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Phosphine-Mediated Dehalogenation Reactions of Trichloro(*N*-silyl)phosphoranimines

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The reaction of *N*-(trimethylsilyl)phosphoranimine $Cl_3P{=}NSiMe_3$ (**1**) with $^nBu_3P$ or Ph_3P yields the *N*-(dichlorophosphino)phosphoranimines $^nBu_3P{=}NPCl_2$ (**4a**) or $Ph_3P{=}NPCl_2$ (**4b**), respectively. Detailed studies of this reaction indicate a mechanism that involves the reductive dechlorination of **1** by the tertiary phosphine to yield $^nBu_3PCl_2$ (**5a**) or Ph_3PCl_2 (**5b**) with the apparent formation of the transient chlorophosphinimine $ClP{=}NSiMe_3$ (**6**), followed by condensation of **5a** or **5b** with **1** to form **4a** or **4b** and Me_3SiCl. Convincing evidence for the proposed mechanism was revealed by studies of the analogous reaction between the *N*-(triphenylsilyl)phosphoranimine $Cl_3P{=}NSiPh_3$ (**8**) with $^nBu_3P$ and Ph_3P. These reactions quantitatively generated **5a** and **5b** and also allowed the correspondingly more stable chlorophosphinimine $ClP{=}NSiPh_3$ (**10**) to be identified.

Introduction

The chemistry of halogen-rich phosphoranimines of the type $X_3P{=}NR$ (X = halogen; R = alkyl, aryl, silyl) represents a very fertile area of main-group chemistry.[1] For example, compounds of this type are precursors to a large array of novel phosphoranimines through selective halogen substitution at the phosphorus center using a wide range of organic[2] and organometallic nucleophiles.[3] Moreover, trihalogenophosphoranimines play important roles as synthons in the preparation of a wide variety of inorganic heterocycles.[4] Recently, such compounds have been employed in imine metathesis chemistry and used as aza-Wittig reagents.[5] Furthermore, the *N*-(trimethylsilyl)phosphoranimine $Cl_3P{=}NSiMe_3$ (**1**)[6] functions as a monomer for the preparation of poly(dichlorophosphazene) $[Cl_2P{=}N]_n$ with a narrow molecular weight distribution and molecular weight control at ambient temperature using the Lewis acid catalyst PCl_5 as the initiator.[7] This process represents a rare example of a living cationic, chain-growth polycondensation and exhibits some significant advantages over the conventional thermal

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ring-opening polymerization of the hexachlorophosphazene trimer $[NPCl_2]_3$, where high temperatures are necessary, molecular weight distributions are broad, and chain-length control is not possible.[8] Moreover, it has recently been shown that the phosphoranimine need not be isolated and purified to achieve a high-molecular-weight polymer with molecular weight control.[9] Recently, Wang has demonstrated that the phosphoranimine **1** can be generated in situ and treated with catalytic quantities of PCl_5 to obtain high-molecular-weight polyphosphazenes with narrow polydispersities.

Although **1** has been known for over 30 years, the chemistry of this interesting species remained relatively unexplored until recently, in part because of its low-yield preparation starting from PCl_5.[6] With the discovery of an improved high-yield synthesis starting from PCl_3 in 2002, the synthetic potential of **1** can now be fully realized more easily. For example, the reactive silyl functionality in **1** readily participates in chlorosilane elimination reactions with a number of halogenated substrates such as group 13 halides.[10] Moreover, the clean condensation of stoichiometric amounts of **1** with the phosphazene salt $[Cl_3P{=}N{=}PCl_3]Cl$ afforded a series of linear phosphazene salts, $[Cl_3P{=}N(PCl_2{=}N)_x{=}PCl_3]Cl$ ($x = 1-3$), which have provided both a snapshot of the P−N bonding and chain conformation within oligomeric phosphazenes and also insight into the initial steps in the cationic chain-growth polymerization of **1**.[11] The phosphoranimine **1** has also been used as a ligand precursor in the synthesis of a series of transition-metal phosphoranimate complexes[12] and, more recently, used to prepare novel lithium imidophosphate clusters and spirocycles.[13]

In this paper, we report our detailed studies of an unexpected reaction of the trichloro(*N*-silyl)phosphoranimine **1** with tertiary phosphines, which generates *N*-(phosphino)-phosphoranimines, $R_3P{=}N{-}PCl_2$, as final reaction products.

Experimental Section

General Procedures. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen or argon (Air Products) using common Schlenk techniques or an inert-atmosphere glovebox (M-Braun). Hexanes were dried and collected using a Grubbs-type solvent purification system manufactured by M-Braun.[14] CH_2Cl_2 was dried at reflux over CaH_2, while Et_2O was dried at reflux over sodium benzophenone. ^1H, $^{13}C\{^1H\}$, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian Gemini 300 spectrometer (300.1, 75.4, 282.3, and 121.5 MHz, respectively) and were referenced either to protic impurities in the solvent (^1H) or externally to $SiMe_4$ ($^{13}C\{^1H\}$), $CFCl_3$ (^{19}F) in $CDCl_3$, and 85% H_3PO_4 ($^{31}P\{^1H\}$) in $CDCl_3$. ^{31}P NMR integrations are approximate and are estimated to be accurate within ca. ±10% in the case of identical coordination numbers (e.g., R_4P^+ and $R_3P{=}E$) and within ±20% in the case of mixed coordination numbers (e.g., $R_3P{=}E$ and R_3P). Elemental analyses were performed at the University of Toronto using a Perkin-Elmer 2400 series CHN analyzer. $^nBu_3P$, Ph_3P, Ph_3PCl_2 (**5b**), PCl_5, Ph_3SiNH_2, and ^{n}BuLi (1.6 M/hexanes) were purchased from Aldrich and used as received. PCl_3 and SO_2Cl_2 were purchased from Aldrich and distilled under nitrogen prior to use. Triethylamine was purchased from Aldrich, dried at reflux over CaH_2, and distilled under nitrogen prior to use. $Cl_3P{=}NSiMe_3$ (**1**)[6a] and $^nBu_3PCl_2$ (**5a**)[15] 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 ($\lambda = 0.710\ 73$ 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.[16] The structures were solved and refined with the *SHELXTL* PC version 6.12 software package.[17] 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.

Reaction between 1 and $^nBu_3P$. To a solution of **1** (0.52 g, 2.3 mmol) in 5 mL of CH_2Cl_2 was added $^nBu_3P$ (0.60 mL, 2.4 mmol) dropwise. Analysis of the resulting yellow solution by $^{31}P\{^1H\}$ NMR after 1 h revealed the formation of $^nBu_3P{=}N{-}PCl_2$ (**4a**)[18] [δ 40.7 (d, $^2J_{PP} = 77.5$ Hz, $^nBu_3\mathit{P}{=}N-$), 159.5 (d, $^2J_{PP} = 76.9$ Hz, $-\mathit{P}Cl_2$); 1:1 ratio; ca. 45%] and **5a** [δ 107.2 (s, ca. 55%)].

Reaction between 1 and Ph_3P. A solution of Ph_3P (0.34 g, 1.30 mmol) in 3 mL of CH_2Cl_2 was added to a solution of **1** (0.29 g, 1.30 mmol) in 2 mL of CH_2Cl_2. The reaction was stirred for 7 days, and removal of the volatiles afforded a white solid, which was characterized as the previously known phosphoranimine $Ph_3P{=}NPCl_2$ (**4b**)[18b,19] (ca. 75%) and Ph_3PCl_2 (**5b**) (ca. 25%). Repeating the reaction in CD_2Cl_2 also identified $ClSiMe_3$ as a byproduct [^1H NMR: δ 0.51 (s)]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 15.8 (d, $^2J_{PP} = 75.0$ Hz, $Ph_3\mathit{P}{=}N$), 54.2 (s, Ph_3PCl_2), and 165.6 (d, $^2J_{PP} = 75.0$ Hz, $N\mathit{P}Cl_2$). ^1H NMR (CD_2Cl_2): δ 7.5−8.0 (m).

Preparation of $[^nBu_3P{=}N{=}PCl_3]Cl$ ([7a]Cl). A 5 mL solution of **1** (0.94 g, 4.19 mmol) was slowly added to a 10 mL CH_2Cl_2 solution of **5a** (1.14 g, 4.19 mmol) and stirred for 3 h. The resulting clear colorless solution was reduced to dryness, yielding a crystalline white solid (1.20 g, 74%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −13.4 (d, $^2J_{PP} = 18.7$ Hz, $Bu_3\mathit{P}{=}N$), and 55.3 (d, $^2J_{PP} = 18.8$ Hz, $N{=}\mathit{P}Cl_3$). ^1H NMR ($CDCl_3$): δ 0.77 (t, $^3J_{HH} = 7.2$ Hz, CH_3, 3H), 1.34 (m, CH_2, 4H), and 2.38 (pseudo q, $^2J_{HP} = 9.0$ Hz, $^3J_{HH} = 8.1$ Hz, CH_2, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.4 (s, CH_3), 23.4 (s, CH_2), 23.6 (s, CH_2), and 24.8 (d, $^1J_{CP} = 59.5$ Hz, CH_2). Anal. Calcd for $C_{12}H_{27}$-

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NP_2Cl_4 (389.11): C, 37.04; H, 6.99; N, 3.60. Found: C, 36.70; H, 7.18; N, 3.87.

Preparation of [Ph_3P═N═PCl_3]Cl ([7b]Cl). To a 50 mL CH_2Cl_2 solution of Ph_3PCl_2 (2.61 g, 7.84 mmol) was slowly added a 10 mL CH_2Cl_2 solution of **1** (1.76 g, 7.84 mmol), and the resulting solution was stirred for 3 h. All volatiles were removed in vacuo, yielding a pale-yellow solid. Recrystallization at −30 °C from a 9:1 $CHCl_3$/hexanes mixture afforded large colorless crystals of [**7b**]Cl (2.49 g, 71%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 2.8 (d, $^2J_{PP}$ = 1.9 Hz, Ph_3P═N), and 27.7 (d, $^2J_{PP}$ = 1.9 Hz, N═PCl_3). ^1H NMR ($CDCl_3$): δ 7.60−7.83 (br m, Ar−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 129.1 (d, $^1J_{CP}$ = 13.2 Hz, *i*-C), 130.6 (d, $^3J_{CP}$ = 13.8 Hz, *m*-C), 132.6 (d, $^2J_{CP}$ = 12.5 Hz, *o*-C), and 135.8 (d, $^4J_{CP}$ = 3.8 Hz, *p*-C). Anal. Calcd for $C_{18}H_{15}NP_2Cl_4$ (449.08): C, 48.14; H, 3.37; N, 3.12. Found: C, 48.05; H, 3.54; N, 3.13.

Reaction between [7a]Cl and ^{n}Bu_3P. A 1 mL CH_2Cl_2 solution of ^{n}Bu_3P (50 mg, 0.25 mmol) was added to a 5 mL solution of **[7a]**Cl (96 mg, 0.25 mmol) in CH_2Cl_2, and the resulting solution was stirred for 1 h. The resulting clear colorless solution was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy, which revealed a quantitative conversion of **[7a]**Cl and ^{n}Bu_3P to **4a** (ca. 45%) and **5a** (ca. 55%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 41.4 (d, $^2J_{PP}$ = 77.5 Hz, ^{n}Bu_3P═N), 107.2 (s, ^{n}Bu_3PCl_2), and 159.9 (d, $^2J_{PP}$ = 76.9 Hz, NPCl_2).

Reaction between [7b]Cl and Ph_3P. To a 5 mL solution of **[7b]**Cl (60 mg, 0.13 mmol) in CH_2Cl_2 was added a 1 mL solution of Ph_3P (35 mg, 0.13 mmol) in CH_2Cl_2, and the resulting solution was stirred for 1 h. The resulting clear colorless solution was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy, which revealed a quantitative conversion of **[7b]**Cl and Ph_3P to **4b** (ca. 55%) and **5b** (ca. 45%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 15.5 (d, $^2J_{PP}$ = 74.3 Hz, Ph_3P═N), 55.1 (s, Ph_3PCl_2), and 166.4 (d, $^2J_{PP}$ = 75.1 Hz, NPCl_2).

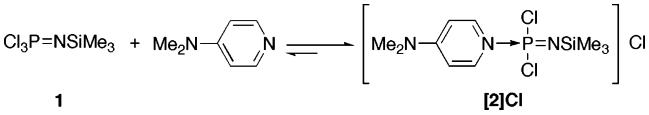
Preparation of Cl_3P═$NSiPh_3$ (8). (a) The silylamine Ph_3SiNH_2 (2.00 g, 7.26 mmol) was dissolved in 100 mL of CH_2Cl_2. To this solution was added Et_3N (1.50 g, 14.82 mmol), and the resulting solution was stirred for 5 min. The resulting clear and colorless solution was slowly added to a 100 mL CH_2Cl_2 solution of PCl_5 (1.51 g, 7.26 mmol) cooled to 0 °C. Upon complete addition of the amine solution, the white suspension was allowed to warm to room temperature and then heated under reflux for 5 h. After cooling to ambient temperature, the suspension was filtered and the filtrate was reduced to dryness, which yielded **8** as a crystalline white solid (2.22 g, 74%). (b) At ambient temperature, Ph_3SiNH_2 (5.00 g, 18.0 mmol) was dissolved in 100 mL of Et_2O. ^{n}BuLi (11.3 mL, 1.6 M solution in hexanes) was then added dropwise over 5 min, and the reaction mixture was refluxed for 1 h. Upon cooling to room temperature, distilled $ClSiMe_3$ (2.0 g, 18.0 mmol) was added and the reaction mixture was allowed to stir for a further 2 h under reflux, yielding a white precipitate (LiCl), at which point a second 1 equiv of ^{n}BuLi was added dropwise over 5 min. Distilled PCl_3 (1.58 mL, 18 mmol) was added following cooling to room temperature and stirring for 30 min at room temperature, resulting in further white precipitate formation (LiCl) and the generation of $Cl_2PN(SiMe_3)(SiPh_3)$ (**9**). $^{31}P\{^1H\}$ NMR: δ 190. Distilled SO_2Cl_2 (1.46 mL, 18 mmol) was added, and the resulting solution was allowed to stir for 30 min at room temperature and then filtered through a 1 cm pad of Celite. The volatiles were removed under reduced pressure (0.01 mmHg) to yield the desired phosphoranimine **8** as a white solid (6.45 g, 87%). Crystals of **8** were grown by vapor diffusion of pentane into a saturated CH_2Cl_2 solution of **8**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −49.6 (s). ^1H NMR ($CDCl_3$): δ 7.30−7.66 (m, ArH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 127.8 (*m*-C), 129.7 (*p*-C), 135.1 (*o*-C), and 135.5 (*i*-C). Anal. Calcd for $C_{18}H_{15}Cl_3NPSi$ (410.72): C, 52.64; H, 3.69; N, 3.41. Found: C, 52.48; H, 4.00; N, 3.36.

Reaction between 8 and ^{n}Bu_3P. To a 1 mL CH_2Cl_2 solution of **8** (95 mg, 0.23 mmol) was added a 1 mL CH_2Cl_2 solution of ^{n}Bu_3P. The clear and colorless solution was stirred for 10 min and then analyzed by $^{31}P\{^1H\}$ NMR, which revealed the quantitative conversion of **8** and ^{n}Bu_3P to **4a** (ca. 65%), **5a** (ca. 25%), and ClP═$NSiPh_3$ (**10**) (ca. 10%). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 35.6 (d, $^2J_{PP}$ = 77.5 Hz, ^{n}Bu_3P═N), 101.5 (s, ^{n}Bu_3PCl_2), 154.0 (d, $^2J_{PP}$ = 76.9 Hz, NPCl_2), 217.1 (s, ClP═$NSiPh_3$). After the solution was stirred for 4 days, the complete consumption of **10** was observed and resulted in the final products **4a** (ca. 80%) and **5a** (ca. 20%).

Results and Discussion

We have previously reported that the stoichiometric reaction between **1** and the strong Lewis base 4-(dimethylamino)pyridine (DMAP) resulted in the quantitative conversion of **1** to the DMAP-stabilized phosphoranimine cation [**2**]$^+$ (Scheme 1).[20] The formation of [**2**]Cl is believed to occur via an associative mechanism, whereby the initial coordination of the strong donor DMAP induces the dissociation of 1 equiv of a chloride anion.[21]

Scheme 1



Encouraged by the ability of DMAP to displace 1 equiv of chloride from **1** to form [**2**]Cl, we attempted to extend this chemistry to include tertiary phosphines as donors. Thus, the preparation of a phosphine-stabilized phosphoranimine cation, a $P^{III} \rightarrow P^V$ adduct, would complement the well-established family of diphosphonium cations $[R_3P-PR_2]^+$, which can be formally regarded as $P^{III} \rightarrow P^{III}$ adducts.[22]

1. Reactions of 1 with R_3P (R = ^{n}Bu and Ph). The direct reaction between **1** and the tertiary phosphines ^{n}Bu_3P and Ph_3P did not result in the expected formation of a phosphine-stabilized phosphoranimine salt [**3**]Cl (Scheme 2). Analysis of the reaction mixture formed from **1** and ^{n}Bu_3P after 1 h by $^{31}P\{^1H\}$ NMR spectroscopy revealed the complete consumption of **1** (δ −54) and the tertiary phosphine (δ −30) and the formation of **5a** (δ 107, ca. 45%) and the known *N*-phosphinophosphoranimine **4a**[18] (δ 41 and 160, $^2J_{PP}$ = 77 Hz, ca. 55%; Scheme 2). On the basis of this surprising result, the reaction was repeated and a $^{31}P\{^1H\}$ NMR spectrum was recorded after 10 min. This revealed the presence of a transient intermediate species, which possessed two doublets with chemical shifts of δ −13 and 55 (J = 19 Hz), in addition to unreacted starting materials. Furthermore, an additional intermediate was observed in the $^{31}P\{^1H\}$ NMR

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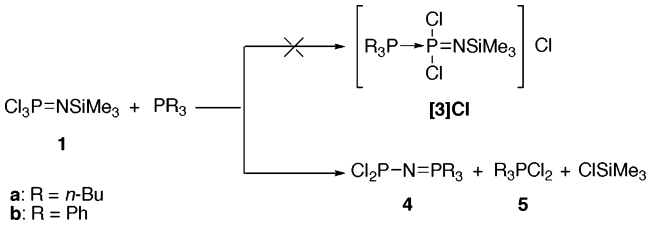
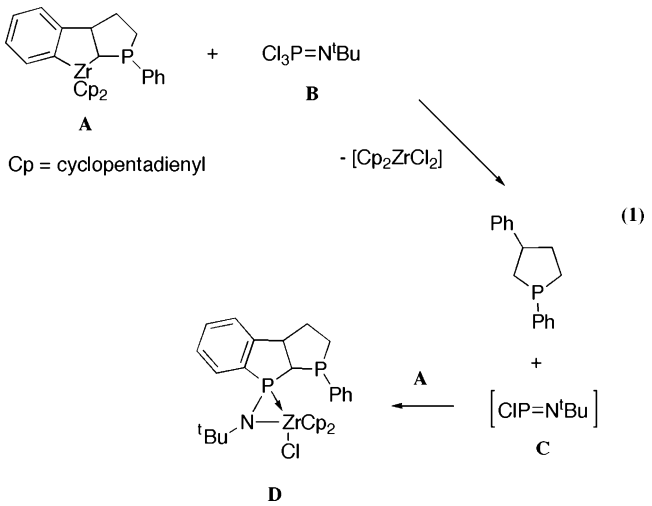
spectrum as a broad singlet centered at δ 227, which subsequently disappeared after 30 min. The identity of these intermediate species will be elaborated upon later, but the species with two doublets is consistent with the formation of a phosphazene salt $[^nBu_3P{=}N{=}PCl_3]^+$ with inequivalent phosphorus environments. Finally, signals corresponding to the previously observed products **4a** (δ 41 and 160, $^2J_{PP}$ = 77 Hz) and **5a** (δ 107) were identified after 30 min.

Scheme 2



When the analogous chemistry was performed using Ph_3P, the corresponding reaction was slower but similar results were obtained. Treatment of **1** in CH_2Cl_2 with Ph_3P resulted in the generation of **5b** (δ 54) and the known **4b**[18b,19] (δ 16 and 166, $^2J_{PP}$ = 75 Hz) after 6 days (Scheme 2), as indicated by $^{31}P\{^1H\}$ NMR. In this case no intermediate species could be detected. The above reactions of **1** with $^nBu_3P$ and Ph_3P were repeated in CD_2Cl_2, and Me_3SiCl (δ 0.51) was also observed by ^1H NMR as a byproduct from the reaction.

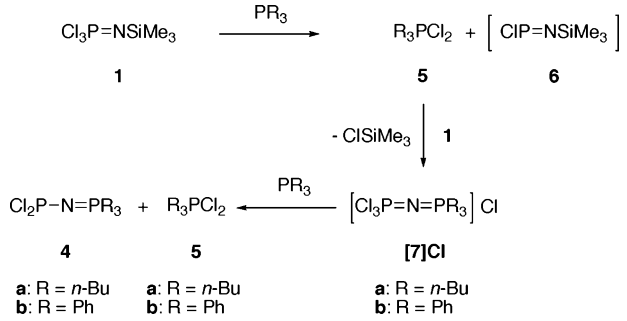
Intrigued by these initial observations, we further investigated the mechanism of this unusual reaction with the goal of identifying the intermediates involved.[23] It has previously been shown that tertiary phosphines and arsines undergo oxidative chlorination reactions with chlorophosphines to respectively yield dichlorophosphoranes or the corresponding arsanes and linear or cyclic phosphines bearing P−P bonds.[24] Very recently, the zirconaindane phospholane **A** has been shown to reductively dechlorinate the phosphoranimine $Cl_3P{=}N^tBu$ **B** to yield zirconocene dichloride, a phospholane, and the transient chlorophosphinimine $ClP{=}N^tBu$ **C** (eq 1). The phosphinimine **C** undergoes a subsequent reaction with an additional 1 equiv of **A**, and this results in the formation of the zirconaspirophosphane **D**.[25]



(1)

With this type of reactivity in mind, we tentatively proposed the following sequence of reactions, which rationalizes the formation of *N*-(phosphino)phosphoranimines and dichlorophosphoranes from **1** and the tertiary phosphines $^nBu_3P$ and Ph_3P (Scheme 3).

Scheme 3



In this proposed mechanism, the tertiary phosphine induces a reductive dechlorination of **1** to yield the dichlorophosphorane **5** and the chlorophosphinimine $ClP{=}NSiMe_3$ (**6**). An additional 1 equiv of **1** then undergoes a condensation reaction with **5** to yield an unsymmetrically substituted bisphosphonioammonium chloride salt [**7**]Cl with the elimination of trimethylchlorosilane. The salt [**7**]Cl further reacts with an additional 1 equiv of tertiary phosphine in a second dechlorination step to generate the final products **4** and **5** (Scheme 3). Thus, the overall stoichiometery for the reaction involves 2 equiv of a tertiary phosphine reacting with 2 equiv of **1** to generate 1 equiv each of **4**−**6** (eq 2). Because chlorophosphinimine **6** is likely to be highly reactive,[26−29] this species might be expected to react further and thus be undetectable as a final isolated product. Therefore, to provide evidence for the proposed mechanism, each proposed step was independently studied.

$$\underset{\mathbf{1}}{2Cl_3P{=}NSiMe_3} + 2PR_3 \rightarrow \underset{\mathbf{4}}{Cl_2PN{=}PR_3} + \underset{\mathbf{5}}{R_3PCl_2} + \underset{\mathbf{6}}{[ClP{=}NSiMe_3]} + ClSiMe_3 \quad (2)$$

(23) Our initial postulate based on our preliminary results (ref 20) was that the reaction of **1** with phosphines PR_3 to form the observed *N*-phosphinophosphoranimine products **4a** and **4b** involved imine transfer because the later species might be expected to result from the reaction of PCl_3 with $R_3P{=}NSiMe_3$, the expected initial products of a metathesis type process between **1** and PR_3. Our in depth studies reported here show that this original proposal is not correct.

(24) (a) Holmes R. R.; Bertant, E. F. *J. Am. Chem. Soc.* **1958**, *80*, 2983−2985. (b) Coates, G. E.; Livingstone, J. G. *Chem. Ind.* **1958**, 1366. (c) Braddock, J. M. F.; Coates, G. E. *J. Chem. Soc.* **1961**, 3208−3211. (d) Frazier, S. E.; Nielson, R. P.; Sisler, H. H. *Inorg. Chem.* **1964**, *3*, 292−294. (e) Seidel, V. W. *Z. Anorg Allg. Chem.* **1964**, *330*, 141−150. (f) Jain, S. R.; Sisler, H. H. *Inorg. Chem.* **1968**, *7*, 2204−2207. (g) Spangenberg, S. F.; Sisler, H. H. *Inorg. Chem.* **1969**, *8*, 1006−1010.

(25) Owsianik, K.; Zablocka, M.; Donnadieu, B.; Majoral, J.-P. *Angew. Chem., Int. Ed.* **2003**, *42*, 2176−2179.

(26) Although assigned as a monomeric species, the phosphinimine **6** may well exist in equilibrium with corresponding cyclic dimer $[ClPNSiMe_3]_2$. Only one example of a 2,4-dichloro-1,3-disila-1,3,2,4-diazadiphosphetidine is known, $\{ClPNSiF(OSiMe_3)[N(SiMe_3)_2]\}_2$, which has a $^{31}P\{^1H\}$ NMR resonance at 220 ppm in CD_2Cl_2. See: Clegg, W.; Klingebiel, U.; Sheldrick, G. M. *Z. Naturforsch.* **1982**, *37B*, 423−431.

Table 1. Crystal Data for [**7b**]Cl and **8**

	[**7b**]Cl·3CHCl$_3$	**8**
empirical formula	$C_{21}H_{18}Cl_{13}NP_2$	$C_{18}H_{15}Cl_3NPSi$
fw	807.15	410.72
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a (Å)	9.9089(3)	8.2984(17)
b (Å)	25.4558(10)	29.260(6)
c (Å)	13.8683(5)	7.7958(16)
α (deg)	90	90
β (deg)	108.910(2)	93.95(3)
γ (deg)	90	90
V (Å^3)	3309.2(2)	1888.4(7)
Z	4	4
D_c (mg m^{-3})	1.620	1.445
T (K)	150(1)	150(2)
R [$I > 2\sigma(I)$]	0.0637	0.0652
wR [$I > 2\sigma(I)$]	0.1628	0.1916
GOF on F^2	1.006	1.085

Table 2. Selected Bond Lengths and Angles for [**7b**]Cl and Related Species

	P(1)−N(1) [Å]	P(2)−N(1) [Å]	P(1)−N(1)−P(2) [deg]
[**7b**]Cl	1.610(5)	1.520(5)	142.7(4)
[**7b**]$_2$[PCl$_6$][ClHCl][30]	1.609(2)	1.525(2)	140.5(1)
[Ph$_3$PNPPh$_3$]Cl[31]	1.575(6)	1.583(6)	139.2(5)
[Cl$_3$PNPCl$_3$]PCl$_6$[32]	1.560(3)	1.562(3)	133.3(2)

2. Reactions of 1 with R_3PCl_2 5a (R = ^{n}Bu) and 5b (R = Ph). The second step of the proposed mechanism outlined in Scheme 3 involves the reaction between the phosphoranimine **1** and dichlorophosphoranes **5**. The direct condensation between **1** and **5** cleanly afforded the unsymmetrically substituted bisphosphonioammonium chloride salts [**7a**]Cl and [**7b**]Cl along with $ClSiMe_3$ as a byproduct. In the preparation of the salt [**7a**]Cl, a CH_2Cl_2 solution of **1** was slowly added to a rapidly stirring solution of **5a** in CH_2Cl_2. A slow rate of addition was necessary because the rapid addition of **1** resulted in the formation of copious amounts of poly(dichorophosphazene), as determined by $^{31}P\{^1H\}$ NMR spectroscopy (δ −18).[7] Workup of the reaction mixture after 3 h afforded [**7a**]Cl as a white solid in 74% yield, which was characterized by multinuclear NMR spectroscopy and elemental analysis. The salt [**7a**]Cl appears in the $^{31}P\{^1H\}$ NMR spectrum as two doublets with chemical shifts δ −13 and 55 ($^2J_{PP}$ = 19 Hz). Significantly, the chemical shifts for this salt directly coincide with the intermediate species from the reaction between **1** and ^{n}Bu$_3$P after 10 min.

The preparation of [**7b**]Cl was carried out in a similar manner.[30] The dichlorophosphorane **5b** in CH_2Cl_2 was treated slowly with a CH_2Cl_2 solution of **1**. The product was isolated, after 3 h, as a crystalline white solid in 71% yield and was characterized by NMR spectroscopy and elemental analysis. Single crystals of [**7b**]Cl suitable for X-ray diffraction studies were grown from a saturated $CHCl_3$ solution and characterized in the solid state (Table 1). Selected bond lengths and angles for [**7b**]Cl are given in Table 2, along with comparable data for related compounds.

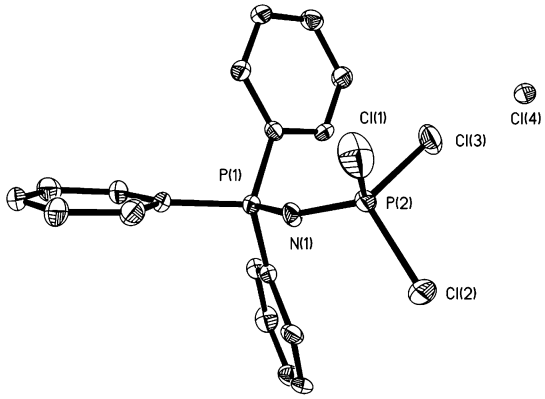


Figure 1. Thermal ellipsoid plot of [**7b**]Cl·3CHCl$_3$ at the 50% probability level. $CHCl_3$ solvate molecules and hydrogen atoms are omitted for clarity.

The cation [**7b**]$^+$ (Figure 1) exhibits a P(1)−N(1) bond length of 1.610(5) Å, which is slightly elongated from the P−N bond lengths found in [Ph$_3$P═N═PPh$_3$]$^+$ [1.575(6) and 1.583(6) Å].[31] Similarly, the P(2)−N(1) bond length of 1.520(5) Å is shorter than that found in [Cl$_3$P═N═PCl$_3$]$^+$ [1.561(3) Å].[32] The difference between the two P−N bond lengths in [**7b**]$^+$ may be attributed to the greater electronegativity for chlorine substituents compared to phenyl groups, thus resulting in a shorter P−N bond length, and can thus be represented as [Ph$_3$P−N═PCl$_3$]$^+$. Alternatively, the difference could be accounted for by the varied degrees of hyperconjugation between the two P−N bonds and could also be represented by the zwitterionic structure [Ph$_3$P(+)−N(−)−P(+)Cl$_3$]$^+$. The bond angle at nitrogen for [**7b**]$^+$ is relatively wide at 142.7(4)° compared to those found in [Ph$_3$P═N═PPh$_3$]$^+$ [139.2(5)°] and [Cl$_3$P═N═PCl$_3$]$^+$ [133.3-(2)°].

3. Reactions of [R_3P═N═PCl_3]Cl [7a]$^+$ (R = ^{n}Bu) and [7b]$^+$ (R = Ph) with R_3P (R = ^{n}Bu and Ph). The last step of the proposed mechanism outlined in Scheme 3 involves a reductive dechlorination of the bisphosphonioammonium chlorides salts [**7a**]Cl and [**7b**]Cl by the tertiary phosphines ^{n}Bu$_3$P and Ph$_3$P to generate the observed final products **4a**/**4b** and **5a**/**5b**, respectively. In line with our proposed mechanism, treatment of a pure sample of [**7a**]Cl with ^{n}Bu$_3$P in CH_2Cl_2 yielded the quantitative formation of **4a** (δ 41 and 160, $^2J_{PP}$ = 77 Hz) and **5a** (δ 107) after 1 h, as

(27) Phosphinimines of the general formula RP═NR′ have been well-documented. For a review, see: Niecke, E.; Gudat, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 217−237.

(28) The dimerization behavior of *N*-alkyl/arylphosphinimines is well-known. For example, see: (a) Burford, N.; Cameron, T. S.; Conroy, K. D.; Ellis, B.; Lumsden, M.; Macdonald, C. L. B.; McDonald, R.; Phillips, A. D.; Ragogna, P. J.; Schurko, R. W.; Walsh, D.; Wasylishen, R. E. *J. Am. Chem. Soc.* **2002**, *124*, 14012−14013. (b) Lehousse, C.; Haddad, M.; Barrans, J. *Tetrahedron Lett.* **1982**, *23*, 4171−4174.

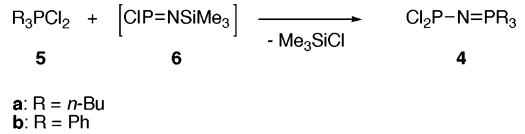
(29) The phosphinimine **6** has been prepared via thermolysis of Cl$_2$PN(SiMe$_3$)$_2$ and identified in the gas phase by UV photoelectron spectroscopy. See: Miqueu, K.; Sotiropoulos, J.-M.; Pfister-Suillouzo, G. Romanenko, V. D. *New J. Chem.* **2001**, *25*, 930−938.

(30) The cation [Ph$_3$P═N═PCl$_3$]$^+$ has been very recently prepared as a mixed salt with [PCl$_6$]$^-$ and [ClHCl]$^-$ counteranions from the reaction 2PCl$_3$ + 2ClNPPh$_3$ + PCl$_5$ + HCl → [Ph$_3$P═N═PCl$_3$]$_2$[PCl$_6$][ClHCl]. See: Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1471−1476.

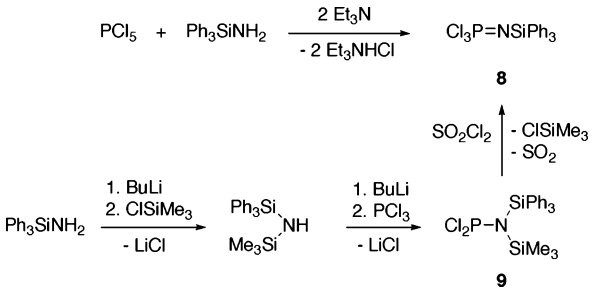
(31) Weller, F.; Nusshaer, D.; Dehnicke, K. *Z. Kristallogr.* **1993**, *208*, 322−325.

(32) Belaj, F. *Acta Crystallogr.* **1998**, *C54*, 1735−1737. For structural information on the cation [Cl$_3$P═N═PCl$_3$]$^+$ with transition-metal halide counterions, see: Rivard, E.; McWilliams, A. R.; Lough, A. J.; Manners, I. *Acta Crystallogr.* **2002**, *C58*, i114−i118.

Scheme 4



Scheme 5



determined by $^{31}P\{^{1}H\}$ NMR spectroscopy. Analogous chemistry involving the reaction of [**7b**]Cl with Ph_3P also resulted in the dechlorination of the salt, which converted Ph_3P (δ −5) to **5b** (δ 54) to quantitatively form **4b** (δ 16 and 166, $^{2}J_{PP}$ = 75 Hz), as shown by $^{31}P\{^{1}H\}$ NMR spectroscopy.

4. Studies of the Fate of ClP═NSiMe$_3$. Reaction between 8 and ^{n}Bu$_3$P. The reaction between **1** and the tertiary phosphines $^{n}Bu_3P$ and Ph_3P resulted in the dechlorination of **1** to give the oxidation products **5a** and **5b**. A ^{31}P NMR resonance tentatively assigned to the transient reductive dechlorination product **6**[26−29] (δ 227) was also detected by $^{31}P\{^{1}H\}$ NMR spectroscopy after 10 min from the reaction between **1** and $^{n}Bu_3P$, but this peak slowly disappeared. The dichlorophosphoranes **5a** and **5b** undergo a further reaction with **1** to yield the salts [**7a**]Cl and [**7b**]Cl, which subsequently also chlorinate the remaining tertiary phosphines, which results in the final reaction products **4** and **5**. However, the fate of the proposed transient chlorophosphinimine **6** (δ 227; Scheme 3) remained unclear. This presumably highly reactive species could, for example, undergo a reaction with the phosphoranes **5** generated in solution to yield the final reaction product **4** (Scheme 4). This alternate pathway may account for the nonstoichiometric production of **4b** and **5b** from the reaction between **1** and Ph_3P and the fact that the intermediate [**7b**]Cl was not observed in solution.

In an effort to characterize a more stable analogue of the proposed species **6**, we prepared the new phosphoranimine **8** based on the assumption that the Ph_3Si group would render the species less reactive toward chlorosilane elimination, compared to **1**. The phosphoranimine **8** was prepared from the treatment of triphenylsilylamine with PCl_5 in the presence of Et_3N.[33] Alternatively, **8** can be prepared via the oxidative chlorination of the unsymmetrically substituted *N*-silylaminophosphine **9** with SO_2Cl_2 (Scheme 5).[6a]

The phosphoranimine **8** represents one of only a few trichlorophosphoranimines that does not exist in equilibrium with its cyclic dimer.[34,35] Such an equilibrium is common

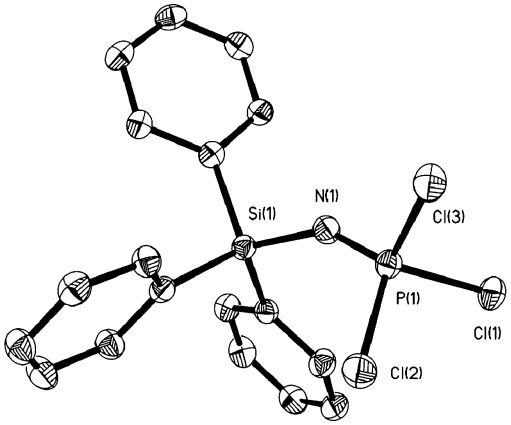
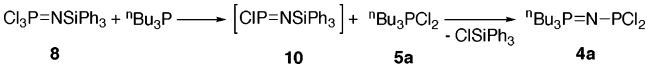


Figure 2. Thermal ellipsoid plot of **8** at the 50% probability level. Hydrogen atoms are omitted for clarity.

Scheme 6



for trichlorophosphoranimines because of the electron-withdrawing ability and small size of the chlorine atoms.[36] The solid-state structure of **8** (Table 1 and Figure 2), determined by single-crystal X-ray crystallography, displays a P(1)−N(1) bond length of 1.490(3) Å and is significantly shorter than typical phosphoranimine P−N bonds.[37] Moreover, the P(1)−N(1)−Si(1) angle is relatively wide [145.7-(2)°] and is similar to those observed in other silylated phosphoranimines.[18]

Treatment of the phosphoranimine **8** with $^{n}Bu_3P$ in CH_2Cl_2 resulted in the quantitative consumption of the reactants, was revealed by $^{31}P\{^{1}H\}$ NMR spectroscopy, after 10 min. More importantly, a resonance at δ 217 was assigned to the chlorophosphinimine **10**[38,39] in addition to the formation of **4a** (δ 41 and 160, $^{2}J_{PP}$ = 77 Hz) and **5a** (δ 107) as revealed by ^{31}P NMR spectroscopy. However, in the reaction between **8** and $^{n}Bu_3P$ after 10 min, **4a** was the predominant species in solution (ca. 65%) while **5a** (ca. 25%) and **10** (ca. 10%) were the minor products. Interestingly, because the reaction was allowed to proceed over 4 days, the chloro-

(33) Kirsanov, A. V. *Izv. Akad. Nauk SSR, Ser. Khim.* **1950**, 426.

(34) Burford, N.; Clyburne, J. A. C.; Gates, D. P.; Schriver, M. J.; Richardson, J. F. *J. Chem. Soc., Dalton. Trans.* **1994**, 997−1001.

(35) (a) Antipin, M. Y.; Struchkov, Y. T.; Urchenko, V. M.; Kozlov, E. S. *J. Struct. Chem. (Engl. Transl.)* **1982**, *23*, 227. (b) Antipin, M. Y.; Struchkov, Y. T.; Kozlov, E. S. *J. Struct. Chem. (Engl. Transl.)* **1986**, *26*, 575.

(36) (a) Zhmurova, I. N.; Kisilenko, A. A.; Kirsanov, A. V. *Zh. Obsch. Khim.* **1962**, *32*, 2580−2586. (b) Zhmurova, I. N.; Drach, B. S. *Zh. Obsch. Khim.* **1964**, *34*, 1441−1446. (c) Becke-Goehring, M.; Leichner, L.; Scharf, B. *Z. Anorg. Allg. Chem.* **1966**, *343*, 154−164. (d) Fluck, E.; Wachtler, D. *Liebigs Ann. Chem.* **1980**, 1651−1658.

(37) Typical P═N bond lengths range from 1.54 to 1.58 Å. See: Allen, C. W. *Coord. Chem. Rev.* **1994**, *130*, 137−173.

(38) Considerations similar to those previously noted for **6** exist for phosphinimine **10**; this species may be in equilibrium with the cyclic dimer, which may be expected to have a similar ^{31}P NMR chemical shift (see ref 26).

(39) The $^{31}P\{^{1}H\}$ NMR δ 217 has been tentatively assigned to the phosphinimine **10**. We base this assignment on the difference in chemical shift between **8** (δ −50) and **10** and draw the analogy from the chemical shift difference between the phosphoranimine Cl_3P═NMes* (δ −95) (ref 34) and the phosphinimine ClP═NMes* (δ 135) (Mes* = 2,4,6-tri-*tert*-butylphenyl). For the first report on ClP═NMes*, see: Niecke, E.; Nieger, M.; Reichert, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1715−1716.

phosphinimine **10** was consumed and quantitatively yielded **4a** (ca. 80%) in addition to **5a** (ca. 20%) (Scheme 6).

Summary

The *N*-(trimethylsilyl)phosphoranimine **1** undergoes reactions with tertiary phosphines and yields *N*-(dichlorophosphino)phosphoranimines **4** and dichlorophosphoranes (**5**). The reaction pathway proceeds via a sequence of dechlorination/chlorination, condensation, and dechlorination/chlorination steps.[23] In the process of elucidation of the mechanism, the unsymmetrically substituted bisphosphonioammonium salts ([**7**]Cl) were identified. These salts may serve as effective monofunctional initiators for the polymerization of **1**. Future goals include the design of a convenient and reactive byproduct-free synthetic route to the phosphinimine **10**, which may be a valuable synthetic precursor to interesting species. In addition, we are currently investigating the preparation of phosphine-stabilized phosphoranimine cations from phosphoranimines that are resistant to dehalogenation with phosphines.

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Supporting Information Available: Crystallographic information files (CIF) and other crystollographic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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