

A New, Convenient Synthesis of the Linear Phosphazene Salt $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]\text{Cl}$: Preparation of Higher Linear Homologues $[\text{Cl}_3\text{P}=\text{N}-(\text{PCl}_2=\text{N})_x=\text{PCl}_3]\text{Cl}$ ($x = 1-3$) and the 16-Membered Macrocycle $[\text{NCCl}(\text{NPCl}_2)_3]_2$

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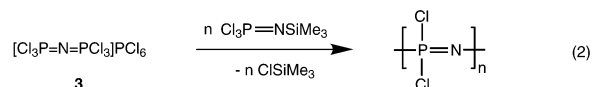
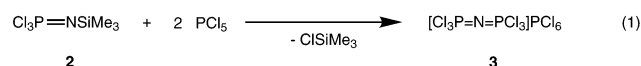
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An improved synthetic route to the linear phosphazene salt $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]\text{Cl}$ is reported. This species is a useful precursor to higher linear homologues and also to heterocycles such as the 16-membered carbophosphazene macrocycle $[\text{NCCl}(\text{NPCl}_2)_3]_2$.

Inorganic rings and chains based on skeletons of nitrogen, phosphorus, and/or heteroelements have attracted considerable attention from the standpoints of structure and reactivity, and also offer potential access to new materials with interesting properties.¹⁻⁵ The phosphazene salt $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]\text{Cl}$ (**1**) has been successfully employed as a reaction precursor for the preparation of various halogenated, polymerizable rings (e.g., $[\text{NCCl}(\text{NPCl}_2)_2]$).^{3,6} Unfortunately, the synthesis of **1** is plagued by multistep procedures which often involve the manipulation of highly toxic and corrosive reagents.⁷ Although analogues of **1** with alternative counter-

ions such as $[\text{PCl}_6]^-$ are easier to prepare, their synthetic utility is severely restricted due to competing side reactions involving the anion.⁸ In this communication, we report a convenient solution to this problem with an improved preparation of **1**. We also show that **1** can be used to prepare higher linear chain homologues and macrocycles, which are possible polymer precursors.

We arrived upon the improved preparation of $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]\text{Cl}$ (**1**) as a result of our investigations of the chemistry of the *N*-silylphosphoramimine $\text{Cl}_3\text{P}=\text{NSiMe}_3$ (**2**).^{9,10} It was found that catalytic quantities of the Lewis acid, PCl_5 , initiated the ambient temperature, living cationic, chain-growth polymerization of **2** to give poly(dichlorophosphazene) with controlled molecular weights and narrow polydispersities.¹¹ This reaction has been shown to proceed via the initial formation of the phosphazene salt $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]\text{PCl}_6$ (**3**), followed by the sequential addition of **2** at the reactive chain ends of **3** to give poly(dichlorophosphazene) and ClSiMe_3 as the byproduct (eqs 1 and 2).



Intrigued by the structural similarities between **3** and the target salt $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]\text{Cl}$ (**1**), we sought a reagent that

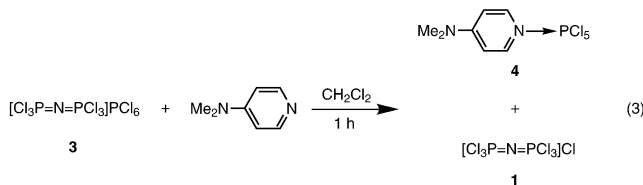
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would effectively remove an equivalent of PCl_5 from the hexachlorophosphate ion within **3**. In this regard, we chose the strong donor, 4-(dimethylamino)pyridine (DMAP).^{12,13} When 1 equiv of DMAP was added portionwise to freshly prepared **3** (see eq 3) in CH_2Cl_2 , the immediate formation of a bright yellow solution over a white precipitate was observed. Analysis of the soluble fraction of the reaction mixture by ^{31}P NMR spectroscopy indicated the presence of a single resonance at -238 ppm which was assigned to $\text{DMAP}\cdot\text{PCl}_5$ (**4**). The insoluble white precipitate was isolated by filtration and identified as the desired salt $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]\text{Cl}$ (**1**) on the basis of NMR (in tetrachloroethane) and subsequent reactivity studies (*vide infra*); ^{31}P NMR spectroscopy was particularly informative as the resonance belonging to the $[\text{PCl}_6]^-$ anion ($\delta = -296$ ppm) was absent. The synthesis of **1** can be performed in a single reaction vessel with routine yields of pure **1** exceeding 75% due to the simple nature of the workup procedure.



With **1** conveniently in hand, we explored the use of this species for the construction of the higher molecular weight linear analogues $[\text{Cl}_3\text{P}=\text{N}-(\text{PCl}_2=\text{N})_x=\text{PCl}_3]\text{Cl}$ ($x \geq 1$). Compared to the relatively well-known phosphazene derivative **1**, longer chains that belong to this family have been scarcely studied, and of these reports, most have focused on the preparation and chemistry of the synthetically problematic $[\text{PCl}_6]^-$ salts.¹⁴ Following the protocol used to synthesize poly(dichlorophosphazene), 1 equiv of **2** was added to a suspension of **1** in CH_2Cl_2 . After 1 h, ^{31}P NMR spectroscopic analysis of the resulting clear and colorless solution revealed that the consumption of **2** ($\delta = -54$ ppm) had transpired to yield a new species with an AB_2 spin pattern [$\delta = 13.8$ (d) and -11.5 (t) ppm; 2:1 ratio; $^2J_{\text{PP}} = 40.1$ Hz]. Large well-formed plates were subsequently obtained and identified as the five-membered chain $[\text{Cl}_3\text{P}=\text{N}-\text{PCl}_2=\text{N}=\text{PCl}_3]\text{Cl}$ (**5**) (59% yield; Figure 1) as a CH_2Cl_2 solvate.^{15a}

Compound **5** represents the first five-membered cationic phosphazene chain to be characterized by X-ray crystallography. This chain adopts a *cis-trans* geometry^{15b} with an acute central $\text{N}(1)-\text{P}(2)-\text{N}(2)$ angle of $118.16(16)^\circ$ and

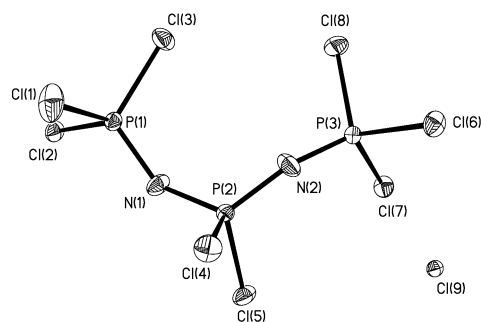


Figure 1. Molecular structure of **5** with thermal ellipsoids at the 50% probability level. CH_2Cl_2 solvate molecule omitted for clarity.

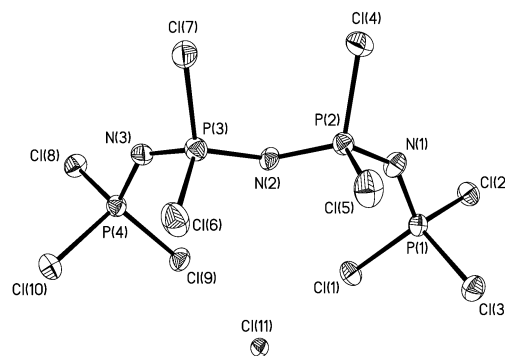
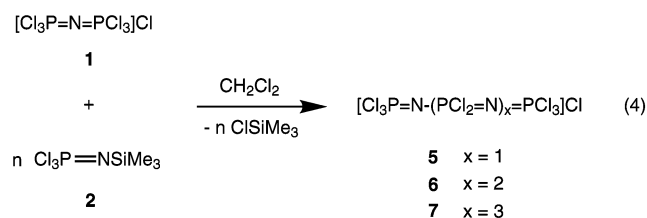


Figure 2. Molecular structure of **6** with thermal ellipsoids at the 50% probability level. CH_2Cl_2 solvate molecule omitted for clarity.

widened terminal $\text{P}-\text{N}-\text{P}$ angles of $140.73(18)^\circ$ and $156.7(2)^\circ$, respectively. All three P atoms in **5** display distorted tetrahedral geometry. The $\text{P}-\text{N}$ bond lengths within **5** range from $1.531(3)$ to $1.561(2)$ Å and suggest significant bond delocalization; a similar bonding arrangement can be found within $[\text{Cl}_2\text{P}=\text{N}]_n$.¹⁶

Repeating the reaction between **1** and increased amounts of **2** (2 and 3 equiv) provided the seven- and nine-membered phosphazene chains $[\text{Cl}_3\text{P}=\text{N}-(\text{PCl}_2=\text{N})_x=\text{PCl}_3]\text{Cl}$ ($x = 2$ and 3; **6** and **7**) in moderate yield (42% and 55%) (eq 4).



Highly moisture-sensitive crystals were obtained for **6** (Figure 2) whereas the nine-membered analogue **7** was obtained as an oil.

The crystal lattice of **6** contained disordered CH_2Cl_2 (0.5 mol equiv) which could not be satisfactorily modeled.¹⁷ Despite this difficulty, the overall geometry of the chain could be resolved. As with **5**, alternate *cis* and *trans*

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(15) (a) **5**· CH_2Cl_2 (CH_2Cl_2 , N_3P_3): MW = 524.91, colorless plate, collection temperature 150(1) K, monoclinic, space group $P2_1/c$, $a = 10.6850(4)$ Å, $b = 12.6600(5)$ Å, $c = 12.9850(3)$ Å, $\alpha = 90^\circ$, $\beta = 96.760(2)^\circ$, $\gamma = 90^\circ$, $V = 1744.30(10)$ Å³, $R_1 = 0.0338$ [$I > 2\sigma(I)$], GOF = 1.017. (b) *cis* relative to $\text{N}(1)-\text{P}(2)$ and *trans* relative to $\text{P}(2)-\text{N}(2)$.

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(17) **6**· $0.5 \text{CH}_2\text{Cl}_2$ ($\text{C}_{0.5}\text{HCl}_{1.2}\text{N}_3\text{P}_4$): MW = 598.32, colorless plate, collection temperature 150(1) K, monoclinic, space group $P2_1/c$, $a = 14.9781(6)$ Å, $b = 11.2624(8)$ Å, $c = 14.9417(10)$ Å, $\alpha = 90^\circ$, $\beta = 115.594(3)^\circ$, $\gamma = 90^\circ$, $V = 2273.2(2)$ Å³, $R_1 = 0.1090$ [$I > 2\sigma(I)$], GOF = 1.062. The degree of disorder within the CH_2Cl_2 solvate molecules was so severe that the data were refined without solvent. However, CH_2Cl_2 was included in the calculation of crystal density.

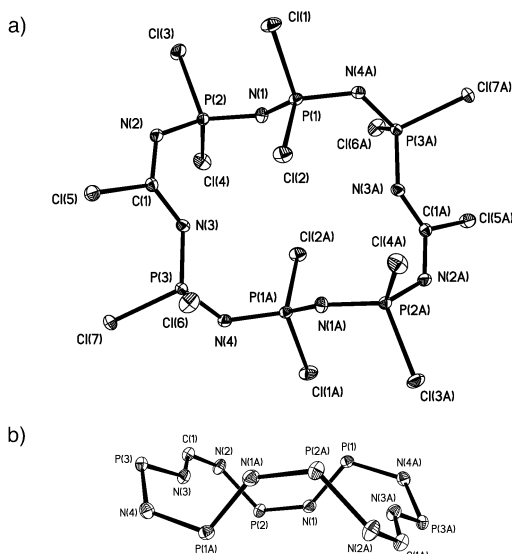


Figure 3. Molecular structure of **8** with thermal ellipsoids at the 50% probability level. All chlorine atoms have been omitted from the side view (b).

geometries exist along the phosphazene backbone of **6** with P–N bond lengths in the range 1.554(10)–1.580(9) Å. In addition, the internal N–P–N angles [114.2(6)° and 114.3(5)°] are narrowed in comparison to the P–N–P angles within the chain [134.0(7)–140.2(7)°]. The [PCl₆][−] analogue to **6** has also been characterized by X-ray crystallography and shown to possess an all *trans* geometry;^{14a} the reason this species has a different geometry than **5** and **6** (*cis*–*trans*) is unclear at the present time but is presumably related to the difference in counterions.

Given the successful use of **1** to construct halogenated heterocycles for ring-opening polymerization (ROP),^{3,6} we reacted the longer phosphazene chain **5** with Me₃SiN=C=NSiMe₃.¹⁸ A ³¹P NMR spectrum of the reaction mixture revealed the presence of two species (ca. 1:1 ratio) each with AB₂ coupling patterns, and consistent with the formation of the carbophosphazene macrocycles [NCCl(NPCl₂)₃]_x (*x* ≥ 1). Fortunately, the less soluble component of the reaction mixture was isolable in pure form by crystallization, and X-ray crystallography identified this species as the novel 16-membered macrocycle [NCCl(NPCl₂)₃]₂ (**8**) (isolated yield 24%; Figure 3).¹⁹ The more soluble product has been

tentatively assigned as the eight-membered derivative [NCCl(NPCl₂)₃] (**9**) (eq 5).

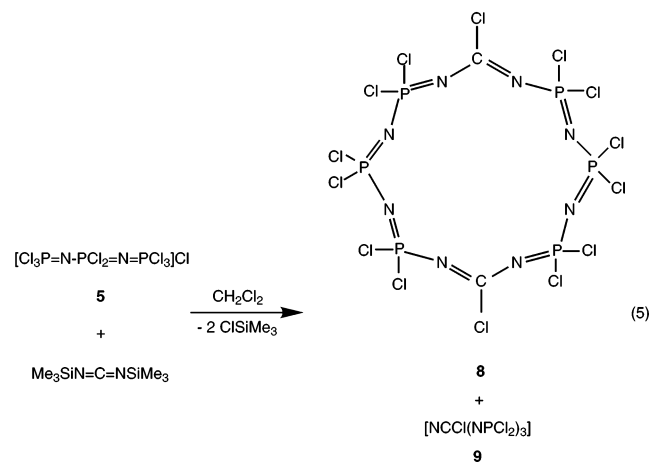
Heterocycle **8** represents, to our knowledge, the largest discrete carbophosphazene ring to be characterized crystallographically.²⁰ The 16-membered ring within **8** is significantly nonplanar with a crystallographic inversion center positioned in the middle of the “double crown” ring.

The carbon atoms within **8** are sp² hybridized as evidenced by a planar geometry [angle sum about C(1): 360.0(2)°] and proximal C–N bond lengths of 1.303(3) and 1.307(2) Å, which are consistent with a bond order of 1.5. Two distinct P–N bond lengths are also found within the ring: long P–N distances [1.5915(16) and 1.6078(16) Å] arise when a phosphorus atom is linked to a carbon-bound nitrogen atom [i.e., N(2) and N(3)], while the remaining P–N bonds are significantly shorter [1.5612(17)–1.5664(16) Å]; thus, the nitrogen atoms appear to π-bond preferentially to carbon. The P–N–P angles within **8** range from 130.54(11)° to 136.92(11)° and compare well with the P–N–P angles observed within the related sulfur-containing 24-membered macrocycle [NS(O)Cl(NPCl₂)₂]₄ [134.8(6)° to 138.9(5)°];²¹ this would suggest a similar, negligible degree of ring-strain is found within both species. The large cavity within **8** [transannular distances from 5.1 to 7.6 Å], coupled with the presence of eight basic, intraring nitrogen centers, makes this species a potential candidate for the encapsulation of metal ions (i.e., as an inorganic “crown” ligand).²²

In summary, an improved preparation of [Cl₃P=N=PCl₃]-Cl (**1**) has been achieved, and the construction of novel phosphazene chains and macrocycles from this versatile reagent has been described. Studies aimed at the construction of new macrocycles from the linear phosphazene chains presented herein are underway, along with their possible use as ROP precursors.

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Supporting Information Available: Experimental details (PDF) along with crystallographic data for **5**, **6**, and **8** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>. IC049955Z



(18) The reaction of **1** with Me₃SiN=C=NSiMe₃ gives the carbophosphazene ring [NCCl(NPCl₂)₂]. Rivard, E.; Manners, I. Unpublished results. For the analogous preparation of [NSCl(NPCl₂)₂], see: Allcock, H. R.; Dodge, J. A.; Manners, I. *Macromolecules* **1993**, *26*, 11.

(19) **8** (C₂Cl₁₄N₈P₆): MW = 818.22, colorless block, collection temperature 150(1) K, monoclinic, space group *P*2₁/*c*, *a* = 10.5670(2) Å, *b* = 12.7427(2) Å, *c* = 10.3853(2) Å, α = 90°, β = 111.1100(10)°, γ = 90°, *V* = 1304.67(4) Å³, *R*₁ = 0.0252 [*I* > 2σ(*I*)], GOF = 1.099.

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