

Isolation of donor-stabilized *N*-silylphosphoranimine cations and the discovery of an ambient temperature route to Poly(alkyl/aryl)phosphazenes [☆]

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Abstract

This account describes the formation of nitrogen and phosphorus donor-stabilized phosphoranimine cations from *N*-silylphosphoranimines. A novel phosphine-mediated dehalogenation reaction is also described, as well as the discovery of an ambient temperature route to poly(alkyl/aryl)phosphazenes.

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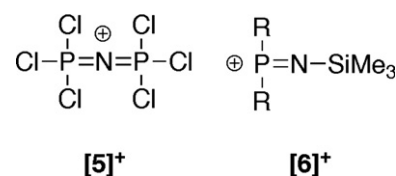
1. Introduction

The study of phosphoranimines with the general formula $R_3P=NR'$ (R = alkyl, aryl, or halogen; R' = alkyl, aryl, or silyl) have made a significant contribution in the development of main-group chemistry [1]. In addition to providing a fundamental understanding into the structure, bonding and reactivity of the phosphorus(V)-nitrogen bond [2], phosphoranimines have been utilized as ligands in main-group [3] and transition–metal coordination chemistry [4]. In particular, early transition–metal (Ti and Zr) complexes which employ the $R_3P=N^-$ ligand has proven to be highly effective catalysts in olefin polymerization [5].

Phosphoranimines also play an integral role in inorganic polymer chemistry as they are molecular precursors to polyphosphazenes. The preparation of polydichlorophosphazene (**1**) can be achieved from the PCl_5 catalyzed living cationic chain-growth condensation polymerization of the *N*-silylphosphoranimine monomer $Cl_3P=NSiMe_3$ (**2**)

(Scheme 1) [6]. The route to the corresponding alkyl and aryl substituted polyphosphazenes (**3**), which was reported much earlier, involves the thermal (150–200 °C) condensation polymerization of an appropriate phosphoranimine with the general formula $(CF_3CH_2O)R_2P=NSiMe_3$ (**4**) (Scheme 2) [7].

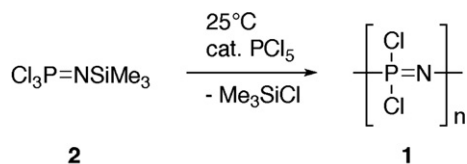
Cationic derivatives of phosphoranimines have been implicated as important intermediates in phosphazene polymerizations. For example, the living cationic chain-growth polymerization of **2** proceeds through the initial formation of the cationic initiator $[Cl_3P=N=PCl_3]^+$ (**[5]⁺**) [6a], and the thermal polycondensation of **4** has been tentatively proposed to proceed through the initial formation of a cationic intermediate $[R_2P=NSiMe_3]^+$ (**[6]⁺**) from the ionization of a P–O bond, followed by **[6]⁺** functioning as an initiator by inducing the chain-growth polymerization of the remaining phosphoranimine monomers [7c].



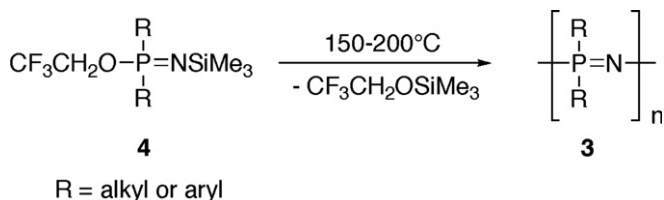
[☆] Based on the presentation given at IRIS XI, July 30 to August 4, 2006, University of Oulu, Finland.

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Scheme 1.



Scheme 2.

The cation **[6]**⁺ is expected to be extremely Lewis acidic and thus highly reactive due to the presence of a coordinatively unsaturated phosphorus(V) center and would likely require additional stabilization to permit isolation. In this account we provide an overview of our recent work which has aimed at the study of these reactive cationic species.

2. Formation of N-donor stabilized phosphoranime cations

The initial strategy for the preparation of cationic phosphoranimes involved chloride abstraction from the phosphoranime monomer $\text{Cl}_3\text{P}=\text{NSiMe}_3$ (**2**) [8]. The halide abstracting agent AgOTf (OTf = OSO_2CF_3) was chosen since AgOTf has proven to be effective in the preparation of main-group and organometallic cations. Treatment of $\text{Cl}_3\text{P}=\text{NSiMe}_3$ with AgOTf did not yield the anticipated phosphoranime derivative $(\text{TfO})\text{Cl}_2\text{P}=\text{NSiMe}_3$ (**7**). Instead, the quantitative formation of polydichlorophosphazene $[\text{Cl}_2\text{P}=\text{N}]_n$ (**1**) and TfOSiMe_3 was observed. This result suggested that upon halide abstraction, the transient $(\text{TfO})\text{Cl}_2\text{P}=\text{NSiMe}_3$ (**7**) immediately polymerizes due to the labile triflate group at phosphorus.

Recent studies have shown that pyridine-based ligands are exceptionally effective in stabilizing reactive cationic phosphorus(III)[9] and phosphorus(V) [9c,10] centers and consequently this synthetic strategy was employed in the present system. The reaction of $\text{Cl}_3\text{P}=\text{NSiMe}_3$ with a stoichiometric amount of AgOTf in the presence of the strong base DMAP (DMAP = 4-dimethylaminopyridine) results

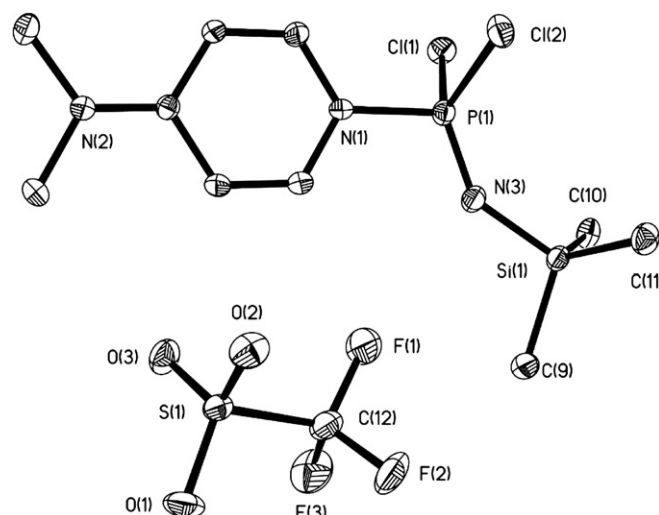


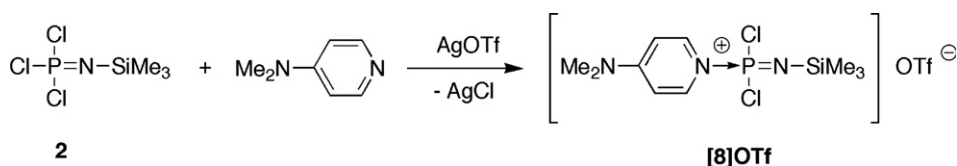
Fig. 1. Molecular structure of **[8]OTf** by X-ray diffraction. Reproduced from Ref. [11] with permission.

in the quantitative conversion of $\text{Cl}_3\text{P}=\text{NSiMe}_3$ to the novel DMAP-stabilized phosphoranime salt $[\text{DMAP} \bullet \text{PCl}_2=\text{NSiMe}_3]\text{OTf}$ (**[8]OTf**) (Scheme 3) [11]. Surprisingly, it was found that AgOTf is not necessary for the preparation of the cation **[8]**⁺. The salt **[8]Cl** can be prepared from the direct reaction between $\text{Cl}_3\text{P}=\text{NSiMe}_3$ and DMAP (see Fig. 1).

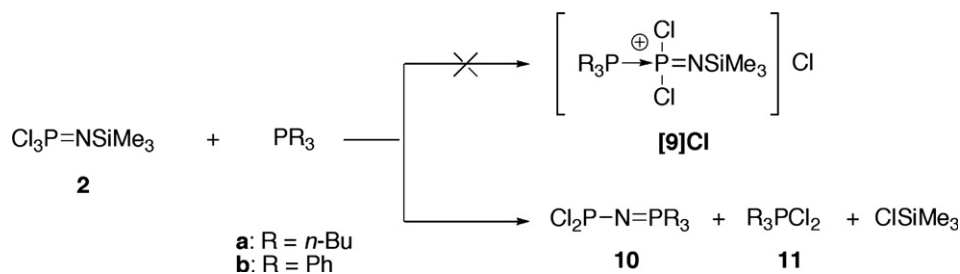
3. Phosphine-mediated dehalogenation reactions

Encouraged by the ability of DMAP to displace one equivalent of chloride from **2** to form **[8]Cl** without the use of a halide abstractor, the extension of this chemistry to tertiary phosphines as donors was attempted. The preparation of a phosphine-stabilized phosphoranime cation, a P(III) → P(V) adduct, would complement the well-established family of diphosphonium cations $[\text{R}_3\text{P}-\text{PR}_2]^+$, which are formally regarded as P(III) → P(III) adducts [12]. Surprisingly, treatment of $\text{Cl}_3\text{P}=\text{NSiMe}_3$ with the tertiary phosphines ^tBu₃P and Ph₃P does not yield the expected phosphine-stabilized phosphoranime salt **[9]Cl** (Scheme 4). Instead the quantitative generation of N-phosphinophosphoranimes $\text{R}_3\text{P}=\text{N}-\text{PCl}_2$ (**10**) and dichlorophosphoranes R_3PCl_2 (**11**) were observed in solution.

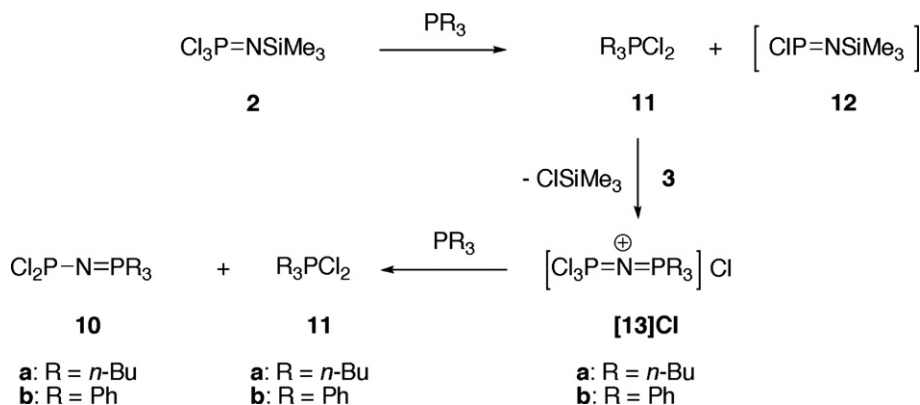
Detailed mechanistic studies concerning this unusual reaction were performed and a reaction pathway which rationalizes the formation of N-phosphinophosphoranimes (**10**)



Scheme 3.



Scheme 4.



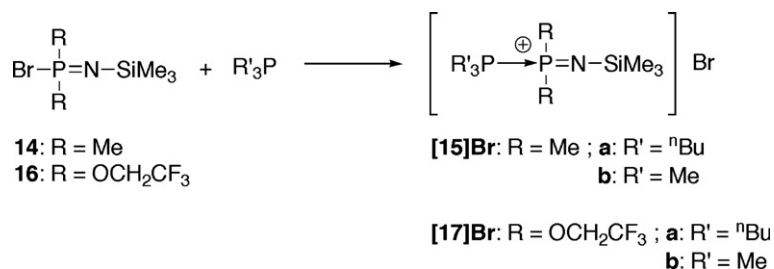
Scheme 5.

and dichlorophosphoranes (**11**) from **2** and tertiary phosphines (Scheme 5) has been proposed.

The reductive dechlorination of **2** is induced by the tertiary phosphine which yields the dichlorophosphorane **11** and the transient chlorophosphinimine intermediate $\text{ClP}=\text{NSiMe}_3$ (**12**). The dichlorophosphorane **11** undergoes a condensation reaction with an additional equivalent of **2** to yield an unsymmetrically substituted bisphosphonioammonium chloride salt $[\text{R}_3\text{P}^{\oplus}=\text{N}=\text{PCl}_2]\text{Cl}$ (**[13]Cl**) with the elimination of trimethylchlorosilane. The salt **[13]Cl** further reacts with an additional equivalent of tertiary phosphine by undergoing a second dechlorination step to generate the final products **10** and **11**. Thus, the overall stoichiometry for the reaction is two equivalents of a tertiary phosphine react with two equivalents of **2** to generate one equivalent each of **10**, **11**, and **12** [13].

4. Formation of P-donor stabilized phosphoranimine cations

It is immediately apparent that the goal of preparing phosphine-stabilized phosphoranimine cations cannot be realized in the presence of a trihalogeno functionality on the phosphoranimine. Therefore, the next logical step in the pursuit of phosphine-stabilized phosphoranimine cations involved monohalogeno(diorgano)phosphoranimines. In the direct reaction between the $\text{BrMe}_2\text{P}=\text{NSiMe}_3$ (**14**) [14] and the tertiary phosphines R_3P ($\text{R} = n\text{-Bu}$ and Me) the novel phosphine-stabilized cationic phosphoranimine salts $[\text{R}_3\text{P}^{\oplus}\text{PMe}_2=\text{NSiMe}_3]\text{Br}$ (**[15]Br**) were obtained (Scheme 6). Interestingly, these salts exhibit remarkably small one-bond phosphorus–phosphorus coupling constants [$^1J_{\text{PP}} = 23 \text{ Hz}$ ($\text{R} = n\text{-Bu}$) and 13 Hz ($\text{R} = \text{Me}$)] [15,16] (see Fig. 2).



Scheme 6.

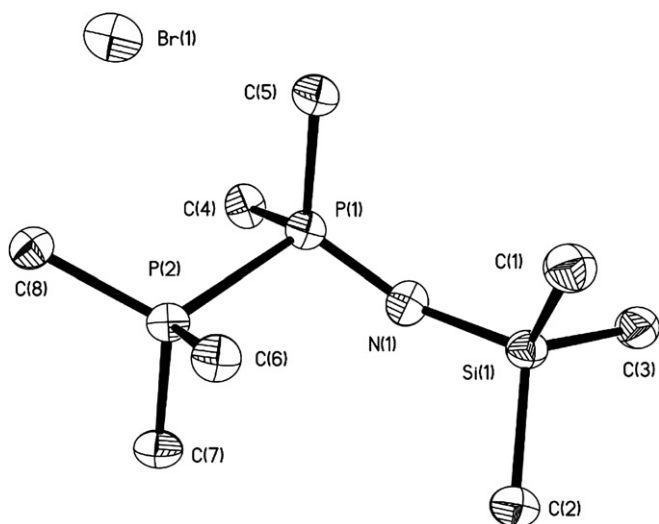


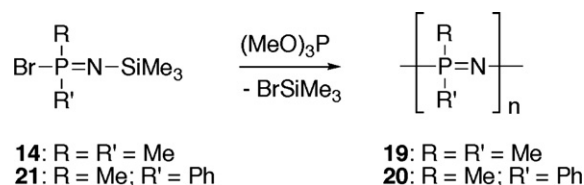
Fig. 2. Molecular structure of **[17b]Br** by X-ray diffraction. Reproduced from Ref. [16] with permission.

We expanded this chemistry to the phosphoranimine $\text{Br}(\text{CF}_3\text{CH}_2\text{O})_2\text{P}=\text{NSiMe}_3$ (**16**) [14], which bears electron-withdrawing trifluoroethoxy substituents (Scheme 6). Treatment of $\text{Br}(\text{CF}_3\text{CH}_2\text{O})_2\text{P}=\text{NSiMe}_3$ with ${}^n\text{Bu}_3\text{P}$ or Me_3P the generation of analogous phosphine-stabilized phosphoranimine cations $[\text{R}_3\text{P}\bullet\text{P}(\text{CF}_3\text{CH}_2\text{O})_2=\text{NSiMe}_3]^+\text{Br}^-$ (**[17]Br**) were obtained. However, the one-bond phosphorus–phosphorus coupling constant observed for these species were normal [${}^1J_{\text{PP}} = 277$ Hz ($\text{R} = {}^n\text{Bu}$) and 324 Hz ($\text{R} = \text{Me}$)] [16].

The above NMR results suggest a close association between the magnitude of the ${}^1J_{\text{PP}}$ observed for these complexes and the phosphorus substituents. Normal values of ${}^1J_{\text{PP}}$ were observed for the phosphine-stabilized phosphoranimine cations **[17a]**⁺ and **[17b]**⁺ (277 and 324 Hz, respectively) where electron-withdrawing substituents are present on the phosphoranimine center, and small values of ${}^1J_{\text{PP}}$ were observed for **[15a]**⁺ and **[15b]**⁺ (23 and 13 Hz, respectively) where electron-donating Me substituents are present on the phosphoranimine center. These observations suggest that the magnitude of the ${}^1J_{\text{PP}}$ observed in these systems are significantly influenced by the substituent identity and that an electron push–pull mechanism may be operating.

5. Ambient temperature preparation of poly(alkyl/aryl)phosphazenes

The unusual observation of coupling constant dependence on the choice of substituent and the abnormally small ${}^1J_{\text{PP}}$ observed for **[15]**⁺ prompted further exploration in the preparation of phosphine-stabilized phosphoranimine cations using different phosphorus donors. If an electron push–pull mechanism was indeed operating within the phosphoranimine cations **[15]**⁺ and **[17]**⁺, then large coupling constants would be anticipated when electron-withdrawing



Scheme 7.

substituents are present on the phosphorus donor and electron-donating substituents are present on the phosphoranimine acceptor. This postulation was investigated through our reactivity studies between $\text{BrMe}_2\text{P}=\text{NSiMe}_3$ (**14**) and the phosphorus donor $(\text{MeO})_3\text{P}$.

In a stoichiometric reaction between $\text{BrMe}_2\text{P}=\text{NSiMe}_3$ and $(\text{MeO})_3\text{P}$, the expected P–P complex $[(\text{MeO})_3\text{P}\bullet\text{PMe}_2=\text{NSiMe}_3]\text{Br}$ (**18**) was not observed. Significantly, the phosphoranimine $\text{BrMe}_2\text{P}=\text{NSiMe}_3$ was quantitatively converted to the known polymer $[\text{Me}_2\text{P}=\text{N}]_n$ (**19**) [7a] (Scheme 7).

Encouraged by this unexpected result, we proceeded to prepare the polymer $[\text{MePhP}=\text{N}]_n$ (**20**) [7b] from the phosphoranimine monomer $\text{BrMePhP}=\text{NSiMe}_3$ (**21**) [14]. Treatment of **21** with a stoichiometric amount of $(\text{MeO})_3\text{P}$ also quantitatively yielded $[\text{MePhP}=\text{N}]_n$ [7b] after 3 h. In an effort to diversify the polymerization chemistry, the polymer **20** was prepared under a variety of conditions such as the use of substoichiometric amounts of $(\text{MeO})_3\text{P}$, employment of different phosphites such as $(\text{EtO})_3\text{P}$ and $(\text{PhO})_3\text{P}$, and different solvents such as THF and toluene. In all cases, high molecular weight **20** ($M_w > 10^5$ g/mol) was obtained [16]. This new polymerization route offers significant potential advantages over the conventional thermal condensation route which requires reaction temperatures of up to 190 °C under vacuum and reaction times in the order of days [7b].

6. Summary

Cationic P(V)–N compounds are proposed intermediates in a variety of polymerization routes to polyphosphazenes. Many of these intermediates are integral in the understanding of polymerization mechanisms, yet have eluded isolation thus far due to their reactive nature. Thus, the nitrogen- and phosphorus-donor-stabilized phosphoranimine cations, which were prepared from the parent phosphoranimine monomers, represents excellent model complexes for these reactive intermediates. Moreover, the pursuit of phosphine-stabilized phosphoranimine cations have led to the discovery of a novel phosphine-mediated dehalogenation reaction. The preparation of phosphine-stabilized phosphoranimine cations was realized by employment of monohalogeno(diorgano)phosphoranimes and these complexes have shown to exhibit an unusual relationship between the magnitude of the observed ${}^1J_{\text{PP}}$ and the choice of organic substituent. We are currently in the process of investigating the origin of this

phenomenon through in depth NMR studies. Attempted expansion of the donor-stabilization chemistry to involve phosphites has led to the discovery of an ambient temperature route to poly(alkyl/aryl)phosphazenes. Investigations aimed at elucidating the polymerization mechanism are underway. This new polymerization method offers new synthetic opportunities for polymerization of phosphoranimine monomers which are unreactive or yield undesirable by-products via the traditional thermal condensation route.

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