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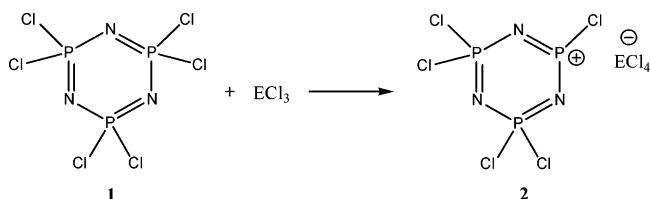
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Cations derived from $(\text{NPCl}_2)_3$, hexachloro-*cyclo*-triphosphazene, the weakly basic precursor of phosphazene polymers, have been prepared using strongly electrophilic reagents based on carborane anions. N-protonated, N-methylated, and N-silylated adducts of $(\text{NPCl}_2)_3$ have been isolated and characterized by X-ray crystallographic and spectroscopic methods. The normally potent chloride-abstracting silyl reagents of the type R_3Si (carborane) are unable to abstract chloride from $(\text{NPCl}_2)_3$, even though the coordinatively unsaturated $\text{N}_2\text{P}_2\text{Cl}_5^+$ cation is widely accepted as a reactive intermediate in the ring-opening polymerization of $(\text{NPCl}_2)_3$.

Polyphosphazenes, $[\text{NPR}_2]_n$, are an important class of inorganic polymers noted for their high thermal stability and functional diversity.^{1a,2} They are typically prepared by substitution reactions on poly(dichlorophosphazene), $[\text{NPCl}_2]_n$, which is accessed by high-temperature, ring-opening polymerization (ROP) of the cyclic trimeric dichlorophosphazene, $(\text{NPCl}_2)_3$ (**1**), at 250 °C. Certain Lewis acids such as BCl_3 or AlCl_3 catalyze the reaction, allowing the process temperature to be reduced to ca. 200 °C, but the lack of wide generality of Lewis acid catalysis and reports of inconsistent processing reproducibility suggest that this chemistry deserves closer scrutiny.^{2c,d} The favored mechanism for ROP of **1** involves the formation of the cationic intermediate **2**⁺ via thermally induced or ECl_3 Lewis acid assisted loss of chloride ion, followed by electrophilic attack of **2**⁺ at N on **1**, with ring opening via P–N bond cleavage, i.e., typical cationic polymerization.^{1b}



Cationic chlorophosphazenes of any kind are rare,^{3,4} and coordinatively unsaturated intermediates of type **2**⁺ are

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(1) Allcock, H. R. *Phosphorus–Nitrogen Compounds*; Academic: New York, 1972; (a) pp 3–7; (b) pp 329–335; (c) pp 249–266; (d) pp 230–238; (e) pp 45–46.

completely unknown. Instead of producing the $\text{N}_3\text{P}_3\text{Cl}_5^+$ cation, the reaction of Lewis acids with $(\text{NPCl}_2)_3$ produces neutral adducts at the N atom, $(\text{PCl}_2\text{N})_3 \cdot \text{ECl}_3$.^{1d} Their σ -complex coordinate structures have recently been confirmed by X-ray structure determination.⁵ Silver ion is also ineffective for the removal of chloride from **1**, forming instead coordinate bonds at N, similar to the ECl_3 adducts.⁶ The coordinating ability of **1** toward silver ion is somewhat greater than that of CH_2Cl_2 ,⁶ consistent with the low basicity and low nucleophilicity of $(\text{NPCl}_2)_3$.

Herein we explore the formation of cations from $(\text{NPCl}_2)_3$ with protic, alkyl, and silylium electrophilic reagents (Scheme 1). We choose electrophilic reagents based on carborane anions, $\text{CHB}_{11}\text{R}_5\text{X}_6^-$ (R = H, Me, X; X = Cl, Br), because they are more powerful than their triflate counterparts in reactions with weakly basic molecules.^{7,8} In addition, the good crystallizing properties of their salts frequently allow the isolation of reactive cations that are otherwise difficult to stabilize. Given the proposal of **2**⁺ as the key intermediate in ROP, the challenge is to find a reagent that favors chloride ion extraction from P over adduct formation at N.

Phosphazene **1** is a weak Brønsted base ($\text{p}K_a < -6$ in nitrobenzene)⁹ and reacts only with strong acids.³ Treatment

- (2) (a) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541–562. (b) D’Halluin, G.; De Jaeger, R.; Chambrette, J. P.; Potin, P. *Macromolecules* **1992**, *25*, 1254–1258. (c) Allcock, H. R. *Chemistry and Applications of Polyphosphazenes*; Wiley-Interscience: New York, 2003. (d) Sulkowski, W. W. In *Synthesis and Characterizations of Poly(organophosphazenes)*; Gleria, M., De Jaeger, R., Eds.; Nova Science: New York, 2004.
- (3) Cations apparently involving mono- and possibly diprotonated **1** were isolated from perchloric acid many years ago but not structurally characterized. See: Bode, H.; Butow, K.; Lienau, G. *Chem. Ber.* **1948**, *81*, 547–552. A number of other protonated phosphazenes have been prepared since then but only when most or all of the chloride substituents on P are replaced by electron-donating groups such as methyl or amino groups. See: Reference 1c. These show protonation on a ring N atom, consistent with the basicity expressed in Lewis acid adduct formation with $(\text{NPCl}_2)_3$.
- (4) Heston, A. J.; Panzner, M.; Youngs, W. J.; Tessier, C. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *179*, 831–837.
- (5) Heston, A. J.; Panzner, M. J.; Youngs, W. J.; Tessier, C. A. *Inorg. Chem.* **2005**, *44*, 6518–6520.
- (6) Gonsier, M.; Antonijevic, S.; Krossing, I. *Chem.–Eur. J.* **2006**, *12*, 1997–2008.
- (7) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133–139.
- (8) Reed, C. A. *Chem. Commun.* **2005**, 1669–1677.
- (9) Feakins, D.; Last, W. A.; Neemuchwala, N.; Shaw, R. A. *J. Chem. Soc.* **1965**, 2804–2811.

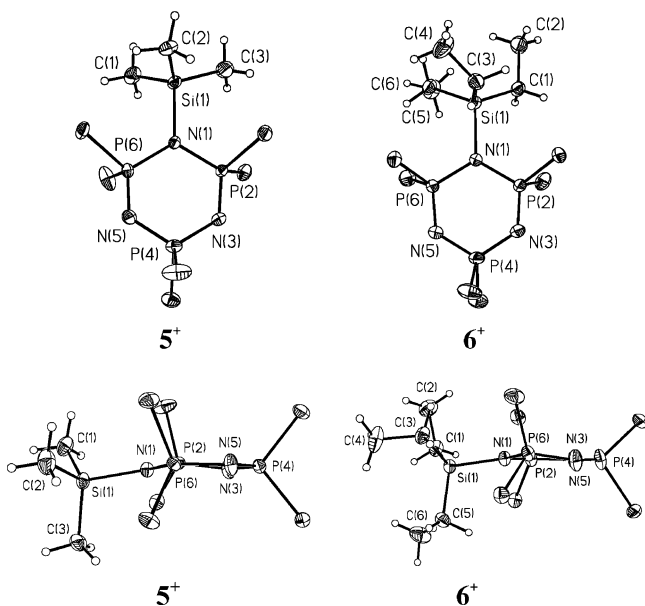


Figure 2. Thermal ellipsoid representations (50%) of N-silylated phosphazene cations showing front and side views of the ring conformations in the X-ray structures of **5** and **6**.

an attempt to prepare the coordinatively unsaturated cation 2^+ was a trialkylsilylium carborane reagent, possibly the most potent halide-abstracting reagent presently available.¹³ Treatment of **1** with the trimethyl- or triethylsilyl reagents $\text{Me}_3\text{Si}(\text{CHB}_{11}\text{Cl}_{11})$ or $\text{Et}_3\text{Si}(\text{CHB}_{11}\text{Cl}_{11})$ in *o*-dichlorobenzene, nevertheless, gave N-atom addition products (Scheme 1). NMR data for the products, $[\text{Me}_3\text{Si}(\text{N}_3\text{P}_3\text{Cl}_6)][\text{CHB}_{11}\text{Cl}_{11}]$ (**5**) and $[\text{Et}_3\text{Si}(\text{N}_3\text{P}_3\text{Cl}_6)][\text{CHB}_{11}\text{Cl}_{11}]$ (**6**), are similar to the

N-methylated derivative, as are the X-ray structures (Figure 2). Similar compounds were produced with trialkylsilylium reagents based on other carborane counterions: $[\text{Et}_3\text{Si}(\text{N}_3\text{P}_3\text{Cl}_6)][\text{CHB}_{11}\text{H}_5\text{Br}_6]$ (**7**) and $[\text{Et}_3\text{Si}(\text{N}_3\text{P}_3\text{Cl}_6)][\text{CHB}_{11}\text{Me}_5\text{Br}_6]$ (**8**).

Different distortions from planarity and different types of puckering are seen in the cations of **3–6** (Figures 1 and 2). This is not unlike neutral phosphazenes, where negligible energy costs appear to exist for departures from planarity, giving a variety of puckered conformations.^{1e}

In summary, despite its low basicity and low nucleophilicity, a variety of cations of **1** can be prepared by reaction with appropriately reactive electrophiles. N-protonated, N-methylated, and N-silylated cations of **1** can be isolated as carborane salts. No evidence has been found for 2^+ , the putative cationic intermediate in the ROP of **1**, despite the use of potent halide-abstracting reagents.

We are currently testing the efficacy of these cations as initiators of ROP of **1** and exploring other chemistry that might give evidence for the existence of the elusive unsaturated cation 2^+ .

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Supporting Information Available: Full experimental details: syntheses, NMR characterization, and X-ray data. This material is available free of charge on the Internet at <http://pubs.acs.org>.

(13) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325–332.