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Synthesis of Linear and Cyclic Carbophosphazenes via an Oxidative Chlorination Strategy

Eric Rivard,[†] Alan J. Lough,[†] Tristram Chivers,[‡] and Ian Manners*[,†]

Departments of Chemistry, University of Toronto, Toronto, Ontario, Canada, M5S 3H6, and University of Calgary, Calgary, Alberta, Canada T2N 1N4

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The use of a mild, oxidative chlorination route for the synthesis of linear and cyclic carbophosphazenes is described. For example, chlorination of the linear PNCN chain $Ph_2P–N{=}C(Ph)–N(SiMe_3)_2$ (**1**) with C_2Cl_6 led to the clean formation of the previously known 8- and 6-membered rings $[Ph_2PNC(Ph)N]_2$ (**2**) and $[Ph_2PNC(Ph)NP(Ph)_2N]$ (**3**), respectively. In a similar fashion, the N-alkyl-substituted PNCN derivatives, $Ph_2P–N{=}C(Ph)–N(^tBu)SiMe_3$ (**4**) and $Ph_2P–N{=}C(Ph)–N^iPr_2$ (**7**) were readily converted by C_2Cl_6 into the halogenated derivatives $ClPh_2P{=}N–C(Ph){=}N^t$-Bu (**5**) and $[ClPh_2P{=}N{=}C(Ph)–N^iPr_2]Cl$ (**8**), respectively. Protonation of **5** was accomplished using HCl and gave the carbophosphazenium salt $[ClPh_2P{=}N–C(Ph){=}N(^tBu)H]Cl$ (**6**). In addition, the isolation of a rare 8-membered $P_2N_4C_2$ heterocycle $[(Cl_3P{=}N)ClPNC(Ph)NP(Cl)_2NC(Ph)N]$ (**9**) from the reaction of PCl_5 and $Li[PhC(NSiMe_3)_2]$ is reported. Treatment of **9** with one equivalent of $GaCl_3$ led to the discovery of an unusual Lewis acid-induced ring contraction reaction whereby the $(PNCN)_2$ ring in **9** is converted into the novel 6-membered P_2N_3C heterocyclic adduct $[(Cl_3P{=}N)ClPNP(Cl)_2NC(Ph)N]{\cdot}GaCl_3$ (**10**) with concomitant release of PhCN. Structural characterization of compounds **1**, **5**, **6**, and **8**–**10** by single-crystal X-ray diffraction is also provided.

Introduction

N-Silylated phosphoranimines, $R_3P{=}NSiMe_3$, have been used as precursors to main group and transition metal phosphoraniminato complexes which adopt a variety of structural motifs,[1] and often display unusual reactivity.[2] In addition, phosphoraniminato complexes have recently been explored as a new class of non-metallocene olefin polymerization catalysts.[3] With a judicious choice of substituents and reaction conditions, N-silylated phosphoranimines can be used as suitable monomers for the preparation of high molecular weight polyphosphazenes via condensation polymerization (whereby a volatile silane is released during the course of the reaction). In this context, a number of elegant thermal routes to aryl/alkyl-,[4] alkoxy-,[5] and halogen-substituted[6] polyphosphazenes have been developed. Recently, we showed that the chlorinated phosphoranimine, $Cl_3P{=}NSiMe_3$, could be polymerized under ambient conditions using PCl_5 as a catalyst to give poly(dichlorophosphazene) with controlled molecular weights and narrow polydispersities due to the living nature of the polymerization (Scheme 1).[7]

Bearing in mind the wealth of interesting chemistry associated with phosphoranimines, we have now targeted the

* Author to whom correspondence should be addressed. E-mail: imanners@chem.utoronto.ca. Fax: (+1) 416-978-2450.
† University of Toronto.
‡ University of Calgary.

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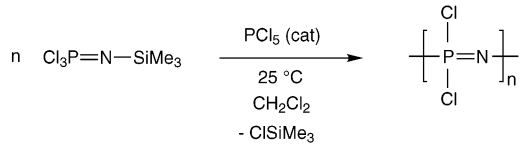
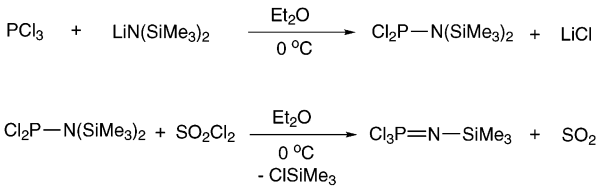
Scheme 1



Scheme 2



synthesis of related heterophosphazene chains with the aim of investigating their suitability as monomers for polymerization.[8] Specifically, we focused on monomers with similar reactive terminal groups as the phosphoranimine $Cl_3P{=}NSiMe_3$ but with their separation by a longer spacer group. As an initial synthetic goal, we chose the linear carbophosphazene $ClR_2P{=}N{-}C(R'){=}NSiMe_3$. We anticipated that polymerization of this monomer might yield the novel material $[R_2PNC(R')N]_n$, which would be expected to possess interesting properties.[9,10] This paper reports full details of our initial explorations in this area.

Results and Discussion

Attempted Synthesis of $SiMe_3$-Terminated Linear Carbophosphazenes. Prior to initiating this work, to our knowledge, no examples of the desired carbophosphazene monomers $ClR_2P{=}N{-}C(R'){=}NSiMe_3$ had been prepared. However, it has been shown that SO_2Cl_2 cleanly converts the chlorophosphine $Cl_2P{-}N(SiMe_3)_2$ to the phosphoranimine $Cl_3P{=}NSiMe_3$ with SO_2 and $ClSiMe_3$ as byproducts (Scheme 2).[11,12] As a consequence, a similar chlorination strategy was explored for the synthesis of the desired PNCN heterophosphazene chains. When the linear precursor $Ph_2P{-}N{=}C(Ph){-}N(SiMe_3)_2$ (**1**), prepared from in situ generated $Li[PhC(NSiMe_3)_2]$ and Ph_2PCl,[13,14] was reacted with one equivalent of SO_2Cl_2 in Et_2O, we obtained a complex mixture of products (by ^{31}P NMR spectroscopy) from which no single phosphorus-containing species could be isolated. Analysis of the mixture by ^1H NMR spectroscopy suggested that an almost quantitative elimination of the $SiMe_3$ groups derived from **1** had occurred as only very small signals for trimethylsilyl groups were detected. One possible reason for the generation of multiple products during the chlorination is that an undesired condensation reaction occurred between the S−Cl bonds of SO_2Cl_2 and the silylated nitrogen atoms of either **1** or an oxidatively chlorinated intermediate (e.g., $ClPh_2P{=}N{-}C(Ph){=}NSiMe_3$).

To circumvent any possible side reactions during the chlorination, we therefore explored the reaction of **1** with the milder chlorinating agent hexachloroethane, C_2Cl_6. Rather than producing a complex mixture, two predominant products were obtained which were identified as the known 8- and 6-membered cyclocarbophosphazenes **2** and **3** (Scheme 3). Heterocycles **2** and **3** were previously obtained by Chivers et al. from the reaction of Ph_2PCl_3 with $Li[PhC(NSiMe_3)_2]$.[14] The formation of the high oxidation state, phosphorus(V)-containing heterophosphazenes **2** and **3** suggested that the oxidative chlorination of **1** was successful. However, it appears that the targeted carbophosphazene, $ClPh_2P{=}N{-}C(Ph){=}NSiMe_3$, is unstable at ambient temperatures and subsequently undergoes a self-condensation reaction to give the dimer **2** and **3** (presumably via the loss of PhCN from **2**).[15] When the reaction was repeated at −78 °C, an intermediate species with a ^{31}P NMR resonance at 29 ppm was observed. However, when the reaction mixture was warmed to −10 °C, this intermediate, whose possible structure we will return to later, was rapidly (<20 min) converted into compounds **2** and **3**. Similar results were obtained in more concentrated reaction media implying a clear thermodynamic preference for the formation of cyclic carbophosphazenes rather than linear oligomeric or polymeric products.

Synthesis of the PNCN Chain, $Ph_2P{-}N{=}C(Ph){-}N(^tBu)SiMe_3$ (4), and Its Oxidative Chlorination with C_2Cl_6: Isolation of $ClPh_2P{=}N{-}C(Ph){=}N^tBu$ (5) and the Salt $[ClPh_2P{=}N{-}C(Ph){=}N(^tBu)H]Cl$ (6). To further understand the route by which cyclocarbophosphazenes **2** and **3** are formed when precursor **1** is chlorinated, we synthesized the *N-tert*-butyl-substituted analogue $Ph_2P{-}N{=}C(Ph){-}N(^tBu)SiMe_3$ (**4**) and explored its reaction with C_2Cl_6. Compound **4** was synthesized in high yield (80%) using a similar synthetic protocol as that used to prepare **1**. When **4** was allowed to react with C_2Cl_6 in diethyl ether, conversion of **4** (^{31}P: 40.5 ppm) into a new species with a ^{31}P NMR resonance at 4.0 ppm was observed after 16 h. A white solid was subsequently isolated which gave NMR data consistent with the elimination of the $SiMe_3$ group at nitrogen to give the linear carbophosphazene $ClPh_2P{=}N{-}C(Ph){=}N^tBu$ (**5**) (Scheme 4). The ^1H NMR spectrum of **5** consisted of a

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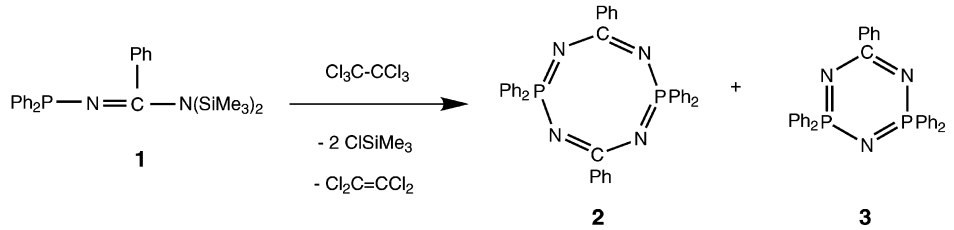
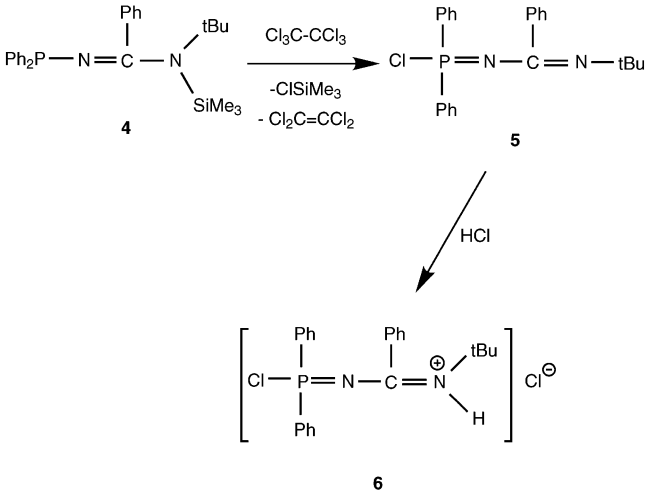
(15) The facile elimination of RCN from an 8-membered $(SNCN)_2$ ring has been reported: Chivers, T.; Richardson, J. F.; Smith, N. R. M. *Inorg. Chem.* **1986**, *25*, 47. One reviewer suggested that the formation of **3** might occur directly from the cyclocondensation of the linear intermediate $ClPh_2P{=}N{-}C(Ph){=}NSiMe_3$ [i.e., from a [4 + 2] cyclocondensation reaction which eliminates PhCN in the process]. This pathway is also entirely plausible. An analogous process may account for the formation of **9**.

Scheme 3



Scheme 4. Preparation of the Linear Carbophosphazenes **5** and **6**



singlet at 1.44 ppm due to the nitrogen-bound ^{t}Bu group, together with a series of resonances at 7−8 ppm associated with the aromatic (phenyl) protons. Furthermore, the initially present singlet for the $SiMe_3$ group in **4** (δ 0.25) was no longer detectable. Interestingly, the ^{31}P NMR spectrum of **5** in $CDCl_3$ gave a singlet at 8.9 ppm which was substantially shifted from the resonance observed in Et_2O and THF [δ 3.9 (s) and 5.0 (br), respectively]. For comparison, the ^{31}P NMR chemical shift for the related phosphoranimine, $ClPh_2P{=}NSiMe_3$, is quite similar with a reported value of 11.3 ppm (in $CDCl_3$),[16] and further supports the assigned structure of **5**. Compound **5** gave a mass spectrum consistent with the presence of a monomeric PNCN chain (M^+ detected), and the structure of **5** was confirmed by single-crystal X-ray crystallography (described below).

To provide a useful structural comparison, we first examined the solid state structure of **1** by single-crystal X-ray crystallography (Table 1). Despite the extensive use of $Ph_2P{-}N{=}C(Ph){-}N(SiMe_3)_2$ (**1**) as a precursor to both novel transition metal complexes[17] and main group radicals,[18] the structure of this compound has not been investigated. Yellow plates of **1** suitable for single-crystal X-ray crystallography were obtained from a cold diethyl ether solution (−30 °C) and indicated the presence of a cis PNCN arrangement (Figure 1). The P−N bond length within **1** was found to be 1.7271(18) Å (Table 3) and lies within the anticipated values

Table 1. Relevant Crystallographic Data for Compounds **1**, **5**, and **6**

	1	**5**	**6**
chemical formula	$C_{25}H_{33}N_2PSi_2$	$C_{23}H_{24}ClN_2P$	$C_{23}H_{25}Cl_2N_2P$
formula weight	448.68	394.86	431.32
crystal system	monoclinic	triclinic	orthorhombic
space group	$P2_1/c$	$P\bar{1}$	*Pbca*
temp, K	150(1)	150(1)	150(1)
a, Å	13.0491(3)	9.6700(2)	22.47100(10)
b, Å	11.6549(3)	10.5020(2)	8.7260(4)
c, Å	17.0704(4)	10.6120(2)	22.9941(5)
α, deg	90	98.5040(12)	90
β, deg	96.5890(10)	91.0030(12)	90
γ, deg	90	106.5820(11)	90
V, Å^3	2579.02(11)	1019.49(3)	4508.7(2)
Z	4	2	8
μ(Mo Kα), mm^{-1}	0.214	0.276	0.370
θ range/deg	2.72−27.52	2.59−27.59	2.66−27.50
no. of reflns collcd	19724	15494	36451
no. of indp reflns/R_{int}	5898/0.074	4693/0.0542	5178/0.1330
no. of refined params	272	245	258
R (%) ($I > 2\sigma[I]$)[a]	4.85	3.72	5.49
R_w (%)[b]	13.38	10.82	14.82

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

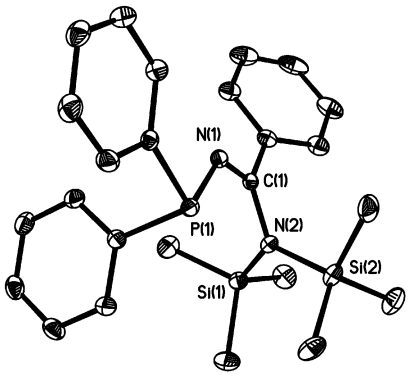


Figure 1. Molecular structure of **1**. All hydrogen atoms have been omitted for clarity. Selected bond lengths and angles are presented in Table 3.

for a typical P−N single bond (1.69 to 1.73 Å).[19] The length of the adjacent C−N bond, [C(1)−N(1)], was determined to be 1.277(3) Å and was much shorter than the neighboring C(1)−N(2) bond [1.427(3) Å]; these bond lengths lie within the values generally observed for double and single bonds, respectively, and are consistent with the canonical representation of the bonding within **1** depicted in Scheme 3. Reflecting the presence of a lone pair at phosphorus, a pyramidal geometry was observed with bond angles substantially narrowed from those of an ideal tetrahedron [range from 98.97(9)° to 100.14(9)°].

An X-ray diffraction study of the ^{t}Bu-terminated carbophosphazene, $ClPh_2P{=}NC(Ph){=}N^tBu$ (**5**), revealed that this

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Table 2. Relevant Crystallographic Data for Compounds **8**−**10**

	8·CH_2Cl_2	**9**	**10**
chemical formula	$C_{26}H_{31}Cl_4N_2P$	$C_{14}H_{10}Cl_6N_5P_3$	$C_7H_5Cl_9GaN_4P_3$
formula weight	544.30	553.88	626.83
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
temp, K	150(1)	150(1)	150(1)
a, Å	11.1470(3)	12.5680(4)	9.1460(2)
b, Å	10.0030(3)	8.6020(3)	10.0440(3)
c, Å	24.7400(6)	19.7070(5)	12.4390(4)
α, deg	90	90	103.6300(9)
β, deg	90.3240(17)	93.5260(17)	109.1460(10)
γ, deg	90	90	91.4420(14)
V, Å^3	2758.55(13)	2126.49(11)	1042.52(5)
Z	4	4	2
μ(Mo Kα), mm^{-1}	0.505	1.046	2.704
θ range/deg	2.62−27.50	2.55−27.48	2.99−27.50
no. of reflns collcd	17475	12270	13106
no. of indp reflns/R_{int}	6298/0.0489	4846/0.0386	4743/0.0599
no. of refined params	299	254	218
R (%) ($I > 2\sigma[I]$)[a]	4.78	4.07	3.88
R_w (%)[b]	12.48	11.01	9.92

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compounds **1**, **5**, **6**, and **8** with Estimated Standard Deviations in Parentheses

	1	**5**	**6**	**8**
P−N	1.7271(18)	1.5417(12)	1.564(2)	1.5785(19)
C−N (internal)	1.277(3)	1.4005(18)	1.332(3)	1.330(3)
(internal)		1.2788(19)	1.315(3)	1.322(3)
(terminal)	1.427(3)	1.4829(18)	1.494(3)	1.495(3)
				1.495(3)
P−Cl		2.0801(5)	2.0259(8)	2.0103(8)
P−N−C (internal)	122.17(15)	132.73(10)	138.38(18)	132.55(17)
N−C−N (internal)	126.61(19)	126.68(13)	121.6(2)	119.6(2)
C−N−C (internal)		123.71(13)	126.5(2)	122.08(19)
				122.26(19)
C−N−Si	117.76(13)			
	117.69(14)			

species exists as a monomer in the solid state (Figure 2) with a significantly shorter P−N distance of 1.5417(12) Å when compared to that of the phosphorus(III)-containing PNCN chain **1**. Furthermore, the observed P−N bond length within **5** is similar to those found within the bis(trichlorophosphine)-iminium cation $[Cl_3P{=}N{=}PCl_3]^+$ (1.5−1.6 Å)[20] and suggests the presence of significant multiple bond character. A localized bonding arrangement is present within the adjacent C−N bonds of the chain, with an internal (imine) C−N bond length [C(1)−N(2)] of 1.4005(18) Å and a shortened terminal C−N distance [C(1)−N(1)] of 1.2788(19) Å. For comparison, the remaining C−N single bond involving the quaternary carbon atom of the ^{t}Bu group [C(8)−N(1)] was 1.4829(18) Å. The P−Cl bond length within **5** was 2.0801(5) Å and is typical for a phosphorus(V)−chlorine bond.[20]

As compound **5** was anticipated to be a strong base, reaction with HCl to form the protonated derivative, $[ClPh_2P{=}N{-}C(Ph){=}N(^tBu)H]Cl$ (**6**), was expected to be facile. Indeed, when **5** was allowed to react with one equivalent of HCl, quantitative formation of a new product with a downfield-shifted ^{31}P NMR resonance at 32.9 ppm was detected. A white solid was subsequently isolated in

(20) Rivard, E.; McWilliams, A. R.; Lough, A. J.; Manners, I. *Acta Crystallogr.* **2002**, *58C*, i114 and references therein.

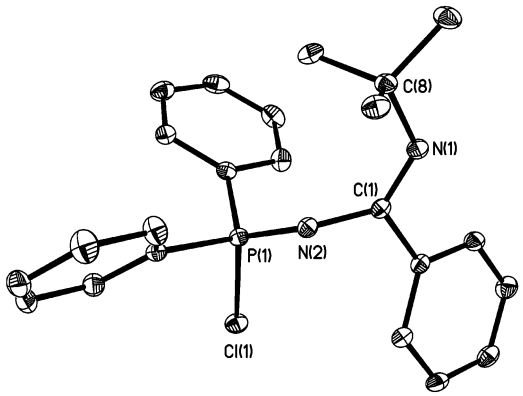


Figure 2. Molecular structure of **5**. All hydrogen atoms have been omitted for clarity. Selected bond lengths and angles are presented in Table 3.

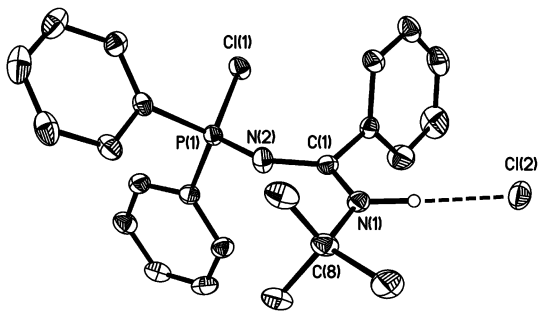


Figure 3. Molecular structure of **6**. All hydrogen atoms bound to carbon have been omitted for clarity. Selected bond lengths and angles are presented in Table 3.

67% yield which gave a ^{1}H NMR spectrum similar to that of **5** except for an additional broad signal at 11.6 ppm, consistent with the presence of an iminium proton. The resonance associated with the ^{t}Bu group within **6** was located at 1.66 ppm and, as a result of the increase in cationic character within the PNCN unit, lies considerably downfield with respect to the ^{t}Bu resonance in the neutral PNCN chain **5** [δ 1.47]. The spectroscopic data, coupled with a single-crystal X-ray diffraction study (Figure 3), conclusively identified the product as the terminally protonated carbophosphazene $[ClPh_2P{=}N{-}C(Ph){=}N(^tBu)H]Cl$ (**6**).

Inspection of the metrical parameters of **6** indicates the presence of a delocalized bonding scheme within the PNCN chain, with similar internal C−N bond lengths of 1.315(3) and 1.332(3) Å, and a P−N distance of 1.564(2) Å. These bond lengths illustrate that, to a significant extent, the cationic charge is delocalized throughout the entire PNCN framework. As a consequence of increased cationic character at phosphorus, a contracted P−Cl bond length [2.0259(8) Å] is observed when compared to the P−Cl bond within the neutral analogue **5** [2.0801(5) Å]. A weak intramolecular hydrogen bonding interaction is also present involving the iminium proton bound to N(1) and the counterion Cl(2) [2.04(4) Å]. No intermolecular hydrogen bonding was present between the N−H moiety and the P−Cl bond of the cation.

Preparation of $Ph_2P{-}N{=}C(Ph){-}N^iPr_2$ (7) and the Carbophosphazenium Salt $[ClPh_2P{=}N{=}C(Ph){-}N^iPr_2]Cl$ (8): Insight into the Oxidative Chlorination Mechanism. With the goal of gaining a better understanding of the initial steps involved in the chlorination of **1**, we decided to explore

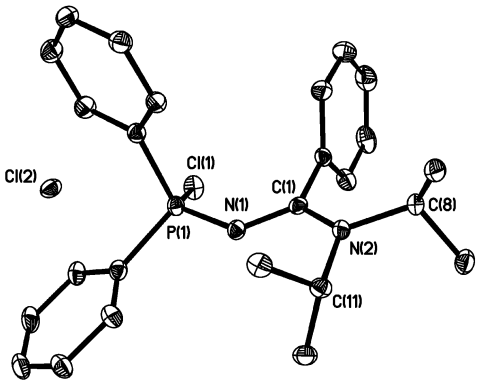
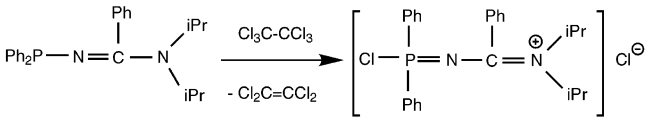


Figure 4. Molecular structure of **8**. All hydrogen atoms have been omitted for clarity. Selected bond lengths and angles are presented in Table 3.

Scheme 5. Synthesis of the Carbophosphazenium Salt **8**



7 8

the chlorination of a PNCN chain where the elimination of a silyl halide was not possible. To facilitate the isolation of an amido-terminated ($-NR_2$) linear carbophosphazene, the reactive silyl groups at the terminal nitrogen atom of the PNCN precursor were replaced by sterically similar, yet elimination-resistant isopropyl groups. Following the established procedure for the construction of PNCN chains, the isopropyl-substituted derivative $Ph_2P-N=C(Ph)-N^iPr_2$ (**7**) was synthesized (yellow solid, 79% yield) from the reaction of Ph_2PCl with in situ generated $Li[N=C(Ph)-N^iPr_2]$. Upon the addition of Cl_3C-CCl_3 in Et_2O, a pale yellow precipitate was obtained within a few minutes. This product was readily soluble in chlorinated solvents and gave a ^{31}P NMR signal at 37.1 ppm in $CDCl_3$. The location of this chemical shift was similar to the observed resonances for the cationic linear carbophosphazene **6** (δ 32.9), suggesting that the isolated species was the carbophosphazenium salt $[ClPh_2P=N=C(Ph)-N^iPr_2]Cl$ (**8**) (Scheme 5), rather than the constitutional isomer $Cl_2Ph_2P-N=C(Ph)-N^iPr_2$.[21] The ^1H and $^{13}C\{^1H\}$ NMR spectra of **8** revealed that there was restricted rotation about the terminal C−N bond in solution, as indicated by the presence of two distinct sets of resonances due to diastereotopically positioned ^{i}Pr groups; a similar situation was also noted for the precursor **7**. Final confirmation for the formation of **8** was obtained from single-crystal X-ray crystallography (Figure 4).

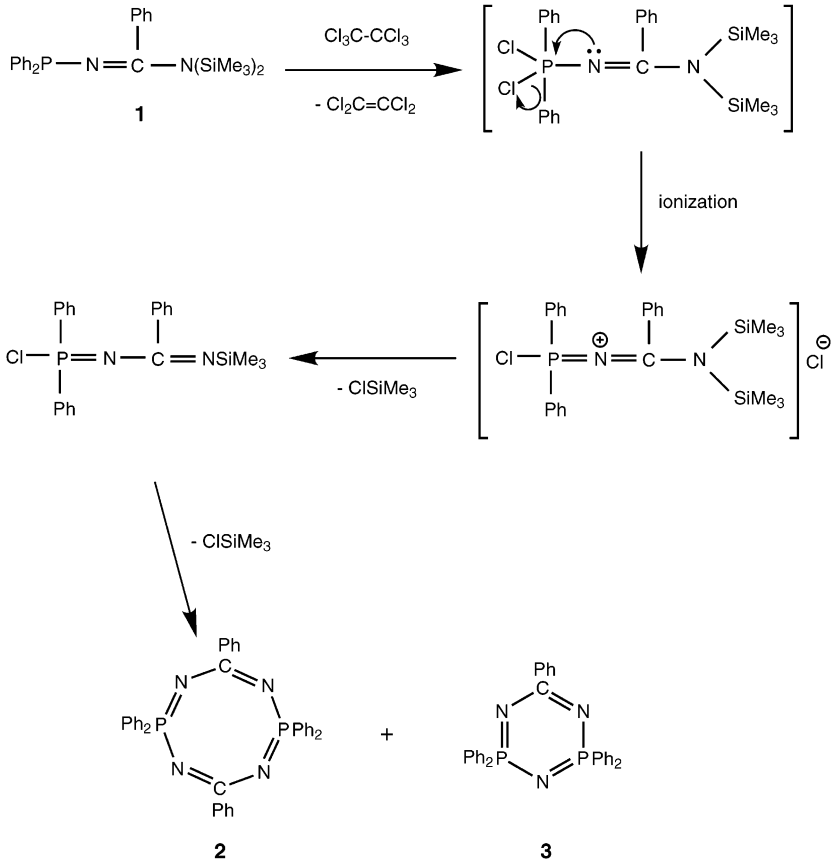
(21) Although the structure of **8** was confirmed to be a salt in the solid state, we could not immediately rule out the possibility that **8** existed as the pentacoordinate species $Cl_2Ph_2P-N=C(Ph)-N^iPr_2$ in solution. To probe the structure of **8** in solution, we reacted **8** with one equivalent of the halide abstractor, $Ag[BF_4]$, in dichloromethane. Upon the addition of $Ag[BF_4]$ an immediate reaction was observed (as evinced by the formation of a white precipitate, presumably AgCl). The ^{31}P NMR spectra remained unchanged throughout the reaction [δ = 36.9 (s) ppm] while ^{19}F NMR spectroscopy revealed the presence of the BF_4^- ion [δ −152.7 (s)]. These results suggest that a simple anion exchange had occurred (BF_4^- for Cl^-) to give $[ClPh_2P=N=C(Ph)-N^iPr_2]BF_4$, and therefore, **8** is also ionized in solution.

Compound **8** crystallized in the $P2_1/c$ space group with one equivalent of solvate CH_2Cl_2 as part of the crystal lattice (Table 2). The PNCN unit within **8** is formally positively charged with no close contacts (<5.0 Å) between the cationic $[ClPh_2P=N=C(Ph)-N^iPr_2]^+$ unit and the chloride counterion. As with the carbophosphazene salt **6**, significant multiple bond character is present throughout the PNCN chain. The P−N bond length was determined to be 1.5785(19) Å, which is slightly longer than that in **6** [1.564(2) Å]. The internal C−N bond distances were 1.330(3) Å and 1.322(3) Å, respectively, and are comparable to those observed within **6**; this delocalized arrangement is in contrast to the neutral derivative **5** where substantial bond alternation is found. The geometry about the phosphorus atom in **8** is distorted tetrahedral and consistent with the presence of a high oxidation state (+5) phosphorus center as a lone pair is no longer present.

Based upon the isolation of **8** and the reactivity studies described above, we can postulate a generalized reaction pathway for the oxidative chlorination of **1** (Scheme 6). The initial step of the chlorination likely involves oxidation of phosphorus from the +3 to +5 oxidation state to produce the carbophosphazenium salt $[ClPh_2P=N=C(Ph)-N(SiMe_3)_2]Cl$ (analogous to the formation of **8**) which can be formally derived from a pentacoordinate phosphorus precursor via ionization of a P−Cl bond (cf. the autoionization of PCl_5). If reactive silyl groups are present at the terminal nitrogen atom, then intramolecular attack by a chloride ion can subsequently take place to give the neutral PNCN chain, $ClPh_2P=N-C(Ph)=NSiMe_3$ with release of $ClSiMe_3$ as a byproduct. Oligomerization of this intermediate can then occur to give the cyclocarbophosphazenes **2** and **3**. As mentioned earlier, an intermediate with a ^{31}P NMR resonance of 29 ppm was detectable during the oxidative chlorination of **1**. From the subsequent data obtained, it appears that this species is the carbophosphazenium salt $[ClPh_2P=N=C(Ph)-N(SiMe_3)_2]Cl$ as the related N-isopropyl-substituted and *N-tert*-butyl substituted salts **8** and **6** have similar ^{31}P NMR resonances (δ 37.0 and 32.9, respectively). Of note, the intermediate $ClPh_2P=N-C(Ph)=NSiMe_3$ is anticipated to have a much different chemical environment, and consequently ^{31}P NMR chemical shift, than the ionized compound $[ClPh_2P=N=C(Ph)-N(SiMe_3)_2]Cl$, as nearly a 24 ppm difference in the ^{31}P NMR chemical shift exists between that of the neutral PNCN derivative **5** [δ 8.9] and the closely related protonated derivative **6** [δ 32.7].

Formation and the Structure of the Eight-Membered Carbophosphazene Heterocycle, $[(Cl_3P=N)ClPNC(Ph)-NP(Cl)_2NC(Ph)N]$ (9). As our attempts to generate the perhalogenated polymer precursor $Cl_3P=N-C(Ph)=NSiMe_3$ using the above-mentioned strategies were unsuccessful, we explored alternative routes toward this PNCN chain. One plausible synthetic pathway involves the direct reaction of PCl_5 with the lithium salt $Li[PhC(NSiMe_3)_2]$ (with LiCl and $ClSiMe_3$ as byproducts). The related reaction involving PCl_5 and $Me_3SiN=C(Ph)-N(SiMe_3)_2$ was explored previously by Chivers and co-workers, and was shown to yield a complex mixture of products including potentially oligomeric carbo-

Scheme 6. Possible Mechanism for the Oxidative Chlorination of **1**



phosphazenes based on the observation of broad ^{31}P NMR signals from 20 to −12 ppm, and a sharp resonance at 40.2 ppm.[14] Intrigued by the possibility of polymer formation (or the potential isolation of the desired PNCN polymer precursor), we reacted Li[PhC(NSiMe$_3$)$_2$] with PCl_5 and obtained a pale yellow, air- and moisture-sensitive oil after 4 h (in Et_2O) which gave a sharp ^{31}P NMR resonance at 42 ppm along with numerous resonances superimposed upon a broad halo from 5 to −10 ppm.[22] A fibrous, yellow solid was subsequently isolated via precipitation into hexanes and gave an equally complex ^{31}P NMR spectrum as the reaction mixture. Unfortunately, all attempts to obtain an air- and moisture-stable material by functionalizing the reactive P−Cl groups with aryloxides were unsuccessful, thus precluding any molecular weight characterization by gel permeation chromatography (GPC). However, light scattering studies performed on the fibrous yellow solid in CH_2Cl_2 (under nitrogen) indicated the presence of only low molecular weight species.[23] With the intention of isolating possible intermediates or side products from the reaction mixture, a toluene/dichloromethane solution of the hexanes−soluble fraction was cooled to −40 °C. Within two weeks, large well-formed colorless blocks were isolated and identified as the novel cyclocarbophosphazene [(Cl_3P═N)ClPNC(Ph)NP(Cl)$_2$-NC(Ph)N] (**9**) (overall yield 5%; Figure 5).

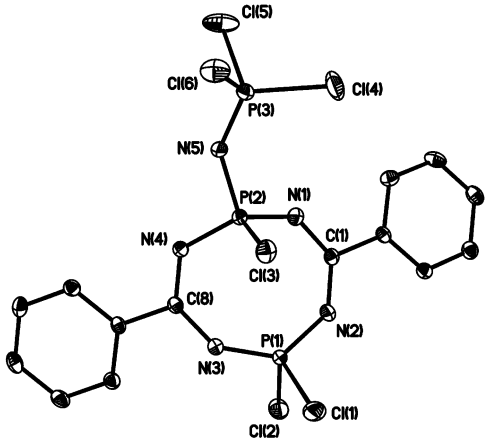


Figure 5. Molecular structure of **9**. All hydrogen atoms have been omitted for clarity. Selected bond lengths and angles are presented in Table 4.

In contrast to the numerous structurally characterized derivatives of the 6-membered carbophosphazenes,[24] only a few examples of well-characterized 8-membered (PNCN)$_2$ rings are known.[14,25] The (PNCN)$_2$ heterocycle within **9** adopts a boat-twist conformation with a phosphoraniminato (Cl_3P═N) ligand positioned *exo* to the ring. The P−N bond within the Cl_3P═N ligand [1.518(2) Å] is considerably shorter than the remaining P−N bonds within the heterocycle

(22) The sharp resonance at 42 ppm could be due to the presence of the 6-membered cyclocarbophosphazene [NCPh(NPCl$_2$)$_2$] (lit. ^{31}P chemical shift: 41.6 ppm in CH_2Cl_2): Schmidpeter, A. *Inorg. Synth.* **1989**, *25*, 24. Attempts to isolate this product in pure form have not been successful.

(23) Dynamic light scattering revealed only the presence of species with a hydrodynamic radius (R_h) of <0.5 nm indicating that the product had a low molecular weight. For comparison, a polymer with a molecular weight of 5000 would be expected to have $R_h \sim 1$ nm; see: Dorn, H.; Singh, R. A.; Massey, J. A.; Nelson, J. M.; Jaska, C. A.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 6669.

Table 4. Selected Bond Lengths (Å) for **9** with Estimated Standard Deviations in Parentheses

P(1)−N(2)	1.578(2)	N(3)−C(8)	1.341(3)
P(1)−N(3)	1.544(2)	N(4)−C(8)	1.314(3)
P(2)−N(1)	1.585(2)	P(1)−Cl(1)	2.0067(10)
P(2)−N(4)	1.608(2)	P(1)−Cl(2)	2.0079(10)
P(2)−N(5)	1.606(2)	P(2)−Cl(3)	2.0498(10)
P(3)−N(5)	1.518(2)	P(3)−Cl(4)	1.9701(11)
N(1)−C(1)	1.329(3)	P(3)−Cl(5)	1.9575(12)
N(2)−C(1)	1.318(3)	P(3)−Cl(6)	1.9686(10)
N(2)−P(1)−N(3)	129.46(13)	P(2)−N(1)−C(1)	133.0(2)
N(1)−P(2)−N(4)	122.54(12)	P(1)−N(2)−C(1)	134.8(2)
N(1)−P(2)−N(5)	108.62(13)	P(1)−N(3)−C(8)	139.7(2)
N(4)−P(2)−N(5)	103.71(11)	P(2)−N(4)−C(8)	124.93(18)
N(1)−C(1)−N(2)	130.0(2)	Cl(3)−P(2)−N(5)	105.95(10)
N(3)−C(8)−N(4)	127.2(2)	P(2)−N(5)−P(3)	136.69(15)

[1.554(2) to 1.608(2) Å] (Table 4). For comparison, the endocyclic P−N bond lengths within the related $P_2N_4C_2$ ring $[Ph_2PNC(4\text{-}MeC_6H_4)N]_2$ range from 1.592(4) to 1.615(4) Å.[14] The observed N−C−N angles [127.2(2) and 130.0(2) °] and C−N distances [1.314(3) to 1.341(3) Å] within **9** suggest a C−N bond order of approximately 1.5, thus significant π-electron delocalization is present. The geometry about the phosphorus atoms can be described as distorted tetrahedral with the longest P−Cl bond involving P(2)−Cl(3) [2.0498(10) Å; remaining P−Cl bonds range from 1.9575(12) to 2.0079(10) Å]. The mechanism by which compound **9** is formed is not clear at the present time as no other intermediates could be isolated in pure form. One possibility involves the initial formation of a 12-membered halogenated PNCN cyclic trimer, $[Cl_2PNC(Ph)N]_3$,[26] followed by elimination of one equivalent of benzonitrile, PhCN, to yield a 10-membered heterocycle (vide supra).[15] Lewis acid (e.g., PCl_5) catalyzed rearrangement of the resulting 10-membered $(PNCN)_2PN$ ring might then occur to place a phosphoraniminato ligand ($Cl_3P{=}N$) *exo* to the ring to give **9**.[27]

Formation of the 6-Membered Cyclic Carbophosphazene Adduct $[(Cl_3P{=}N)ClPNP(Cl)_2NC(Ph)N]\cdot GaCl_3$ (10). In previous studies we showed that halide abstraction from cyclic boron-containing heterophosphazenes was readily accomplished using group 13 halides (e.g., $GaCl_3$ and $AlCl_3$) to give planar cationic borazine−phosphazene hybrid rings.[28] As **9** contains an elongated P−Cl bond at P(2), we hoped that treatment of this compound with the potential halide acceptor, $GaCl_3$, would produce a cationic cyclocarbophosphazene as a tetrachlorogallate salt. The formation of such a species has fundamental importance as cationic heterocycles are often postulated as intermediates during the ring-opening polymerization (ROP) of various inorganic rings (e.g., in the thermal polymerization of $[Cl_2PN]_3$ to give linear poly(dichlorophosphazene)).[29,30]

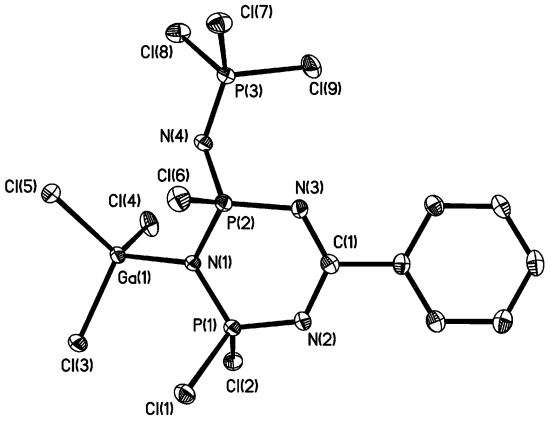
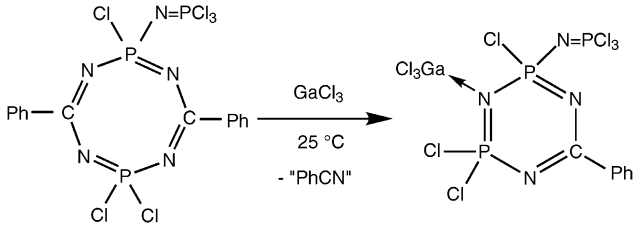


Figure 6. Molecular structure of **10**. All hydrogen atoms have been omitted for clarity. Selected bond lengths and angles are presented in Table 5.

Scheme 7. Lewis Acid-Mediated Ring Contraction of **9**



9 **10**

When a solution of **9** was treated with one equivalent of $GaCl_3$ (in CH_2Cl_2), quantitative conversion (by ^{31}P NMR spectroscopy) into a new species was observed after 16 h. Specifically, a series of broadened resonances were detected at 4.0, 9.4, and 40.3 ppm, respectively (1:1:1 ratio). These signals were shifted downfield compared to the resonances associated with **9** (−2.1 to 1.6 ppm) and suggested the retention of three distinct (possibly cationic) phosphorus environments within the product. X-ray quality crystals were subsequently obtained which enabled conclusive identification of the species as the unusual 6-membered cyclic carbophosphazene adduct $[(Cl_3P{=}N)ClPNP(Cl)_2NC(Ph)N]\cdot GaCl_3$ (**10**) (Scheme 7; Figure 6). The isolation of a ring-contracted product was somewhat surprising given our expectations outlined above. Furthermore, the coordination of $GaCl_3$ to one of the nitrogen atoms within the CN_3P_2 ring represents a rare example of a structurally characterized

(24) For selected examples of structurally characterized 6-membered carbophosphazenes, see: (a) Dastagiri Reddy, N.; Elias, A. J.; Vij, A. *J. Chem. Soc., Dalton Trans.* **1999**, 1515. (b) For the structure of **3**, see: Chandrasekhar, V.; Chivers, T.; Parvez, M. *Acta Crystallogr.* **1993**, *49C*, 393. (c) Allcock, H. R.; Coley, S. M.; Manners, I.; Visscher, K. B.; Parvez, M.; Nuyken, O.; Renner, G. *Inorg. Chem.* **1993**, *32*, 5088.

(25) Estradayanez, M. R.; Roesky, H. W.; Scholz, U.; Noltemeyer, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *47*, 145.

(26) It is known that the formation of large macrocycles generally becomes more favorable when smaller substitutents are located about the ring: (a) Ni, Y.; Lough, A. J.; Rheingold, A. L.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 998. (b) The 12-membered ring $[Cl_2PNC(Cl)N]_3$ has also been structurally characterized: Hausen, H.-D.; Rajca, G.; Weidlein, J. *Z. Naturforsch.* **1986**, *41B*, 839.

(27) For a related rearrangement of cyclophosphazenes, see: Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Whittle, R. R. *Organometallics* **1984**, *3*, 663.

(28) (a) Gates, D. P.; Ziembinski, R.; Rheingold, A. L.; Haggerty, B. S.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2277. (b) Gates, D. P.; McWilliams, A. R.; Ziembinski, R.; Liable-Sands, L. M.; Guzei, I. A.; Yap, G. P. A.; Rheingold, A. L.; Manners, I. *Chem. Eur. J.* **1998**, *4*, 1489.

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

(30) (a) Gates, D. P.; Edwards, M.; Liable-Sands, L. M.; Rheingold, A. L.; Manners, I. *J. Am. Chem. Soc.* **1998**, *120*, 3249. (b) McWilliams, A. R.; Gates, D. P.; Edwards, M.; Liable-Sands, L. M.; Guzei, I.; Rheingold, A. L.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 8848.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **10** with Estimated Standard Deviations in Parentheses

Ga(1)−N(1)	1.997(2)	P(2)−N(4)	1.589(3)
P(1)−N(1)	1.637(3)	P(3)−N(4)	1.534(3)
P(1)−N(2)	1.573(3)	C(1)−N(2)	1.350(4)
P(2)−N(1)	1.654(2)	C(1)−N(3)	1.323(4)
P(2)−N(3)	1.596(3)	P(2)−Cl(6)	2.0072(11)
Ga(1)−N(1)−P(1)	124.24(13)	N(3)−P(2)−N(4)	113.55(14)
Ga(1)−N(1)−P(2)	122.34(15)	P(2)−N(4)−P(3)	132.46(18)
P(1)−N(1)−P(2)	113.41(15)	C(1)−N(2)−P(1)	122.9(3)
N(1)−P(1)−N(2)	115.23(14)	C(1)−N(3)−P(2)	122.6(2)
N(1)−P(2)−N(3)	113.29(14)	N(2)−C(1)−N(3)	126.5(3)
N(1)−P(2)−N(4)	107.16(13)		

Lewis acid−base adduct involving a skeletal ring atom within a heterophosphazene.[31] The ease of adduct formation within **10** is likely due to the presence of a relatively electron-donating phosphoraniminato ($Cl_3P{=}N$) group which increases the basicity of the nitrogen atoms within the CN_3P_2 ring. Consistent with the above postulate is the observation that the related halogenated heterocycles $[Cl_2PN]_3$ and $[Cl_2PNC(Cl)NC(Cl)N]$ exhibit no detectable coordination chemistry with $GaCl_3$ at room temperature.[32]

The influence of $GaCl_3$ on the bonding within **10** becomes clear when the metrical parameters within this heterocycle are examined. The P−N bond distances involving the three-coordinate N(1) atom are significantly lengthened [1.637(3) and 1.654(2) Å] when compared to the remaining P−N distances within **10** [1.534(3) Å to 1.596(3) Å] (Table 5), and this suggests a decrease in electron density about the Ga-bound nitrogen atom (which is expected to reduce the strength of the bonding interaction with the neighboring phosphorus atoms). The Ga−N distance was determined to be 1.997(2) Å and compares well with the Ga−N dative bond distance found within the boraamidinate complex $(THF)_4Li\{[PhB(\mu\text{-}N^tBu)_2GaCl_2]\cdot GaCl_3\}$ [1.966(2) Å].[33] The bonding arrangement within the *exo* $Cl_3P{=}N$ ligand remains relatively unaffected by the presence of $GaCl_3$, with a similar P−N bond length [1.534(3) Å] and $P_{exo}-N-P_{ring}$ angle [132.46(18)°] as in **9** [1.554(2) Å and 136.69(15)° respectively]. The C−N bond lengths within the heterocycle were 1.323(4) and 1.350(4) Å, and indicate retention of considerable multiple bond character (cf. bonding discussion for **9**).

The mechanism by which **10** is formed is unclear at the present time; however, the extrusion of a skeletal CN fragment (as PhCN) from **9** is likely to be a thermodynamically favorable process in light of the strong C≡N bond strength. In addition, a similar extrusion pathway is possibly involved in the formation of **3**.[15,34] Therefore, the Lewis acid-mediated extrusion of cyanide derivatives from cyclic 8-membered $C_2N_4P_2$ heterophosphazenes may be a general reaction and could limit the use of these species as precursors to polymers via ROP. This highlights the need for suitable linear PNCN precursors for condensation polymerization.

Summary

We report the application of a new, mild, chlorination route toward the synthesis of linear and cyclic hybrid PNCN carbophosphazenes. This strategy allows for the facile creation of halogenated phosphorus(V) centers, which is crucial for the development of the linear PNCN derivatives as polymer precursors via condensation polymerization.[35] In addition, a possible mechanistic pathway for the chlorination of **1** with C_2Cl_6 was presented. Furthermore, the novel heterocycle **9** was isolated from the complex reaction between PCl_5 and $Li[PhC(NSiMe_3)_2]$. Compound **9** was shown to undergo a Lewis acid-induced ring contraction to produce the unusual, ring-contracted 6-membered cyclic carbophosphazene adduct **10**. Future work will involve studying the mechanism by which **9** is formed and the factors that govern the possibly general ring contraction of cyclic 8-membered carbophosphazenes. Given the formation of the cyclic species **2** and **3** during the chlorination of the silylated PNCN chain **1**, silyl-terminated derivatives such as $ClPh_2P{=}N-C(Ph){=}NSiMe_3$ likely display a propensity toward self-condensation. This implies a greater reactivity of N-silyl carbophosphazenes when compared to the related N-silyl phosphoranimines, $ClR_2P{=}NSiMe_3$, which can be distilled at elevated temperatures without significant oligomerization.[4,11,12] Future work will concentrate on improving the stability of linear silylated PNCN heterophosphazenes in order to facilitate their use as polymer precursors by controlled condensation polymerization.[7]

Experimental Section

Materials and Instrumentation. All reactions and manipulations were carried out strictly under an atmosphere of prepurified nitrogen or argon gas (BOC) using common Schlenk techniques or an inert atmosphere glovebox (M-Braun). Solvents were dried and collected using a Grubbs-type solvent system manufactured by M-Braun.[36] ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian Gemini 300 spectrometer (300.1 and 121.5 MHz) and were referenced either to protio impurities in the solvent (^1H) or externally to 85% H_3PO_4 ($^{31}P\{^1H\}$) in $CDCl_3$ or D_2O]. $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra were obtained on a Varian Unity 400 spectrometer (100.5 and 79.4 MHz) and were both referenced externally to $SiMe_4$ (TMS) in $CDCl_3$. Mass spectra were obtained with the use of a VG-250S mass spectrometer using a 70 eV electron impact ionization source. Melting points (uncorrected) were obtained in 0.5 mm (o.d.) glass capillaries which were flame sealed under an atmosphere of nitrogen. Elemental analyses were performed at the University of Toronto using a Perkin-Elmer 2400 series CHN analyzer. Dynamic light scattering (DLS) was carried out as described in detail

(31) A series of N-bonded complexes of PNSN heterocycles involving Pt and Pd have been prepared: (a) Chivers, T.; Hilts, R. W. *Inorg. Chem.* **1992**, *31*, 5272. (b) Chivers, T.; Hilts, R. W.; Krouse, I. H.; Cordes, A. W.; Hallford, R.; Scott, S. R. *Can. J. Chem.* **1992**, *70*, 2602. (c) Chivers, T.; Doxsee, D. D.; Hilts, R. W.; Parvez, M. *Can. J. Chem.* **1993**, *71*, 1821.

(32) Rivard, E.; Manners, I. Unpublished results.

(33) Chivers, T.; Fedorchuk, C.; Schatte, G.; Parvez, M. *Inorg. Chem.* **2003**, *42*, 2084.

(34) Compound **2** is stable for indefinite periods of time in chlorinated solvents (CH_2Cl_2 and $CHCl_3$) when no extraneous Lewis acids are present. Rivard, E.; Manners, I. Unpublished results

(35) Previous routes to linear carbophosphazenes of the form $R_3P{=}N-C(Ph){=}NR$ (R = alkyl or aryl) are not amenable to the synthesis of halogenated analogues due to the likely instability of the required precursors (e.g., $[ClPh_2P{=}N]Li$ for the synthesis of **5**). See the following for details: Yoshida, H.; Ogata, T.; Inokawa, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1541.

(36) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

elsewhere.[23] Hexachloroethane, $Li[N(SiMe_3)_2]$, PCl_5, HCl (1.0 M solution in ether), and lithium diisopropylamide (LDA, 2.0 M solution in heptane/THF/ethylbenzene) were purchased from Aldrich and used as received. Ph_2PCl was also purchased from Aldrich and was vacuum distilled prior to use. Benzonitrile was obtained from BDH Chemicals and was dried over P_2O_5 and distilled under nitrogen immediately before use. SO_2Cl_2 (BDH) and was distilled under nitrogen immediately prior to use. $LiN(^tBu)SiMe_3$ was prepared according to a literature procedure.[37]

Preparation of $Ph_2P-N=C(Ph)-N(SiMe_3)_2$ (1). Compound **1** was prepared according to a literature procedure,[14] and crystals suitable for a single-crystal X-ray diffraction experiment were grown from a diethyl ether solution at −30 °C. ^{31}P NMR ($CDCl_3$): 35.2 (s). ^1H NMR ($CDCl_3$): 0.16 (s, 18H, $SiMe_3$), 7.35−7.65 (m, 15H, Ph). $^{13}C\{^1H\}$ ($CDCl_3$): 3.0 (s, $SiMe_3$), 127.9 (s, CH_{aryl}), 128.2 (d, J_{CP} = 6.6 Hz, CH_{aryl}), 128.5 (s, CH_{aryl}), 129.5 (br, CH_{aryl}), 130.2 (s, CH_{aryl}), 132.6 (d, J_{CP} = 21.1 Hz, CH_{aryl}), 140.2 (d, J_{CP} = 5.1 Hz, C_{aryl}), 143.3 (d, J_{CP} = 9.1 Hz, C_{aryl}), 172.6 (d, $^2J_{CP}$ = 20.4 Hz, N*C*N). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): 5.8 (s). Mp (°C): 71.5−72.0 (Et_2O); lit. 71−2 (pentane).[14] EI-MS (70 eV, *m*/*z*, %): 448 (M^+, 1), 433 ($M^+ - Me$, 14), 375 ($M^+ - SiMe_3$, 1), 371 ($M^+ - Ph$, 2), 303 ($M^+ - 2SiMe_3$, 1), 272 ($M^+ - PhCN(SiMe_3)$, 5), 176 ($PhCN(SiMe_3)^+$, 100), 73 ($SiMe_3^+$, 57).

Chlorination of 1 with C_2Cl_6: Isolation of $[Ph_2PNC(Ph)N]_2$ (2) and $[Ph_2PNP(Ph_2)NC(Ph)N]$ (3). A solution of **1** (3.10 g, 6.92 mmol) in 20 mL of Et_2O was cooled to −78 °C, and a solution of C_2Cl_6 (1.64 g, 6.93 mmol) in 15 mL of Et_2O was added dropwise. The initially yellow solution was warmed to room temperature and stirred for 16 h to give a pale beige solution over a white precipitate. Filtration of the reaction mixture followed by removal of the volatiles gave a white solid as the Et_2O-insoluble fraction (1.27 g) along with a pale yellow highly sticky solid (0.38 g) as the Et_2O-soluble fraction. Analysis of the products by ^{31}P NMR spectroscopy identified the previously characterized 8- and 6-membered heterocycles (**2** and **3**) as the products (estimated yield based on ^{31}P NMR spectroscopy and total weight of both fractions: **2**, 27%; **3**, 15%: considerable sample loss occurred during the isolation of the soluble fraction).

Data for Et_2O-Soluble Fraction. ^{31}P NMR ($CDCl_3$): −0.7 (s) (58%, **2**) and 18.4 (s) (42%, **3**). ^1H NMR ($CDCl_3$): 7.2−8.8 (m, Ph). EI-MS (70 eV, *m*/*z*, %): 604 (**2**$^+$, 46), 527 (**2**$^+ - Ph$, 35), 500 (**3**$^+$ and/or **2**$^+ - PhCN$, 100), 424 (**3**$^+ - Ph$, 85), 397 (**3**$^+ - PhCN$, 21), 319 (**3**$^+ - PhCN - Ph$, 40), 180 (Ph_2CN^+, 95), 104 ($PhCN^+$, 93), 77 (Ph^+, 35).

Data for Et_2O-Insoluble Fraction. ^{31}P NMR ($CDCl_3$): −0.7 (s) (90%, **2**) and 18.6 (s) (10%, **3**). ^1H NMR ($CDCl_3$): EI-MS (70 eV, *m*/*z*, %): 604 (**2**$^+$, 37), 527 (**2**$^+ - Ph$, 27), 500 (**3**$^+$ and/or **2**$^+ - PhCN$, 100), 424 (**3**$^+ - Ph$, 67), 397 (**3**$^+ - PhCN$, 26), 319 (**3**$^+ - PhCN - Ph$, 20), 180 (Ph_2CN^+, 65), 77 (Ph^+, 30).

Preparation of $Ph_2P-N=C(Ph)-N(^tBu)SiMe_3$ (4). $LiN(^tBu)SiMe_3$ (1.38 g, 9.12 mmol) was dissolved in 30 mL of Et_2O to give a colorless solution. PhCN (1.10 mL, 10.8 mmol) was then added dropwise to give a yellow solution after 30 min. A solution of Ph_2PCl (1.85 mL, 10.3 mmol) in 5 mL of THF was then slowly added to give a yellow, cloudy mixture. The reaction was stirred overnight (16 h) and filtered. Removal of the volatiles gave a highly viscous yellow oil (3.45 g, 87%). This product was ca. 90% pure by ^1H NMR spectroscopy, and all attempts to obtain an analytically pure sample either by vacuum distillation or by crystallization were unsuccessful. ^{31}P NMR ($CDCl_3$): 38.8 (s). ^1H NMR ($CDCl_3$): 0.38 (s, 9H, $SiMe_3$), 1.18 (s, 9H, ^tBu), 7.0−7.6 (m, 15 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 4.4 (d, $^5J_{CP}$ = 3.8 Hz, $SiMe_3$), 31.9 (s, Me in ^tBu), 54.5 (s, *C*−Me in ^tBu), 127.4 (s, CH_{aryl}), 127.7 (s, CH_{aryl}), 127.9 (d, J_{CP} = 4.5 Hz, CH_{aryl}), 128.1 (br, CH_{aryl}), 128.9 (d, J_{CP} = 3.8 Hz, CH_{aryl}), 131.9 (d, J_{CP} = 19.8 Hz, CH_{aryl}), 138.7 (d, J_{CP} = 6.0 Hz, C_{aryl}), 161.8 (d, $^2J_{CP}$ = 22 Hz, N*C*N). Ph−C(ipso) not located. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): 6.7 (s). EI-MS (70 eV, *m*/*z*, %): 432 (M^+, 3), 417 ($M^+ - Me$, 11), 375 ($M^+ - {}^tBu$, 10), 360 ($M^+ - SiMe_3$, 35), 355 ($M^+ - Ph$, 17), 303 ($M^+ - SiMe_3 - {}^tBu$, 20), 283 ($M^+ - Ph - SiMe_3$, 3), 272 ($M^+ - PhCN(^tBu)$, 50), 262 (Ph_3P^+, 40), 185 (Ph_2P^+, 22), 176 ($PhCN(SiMe_3)^+$, 84), 160 ($PhCN(^tBu)^+$, 66), 104 ($PhCN^+$, 85), 73 ($SiMe_3^+$, 45), 57 ($^tBu^+$, 100). HR-MS (70 eV): $M^+ - Me$ ($C_{25}H_{30}N_2PSi$), calcd 417.1916. Found: 417.1931.

Reaction of 4 with C_2Cl_6: Preparation of $ClPh_2P=N-C(Ph)=N^tBu$ (5). A colorless solution of C_2Cl_6 (1.72 g, 7.27 mmol) in 15 mL of Et_2O was added dropwise to a solution of **4** (3.03 g, 7.00 mmol) at 0 °C. Upon warming the reaction to room temperature, the initially yellow solution became cloudy. The reaction mixture was stirred for 2 h, and the mixture was filtered. Removal of the volatiles gave a viscous, highly lipophilic, yellow oil, which was recrystallized from a 2:1 hexanes/CH_2Cl_2 mixture (−30 °C, 2 weeks) to give X-ray quality colorless crystals (0.78 g, 27%). ^{31}P NMR ($CDCl_3$): 8.9 (br). ^1H NMR ($CDCl_3$): 1.47 (s, 9H, ^tBu), 7.1−7.9 (m, 15 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 29.9 (s, Me in ^tBu), 53.8 (s, *C*−Me in ^tBu), 127.5 (d, J_{CP} = 1.5 Hz, CH_{aryl}), 127.9 (s, CH_{aryl}), 128.6 (d, J_{CP} = 14.5 Hz, CH_{aryl}), 131.4 (d, J_{CP} = 12.2 Hz, CH_{aryl}), 132.4 (br, CH_{aryl}), 132.5 (s, CH_{aryl}), 133.2 (d, J_{CP} = 2.9 Hz, C_{aryl}) 142.6 (d, J_{CP} = 4.7 Hz, C_{aryl}), and 155.7 (d, $^2J_{CP}$ = 9.3 Hz, N*C*N). Mp (°C): 57.5−59.5. MS-EI (70 eV, *m*/*z*, %): 395 ($M^+ + H$, 2), 394 (M^+, 2), 379 ($M^+ - Me$, 48), 360 ($M^+ - Cl + H$, 3), 344 ($M^+ - Me - Cl$, 1), 337 ($M^+ - {}^tBu$, 5), 321 ($M^+ - Me - {}^tBu - H$, 1), 303 ($M^+ - Me - Ph + H$, 1), 276 ($M^+ - Me - PhCN + H$, 9), 235 ($ClPPh_2NH^+$, 85), 220 (Ph_2PCl^+, 8), 201 ($Ph_2PNH_2^+$, 62), 144 ($PhPClH^+$, 36), 122 ($PhPN^+$, 6), 104 ($PhCN^+$, 55), 77 (Ph^+, 100), 57 ($^tBu^+$, 14). Anal. Calcd for $C_{23}H_{24}ClN_2P$: C, 69.96; H, 6.13; N, 7.09. Found: C, 69.96; H, 6.12; N, 6.99.

Preparation of $[ClPh_2P=N-C(Ph)=N(^tBu)H]Cl$ (6). HCl (1.0 M solution in Et_2O, 0.50 mL, 0.50 mmol) was added dropwise to a 4 mL solution of **5** (0.19 g, 0.48 mmol) in CH_2Cl_2. The reaction mixture was stirred for 1 h, whereby the initially clear, pale yellow solution went somewhat cloudy. Removal of the volatiles afforded **6** (0.14 g, 67%) as a white solid. Crystals suitable for single-crystal X-ray crystallography were grown from slow evaporation of a solution of **6** in 1:1 hexanes/CH_2Cl_2. ^{31}P NMR ($CDCl_3$): 32.9 (br). ^1H NMR ($CDCl_3$): 1.66 (s, 9H, ^tBu), 7.3 and 7.6−7.8 (m, 15 H, Ph), 11.6 (br, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 28.7 (s, Me in ^tBu), 56.4 (s, *C*−Me in ^tBu), 128.2 (s, CH_{aryl}), 128.3 (s, CH_{aryl}), 129.7 (d, J_{CP} = 15.2 Hz, CH_{aryl}), 131.3 (d, J_{CP} = 12.1 Hz, CH_{aryl}), 131.5 (s, CH_{aryl}), 134.7 (d, J_{CP} = 3.1 Hz, CH_{aryl}), 169.4 (br, N*C*N). Ipso Ph−C and Ph−P not located. Mp (°C): 56−58. Anal. Calcd for $C_{23}H_{25}Cl_2N_2P$: C, 64.04; H, 5.84; N, 6.49. Found: C, 63.43; H, 5.96; N, 6.36.

Preparation of $Ph_2P-N=C(Ph)-N^iPr_2$ (7). PhCN (1.7 mL, 17 mmol) was added dropwise to a solution of LiN^iPr_2 (8.0 mL, 2.0 M solution in heptane/THF/ethylbenzene, 16 mmol) in 20 mL of THF at −78 °C, and the reaction mixture was stirred for 1 h to give a tan colored suspension. Ph_2PCl (2.90 mL, 16.2 mmol) was then added dropwise to give a clear orange solution. The mixture was warmed to room temperature and stirred for 1 h and then concentrated to a volume of 5 mL. Diethyl ether (50 mL) was added and the resulting solution was filtered. Removal of the volatiles from the filtrate produced a yellow oil that gradually crystallized (15 °C) over a period of 24 h to give bright yellow needles of **7**

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(4.92 g, 79%). ^{31}P NMR (C_6D_6): 41.7 (s). ^{1}H NMR (C_6D_6): 0.80 (v br, Me in ^{i}Pr, 6H), 1.80 (v br, Me in ^{i}Pr, 6H), 3.50 (v br, CH in ^{i}Pr, 2H), 7.0−7.8 (m, Ph) and 7.8−8.1 (m, Ph). ^{13}C{^{1}H} (C_6D_6): 20.5 (s, Me in ^{i}Pr), 46.4 (br, CH in ^{i}Pr), 50.4 (br, CH in ^{i}Pr), 126.3 (d, J_{CP} = 3.4 Hz, CH_{aryl}), 127.6 (d, J_{CP} = 13.2 Hz, CH_{aryl}), 127.7 (s, CH_{aryl}), 127.8 (s, CH_{aryl}), 128.2 (s, CH_{aryl}), 138.3 (d, J_{CP} = 9.8 Hz, C_{aryl}), 146.4 (d, J_{CP} = 16.1 Hz, C_{aryl}), 166.2 (d, $^2J_{CP}$ = 29.8 Hz, N*C*N). Mp (°C): 84−86. EI-MS (70 eV, *m*/*z*, %): 388 (M^+, 46), 345 ($M^+ - {}^i$Pr, 50), 311 (M^+ − Ph, 15), 303 ($M^+ - 2\ {}^i$Pr, 4), 288 ($M^+ - N^iPr_2$, 4), 285 (M^+ − PhCN, 10), 242 (M^+ − PhCN − ^{i}Pr, 14), 228 ($Ph_2P^iPr^+$, 30), 185 (Ph_2P^+, 100), 104 ($PhCN^+$, 47), 100 ($N^iPr_2^+$, 60). HR-MS (70 eV): M^+ ($C_{25}H_{29}N_2P$), calcd: 388.2068. Found: 388.2070. Anal. Calcd for $C_{25}H_{29}N_2P$: C, 77.29; H, 7.52; N, 7.21. Found: C, 76.51; H, 7.17; N, 7.82.

Chlorination of 7 with C_2Cl_6: Preparation of [$ClPh_2P$═N═C(Ph)−N^iPr_2]Cl (8). To a solution of **7** (0.30 g, 0.77 mmol) in 10 mL of Et_2O was added a 1 mL solution of C_2Cl_6 (0.19 g, 0.80 mmol) in ether. Upon the addition of hexachloroethane, a pale yellow precipitate was observed. Fresh diethyl ether (15 mL) was then added to the suspension, and the reaction mixture was stirred for 30 min. The precipitate was allowed to settle and the mother liquor (colorless) was decanted to afford a pale yellow solid. This material was dissolved in a minimum of CH_2Cl_2, and an equal volume of Et_2O was carefully layered on top. Cooling to −30 °C for 1 week produced large well-formed yellow blocks of **8** (0.24 g, 67%). ^{31}P{^{1}H} NMR ($CDCl_3$): 37.1 (s). ^{1}H NMR ($CDCl_3$): 1.31 (d, J = 6.6 Hz, Me in ^{i}Pr, 6H), 1.78 (d, J = 6.6 Hz, Me in ^{i}Pr, 6H), 3.95 (m, CH in ^{i}Pr, 1H), 4.10 (m, CH in ^{i}Pr, 1H), 7.1−7.7 (m, Ph, 15 H). ^{13}C{^{1}H} NMR ($CDCl_3$): 20.1 (s, Me in ^{i}Pr), 20.4 (s, Me in ^{i}Pr), 49.9 (s, CH in ^{i}Pr), 55.5 (s, CH in ^{i}Pr), 125.3 (s, CH_{aryl}), 129.7 (s, CH_{aryl}), 130.0 (d, J_{CP} = 15.3 Hz, CH_{aryl}), 131.0 (s, C−Ph, ortho or meta), 131.3 (d, J_{CP} = 12.6 Hz, CH_{aryl}), 132.3 (d, P−Ph, J_{PC} = 8.3 Hz, CH_{aryl}), 135.1 (s, CH_{aryl}), 168.6 (br, N*C*N). Ipso C (C−Ph) not located. Mp (°C): 76−79. Anal. Calcd for $C_{25}H_{29}Cl_2N_2P$: C, 65.36; H, 6.36; N, 6.10. Found: C, 65.22. H, 6.81; N, 5.96.

Preparation of [(Cl_3P═N)ClPNC(Ph)NP(Cl_2)NC(Ph)N] (9). To a cold (−78 °C) solution of Li[PhC($NSiMe_3$)$_2$] (31.1 mmol; generated in situ from 5.20 g of LiN($SiMe_3$)$_2$ and 3.2 mL of PhCN in 250 mL of Et_2O, 3 h at room temperature) was added PCl_5 (6.48 g, 31.1 mmol) portionwise over 20 min. The resulting yellow mixture was warmed to room temperature and stirred for 4 h. ^{31}P NMR spectroscopy showed a broad signal centered at 42 ppm along with numerous sharpened resonances superimposed on a broad halo from 5 to −10 ppm. Filtration of the reaction mixture followed by the removal of the volatiles gave a viscous yellow oil. Extraction of the oil into 10 mL of Et_2O and subsequent precipitation into vigorously stirring hexanes (200 mL) gave a yellow tacky solid along with a colorless supernatant. The precipitate was isolated by filtration, dried in vacuo, and redissolved in 5 mL of CH_2Cl_2. This solution was precipitated into 250 mL of hexanes to give a fibrous yellow solid when isolated and dried (1.45 g, see below for characterization). The hexanes−soluble fractions from the above precipitations were combined and the volatiles were removed to give a pale yellow residue. Dissolution of the residue into a 1:1 toluene/CH_2Cl_2 mixture, followed by cooling to −40 °C, afforded colorless blocks of **9** (0.30 g, 5%). ^{31}P NMR ($CDCl_3$): 1.6 (d, $^4J_{PP}$ = 4.5 Hz, −*P*Cl_2−), −0.2 (d of d, $^2J_{PP}$ = 35.6 Hz; $^4J_{PP}$ = 4.5 Hz, −N(Cl_3P═N)*P*ClN−), −2.1 (d, br, $^2J_{PP}$ = 34 Hz, Cl_3*P*═N−). ^{13}C-{^{1}H} NMR ($CDCl_3$): 128.1 (s, CH_{aryl}), 130.6 (s, CH_{aryl}), 132.8 (s, CH_{aryl}), 137.8 (t, $^3J_{CP}$ = 25 Hz, C_{aryl}). The resonance for N*C*N was not located. ^{1}H NMR ($CDCl_3$): 7.4−7.6 (m), 8.3 (m). Mp (°C): 146−151 (dec). EI-MS (70 eV, *m*/*z*, %): 553 (M^+, 1), 518 (M^+ − Cl, 1), 450 (M^+ − PhCN, 1), 415 (M^+ − PhCN − Cl, 2), 103 ($PhCN^+$, 100), 73 (Ph^+, 42). Anal. Calcd for $C_{14}H_{10}Cl_6N_5P_3$: C, 30.36; H, 1.82; N, 12.64. Found: C, 30.41; H, 1.86; N, 12.36.

Data for Precipitated Material. ^{31}P NMR ($CDCl_3$): 42.3 (br) and many signals from 10 to −30 ppm (br). ^{1}H NMR ($CDCl_3$): 7.3 (br, Ph) and 8.3 (br, Ph). DLS (CH_2Cl_2, 50 mg/mL, under N_2): observed hydrodynamic radii < 0.5 nm; therefore the material was of very low molecular weight.[23]

Synthesis of [(Cl_3P═N)ClPNP(Cl_2)NC(Ph)N]·$GaCl_3$ (10). $GaCl_3$ (19 mg, 0.11 mmol) and **9** (57 mg, 0.10 mmol) were allowed to react in 1.5 mL of CH_2Cl_2 for 16 h. Hexanes (1.5 mL) were added to the resulting colorless solution until clouding was observed. The solution was slowly allowed to evaporate under an atmosphere of nitrogen. Within 2 days, colorless needles were obtained, which were isolated and washed with hexanes (2 × 2 mL) and dried to afford the 6-membered heterocycle **10** (26 mg, 42%). ^{31}P{^{1}H} NMR ($CDCl_3$): 4.0 (d, $^2J_{PP}$ = 46.0 Hz), 9.4 (br) and 40.3 (br). ^{1}H NMR ($CDCl_3$): 7.5−8.3 (m, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): 128.6 (d, J_{CP} = 13.2 Hz, CH_{aryl}), 130.0 (s, CH_{aryl}), 130.5 (s, CH_{aryl}) and 134.6 (br, C_{aryl}). The resonance for N*C*N was not located. EI-MS (70 eV, *m*/*z*, %): 450 (M^+ − $GaCl_3$, 22), 415 (M^+ − $GaCl_3$ − Cl, 65), 312 (M^+ - $GaCl_3$ − Cl − PhCN, 31), 176 ($GaCl_3^+$, 3), 103 ($PhCN^+$, 100), 76 (Ph^+, 43). Anal. Calcd for $C_7H_5Cl_9GaN_4P_3$: C, 13.41; H, 0.80; N, 8.94. Found: C, 14.61; H, 0.92; N, 8.85.

Single-Crystal X-ray Structural Determination of 1, 5, 6, and 8−10. Data were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A combination of 1° ϕ and ω (with κ offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.[38] The structures were solved and refined with the SHELXTL-PC v6.12 software package.[39] Refinement was by full-matrix least squares on F^2 using data (including negative intensities) with hydrogen atoms bonded to carbon atoms included in calculated positions and treated as riding atoms, while those attached to nitrogen were located and refined with isotropic parameters. All molecular structures are presented with thermal ellipsoids at the 30% probability level.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1**, **5**, **6**, **8**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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