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Zhang, Yun Tham, Fook S Reed, Christopher A

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# **Phosphazene Cations**

#### Yun Zhang, Fook S. Tham, and Christopher A. Reed\*

Center for S and P Block Chemistry, Department of Chemistry, University of California, Riverside, California 92521

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Cations derived from (NPCl<sub>2</sub>)<sub>3</sub>, 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<sub>2</sub>)<sub>3</sub> have been isolated and characterized by X-ray crystallographic and spectroscopic methods. The normally potent chloride-abstracting silyl reagents of the type  $R_3 Si(carborane)$  are unable to abstract chloride from (NPCl<sub>2</sub>)<sub>3</sub>, even though the coordinatively unsaturated  $N_2 P_2 Cl_5{}^+$  cation is widely accepted as a reactive intermediate in the ring-opening polymerization of (NPCl<sub>2</sub>)<sub>3</sub>.

Polyphosphazenes, [NPR<sub>2</sub>]<sub>n</sub>, 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<sub>2</sub>]<sub>n</sub>, which is accessed by high-temperature, ring-opening polymerization (ROP) of the cyclic trimeric dichlorophosphazene, (NPCl<sub>2</sub>)<sub>3</sub> (1), at 250 °C. Certain Lewis acids such as BCl<sub>3</sub> or AlCl<sub>3</sub> 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<sup>+</sup> via thermally induced or ECl<sub>3</sub> 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

completely unknown. Instead of producing the  $N_3P_3Cl_5^+$  cation, the reaction of Lewis acids with (NPCl<sub>2</sub>)<sub>3</sub> produces neutral adducts at the N atom, (PCl<sub>2</sub>N)<sub>3</sub>·ECl<sub>3</sub>.<sup>1d</sup> Their  $\sigma$ -complex coordinate structures have recently been confirmed by X-ray structure determination.<sup>5</sup> Silver ion is also ineffective for the removal of chloride from **1**, forming instead coordinate bonds at N, similar to the ECl<sub>3</sub> adducts.<sup>6</sup> The coordinating ability of **1** toward silver ion is somewhat greater than that of CH<sub>2</sub>Cl<sub>2</sub>,<sup>6</sup> consistent with the low basicity and low nucleophilicity of (NPCl<sub>2</sub>)<sub>3</sub>.

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.<sup>7,8</sup> 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 (p $K_a < -6$  in nitrobenzene)<sup>9</sup> and reacts only with strong acids.<sup>3</sup> 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 (NPCl<sub>2</sub>)<sub>3</sub>.
- (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.

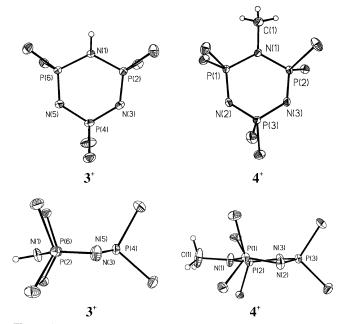
 $<sup>\</sup>ast$  To whom correspondence should be addressed. E-mail: chris.reed@ucr.edu.

<sup>(1)</sup> 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.

of 1 in CH<sub>2</sub>Cl<sub>2</sub> with 1 equiv of a mesitylenium carborane salt, [HC<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>][CHB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub>], <sup>10</sup> a conveniently handled protic acid of about the same strength as H<sub>3</sub>O<sup>+</sup> or HC<sub>60</sub><sup>+</sup> in a benzene solution, gives the protonated adduct [H(NPCl<sub>2</sub>)<sub>3</sub>]-[CHB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub>] (3) in excellent yield. Colorless single crystals of 3 were grown from CH<sub>2</sub>Cl<sub>2</sub>/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<sup>+</sup>-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<sub>2</sub>)<sub>3</sub>][AlBr<sub>4</sub>]<sup>4</sup> and approaches that found in protonated arenes.10

The room temperature  $^1H$  NMR spectrum of **3** in CD<sub>2</sub>Cl<sub>2</sub> 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 meth-



**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**.

ylating agents,<sup>12</sup> and the reaction of **1** with 1 equiv of CH<sub>3</sub>(CHB<sub>11</sub>Me<sub>5</sub>Br<sub>6</sub>) takes place in CH<sub>2</sub>Cl<sub>2</sub> 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<sub>2</sub>Cl<sub>2</sub>.

The  $^{1}$ H NMR spectrum of the methylated product, [(CH<sub>3</sub>)N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub>][CHB<sub>11</sub>Me<sub>5</sub>Br<sub>6</sub>] (**4**), shows a triplet at 3.66 ppm due to the methyl group with coupling to two equivalent P atoms ( $^{3}J_{P-H} = 14.4$  Hz). The  $^{31}$ P NMR spectrum shows two signals, one at 23.3 ppm (dq, 2P,  $^{3}J_{P-H} = 14.6$  Hz) and the other at 17.9 ppm (t, 1P,  $^{2}J_{P-P} = 41.0$  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<sup>+</sup>, 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

<sup>(10)</sup> Reed, C. A.; Kim, K.-C.; Stoyanov, E. S.; Stasko, D.; Tham, F. S.; Mueller, L. J.; Boyd, P. D. W. J. Am. Chem. Soc. 2003, 125, 1796– 1804.

<sup>(11)</sup> Ragogna, P. J.; Manners, I. Personal communication. On the other hand, more basic phosphazenes such as N<sub>3</sub>P<sub>3</sub>Me<sub>6</sub> are readily alkylated. See: Oakley, R. T.; Paddock, N. L. Can. J. Chem. 1977, 55, 3651– 3663.

<sup>(12)</sup> Kato, T.; Stoyanov, E.; Geier, J.; Grutzmacher, H.; Reed, C. A. J. Am. Chem. Soc. 2004, 126, 12451–12457.

#### COMMUNICATION

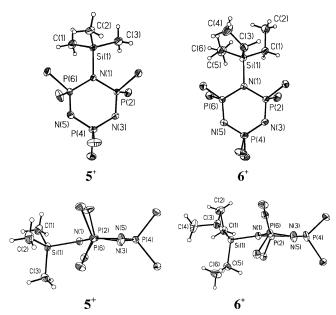


Figure 2. Thermal ellipsoid representations (50%) of N-silylated phosphazene cations showing front and side views of the ring conformations in the X-ray structures of 5 and 6.

an attempt to prepare the coordinatively unsaturated cation 2<sup>+</sup> was a trialkylsilylium carborane reagent, possibly the most potent halide-abstracting reagent presently available.<sup>13</sup> Treatment of 1 with the trimethyl- or triethylsilyl reagents Me<sub>3</sub>Si(CHB<sub>11</sub>Cl<sub>11</sub>) or Et<sub>3</sub>Si(CHB<sub>11</sub>Cl<sub>11</sub>) in *o*-dichlorobenzene, nevertheless, gave N-atom addition products (Scheme 1). NMR data for the products, [Me<sub>3</sub>Si(N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub>)][CHB<sub>11</sub>Cl<sub>11</sub>] (5) and  $[Et_3Si(N_3P_3Cl_6)][CHB_{11}Cl_{11}]$  (6), are similar to the

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

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, Nmethylated, and N-silvlated 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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