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Probing the Mechanism of the PCl_5−Initiated Living Cationic Polymerization of the Phosphoranimine $Cl_3P{=}NSiMe_3$ using Model Compound Chemistry

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Abstract: New insight into the mechanism of the ambient temperature PCl_5-initiated living cationic chain growth polycondensation of the *N*-silylphosphoranimine $Cl_3P{=}NSiMe_3$ (**1**) to give poly(dichlorophosphazene), $[N{=}PCl_2]_n$, has been provided by studies of model compound chemistry. Investigations of the reactivity of Cl^- salts of the proposed cationic intermediates $[Cl_3P{=}N{=}PCl_3]^+$ ([**2**]$^+$) and $[Cl_3P{=}N{-}PCl_2{=}N{=}PCl_3]^+$ ([**6**]$^+$) toward $Ph_3P{=}NSiMe_3$ (**3a**) provided evidence that under the usual polymerization conditions that involve a high monomer to initiator ratio, propagation occurs at both chain ends. However, analogous studies of near stoichiometric processes suggested that propagation is faster at one chain end, particularly when the chains are short. In addition, experiments involving $[Ph_3P{=}N{=}PPh_3][PCl_6]$ ([**9**][PCl_6]) and the *N*-silylphosphoranimines $R_3P{=}NSiMe_3$ **3a** (R = Ph) and **3b** (R = *p*-$CF_3C_6H_4$), showed that the $[PCl_6]^-$ anion, which is formed in the early stages of the polymerization and has hitherto been assumed to be an innocent spectator counteranion, is actually reactive under the reaction conditions and can initiate oligomerization and polymerization. Finally, the absence of reactions between phosphoranimines **3b** or **1** with the Cl^- salts of the cations $[Ph_3P{=}N{-}PCl_2{=}N{=}PPh_3]^+$ ([**10a**]$^+$), $[Ph_3P{=}N{-}(PCl_2{=}N)_2{=}PPh_3]^+$ ([**5**]$^+$), and $[Ph_3P{=}N{-}(PCl_2{=}N)_3{=}PPh_3]^+$ ([**8**]$^+$) with P−Cl bonds located internally but not at the chain ends have shown that chain branching reactions are unlikely to be significant during the polymerization. These results identify key factors that complicate the living PCl_5-initiated chain growth polycondensation of **1** and potentially lead to a loss of control over molecular weight and broaden the molecular weight distributions, but also indicate that the polymer formed is essentially linear rather than branched.

Introduction

Living polymerizations are important synthetic protocols as the absence of chain transfer and chain termination reactions combined with rapid initiation allows the preparation of polymeric materials with molecular weight control and narrow molecular weight distributions and also multiblock and star architectures.[1] Examples of living polymerizations are mainly limited to chain growth addition and ring-opening processes and involve highly reactive anionic, cationic, radical, or organometallic propagating centers. However, living chain growth polycondensations that are formally analogous to the biological synthesis of proteins from amino acids have also recently been identified.[2] In general, living polymerization processes are well-developed for organic macromolecules whereas for inorganic polymers few examples are known. The anionic polymerization of phosphaalkenes,[3] and the anionic ring-opening polymerization of cyclic siloxanes[4] and strained ferrocenophanes[5] provide rare, well-established examples. The development of new living polymerization routes to inorganic macromolecules is of key importance as it provides a method to prepare well-defined hybrid polymers with controlled architectures that are of interest as functional nanostructured materials.[6]

Polyphosphazenes, $[N{=}PR_2]_n$, are an interesting class of inorganic polymers with uses as high performance elastomers,[7] polymeric electrolytes,[8] and biomedical membranes[9] and with much potential as functional materials for a variety of other applications.[10] The most well-known synthetic route to these materials that opened up the field in the 1960s involves the thermal ring-opening polymerization (ROP) of hexachlorocyclotriphosphazene, $(N{=}PCl_2)_3$, at *ca.* 200−250 °C. This yields poly(dichlorophosphazene), $[N{=}PCl_2]_n$, a versatile reactive intermediate in the formation of a large number of polyphos-

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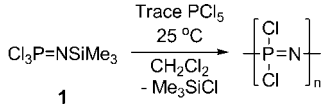
phazenes *via* subsequent nucleophilic substitution reactions.[11] This ROP reaction may also be carried out at room temperature by employing trialkylsilyl carboranes as initiators.[12] An alternative, thermally induced condensation polymerization route to $[N{=}PCl_2]_n$ involves heating the (*N*-phosphoryl)trichlorophosphoranimine $Cl_3P{=}NP(O)Cl_2$ at *ca.* 250 °C, which proceeds with the elimination of $POCl_3$.[13] A wide range of polyphosphazenes such as $[N{=}PMe_2]_n$ and $[N{=}P(OCH_2CF_3)_2]_n$ have also been prepared *via* the condensation polymerization of organo- and alkoxyphosphoranimines (e.g., $RR'(RO)P = NSiMe_3$ and $(RO)_3P = NSiMe_3$),[14] which can be achieved at 100−180 °C and in some cases at ambient temperature.[15] Nevertheless, most of these synthetic routes to polyphosphazenes involve elevated temperatures and the polymerizations are often slow, the yields are moderate, and none, at present, provide easy control of molecular weight and the molecular weight distributions are broad. New and controlled synthetic approaches to polyphosphazenes that proceed under mild conditions are therefore of considerable interest in order to lower costs and to provide access to well-defined structures (e.g., block copolymers)[6,16] to facilitate more widespread development.

In the mid-1990s we and Allcock and co-workers reported the synthesis of poly(dichlorophosphazene) *via* the living cationic chain growth polycondensation of the trichloro(*N*-silyl)phosphoranimine, $Cl_3P{=}NSiMe_3$ (**1**), initiated by catalytic amounts of PCl_5 (Scheme 1).[17−19] This method, the first example

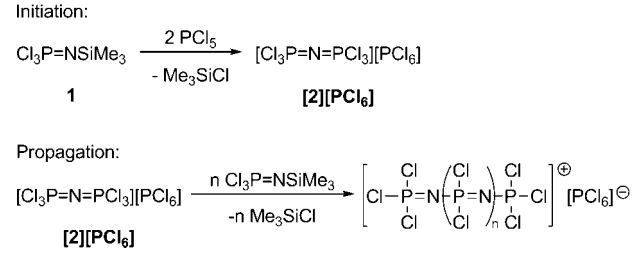
Scheme 1



of a living chain growth polycondensation process,[20] is potentially advantageous over previous routes to $[N{=}PCl_2]_n$ because it occurs at ambient temperature, allows reasonable control of the molecular weight through changes to the monomer to initiator ratio, and forms $[N{=}PCl_2]_n$ in high yield with a relatively narrow molecular weight distribution (PDI = 1.1 - 1.3, up to M_n = *ca.* 60 000). This living polymerization route also provides access to polyphosphazene block copolymers *via* sequential monomer addition.[21,22]

The initiation step for the PCl_5-initiated living cationic polymerization of **1** appears to involve the reaction of one molecule of monomer with two molecules of PCl_5 to produce the species $[Cl_3P{=}N{=}PCl_3][PCl_6]$ ($[\mathbf{2}][PCl_6]$).[17,19,23,24] Propagation by cationic chain growth is proposed to proceed *via* reaction of the cation $[\mathbf{2}]^+$ in $[\mathbf{2}][PCl_6]$ with **1** until all the monomer is consumed to yield a living polymer together with Me_3SiCl, the condensation byproduct (Scheme 2).

Scheme 2



An improved, high yield one-pot synthesis of the phosphoranimine monomer **1**[25] from PCl_3 has facilitated the development of the living cationic route to poly(dichlorophosphazene) as well as novel molecular chemistry.[24,26,27] In addition, recently it has been shown that it is possible to prepare $[N{=}PCl_2]_n$ directly from PCl_3 using a one-pot route at ambient temperature and pressure although the process is not living, the yield is lower, and the molecular weight distribution broader than for the PCl_5-initiated process using isolated **1**.[28]

Although the room temperature living cationic chain growth polymerization of **1** is highly promising route to polyphosphazenes with controlled architectures further improvements are desirable and mechanistic understanding is incomplete. For example, the cationic propagating site in the living polyphosphazene chain (see Scheme 2) is potentially capable of delocalization and it is possible (or even probable) that chain growth may occur at either chain end. Indeed, such bidirectional chain growth involving two propagating sites is suggested by the observation that the molecular weights of polyphosphazenes prepared from **1** using the living cationic polymerization method with PCl_5 as initiator are often approximately double those predicted by the initiator:monomer ratio.[18] In contrast, some recent studies of model reactions of [**2**]Cl with a stoichiometric

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amount of **1** suggested that only one chain end may be active.[24] Another potential complication is the presence of the $[PCl_6]^-$ counteranion, which possesses P−Cl bonds and might also be reactive toward **1**. It is also possible that interior P−Cl bonds in the resulting polyphosphazene $[N{=}PCl_2]_n$ may react with **1** to yield a branched rather than a strictly linear product.

In this paper we use model compound chemistry in order to probe fundamental and unresolved issues concerning the mechanism for the living cationic polymerization of **1.** Our ultimate aim is to facilitate further improvements in the molecular weight control and polydispersity achievable for polyphosphazene homopolymer and block copolymers that can be prepared using this very promising process.

Results

1. Bidirectional versus Monodirectional Chain Growth. Living polymerizations are capable of yielding polymer with a PDI close to 1.0. If the living cationic polymerization of **1** initiated by PCl_5 is indeed bidirectional, and the two propagation sites exhibit different and chain length-dependent reactivity, this might provide an explanation for the non-optimal PDIs of polyphosphazene homopolymers and block copolymers prepared by this route which often reach values of 1.3 or more.[18,21] To provide insight into whether chain growth is mono- or bidirectional we studied the reactions of [**2**]Cl with the chain-terminating triphenyl(*N*-trimethylsilyl)phosphoranimine, $Ph_3P{=}NSiMe_3$ (**3a**), which, unlike **1**, can add to an active chain end only once. The absence of P−Cl bonds in **3a** means that growth of the phosphazene chain would be halted, resulting in oligomers with end groups that should be readily detectable by $^{31}P\{^1H\}$ NMR spectroscopy. This was anticipated to allow more definitive results than were apparent in previous studies of the reaction of [**2**]Cl with **1** which, although suggestive of monodirectional chain growth, led to complex oligomer mixtures that were difficult to analyze.[24] The use of [**2**]Cl rather than [**2**][PCl_6] for these studies removes potential complications associated with the reactivity of the P−Cl bonds in the $[PCl_6]^-$ anion, an issue to which we will return.

(a) Reaction of [2]Cl with One Equivalent of $Ph_3P{=}NSiMe_3$ (3a). When one equivalent of the *N*-silylphosphoranimine **3a** was added to a suspension of [**2**]Cl in CH_2Cl_2 a clear and colorless solution was observed within 10 min. After 1.5 h $^{31}P\{^1H\}$ NMR analysis revealed the consumption of **3a** (δ 0.7) and the quantitative formation of the five-membered chain $[Ph_3P{=}N{-}PCl_2{=}N{=}PCl_3]Cl$ ([**4**]Cl) (Scheme 3) with resonances at δ −15.1 ppm (dd, $^2J_{PP}$ = 13.0 Hz, $^2J_{PP}$ = 27.9 Hz, $N{=}PCl_2$), 7.3 ppm (d, $^2J_{PP}$ = 27.9 Hz, $N{=}PCl_3$) and 23.3 ppm (d, $^2J_{PP}$ = 13.0 Hz, $Ph_3P{=}N$). This product corresponds to the exclusive reaction of **3a** with one phosphorus chain end of [**2**]$^+$. Significantly, no product was detected corresponding to the reaction of **3a** with both of the phosphorus chain ends of [**2**]Cl, which would model bidirectional chain growth. Recrystallization from a mixture of CH_2Cl_2/hexane (3:1) resulted in the formation of colorless blocks (75% yield) of [**4**]Cl suitable for an X-ray diffraction study (Figure 1).

Scheme 3

$$[Cl_3P{=}N{=}PCl_3]Cl \;(\textbf{[2]Cl}) + Ph_3P{=}NSiMe_3\;(\textbf{3a}) \xrightarrow{-\,Me_3SiCl} [Ph_3P{=}N{-}PCl_2{=}N{=}PCl_3]Cl\;(\textbf{[4]Cl})$$

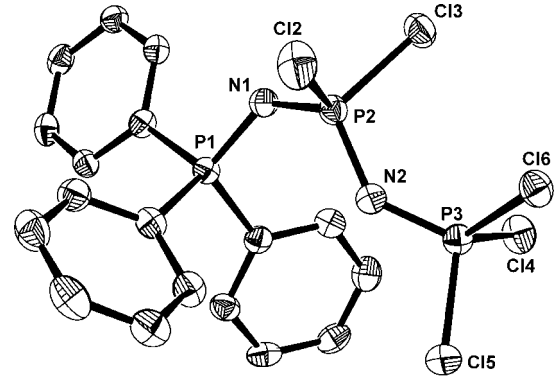


Figure 1. Molecular structure of the cation in [**4**]Cl with thermal ellipsoids at the 50% probability level. Hydrogen atoms and the counterion are omitted for clarity.

The five-membered cationic phosphazene chain [**4**]$^+$ was found to adopt a *cis*−*trans* geometry with an acute central N1−P2−N2 angle of 116.91(14)° and widened terminal P−N−P angles of 127.98(16) and 138.36(19)°, respectively; similar bond angles are found in $[N{=}PCl_2]_n$.[29] All three P atoms adopt a distorted tetrahedral geometry. The P1−N1 bond length of 1.616(3) Å, is slightly longer than the P−N bond lengths found in $[Ph_3P{=}N{=}PPh_3]^+$ (1.575(6) and 1.583(6) Å).[30] The other P−N bond lengths, which range from 1.543(3) to 1.577(3) Å, coincide relatively well with those found in $[Cl_3P{=}N{-}PCl_2{=}N{=}PCl_3]Cl$ [1.531(3) to 1.561(2) Å].[24] The lower electronegativity of phenyl groups compared to chlorine substituents causes lengthening of the P1−N1 bond compared to other P−N bonds. The Cl^- counteranion lies 5.07 Å from P1, and at its closest point it lies 5.05−5.12 Å from the P3 atoms of three different oligomers, and 4.91 Å from the P1 atom of a fourth oligomer.

The key result from this reaction is that the *N*-silylphosphoranimine **3a** reacts preferentially with one end of the initiator, [**2**]Cl. This suggests that the propagation step of the cationic polymerization of **1** is faster at one end and is preferentially monodirectional (Scheme 4, route 1). If both phosphorus centers in [**2**]Cl were equally reactive, a 50:50 mixture of the phosphazene oligomer capped at either end by PPh_3 groups ([**5**]Cl) and unreacted [**2**]$^+$ would have been obtained (Scheme 4, route 2).

Scheme 4

$$[Cl_3P{=}N{=}PCl_3]Cl\;(\textbf{[2]Cl}) + Ph_3P{=}NSiMe_3\;(\textbf{3a}) \xrightarrow[-\,Me_3SiCl]{\text{Route 1}} [Cl_3P{=}N{-}PCl_2{=}N{=}PPh_3]Cl\;(\textbf{[4]Cl})$$

$$[Cl_3P{=}N{=}PCl_3]Cl\;(\textbf{[2]Cl}) + Ph_3P{=}NSiMe_3\;(\textbf{3a}) \xrightarrow[-\,Me_3SiCl]{\text{Route 2}} 0.5\,[Ph_3P{=}N{-}PCl_2{-}N{=}PCl_2{=}N{=}PPh_3]Cl\;(\textbf{[5]Cl})$$

(b) Reaction of [2]Cl with Two Equivalents of $Ph_3P{=}NSiMe_3$ (3a). Polymerization of **1** involves the reaction of $[\mathbf{2}]^+$ with a large excess rather than a stoichiometric amount of the phosphoranimine. Therefore to provide further insight into the reactivity of the chain ends two equivalents of phosphoranimine **3a** were reacted with [**2**]Cl in CH_2Cl_2. After 3 h $^{31}P\{^1H\}$ NMR analysis indicated the formation of [**5**]Cl (Scheme 5) by an AA′XX′ spin pattern with chemical resonances centered at δ −16.7 ppm (N=*P*Cl_2), and 20.1 ppm (Ph_3*P*=N) in which J_{AX} = 14.1 Hz, $J_{AX'}$ = 1.6 Hz, $J_{AA'}$ = 27.8 Hz and $J_{XX'}$ = 0 Hz.[31] The same product was also formed when an equimolar quantity of **3a** was reacted with [**4**]Cl prepared *in situ*.

Scheme 5

$$[Cl_3P{=}N{=}PCl_3]Cl + 2\ Ph_3P{=}NSiMe_3 \xrightarrow[-2\ Me_3SiCl]{} [Ph_3P{=}N\text{-}PCl_2{=}N\text{-}PCl_2{=}N{=}PPh_3]Cl$$

[2]Cl **3a** **[5]Cl**

When the reaction of two equivalents of **3a** with [**2**]Cl was monitored by $^{31}P\{^1H\}$ NMR the formation of both [**4**]Cl and [**5**]Cl were observed (*ca.* 40% and 60%, respectively by integration) in the reaction solution within 5 min. Over a period of 50 min [**4**]Cl was completely converted to [**5**]Cl (Figure 2). The formation of [**5**]Cl suggests that the polymerization of **1** would not be expected to be *exclusively* monodirectional and that in the presence of excess monomer under normal polymerization conditions bidirectional chain growth from **1** with different rates would be expected. This behavior is likely a consequence of preferential ion pairing at one end of the growing polymer chain in solution.[32]

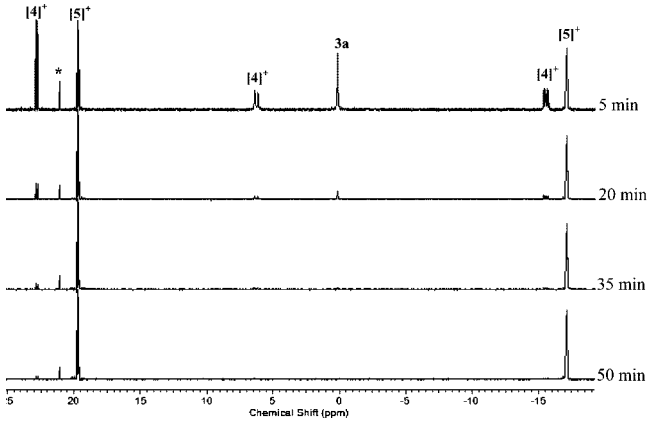


Figure 2. $^{31}P\{^1H\}$ NMR of reaction of [**2**]Cl with 2 equivalents of **3a**. * Hydrolysis product.

Attempts to grow single crystals of [**5**]Cl for X-ray analysis were unsuccessful. To improve crystallizability, [**5**]Cl was converted to the $[PCl_6]^-$ salt by addition of a single equivalent of PCl_5. Single crystals of [**5**][PCl_6] as a CH_2Cl_2 solvate were obtained by slow diffusion of hexane into a dichloromethane solution (1:3) of [**5**][PCl_6] (43% yield; Figure 3).

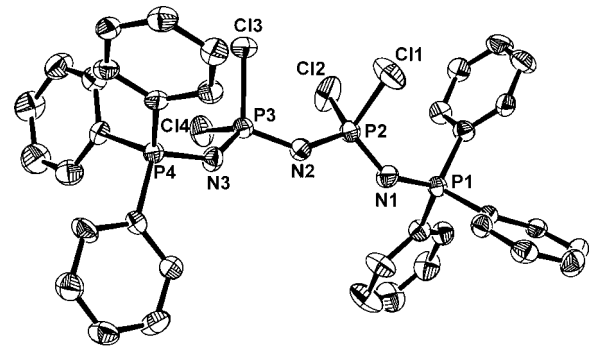


Figure 3. Molecular structure of the cation in [**5**][PCl_6].CH_2Cl_2 with thermal ellipsoids at the 50% probability level. Hydrogen atoms, the counterion, and the CH_2Cl_2 solvate molecule are omitted for clarity.

Unlike the five-membered chain [**4**]Cl, [**5**][PCl_6] adopts an all *trans* geometry, this may be related to the counterion as $[Cl_3P{=}N{-}PCl_2{=}N{-}PCl_2{=}N{=}PCl_3][PCl_6]$ has a planar *trans-trans* geometry[33] while the Cl^- analogue has a *cis*−*trans* geometry.[24] The P1−N2 and P4−N3 bond lengths [1.605(6) and 1.601(6) Å respectively] are slightly elongated in comparison to the other P−N bond lengths which range from 1.523(7) to 1.561(6) Å. The P−N−P bond angles [136.1(4) − 138.9(4)°] are widened in comparison to the N−P−N angles [both 112.9(3)°]. The $[PCl_6]^-$ counteranion lies 5.98 - 6.08 Å from P2−P4 and 7.10 Å from P1 of the same chain, however it lies only 6.76 Å from P1 of an adjacent chain.

(c) Reactions of $[Cl_3P{=}N{-}PCl_2{=}N{=}PCl_3]Cl$ ([6]Cl) with One or Two Equivalents of $Ph_3P{=}NSiMe_3$ (3a). In order to gain insight into the relative reactivity of the propagating chain ends as a function of chain length we studied the analogous reactions of **3a** with the 5 membered chain $[Cl_3P{=}N{-}PCl_2{=}N{=}PCl_3]Cl$, [**6**]Cl (Scheme 6). The latter species has the advantage of being much more soluble than the 3-membered chain [**2**]Cl.

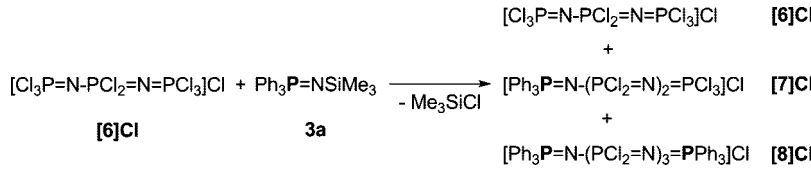
When a CH_2Cl_2 solution of one equivalent of **3a** was added to a solution of [**6**]Cl after 1 h $^{31}P\{^1H\}$ NMR analysis showed the complete consumption of **3a** and the formation of the 7-membered chain, $[Ph_3P{=}N{-}(PCl_2{=}N)_2{=}PCl_3]Cl$ ([**7**]Cl), as the major product (*ca.* 75%) corresponding to preferential reaction at one end of $[\mathbf{6}]^+$. However, the starting 5-membered chain [**6**]Cl was also observed (*ca.* 10%), as were resonances assigned to the 9-membered chain $[Ph_3P{=}N{-}(PCl_2{=}N)_3{=}PPh_3]Cl$ ([**8**]Cl) formed by the reaction of **3a** with both -PCl_3 end groups of [**6**]Cl (15%) (Scheme 7). The presence of $[\mathbf{8}]^+$ and the incomplete consumption of $[\mathbf{6}]^+$ indicate that, although chain growth is preferentially monodirectional resulting in the formation of $[\mathbf{7}]^+$, some bidirectional chain growth does occur to produce $[\mathbf{8}]^+$.

Scheme 6

$$[Cl_3P{=}N\text{-}PCl_2{=}N{=}PCl_3]Cl + x\ Ph_3P{=}NSiMe_3 \longrightarrow \begin{cases} x = 1 \rightarrow [Ph_3P{=}N\text{-}(PCl_2{=}N)_2{=}PCl_3]Cl \ (\mathbf{[7]Cl}) \ (-Me_3SiCl) \\ x = 2 \rightarrow [Ph_3P{=}N\text{-}(PCl_2{=}N)_3{=}PPh_3]Cl \ (\mathbf{[8]Cl}) \ (-2\ Me_3SiCl) \end{cases}$$

[6]Cl **3a**

Scheme 7



The reaction of **3a** with [**6**]Cl was also performed using 2.1 equivalents of the phosphoranimine and this reaction resulted in the exclusive formation of [**8**]Cl. When the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy all three species [**6**]Cl, [**7**]Cl and [**8**]Cl were observed simultaneously in solution immediately after the addition of **3a** (Figure 4).[34] Over a period of *ca.* 20 min, the starting material [**6**]Cl, and [**7**]Cl were both consumed to form [**8**]Cl.

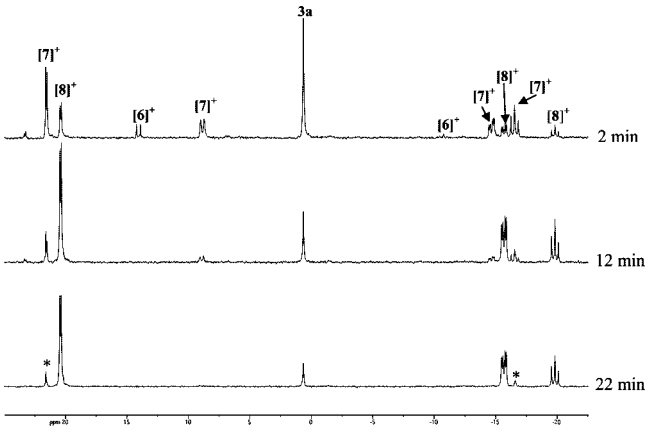


Figure 4. $^{31}P\{^1H\}$ NMR of reaction of [**6**]Cl with 2.1 equivalents of **3a**. * Hydrolysis product.[34]

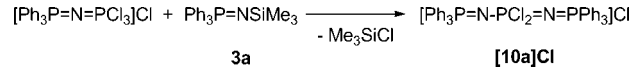
These observations indicate that when the phosphazene chain in the cationic initiator is longer, bidirectional chain growth is more favorable. Thus reaction at both ends of the cationic initiating species is detected when one equivalent of phosphoranimine **3a** is added to the 5-membered cationic initiator $[\mathbf{6}]^+$, in contrast to the case where the 3-membered chain initiator $[\mathbf{2}]^+$ was used under the same conditions. These results suggest that during the PCl_5-initiated cationic polymerization of $Cl_3P{=}NSiMe_3$ bidirectional chain growth would be expected to become increasingly dominant as the chains increase in length.

2. Studies of the Reactivity of the $[PCl_6]^-$ Anion. The $[PCl_6]^-$ counterion is formed as part of the initiation step in the PCl_5-initiated polymerization of **1** (Scheme 2).[17,24] Gas phase studies suggest that $[PCl_6]^-$ is close to the stability threshold so dissociation is possible.[35] The $[PCl_6]^-$ anion contains P−Cl bonds that may be reactive toward **1** and could result in side reactions during the polymerization, thereby decreasing molecular weight and architectural control. To investigate this potential reactivity we carried out reactions between the salt $[Ph_3P{=}N{=}PPh_3][PCl_6]$ ([**9**][PCl_6]), with an inert countercation devoid of P−Cl bonds, and the *N*-silylphosphoranimines **3a**, **3b**, and **1**.

(a) Reactions of $[Ph_3P{=}N{=}PPh_3][PCl_6]$ ([9]PCl_6) with $R_3P{=}NSiMe_3$ (3a R = Ph; 3b R = *p*-$CF_3C_6H_4$; 1 R = Cl). The salt [**9**][PCl_6] was prepared from the commercially available chloride salt by reaction with PCl_5. $^{31}P\{^1H\}$ NMR spectroscopy after 1 h confirmed the complete consumption of PCl_5 and the clean formation of [**9**][PCl_6]. A stoichiometric amount of [**9**][PCl_6] was reacted with the *N*-silylphosphoranimine **3a** in CH_2Cl_2. After 1 h $^{31}P\{^1H\}$ NMR analysis of the reaction solution showed the complete consumption of **3a** and the quantitative formation of a new species with peaks at δ 18.9 ppm (d, $^2J_{PP}$ = 10.4 Hz) and δ −13.3 ppm (t, $^2J_{PP}$ = 10.4 Hz). In addition, a singlet resonance at δ −296.3 ppm was present, indicative of some remaining $[PCl_6]^-$ anions. The structure of the product was assigned as the cationic phosphazene oligomer $[Ph_3P{=}N{-}PCl_2{=}N{=}PPh_3]^+$ ($[\mathbf{10a}]^+$) with mixed $[PCl_6]^-$ or Cl^- counteranions based on the reaction stoichiometry, which implied that only one equivalent of the $[PCl_6]^-$ anion in [**9**][PCl_6] was consumed (Scheme 8).

The structure of the cation $[\mathbf{10a}]^+$ in the product was confirmed by an alternative synthesis (Scheme 9) of a spectroscopically identical species from the reaction of **3a** with $[Ph_3P{=}N{=}PCl_3]Cl$,[27] which was prepared from Ph_3PCl_2 and **1**.

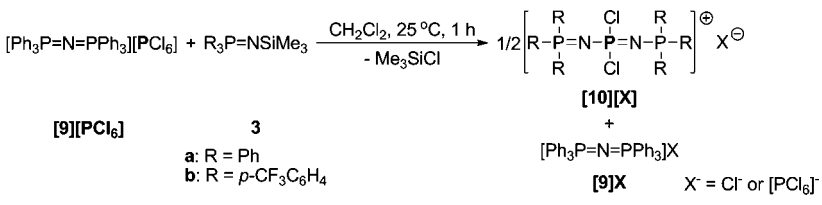
Scheme 9



To improve crystallizability, [**10a**]Cl was converted to the $[PCl_6]^-$ salt by addition of a single equivalent of PCl_5. Recrystallization by slow diffusion of Et_2O into a CH_2Cl_2 solution (1:2) at 25 °C afforded colorless crystals of [**10a**][PCl_6] suitable for an X-ray diffraction study (Figure 5).

The cation $[\mathbf{10a}]^+$ adopts a *cis*−*trans* geometry with a central N1−P2−N2 angle of 117.37(11)° and terminal P−N−P angles of 135.43(14)° and 141.35(15)° similar to those of $[\mathbf{4}]^+$ and $[N{=}PCl_2]_n$.[29] The terminal P1−N1 and N2−P3 bond lengths [1.594(2) and 1.599(2) Å respectively] are slightly elongated in comparison to the interior N1−P2 and P2−N2 bonds [1.565(2) and 1.548(2) Å respectively] presumably due to the lower electronegativity of the phenyl substituents in comparison to Cl. The shortest cation−$[PCl_6]^-$ distance is 6.473 Å to P3, while the distance to P1 is 7.001 Å.

Scheme 8



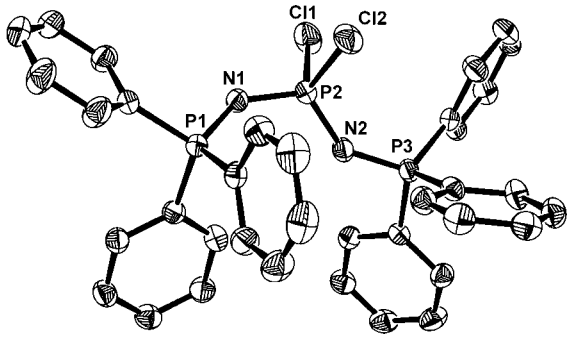
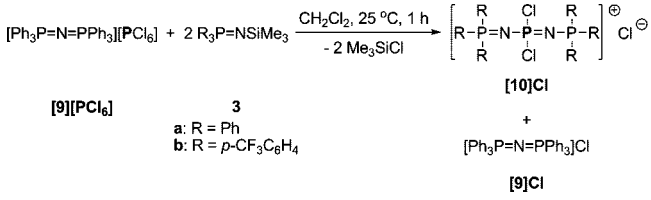


Figure 5. Molecular structure of the cation in [**10a**][PCl_6] with thermal ellipsoids at the 50% probability level. Hydrogen atoms and the counterion are omitted for clarity.

As anticipated, when the reaction of [**9**][PCl_6] was performed with *two* molar equivalents of **3a** after 2 h $^{31}P\{^1H\}$ NMR analysis revealed the formation of [**10a**]$^+$ with the complete consumption of $[PCl_6]^-$ as shown by the absence of a resonance at *ca.* −296 ppm (Scheme 10).

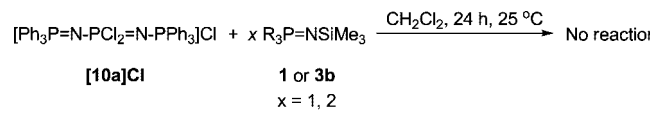
Scheme 10



When the analogous reactions of [**9**][PCl_6] were performed using the *N*-silylphosphoranimine **3b** similar results were obtained. Thus, addition of two equivalents of **3b** to [**9**][PCl_6] in CH_2Cl_2 yielded [**10b**]$^+$ with the complete consumption of $[PCl_6]^-$ within 2 h by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 10). It is important to note that when equimolar quantities of the chloride salt [**9**]Cl and **3b** were stirred in CH_2Cl_2 at room temperature over 3 h no reaction was observed by $^{31}P\{^1H\}$ NMR spectroscopy. This confirmed that the above results are a consequence of the reactivity of the $[PCl_6]^-$ ion.

When one or two equivalents of **1** were reacted with [**9**][PCl_6] the consumption of **1** was observed within 1 h by $^{31}P\{^1H\}$ NMR spectroscopy. Phosphazene oligomers $[Cl_3P{=}N{-}(PCl_2{=}N)_x{=}PCl_3]^+$ ([**11**]$^+$) of various lengths were formed as indicated by a series of multiplets in the regions δ 9.4−11.5 ppm and δ −14.5 to −12.0 ppm characteristic of $-N{=}PCl_3$ end groups and $N{=}PCl_2$- interior groups, respectively (Scheme 11). When one equivalent of **1** was added the major cationic phosphazene oligomer product formed was $[Cl_3P{=}N{-}PCl_2{=}N{-}PCl_2{=}N{=}PCl_3]^+$. This changed to $[Cl_3P{=}N{-}(PCl_2{=}N)_3{=}PCl_3]^+$ when two equivalents of **1** were used.[24] In both cases the $[PCl_6]^-$ anion was not fully consumed, however there was a clear decrease in the amount present in relation to the cation [**9**]$^+$ compared to before the addition of **1** according to $^{31}P\{^1H\}$ NMR integration. Thus, when one equivalent of **1** was used approximately 30% of the $[PCl_6]^-$ anions initially present were consumed, and this increased to *ca.* 65% when two equivalents of **1** were used.

Scheme 12



Clearly the $[PCl_6]^-$ anion is also an effective initiator for the oligomerization of **1**.[36] The incomplete conversion of this anionic species in the reactions of **1** with [**9**][PCl_6] indicates that propagation of the phosphazene chain induced by the resulting phosphazene cations [**11**]$^+$ is faster than for the initiation reaction between **1** and $[PCl_6]^-$. This suggests that in the polymerization of **1** initiated by PCl_5 only part of the $[PCl_6]^-$ formed in the initiation step will be consumed to form new phosphazene oligomers. Nevertheless, this pathway would be expected to complicate molecular weight control by providing another source of initiating sites for chain growth and, as the initiation step is slow, to broaden molecular weight distributions.[36]

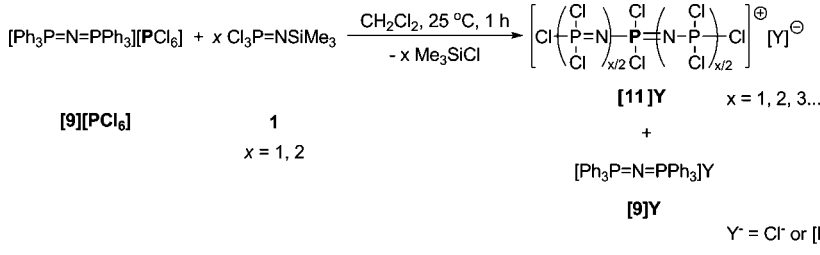
3. Studies of Potential Branching Reactions. In addition to bidirectional chain growth and reaction of monomer **1** with the $[PCl_6]^-$ anion, the living cationic chain growth polycondensation of **1** has the potential for reactions of the latter with the internal PCl_2 units of the growing $[N{=}PCl_2]_n$ chain resulting in branched polymer. Previous studies of the reaction of [**2**]Cl with **1** have identified linear phosphazenes as the major products.[24] However, the formation of small amounts of branched products could not be ruled out. In order to carry out more definitive studies we modeled this possible reactivity using the phosphazene oligomers $[Ph_3P{=}N{-}(PCl_2{=}N)_x{=}PPh_3]Cl$ (x = 1, 2, 3) in which reactivity at both ends is curtailed due to the absence of P−Cl bonds.

(a) Reactions of $[Ph_3P{=}N{-}PCl_2{=}N{=}PPh_3]Cl$ ([10a]Cl) with $(p\text{-}CF_3C_6H_4)_3P{=}NSiMe_3$ (3b). In our initial experiments, the *N*-silylphosphoranimine **3b** was chosen to model monomer **1** so that if branching reactions did occur, the $^{31}P\{^1H\}$ NMR shifts of the new $R_3P{=}N-$ groups would be distinguishable from those of the starting phosphazene oligomer [**10a**]$^+$. When a solution of either one or two equivalents of **3b** in CH_2Cl_2 was added to a solution of [**10a**]Cl in CH_2Cl_2 and the resulting reaction mixture stirred at room temperature for 24 h no reaction was observed by $^{31}P\{^1H\}$ NMR (Scheme 12).

The absence of a reaction between the phosphoranimine **3b** and the reactive P−Cl bonds of the phosphazene oligomer [**10a**]Cl suggests that during the polymerization of **1** branching reactions are unlikely.

(b) Reactions of $[Ph_3P{=}N{-}PCl_2{=}N{=}PPh_3]Cl$ ([10a]Cl) with $Cl_3P{=}NSiMe_3$ (1). To confirm the absence of significant

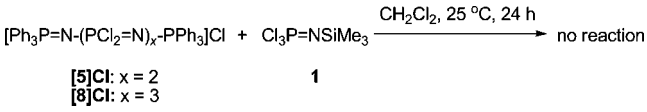
Scheme 11



branching reactions during the PCl_5-initiated polycondensation of **1** we studied the same reactions with the *N*-silylphosphoranimine **1** (Scheme 12). When a solution of either one or two equivalents of **1** in CH_2Cl_2 were added to a solution of [**10a**]Cl in CH_2Cl_2 and stirred at room temperature for 24 h no reaction between the phosphoranimines and the PCl_2 groups of $[\mathbf{10a}]^+$ was observed by $^{31}P\{^1H\}$ NMR. This observation reinforces the above assertion that branching reactions are improbable in the PCl_5-initiated polymerization of **1**.

(c) Reactions of $[Ph_3P{=}N{-}(PCl_2{=}N)_x{=}PPh_3]Cl$ ([5]Cl; $x = 2$ and [8]Cl; $x = 3$) with $Cl_3P{=}NSiMe_3$ (1). In order to model the $[N{=}PCl_2]_n$ backbone more closely and ensure that the lack of reactivity of **1** with $[\mathbf{10a}]^+$ observed above was not a consequence of steric interference by the PPh_3 end groups we repeated the reaction with cationic phosphazene oligomers with either two or three $N{=}PCl_2$ units (Scheme 13). A solution of one equivalent of **1** was added to a solution of [**5**]Cl or [**8**]Cl in CH_2Cl_2 and stirred at 25 °C. After 3 h no reaction was observed by $^{31}P\{^1H\}$ NMR spectroscopy.

Scheme 13



Discussion

Previous work involving the stoichiometric reaction of [**2**]Cl with **1** gave the linear cationic phosphazene oligomer $[Cl_3P{=}N{-}PCl_2{=}N{=}PCl_3]Cl$, [**6**]Cl, in excellent yield consistent with preferential monodirectional chain growth.[24] However analogous polymerizations with PCl_5 as an initator have given molecular weights more consistent with bidirectional chain growth.[18] Our results described in this paper are completely consistent with these seemingly contradictory observations. We have found that stoichiometric reactions of [**2**]Cl and the *N*-silylphosphoranimine **3a** demonstrated that the growth of living phosphazene chains is preferentially monodirectional. However, similar experiments using [**6**]Cl and **3a** indicate that bidirectional chain growth competes increasingly when the phosphazene chain is longer. This may be a consequence of ion pair effects, which lead to more effective steric hindrance at one end of a shorter phosphazene chain whereas the binding is weaker in longer chains where the cationic charge is increasingly delocalized. Bidirectional chain growth of living poly(dichlorophosphazene) where the rate of addition of each monomer molecule of **1** to each propagating site is different and chain length dependent may increase the breadth of the molecular weight distribution. We are currently working on the development of new end-capped initiators, $[R_3P{=}N{=}PCl_3]^+$ (R = non-halogen) for the living cationic chain growth polycondensation of **1**. By capping one end of the initiating species with alkyl or aryl groups, chain growth will be prevented at one end of the chain ensuring monodirectional chain growth and potentially providing greater control of the polymerization.

Significantly, the $[PCl_6]^-$ counterion present in the PCl_5-initiated cationic polymerization of **1** has been shown to react with *N*-silylphosphoraninimines **3a** and **3b** to form the phosphazene oligomers $[\mathbf{10a}]^+$ and $[\mathbf{10b}]^+$, respectively. Monomer **1** similarly reacts with $[PCl_6]^-$ to form phosphazene oligomers of various lengths where the first step is slow.[36] This reactivity has important consequences for the molecular weight and PDI of polyphosphazenes prepared *via* the cationic polymerization of **1** initiated by PCl_5. On the basis of these model compound studies, the $[PCl_6]^-$ anion in the polymerization of **1** will initiate the growth of new polymer chains in addition to PCl_5, resulting in a material with a less predictable molecular weight and a broader molecular weight distribution. A further broadening effect for the molecular weight distribution is expected to result from the apparent slow initiation step with the $[PCl_6]^-$ anion, which will lead to polymer chains starting to grow at different times. In future work we will explore the use of initiators with unreactive counteranions such as $[PF_6]^-$ in our attempts to understand and improve the living polymerization of **1**.

Experiments have shown no evidence for reactions between phosphoranimines **3b** or **1** and the phosphazene cation salts [**10a**]Cl, [**5**]Cl or [**8**]Cl with only internal P−Cl bonds. This suggests that -PCl_3 end-groups are required for reactions with the monomer **1** and that the polyphosphazenes formed by the PCl_5-initiated polymerization of **1** are essentially linear rather than branched.

Summary

Based on model compound studies important new insight has been obtained into the factors that influence the degree of control possible in the living PCl_5-initiated cationic polymerization of **1**. Our results indicate that in CH_2Cl_2, the most common solvent for the polymerization, two propagating sites with different and chain length dependent reactivity are located at the polymer chain ends, presumably a result of ion pairing effects. Significantly, our studies also indicate that the $[PCl_6]^-$ counteranion arising in the initiating step is not unreactive but is actually an active participant in the polymerization.[36] This has important implications for molecular weight control and provides an explanation for the significant polydispersity (1.1−1.3 or higher) detected for $[N{=}PCl_2]_n$ prepared *via* the PCl_5-initiated living cationic polymerization of **1**. The absence of reactions between the phosphazene cations with only internal P−Cl bonds and **1** indicates that the polymer formed is essentially linear. This emphasizes that with improvements, this polymerization should offer the opportunity to generate very well-defined materials. As part of our further attempts to optimize the living cationic polymerization of **1**, future studies will examine the use of cationic initiators with only one active site (e.g., $[R_3P{=}N{=}PCl_3]^+$) and counteranions other than $[PCl_6]^-$.

Experimental Section

General Procedures. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an argon atmosphere glovebox (M

(29) Chatani, Y.; Yatsuyanagi, K. *Macromolecules* **1987**, *20*, 1042.
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(31) The two chemical resonances consisted of a six line spectrum which were analyzed as an AA′XX′ spin pattern.
(32) Macchioni, A. *Chem. Rev.* **2005**, *105*, 2039.
(33) Allcock, H. R.; Tollefson, N. M.; Arcus, R. A.; Whittle, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5166.
(34) The precursor [**6**]Cl and the new species [**7**]Cl and [**8**]Cl are all highly hydrolytically sensitive. This generally led to the detection of very small quantities of hydrolysis products in the ^{31}P NMR spectra.
(35) Gutsev, G. L. *Chem. Phys.* **1994**, *179*, 325.
(36) The polymerization of **1** can be initiated by small amounts of [**9**][PCl_6] (a few mol % in CH_2Cl_2) and is complete within ca. 3.5 h and gives high molecular weight polymer with a PDI > 1.3. In depth studies of these polymerizations will be reported separately.

Braun). Hexanes and Et_2O were dried and collected using a Grubbs system using filtration through an alumina column impregnated with deoxygenated catalysts in oven and *vacuo* dried glassware. CH_2Cl_2 was dried at reflux over CaH_2. $CDCl_3$ was purchased from Cambridge Isotope Laboratories and then dried at reflux over CaH_2 and stored over 4 Å molecular sieves. NMR spectra were recorded on a Jeol Eclipse 300 MHz spectrometer. Chemical shifts are reported relative to residual protonated solvent peaks (^1H and ^{13}C) or externally to 85% H_3PO_4 in $CDCl_3$ (^{31}P). NMR spectra were obtained at 300 MHz (^1H), 121 MHz (^{31}P) or 75 MHz (^{13}C). Elemental analyses were carried out using a Eurovector EA3000 Elemental Analyzer. Due to their high hydrolytic sensitivity most oligomeric products with P−Cl substituents contained trace amounts of hydrolysis products (identified by $^{31}P\{^1H\}$ NMR spectroscopy in independent experiments) and therefore elemental analysis was not performed. Triphenyl(*N*-trimethylsilyl)phosphoranimine ($Ph_3P{=}NSiMe_3$, **3a**) was purchased from Aldrich and recrystallized from dry hexane before use. Phosphorus pentachloride (PCl_5) was purchased from Aldrich and sublimed at 50 °C onto a water-cooled coldfinger. Bis(triphenylphosphoranylidene)ammonium chloride ([$Ph_3P{=}N{=}PPh_3$]Cl, [**9**]Cl) was purchased from Aldrich and recrystallized from dry CH_2Cl_2/Et_2O. [$Cl_3P{=}N{=}PCl_3$]Cl ([**2**]Cl),[24] [$Cl_3P{=}N{-}PCl_2{=}N{=}PCl_3$]Cl ([**6**]Cl),[24] ($p$-$CF_3C_6H_4)_3P{=}NSiMe_3$ (**3b**)[37] and $Cl_3P{=}NSiMe_3$ (**1**)[25] were prepared according to literature procedures.

X-Ray Structure Determination. Data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ 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 all data (including negative intensities). In all structures, hydrogen atoms bonded to carbon atoms were included in calculated positions and treated as riding atoms.

Preparation of [$Ph_3P{=}N{-}PCl_2{=}N{=}PCl_3$]Cl ([4]Cl). A colorless solution of **3a** (0.349 g, 1.0 mmol) in CH_2Cl_2 (1.5 mL) was added dropwise to a stirred white suspension of [**2**]Cl (0.324 g, 1.0 mmol) in CH_2Cl_2 (4 mL) at room temperature. A clear, colorless solution was observed within 10 min and the reaction was stirred for a further 1.5 h. All volatiles were removed under vacuum leaving a white crystalline solid. Recrystallization from 3:1 CH_2Cl_2/hexanes mixture afforded colorless crystals of [**4**]Cl (0.424 g, 75% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.4 (d, $^2J_{PP} = 13.0$ Hz, $Ph_3P{=}N$), 7.3 (d, $^2J_{PP} = 27.9$ Hz, $N{=}PCl_3$) and −15.1 (dd,$^2J_{PP} = 13.0$ Hz, $^2J_{PP} = 27.9$ Hz, $N{=}PCl_2$). ^1H NMR ($CDCl_3$): δ 7.62−7.83 (br m, Ar−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 123.6 (dd, $^1J_{CP} = 107.6$ Hz, $^3J_{CP} = 5.2$ Hz, *i*-C), 130.0 (d, $^2J_{CP} = 13.2$ Hz, *o*-C), 132.4 (d, $^3J_{CP} = 11.5$ Hz, *m*-C), 134.8 (d, $^4J_{CP} = 3.5$ Hz, *p*-C). Due to hydrolytic sensitivity purity levels higher than ca. 95% were not possible, elemental analysis was therefore not attempted. For single crystal X-ray data see Figure 1 and Table 1.

Preparation of [$Ph_3P{=}N{-}PCl_2{=}N{-}PCl_2{=}N{=}PPh_3$]Cl ([5]Cl). A colorless solution of **3a** (0.349 g, 1.0 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a stirred white suspension of [**2**]Cl (0.162 g, 0.5 mmol) in CH_2Cl_2 (4 mL) at room temperature. A clear, colorless solution was observed within 5 min and the reaction was stirred for a further 3 h. All volatiles were removed under vacuum leaving a white solid which was recrystallized from a 4:1 CH_2Cl_2/hexanes mixture (0.32 g, 80%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.1 ($Ph_3P{=}N$), −16.7 ($N{=}PCl_2$), AA′XX′ in which $J_{AX} = 14.1$ Hz, $J_{AX'} = 27.8$ Hz and $J_{XX'} = 0$ Hz. ^1H NMR ($CDCl_3$): δ 7.50−7.71 (br m, Ar−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 124.7 (d, $^1J_{CP} = 107.9$ Hz, *i*-C), 129.4 (d, $^2J_{CP} = 13.8$ Hz, *o*-C), 132.3 (d, $^3J_{CP} = 11.5$ Hz, *m*-C), 134.1 (d, $^4J_{CP} = 2.9$ Hz, *p*-C). Due to hydrolytic sensitivity purity levels higher than ca. 95% were not possible, elemental analysis was therefore not attempted.

Table 1. Crystal Data for [**4**]Cl, [**5**][PCl_6] and [**10a**][PCl_6]

	[**4**]Cl	[**5**][PCl_6]·CH_2Cl_2	[**10a**][PCl_6]
empirical formula	$C_{18}H_{15}Cl_6N_2P_3$	$C_{37}H_{32}Cl_{12}N_3P_5$	$C_{36}H_{30}Cl_8N_2P_4$
fw	564.93	1098.91	898.10
cryst syst	Orthorhombic	Monoclinic	Monoclinic
space group	*Pbca*	$P2_1$	$P2_1/n$
a (Å)	10.6478(3)	11.3728(4)	18.0588(3)
b (Å)	16.6197(4)	17.6718(7)	7.74220(10)
c (Å)	26.3441(4)	13.0181(3)	29.3146(4)
α (deg)	90	90	90
β (deg)	90	107.735(2)	103.2450(9)
γ (deg)	90	90	90
V (Å^3)	4661.94(19)	2492.01(14)	3989.59(10)
Z	8	2	4
D_c (mg m^{-3})	1.610	1.465	1.495
T (K)	150(1)	150(1)	150(2)
R [$I > 2\sigma(I)$]	0.0459	0.0723	0.0424
wR [$I > 2\sigma(I)$]	0.1015	0.1921	0.0990
GOF on F^2	1.058	1.036	1.027

Preparation of [$Ph_3P{=}N{-}PCl_2{=}N{-}PCl_2{=}N{=}PPh_3$][$PCl_6$] ([5][$PCl_6$]). A colorless solution of **3a** (0.349 g, 1.0 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a stirred white suspension of [**2**]Cl (0.162 g, 0.5 mmol) in CH_2Cl_2 (4 mL) at room temperature. A clear, colorless solution was observed within 5 min. After stirring at room temperature for a further 3 h a colorless solution of PCl_5 (0.104 g, 0.5 mmol) in CH_2Cl_2 (2 mL) was added dropwise to the reaction mixture which was then allowed to stir for 1.5 h. All volatiles were removed under vacuum leaving a white crystalline solid. Recrystallization from 3:1 CH_2Cl_2/hexanes mixture afforded colorless crystals of [**5**]PCl_6.CH_2Cl_2 (0.22 g, 43%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.1 ($Ph_3P{=}N$), −16.4 ($N{=}PCl_2$), AA′XX′ in which $J_{AX} = 14.1$ Hz, $J_{AX'} = 1.6$ Hz, $J_{AA'} = 27.8$ Hz and $J_{XX'} = 0$ Hz. ^1H NMR ($CDCl_3$): δ 7.6−7.8 (br m, Ar−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 124.9 (d, $^1J_{CP} = 104.8$ Hz, *i*-C), 129.6 (d, $^2J_{CP} = 13.2$ Hz, *o*-C), 132.6 (d, $^3J_{CP} = 11.5$ Hz, *m*-C), 134.3 (d, $^4J_{CP} = 2.9$ Hz, *p*-C). Anal. Calcd for **5[PCl_6].CH_2Cl_2**, $C_{37}H_{32}Cl_{12}N_3P_5$ (1098.97): %C: 40.44; %H: 2.93; %N: 3.82. Found: %C: 39.79; %H: 2.72; %N: 3.87. For single crystal X-ray data see Figure 3 and Table 1.

Reaction of [$Cl_3P{=}N{-}PCl_2{=}N{=}PCl_3$]Cl ([6]Cl) with One Equivalent of $Ph_3P{=}NSiMe_3$ (3a). A solution of **3a** (0.079 g, 0.23 mmol) in CH_2Cl_2 (1 mL) was added to a solution of [**6**]Cl (1.0 g, 0.23 mmol) in CH_2Cl_2 (1.5 mL) and the reaction was stirred at room temperature for 1 h. An aliquot was removed, $^{31}P\{^1H\}$ NMR showed consumption of **3a**, a small amount of remaining $[\mathbf{6}]^+$ [δ 13.8 (d, $^2J_{PP} = 40.1$ Hz) and −11.5 (t, $^2J_{PP} = 40.1$ Hz)] (∼ 10%),[24] and the formation of [**7**]Cl [δ 21.6 (d, $^2J_{PP} = 14.9$ Hz, $N{=}PPh_3$), 8.8 (d, $^2J_{PP} = 33.5$ Hz, $N{=}PCl_3$), −14.7 (dd, $^2J_{PP} = 14.9$ Hz, $^2J_{PP} = 37.2$ Hz, $N{=}PCl_2$) and −16.5 (t, $^2J_{PP} = 36.3$ Hz, $N{=}PCl_2$)] and [**8**]Cl [δ 20.4 (d, $^2J_{PP} = 14.9$ Hz), −15.7 (d, $^2J_{PP} = 13.0$ Hz, $^2J_{PP} = 34.4$ Hz, $N{=}PCl_2$) and −19.8 (t, $^2J_{PP} = 34.4$ Hz, $N{=}PCl_2$)].

Reaction of [$Cl_3P{=}N{-}PCl_2{=}N{=}PCl_3$]Cl ([6]Cl) with 2.1 Equivalents of $Ph_3P{=}NSiMe_3$ (3a). A solution of **3a** (0.167 g, 0.47 mmol) in CH_2Cl_2 (1 mL) was added to a solution of [**6**]Cl (0.100 g, 0.23 mmol) in CH_2Cl_2 (1.5 mL) and the reaction was stirred at room temperature for 1 h. An aliquot was removed, $^{31}P\{^1H\}$ NMR showed consumption of **3a** and the formation of [**8**]Cl [δ 20.5 (d, $^2J_{PP} = 13.0$ Hz, $N{=}PPh_3$), −15.6 (dd, $^2J_{PP} = 13.0$ Hz, $^2J_{PP} = 34.4$ Hz, $N{=}PCl_2$) and −19.7 (t, $^2J_{PP} = 34.4$ Hz, $N{=}PCl_2$)]. Due to hydrolytic sensitivity purity levels higher than ca. 95% by $^{31}P\{^1H\}$ NMR were not possible, elemental analysis was therefore not attempted.

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Preparation of [$Ph_3P{=}N{=}PPh_3$][PCl_6] ([9][PCl_6]). PCl_5 (316 mg, 1.5 mmol) in CH_2Cl_2 (8 mL) was added to a solution of [**9**]Cl (1.0 g, 1.5 mmol) in CH_2Cl_2 (6 mL). After stirring for 1 h $^{31}P\{^1H\}$ NMR analysis confirmed the consumption of PCl_5 (δ −80.0) and the formation of [**9**][PCl_6] [δ 21.7 (s, $Ph_3P{=}N$) and −296.4 (s, [PCl_6]$^-$)]. The reaction solution was layered with Et_2O (5 mL) and cooled to −40 °C to give off-white crystals over 3 days. The crystals were isolated by decanting the mother liquors then dried under vacuum (1.0 g, 85%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.7 (s, [$Ph_3P{=}N{=}PPh_3$]$^+$) and −296.3 ppm (s, [PCl_6]$^-$). Anal. Calcd for **[9][PCl_6]**, $C_{36}H_{30}Cl_6NP_3$ (782.27): %C: 55.27; %H: 3.87; %N: 1.79. Found: %C: 55.54; %H: 3.88; %N: 2.07.

Reaction between Stoichiometric Amounts of [$Ph_3P{=}N{=}PPh_3$][PCl_6] ([9][PCl_6]) and $Ph_3P{=}NSiMe_3$ (3a). To a CH_2Cl_2 (6 mL) solution of [**9**][PCl_6] (0.29 mmol) was added a solution of **3a** (100 mg, 0.29 mmol) in CH_2Cl_2 (3.3 mL). After stirring at room temperature for 1 h $^{31}P\{^1H\}$ NMR analysis revealed the partial consumption of [PCl_6]$^-$ (δ −296.3) and the formation of [**10a**][PCl_6]/Cl^- [δ 18.9 (d, $^2J_{PP}$ = 10.4 Hz, $Ph_3P{=}N$) and −13.3 (t,$^2J_{PP}$ = 10.4 Hz, $N{=}PCl_2$)] in a 1:2 ratio with [**9**]$^+$ [δ 21.7 (s, $Ph_3P{=}N$)].

Reaction between Stoichiometric Amounts of [$Ph_3P{=}N{=}PPh_3$][PCl_6] ([9][PCl_6]) and (p-$CF_3C_6H_4$)$_3$P=NSiMe$_3$ (3b). To a CH_2Cl_2 (1.75 mL) solution of [**9**][PCl_6] (8.7×10^{-5} mol) was added a solution of **3b** (48 mg, 8.7×10^{-5} mol) in CH_2Cl_2 (1 mL). After stirring at room temperature for 1 h $^{31}P\{^1H\}$ NMR analysis revealed the partial consumption of [PCl_6]$^-$ (δ −296.4) and the formation of [**10b**][PCl_6]/Cl^- [δ 16.7 (d, $^2J_{PP}$ = 18.3 Hz, (p-$CF_3C_6H_4$)$_3$P=N) and −11.6 (t,$^2J_{PP}$ = 18.3 Hz, $N{=}PCl_2$)] in a 1:2 ratio with [**9**]$^+$ [δ 21.7 (s, $Ph_3P{=}N$)].

Reaction between [$Ph_3P{=}N{=}PPh_3$][PCl_6] ([9][PCl_6]) and Two Equivalents of $Ph_3P{=}NSiMe_3$ (3a). To a CH_2Cl_2 (6 mL) solution of [**9**][PCl_6] (0.29 mmol) was added a solution of **3a** (203 mg, 0.58 mmol) in CH_2Cl_2 (3.3 mL). After stirring at room temperature for 1 h $^{31}P\{^1H\}$ NMR analysis revealed the consumption of [PCl_6]$^-$ (δ −296.4) and the formation of [**10a**]Cl [δ 19.0 (d, $^2J_{PP}$ = 10.4 Hz, $Ph_3P{=}N$), −13.3 (t,$^2J_{PP}$ = 10.4 Hz, $N{=}PCl_2$)] in a 1:1 ratio with [**9**]Cl [δ 21.7 (s, $Ph_3P{=}N$)].

Preparation of [$Ph_3P{=}N{-}PCl_2{=}N{-}PPh_3$]Cl ([10a]Cl). [$Ph_3P{=}N{=}PCl_3$]Cl was prepared *in situ* by the addition of a solution of C_2Cl_6 (451 mg, 1.9 mmol) in CH_2Cl_2 (5 mL) to a solution of PPh_3 (500 mg, 1.9 mmol) in CH_2Cl_2 (10 mL) and stirring for 30 min at 25 °C, followed by the dropwise addition of **1** (427 mg, 1.9 mmol) in CH_2Cl_2 (5 mL) and stirring for a further 1 h. To the above solution of [$Ph_3P{=}N{=}PCl_3$]Cl was added **3a** (664 mg, 1.9 mmol) in CH_2Cl_2 (5 mL) and the reaction was stirred for 1 h. All volatiles were removed under vacuum leaving a white solid which after recrystallization from CH_2Cl_2/Et_2O (1:1) afforded colorless crystals (884 mg, 67%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 18.8 (d, $^2J_{PP}$ = 10.4 Hz, $Ph_3P{=}N$), −13.4 (t,$^2J_{PP}$ = 10.4 Hz, $N{=}PCl_2$). ^1H NMR ($CDCl_3$): δ 7.5−7.8 (br m, Ar−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 125.0 (dd, $^1J_{CP}$ = 107.1 Hz, $^3J_{CP}$ = 5.2 Hz, *i*-C), 129.5 (d, $^2J_{CP}$ = 13.4 Hz, *o*-C), 132.4 (d, $^3J_{CP}$ = 11.5 Hz, *m*-C), 134.2 (d, $^4J_{CP}$ = 3.0 Hz, *p*-C). Due to hydrolytic sensitivity purity levels higher than ca. 95% were not possible, elemental analysis was therefore not attempted.

Preparation of [$Ph_3P{=}N{-}PCl_2{=}N{-}PPh_3$][$PCl_6$] ([10a][$PCl_6$]). [$Ph_3P{=}N{=}PCl_3$]Cl was prepared *in situ* by the addition of a solution of C_2Cl_6 (451 mg, 1.9 mmol) in CH_2Cl_2 (5 mL) to a solution of PPh_3 (500 mg, 1.9 mmol) in CH_2Cl_2 (10 mL) and stirring for 30 min at 25 °C, followed by the dropwise addition of **1** (427 mg, 1.9 mmol) in CH_2Cl_2 (5 mL) and stirring for a further 1 h. To the above solution of [$Ph_3P{=}N{=}PCl_3$]Cl was added **3a** (664 mg, 1.9 mmol) in CH_2Cl_2 (5 mL) and the reaction was stirred for 1 h. PCl_5 (396 mg, 1.9 mmol) was added portionwise and the reaction was stirred for a further 1 h. All volatiles were removed under vacuum leaving a crystalline off-white solid. Recrystallization from CH_2Cl_2/Et_2O (2:1) afforded colorless crystals of [**10a**][PCl_6] (1.63 g, 95%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 18.9 (d, $^2J_{PP}$ = 10.4 Hz, $Ph_3P{=}N$), −13.3 (t, $^2J_{PP}$ = 10.4 Hz, $N{=}PCl_2$) and −296.4 (s, [PCl_6]$^-$). ^1H NMR ($CDCl_3$): δ 7.53−7.76 (br m, Ar−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 125.2 (dd, $^1J_{CP}$ = 107.3 Hz, $^3J_{CP}$ = 5.2 Hz, *i*-C), 129.7 (d, $^2J_{CP}$ = 13.4 Hz, *o*-C), 132.6 (d, $^3J_{CP}$ = 11.5 Hz, *m*-C), 134.4 (d, $^4J_{CP}$ = 3.0 Hz, *p*-C). Due to hydrolytic sensitivity purity levels higher than ca. 95% were not possible, elemental analysis was therefore not attempted. For single crystal X-ray data see Figure 5 and Table 1.

Reaction between [$Ph_3P{=}N{=}PPh_3$][PCl_6] ([9][PCl_6]) and Two Equivalents of (p-$CF_3C_6H_4$)$_3$P=NSiMe$_3$ (3b). To a CH_2Cl_2 (3.5 mL) solution of [**9**][PCl_6] (1.8×10^{-4} mol) was added a solution of **3b** (200 mg, 3.6×10^{-4} mol) in CH_2Cl_2 (2 mL). After stirring at room temperature for 2 h $^{31}P\{^1H\}$ NMR analysis revealed the consumption of [PCl_6]$^-$ (δ −296.4) and the formation of [**10b**]Cl [δ 16.7 (d, $^2J_{PP}$ = 18.3 Hz, (p-$CF_3C_6H_4$)$_3$P=N), −11.6 (t, $^2J_{PP}$ = 18.3 Hz, $N{=}PCl_2$)] in a 1:1 ratio with [**9**]Cl [δ 21.7 (s, $Ph_3P{=}N$)].

Attempted Reaction between Stoichiometric Amounts of [$Ph_3P{=}N{=}PPh_3$]Cl ([9]Cl) and (p-$CF_3C_6H_4$)$_3$P=NSiMe$_3$ (3b). A solution of **3b** (48 mg, 8.7×10^{-5} mol) in CH_2Cl_2 (1 mL) was added with stirring to a solution of [**9**]Cl (50 mg, 8.7×10^{-5} mol) in CH_2Cl_2 (1 mL). Analysis of the colorless solution by $^{31}P\{^1H\}$ NMR after 3 h revealed that no reaction had occurred [δ 21.7 (s, $Ph_3P{=}N{=}PPh_3$), −4.0 (s, {p-$CF_3C_6H_4$}$_3$P=NSiMe$_3$)].

Reaction between Stoichiometric Amounts of [$Ph_3P{=}N{=}PPh_3$][PCl_6] ([9][PCl_6]) and $Cl_3P{=}NSiMe_3$ (1). A solution of **1** (67 mg, 0.3 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a solution of [**9**][PCl_6] (0.3 mmol) in CH_2Cl_2 (6 mL). After stirring for 1 h at 25 °C an aliquot was removed. $^{31}P\{^1H\}$ NMR showed the complete consumption of **1** and consumption of a approximately 30% of [PCl_6]$^-$ (based on integration of [$Ph_3P{=}N{=}PPh_3$]$^+$ and [PCl_6]$^-$ peaks before and after addition of **1**) to form [$Cl_3P{=}N{-}(PCl_2{=}N)_x{=}PCl_3$]$^+$ (based on integration of $Cl_3P{=}N{-}$ peaks: x = 1, 27%; x = 2, 73%).[24]

Reaction between [$Ph_3P{=}N{=}PPh_3$][PCl_6] ([9][PCl_6]) and Two Equivalents of $Cl_3P{=}NSiMe_3$ (1). A solution of **1** (135 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a solution of [**9**][PCl_6] (0.3 mmol) in CH_2Cl_2 (6 mL). After stirring for 1 h at 25 °C an aliquot was removed. $^{31}P\{^1H\}$ NMR showed the complete consumption of **1** and consumption of a approximately 60% of [PCl_6]$^-$ (based on integration of [$Ph_3P{=}N{=}PPh_3$]$^+$ and [PCl_6]$^-$ peaks before and after addition of **1**) to form [$Cl_3P{=}N{-}(PCl_2{=}N)_x{=}PCl_3$]$^+$ (based on integration of $Cl_3P{=}N{-}$ peaks: x = 1, 3%; x = 2, 38%; x = 3, 59%).[24]

Attempted Reaction between Stoichiometric Amounts of [$Ph_3P{=}N{-}PCl_2{=}N{-}PPh_3$]Cl ([10a]Cl) and ($p$-$CF_3C_6H_4$)$_3$P=NSiMe$_3$ (3b). A solution of **3b** (80 mg, 0.14 mmol) in CH_2Cl_2 (1.5 mL) was added dropwise to a solution of **[10a]Cl** (100 mg, 0.14 mmol) in CH_2Cl_2 (1.5 mL). After stirring at 25 °C for 24 h no reaction was observed by $^{31}P\{^1H\}$ NMR.

Attempted Reaction between [$Ph_3P{=}N{-}PCl_2{=}N{-}PPh_3$]Cl ([10a]Cl) and Two Equivalents of (p-$CF_3C_6H_4$)$_3$P=NSiMe$_3$ (3b). A solution of **3b** (160 mg, 0.29 mmol) in CH_2Cl_2 (1.5 mL) was added dropwise to a solution of **[10a]Cl** (100 mg, 0.14 mmol) in CH_2Cl_2 (1.5 mL). No reaction was observed by $^{31}P\{^1H\}$ NMR after stirring at 25 °C for 24 h.

Attempted Reaction between Stoichiometric Amounts of [$Ph_3P{=}N{-}PCl_2{=}N{-}PPh_3$]Cl ([10a]Cl) and $Cl_3P{=}NSiMe_3$ (1). A solution of **1** (40 mg, 0.18 mmol) in CH_2Cl_2 (1.5 mL) was added dropwise to a solution of **[10a]Cl** (123 mg, 0.18 mmol) in CH_2Cl_2 (1.5 mL). After stirring at 25 °C for 24 h an aliquot was removed. $^{31}P\{^1H\}$ NMR showed no change in the resonances for [**10a**]$^+$ (δ 18.9 (d, $^2J_{PP}$ = 11.2 Hz, $Ph_3P{=}N$), −13.8 (t, $^2J_{PP}$ = 10.2 Hz, $N{=}PCl_2$)) but **1** (δ = −53.0 ppm) had been consumed to form $N{=}PCl_2]_3$ (δ = 20.3 ppm, 84%) and [$N{=}PCl_2]_4$ (δ = −6.3 ppm, 16%).[40]

Attempted Reaction between [$Ph_3P{=}N{-}PCl_2{=}N{-}PPh_3$]Cl ([10a]Cl) and Two Equivalents of $Cl_3P{=}NSiMe_3$ (1). A solution of **1** (71 mg, 0.32 mmol) in CH_2Cl_2 (1.5 mL) was added dropwise to a solution of **[10a]Cl** (109 mg, 0.16 mmol) in CH_2Cl_2 (1.5 mL). After stirring at 25 °C for 24 h an aliquot was removed. $^{31}P\{^1H\}$

NMR showed no change to the resonances for $[\mathbf{10a}]^+$ (δ 18.5 (d, $^2J_{PP}$ = 9.3 Hz, $Ph_3P{=}N$), −13.8 (t, $^2J_{PP}$ = 10.2 Hz, $N{=}PCl_2$)) but **1** (δ = −53.0 ppm) had been consumed to form $[N{=}PCl_2]_3$ (δ = 20.3 ppm, 83%) and $[N{=}PCl_2]_4$ (δ = −6.3 ppm, 17%).[40]

Attempted Reaction between $[Ph_3P{=}N{-}PCl_2{=}N{-}PCl_2{=}N{-}PPh_3]Cl$ ([5]Cl) and $Cl_3P{=}NSiMe_3$ (1). A solution of **1** (100 mg, 0.45 mmol) in CH_2Cl_2 (1 mL) was added to a solution of [**5**]Cl (0.45 mmol) in CH_2Cl_2 (4 mL) and stirred at 25 °C. After 3 h an aliquot was removed, $^{31}P\{^1H\}$ NMR showed no reaction between $[\mathbf{5}]^+$ (δ = 20.1 and −16.8 ppm, AA′XX′) and **1** (δ = −54.5 ppm). After stirring for a further 21 h $^{31}P\{^1H\}$ NMR still showed no change in the resonances of $[\mathbf{5}]^+$ (δ = 20.1 and −16.8 ppm, AA′XX′) but approximately 35% of **1** (δ = −54.7 ppm) had been converted to $[N{=}PCl_2]_n$ (δ = −17.6 ppm).[40]

Attempted Reaction between $[Ph_3P{=}N{-}(PCl_2{=}N)_3{-}PPh_3]Cl$ ([8]Cl) and $Cl_3P{=}NSiMe_3$ (1). A solution of **1** (100 mg, 0.45 mmol) in CH_2Cl_2 (1 mL) was added to a solution of [**8**]Cl (0.45 mmol) in CH_2Cl_2 (4 mL) and stirred at 25 °C. After 3 h an aliquot was removed, $^{31}P\{^1H\}$ NMR showed no reaction between $[\mathbf{8}]^+$ (δ = 20.5, −15.6 and −19.7) and **1** (δ = −54.5 ppm). After stirring for a further 21 h no change was observed by $^{31}P\{^1H\}$ NMR.

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Supporting Information Available: Crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(40) The formation of $[N{=}PCl_2]_x$ (x = 3, 4, n) arises from the reaction of Cl^- with the monomer **1**. Details of investigations into this reactivity will be published in a future paper.