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Phosphazene Cations

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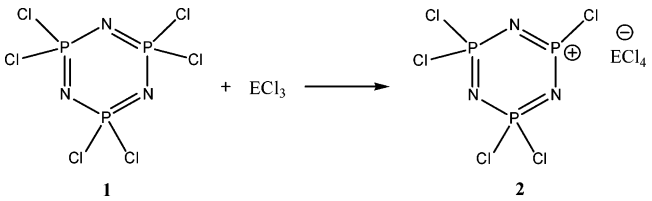
Cations derived from $(NPCl_2)_3$, hexachloro-*cyclo*-triphosphazene, the weakly basic precursor of phosphazene polymers, have been prepared using strongly electrophilic reagents based on carborane anions. N-protonated, N-methylated, and N-silylated adducts of $(NPCl_2)_3$ have been isolated and characterized 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 $(NPCl_2)_3$, even though the coordinatively unsaturated $N_2P_2Cl_5^+$ cation is widely accepted as a reactive intermediate in the ring-opening polymerization of $(NPCl_2)_3$.

Polyphosphazenes, $[NPR_2]_n$, 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), $[NPCl_2]_n$, which is accessed by high-temperature, ring-opening polymerization (ROP) of the cyclic trimeric dichlorophosphazene, $(NPCl_2)_3$ (**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 $\mathbf{2}^+$ via thermally induced or ECl_3 Lewis acid assisted loss of chloride ion, followed by electrophilic attack of $\mathbf{2}^+$ at N on **1**, with ring opening via P−N bond cleavage, i.e., typical cationic polymerization.[1b]



1 **2**

Cationic chlorophosphazenes of any kind are rare,[3,4] and coordinatively unsaturated intermediates of type $\mathbf{2}^+$ are completely unknown. Instead of producing the $N_3P_3Cl_5^+$ cation, the reaction of Lewis acids with $(NPCl_2)_3$ produces neutral adducts at the N atom, $(PCl_2N)_3{\cdot}ECl_3$.[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 $(NPCl_2)_3$.

Herein we explore the formation of cations from $(NPCl_2)_3$ with protic, alkyl, and silylium electrophilic reagents (Scheme 1). We choose electrophilic reagents based on carborane anions, $CHB_{11}R_5X_6^-$ (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 $\mathbf{2}^+$ 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 ($pK_a < -6$ in nitrobenzene)[9] and reacts only with strong acids.[3] Treatment

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(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 $(NPCl_2)_3$.

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(5) Heston, A. J.; Panzner, M. J.; Youngs, W. J.; Tessier, C. A. *Inorg. Chem.* **2005**, *44*, 6518−6520.

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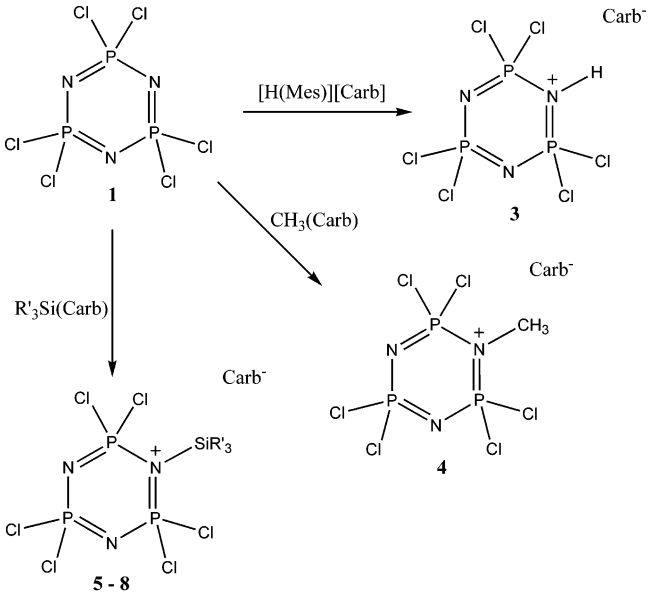
Scheme 1. Reactions of Protic, Methyl, and Silylium Carborane Reagents with **1**



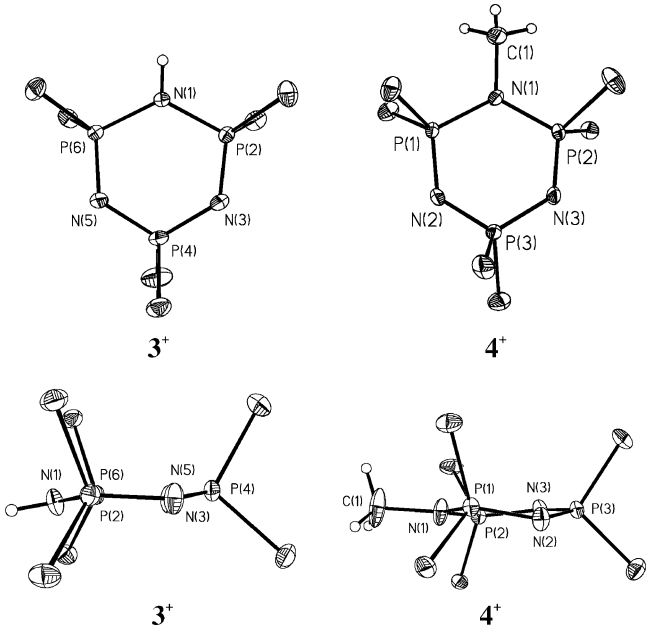


Figure 1. Thermal ellipsoid representations (50%) of N-protonated and N-methylated phosphazene cations showing front and side views of the ring conformations in the X-ray structures of **3** and **4**.

of **1** in CH_2Cl_2 with 1 equiv of a mesitylenium carborane salt, $[HC_6H_3Me_3][CHB_{11}H_5Br_6]$,[10] a conveniently handled protic acid of about the same strength as H_3O^+ or HC_{60}^+ in a benzene solution,[8] gives the protonated adduct $[H(NPCl_2)_3][CHB_{11}H_5Br_6]$ (**3**) in excellent yield. Colorless single crystals of **3** were grown from CH_2Cl_2/*n*-hexane. As illustrated in Figure 1, the X-ray structure shows that protonation occurs on a ring N atom. There is H bonding of the N^+-H bond of the cation to Br atoms of the anion (N···Br = 3.524 and 3.676 Å), similar to C−H···Br interactions seen in arenium ion salts with bromocarborane anions.[10] The phosphazene ring adopts a chair conformation, and the P−N bond lengths involving the protonated N atom show single-bond character with an average bond length of 1.660 Å. The remaining P−N bonds show double-bond character with P2−N3 and P6−N5 bonds (average = 1.555 Å) somewhat shorter than P4−N5 and P4−N3 (average = 1.576 Å). This alternating pattern of bond lengths is similar to that observed in $[H(NPCl_2)_3][AlBr_4]$[4] and approaches that found in protonated arenes.[10]

The room temperature ^{1}H NMR spectrum of **3** in CD_2Cl_2 shows a peak due to the acidic proton at 8.9 ppm. The ^{31}P NMR spectrum shows a single peak at 18.1 ppm (compared to 19.9 ppm for **1**), which does not split when the temperature is lowered to −90 °C. Evidently, the static structure seen in the crystal is fluxional in solution, with the proton sampling all three ring N atoms on the NMR time scale. Mixtures of **1** and **3** do not show separate peaks, indicating that intermolecular proton exchange is occurring.

Methylation of **1** cannot be achieved with methyl triflate, even when used as neat solvent and heated.[11] Methyl carboranes, on the other hand, are more potent methylating agents,[12] and the reaction of **1** with 1 equiv of $CH_3(CHB_{11}Me_5Br_6)$ takes place in CH_2Cl_2 solution at −60 °C. The low temperature is necessary to minimize the reaction of the reagent with the solvent and contamination of the methylated product with protonated product, arising from acid-mediated decomposition of CH_2Cl_2.

The ^{1}H NMR spectrum of the methylated product, $[(CH_3)N_3P_3Cl_6][CHB_{11}Me_5Br_6]$ (**4**), shows a triplet at 3.66 ppm due to the methyl group with coupling to two equivalent P atoms ($^3J_{P-H}$ = 14.4 Hz). The ^{31}P NMR spectrum shows two signals, one at 23.3 ppm (dq, 2P, $^3J_{P-H}$ = 14.6 Hz) and the other at 17.9 ppm (t, 1P, $^2J_{P-P}$ = 41.0 Hz). ^{1}H decoupling reduces the multiplicities to a doublet and a triplet, respectively. These data are consistent with methylation at N. The spectrum of a mixture of **1** and **4** showed separate components indicating that, unlike H^+, methyl group transfer (or migration) does not occur on the NMR time scale.

Prisms of **4** suitable for X-ray analysis, grown from the reaction mixture after *n*-hexane layering, were manually separated from needles of the protonation product. The crystal structure confirmed N-methylation (Figure 1). The phosphazene ring has a mildly twisted conformation. The P−N bond lengths to the methylated N atom (average = 1.666 Å) are marginally longer than the same bonds in **3**, while the other P−N bond distances are very similar. The P1−N2 and P2−N3 bonds average 1.549 Å, and the P3−N2 and P3−N3 bonds average 1.580 Å.

Given that neither carborane acids nor methyl carboranes showed any halide abstraction behavior, the next choice in

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(11) Ragogna, P. J.; Manners, I. Personal communication. On the other hand, more basic phosphazenes such as $N_3P_3Me_6$ are readily alkylated. See: Oakley, R. T.; Paddock, N. L. *Can. J. Chem.* **1977**, *55*, 3651−3663.

(12) Kato, T.; Stoyanov, E.; Geier, J.; Grutzmacher, H.; Reed, C. A. *J. Am. Chem. Soc.* **2004**, *126*, 12451−12457.

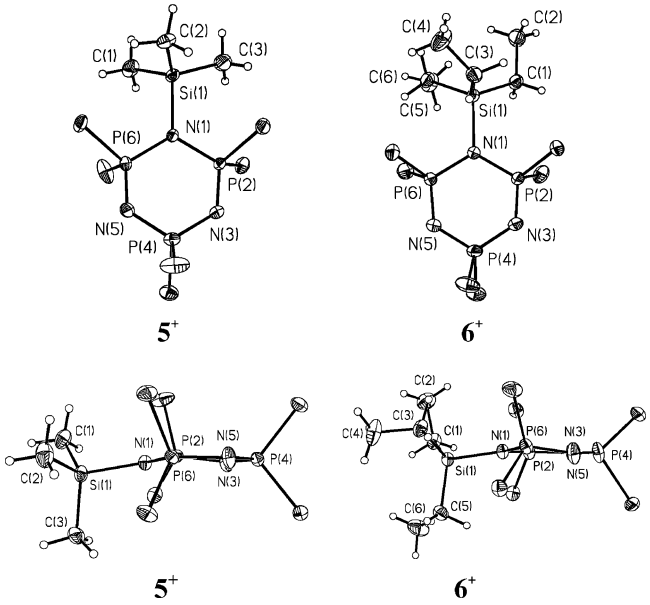

Figure 2. Thermal ellipsoid representations (50%) of N-silylated phosphazene cations showing front and side views of the ring conformations in the X-ray structures of **5** and **6**.

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 $Me_3Si(CHB_{11}Cl_{11})$ or $Et_3Si(CHB_{11}Cl_{11})$ in *o*-dichlorobenzene, nevertheless, gave N-atom addition products (Scheme 1). NMR data for the products, $[Me_3Si(N_3P_3Cl_6)][CHB_{11}Cl_{11}]$ (**5**) and $[Et_3Si(N_3P_3Cl_6)][CHB_{11}Cl_{11}]$ (**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: $[Et_3Si(N_3P_3Cl_6)][CHB_{11}H_5Br_6]$ (**7**) and $[Et_3Si(N_3P_3Cl_6)][CHB_{11}Me_5Br_6]$ (**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.

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