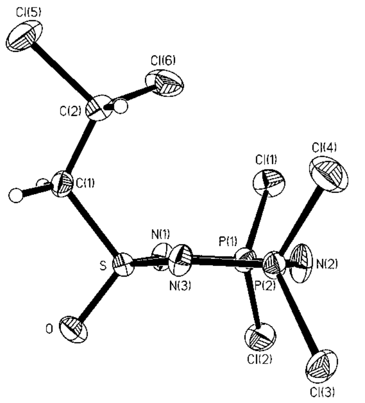

Figure 1. Molecular structure of **5** with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): S−N(1) 1.567(3), N(1)−P(1) 1.583(3), P(1)−N(2) 1.567(3), N(2)−P(2) 1.571(3), P(2)−N(3) 1.582(3), N(3)−S 1.563(3), S−O 1.434(3), S−C(1) 1.784(3); N(1)−S−N(3) 114.5(1), 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).

On the basis of the chemistry observed with Ag[BF$_4$], the triflate anion was chosen as a potentially less reactive counteranion for [**4**]$^+$. Addition of a solution of **1** to a slurry of Ag[OSO$_2$CF$_3$] in CH$_2$Cl$_2$ again resulted in the formation 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 very slightly downfield from that for **1** (δ = 27.1 ppm) and a single new peak in the ^{19}F NMR spectrum at −72.0 ppm. This is consistent with the formation of **6** where the triflate anion is presumably weakly coordinated to the sulfur(VI) center.

After solvent removal, an uncrystallizable elastomeric material was isolated. The soluble fraction exhibited a ^{31}P NMR resonance assigned to **6** and also broad resonances between 0 and −15 ppm. These observations suggested that oligomerization/polymerization (with some crosslinking) had taken place. An attempt was made to stabilize [**4**]$^+$ via coordination of diethyl ether. Indeed, addition of 1.25 equiv of diethyl ether to **6** in CH$_2$Cl$_2$ resulted in the formation a new product with a singlet ^{31}P NMR resonance at 24.7 ppm. However, after recrystallization and sublimation, no ^{19}F NMR resonances were observed and ^{1}H and ^{13}C NMR spectroscopy showed resonances attributed to an ethoxy group.[18] The X-ray structure of the product (**7**) (Figure 2) confirmed that diethyl ether had been cleaved and an ethoxy group had been transferred to sulfur, presumably leading to the elimination of EtOSO$_2$CF$_3$.[19]

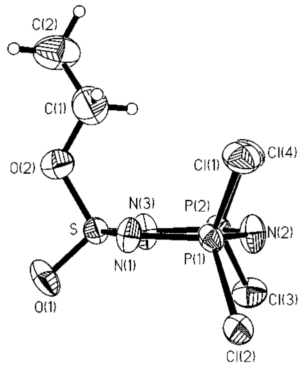

Figure 2. Molecular structure of **7** with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): S−N(1) 1.551(10), N(1)−P(1) 1.572(9), P(1)−N(2) 1.566(10), N(2)−P(2) 1.542(11), P(2)−N(3) 1.572(10), N(3)−S 1.575(10), S−O(1) 1.420(8), S−O(2) 1.557(10); N(1)−S−N(3)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

The high electrophilicity of the sulfur(VI) center in **6** and, in particular, the evidence for intermolecular reactions on attempted isolation of this species suggested that the cation [**4**]$^+$ might initiate the cationic ROP of **1** in solution at ambient temperature. We therefore studied the reaction of **1** with substoichiometric quantities of GaCl$_3$ (5% and 10%).[20] The reactions (in CH$_2$Cl$_2$ at 25 °C) were monitored by ^{31}P NMR, and in both cases, cyclic oligomers and also polymer were indeed formed.[21] When no further increase in the relative amount of **3** (R = Cl) was observed (ca. 48 h for 5% GaCl$_3$; ca. 80 h for 10% GaCl$_3$), the polymer was isolated by precipitation into hexanes (to remove unreacted **1** and macrocyclics) and was then reacted with BuNH$_2$ (15 equiv, 0 °C, CH$_2$Cl$_2$) to form the air- and moisture-stable elastomer poly(*n*-butylamino)thionylphosphazene) **3** (R = NH-*n*-Bu). This material was isolated by precipitation from THF into H$_2$O (typical yields, 50−75%). Analysis by gel permeation chromatography (GPC) gave molecular weight data comparable[20] with that for **3** (R = NH-*n*-Bu) derived from the thermal ROP of **1** (M_w = 49 000, PDI = 2.0).[22]

These results indicate that a highly electrophilic sulfur(VI) species with novel reactivity can be generated via the reaction of **1** with halide acceptors. Further work is in progress aimed at detailed studies of such species and understanding and exploiting the novel ambient temperature ROP of **1**.

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Supporting Information Available: Experimental details and spectroscopic data for **5**−**7** (4 pages). An X-ray crystallographic file, in CIF format, is available via the Web only. Details of the X-ray structural determinations for **5** and **7** have been deposited with the Cambridge Database. See any current masthead page for ordering information and Web access instructions.

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[17] The high (79%) yield preparation of **2** is a significant improvement over the only previously reported route (thermal fluorination of **1** with a large (10-fold) excess of AgF$_2$ (Baalmann, H. H.; van de Grampel, J. C. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 1237).

[18] For **7**: ^{31}P (CDCl$_3$) δ = 24.7; ^{1}H NMR (CDCl$_3$) δ = 1.41 (t, CH_3, $^3J_{HH}$ = 7.1 Hz, 3 H), 4.29 (q, OCHCl$_2$, $^3J_{HH}$ = 7.1 Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ = 14.5 (CH$_3$), 68.3 (OCH$_2$); MS (70 eV, EI) m/z = 339 ($\underline{M}^+$, 1%).

[19] Crystal data for C$_2$H$_5$Cl$_4$N$_3$O$_2$P$_2$S (**7**) (yield 44%): $P\bar{1}$, a = 6.348(1) Å, b = 8.068(1) Å, c = 12.609(3) Å, α = 96.22(1)°, β = 97.90(7)°, γ = 107.61(1)°, V = 602.00(14) Å^3, Z = 2, μ = 13.99 cm^{-1}, Mo Kα (λ = 0.710 73 Å), δ_{calcd} = 1.868 g cm^{-3}, 296 K, diffractometer, see ref 13, colorless crystal (0.12 × 0.23 × 0.24 mm) mounted in a capillary. Of 1723 reflections collected ($7 \leq 2\theta \leq 45$), 1284 were independent (R_{int} = 0.0842) and 861 were observed with $F_o \geq 4\sigma(F_o)$. Solution, see ref 13, R = 0.0564, wR2 = 0.0732, GOF = 1.40, N_o/N_v = 6.8.

[20] Typical experiment with 5% GaCl$_3$: **1** (200 mg, 0.6 mmol); GaCl$_3$ (5 mg, 0.03 mmol); CH$_2$Cl$_2$ (1.5 mL); BuNH$_2$ (0.9 mL, 9 mmol); yield for **3** (R = NH-*n*-Bu) = 230 mg (74%); M_w = 46 000; PDI = 2.0. With 10% GaCl$_3$: **1** (150 mg, 0.4 mmol); GaCl$_3$ (8 mg, 0.05 mmol); CH$_2$Cl$_2$ (2 mL); BuNH$_2$ (0.7 mL, 6.8 mmol); yield of **3** (R = NH-*n*-Bu) = 160 mg (68%); M_w = 34 000; PDI = 1.9.

[21] To our knowledge, this is the first example of an ambient temperature ROP of a phosphazene or heterophosphazene induced by the addition of an initiating reagent. The spontaneous ROP of the highly reactive S(IV) thiophosphazene [NSCl(NPCl$_2$)$_2$] in the liquid state over several days at 25 °C has previously been reported: Allcock, H. R.; Dodge, J. A.; Manners, I. *Macromolecules* **1993**, *26*, 11.

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