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SYNTHESIS AND REACTIVITY OF A NEW (METHYLENE)PHOSPHINE

Robert H. Neilson

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Dept. of Chemistry
Texas Christian University
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Synthesis and Reactivity of a New (Methylene)phosphine

A new, stable (methylene)phosphine $(Me_3Si)_2N-P=CHSiMe_3$ (4) was prepared via dehydrohalogenation of the chlorophosphine, $(Me_3Si)_2N-P(Cl)-CH_2SiMe_3$ (1), using $LiN(SiMe_3)_2$ as the base.

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Compound 1 and the related phosphine, $(Me_3Si)_2NP(CH_2SiMe_3)_2$ (2), were obtained by treating $(Me_3Si)_2NPCl_2$ with either one or two equivalents of Me_3SiCH_2MgCl. Reaction of 1 with t-BuLi proceeded via chloride displacement rather than dehydrohalogenation to afford the t-butylphosphine, $(Me_3Si)_2NP(t\text{-}Bu)CH_2SiMe_3$ (3). Two different modes of reactivity of 4 were observed: methanol added to the pπ bond yielding the methoxyphosphine, $(Me_3Si)_2NP(OMe)$-CH_2SiMe_3 (5), while treatment with Me_3SiN_3 gave the novel imino (methylene)phosphorane, $(Me_3Si)_2NP(=NSiMe_3)(=CHSiMe_3)$ (6). Compound 6 also added methanol to form a P-methoxyphosphinimine, $(Me_3Si)_2NP(OMe)(=NSiMe_3)CH_2SiMe_3$ (7). The reaction of 1 with with Me_3SiN_3 gave the azidophosphine, $(Me_3Si)_2NP(N_3)CH_2SiMe_3$ (8), which on heating underwent elimination of N_2 with formation of th dimeric forms (10a and 10b) of the di (imino) phosphorane $(Me_3SiN=)_2PCH_2SiMe_3$ (9). Decomposition of 8 in the presence of Me_3SiCl, however, gave a P-chlorophosphinimine, $(Me_3Si)_2NP(Cl)$-$(=NSiMe_3)CH_2SiMe_3$ (11). Proton, ^{13}C and ^{31}P NMR spectroscopic data for this new series of compounds are reported.

Contribution from the
Department of Chemistry
Texas Christian University
Fort Worth, TX 76129

Synthesis and Reactivity of a New (Methylene)phosphine

ROBERT H. NEILSON

Received ___________

A new, stable (methylene)phosphine $(Me_3Si)_2N-P=CHSiMe_3$ (4), was prepared via dehydrohalogenation of the chlorophosphine, $(Me_3Si)_2N-P(Cl)-CH_2SiMe_3$ (1), using $LiN(SiMe_3)_2$ as the base. Compound 1 and the related phosphine, $(Me_3Si)_2NP(CH_2SiMe_3)_2$ (2), were obtained by treating $(Me_3Si)_2NPCl_2$ with either one or two equivalents of Me_3SiCH_2MgCl. Reaction of 1 with t-BuLi proceeded via chloride displacement rather than dehydrohalogenation to afford the t-butylphosphine, $(Me_3Si)_2NP(t\text{-}Bu)$-$CH_2SiMe_3$ (3). Two different modes of reactivity of 4 were observed: methanol added to the $p\pi$ bond yielding the methoxyphosphine, $(Me_3Si)_2NP(OMe)CH_2SiMe_3$ (5), while treatment with Me_3SiN_3 gave the novel imino(methylene)phosphorane, $(Me_3Si)_2NP(=NSiMe_3)(=CHSiMe_3)$ (6). Compound 6 also added methanol to form a P-methoxyphosphinimine, $(Me_3Si)_2NP(OMe)$-$(=NSiMe_3)CH_2SiMe_3$ (7). The reaction of 1 with Me_3SiN_3 gave the azidophosphine, $(Me_3Si)_2NP(N_3)CH_2SiMe_3$ (8), which on heating underwent elimination of N_2 with formation of the dimeric forms (10a and 10b) of the di(imino)phosphorane $(Me_3SiN=)_2PCH_2SiMe_3$ (9). Decomposition of 8 in the presence of Me_3SiCl, however, gave a P-chlorophosphinimine, $(Me_3Si)_2NP(Cl)(=NSiMe_3)CH_2SiMe_3$ (11). Proton, ^{13}C and ^{31}P NMR spectroscopic data for this new series of compounds are reported.

Introduction

In recent years there has been considerable interest in the synthesis and reactivity of "low-coordinate" phosphorus compounds which contain P=C or P=N $(p-p)\pi$ bonds. Aside from the well known phosphabenzenes[1], compounds of this type include a relatively few examples of methylenephosphines[2], $R_2C=PR'$, iminophosphines[3], $RN=PR'$, and aminophosphinium cations[4], $(R_2N)_2P^+$. In addition to being significant from a theoretical viewpoint, these $p\pi$-hybridized phosphines appear to have great potential as new ligands in transition metal chemistry[5] and as possible precursors to new phosphorus-based polymer systems. It is this latter aspect to which some of our attention is now being directed.

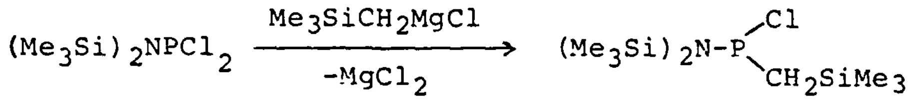
As a major part of our continuing study[6] of the chemistry of compounds which contain the Si-N-P linkage, we have demonstrated that certain easily-prepared N-silylphosphinimines are extremely effective precursors to new polyphosphazenes including $(Me_2PN)_n$[7]. The success of this method is based on the relatively high reactivity of the Si-N bond. We are now attempting to extend this approach to the synthesis of different types of phosphorus-containing polymers. Accordingly, we have begun a study of the synthesis, reactivity, and stereochemistry of new pπ-hybridized phosphorus compounds which contain silicon-nitrogen substituents. In this initial paper we report the synthesis, characterization, and some reactions of a new 2-coordinate P^{III} compound, $(Me_3Si)_2N$-$P{=}CHSiMe_3$.

Results and Discussion

The synthetic route to the P=C bond which we have used in this study involves the dehydrohalogenation of a chlorophosphine bearing the trimethylsilylmethyl, Me_3SiCH_2, substituent. The Me_3Si group serves a threefold purpose: (1) to labilize the adjacent methylene protons, (2) to sterically and electronically stabilize the resulting P=C product, and (3) to function as a potentially reactive site in the product.

A suitable precursor, [bis(trimethylsilyl)amino](chloro)-(trimethylsilylmethyl)phosphine (1) was prepared by the "one-pot" Grignard method (eqs 1 and 2) which we have used previously for the synthesis of a variety of alkyl(silylamino)-phosphines[8]. Similarly, if two equivalents of the silylmethyl Grignard reagent were used (eq 3), the dialkylphosphine 2 was obtained.

$$(Me_3Si)_2NLi \xrightarrow[-LiCl]{PCl_3} (Me_3Si)_2NPCl_2 \qquad (1)$$



$$(Me_3Si)_2NPCl_2 \xrightarrow[-MgCl_2]{Me_3SiCH_2MgCl} (Me_3Si)_2N\text{-}P(Cl)(CH_2SiMe_3) \quad (2)$$

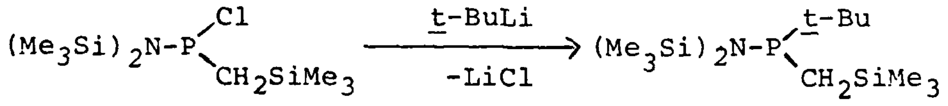
1

$$(Me_3Si)_2NPCl_2 \xrightarrow[-2\ MgCl_2]{2\ Me_3SiCH_2MgCl} (Me_3Si)_2NP(CH_2SiMe_3)_2 \quad (3)$$

2

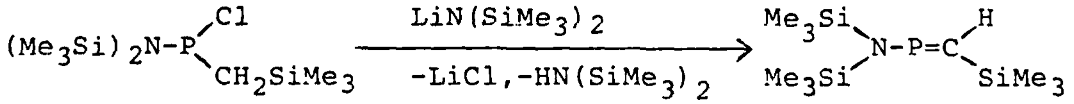
Like most of the compounds described herein, 1 and 2 are air- and moisture-sensitive liquids which were purified by vacuum distillation and characterized by elemental analysis and NMR (^1H, ^{13}C, and ^{31}P) spectroscopy (Table I).

Depending on the steric bulk and relative nucleophilicity of the base employed, the chlorophosphine 1 exhibited two distinct modes of reactivity. With t-butyllithium, chloride displacement (eq 4) was rapid and resulted in the formation of the t-butylphosphine 3. On the other hand, the less nucleophilic base, lithium bis(trimethylsilyl)amide, brought about dehydrohalogenation (eq 5) to afford the novel 2-coordinate P^{III} compound, [bis(trimethylsilyl)amino](trimethylsilylmethylene)-phosphine (4) in 70-75% yield.



$$(Me_3Si)_2N\text{-}P(Cl)(CH_2SiMe_3) \xrightarrow[-LiCl]{t\text{-}BuLi} (Me_3Si)_2N\text{-}P(t\text{-}Bu)(CH_2SiMe_3) \quad (4)$$

1 3

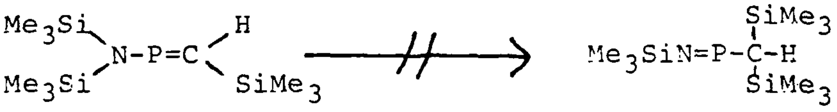


$$(Me_3Si)_2N\text{-}P(Cl)(CH_2SiMe_3) \xrightarrow[-LiCl,-HN(SiMe_3)_2]{LiN(SiMe_3)_2} (Me_3Si)_2N\text{-}P{=}C(H)(SiMe_3) \quad (5)$$

1 4

Compound 4 is an air-sensitive but thermally stable liquid which has a slight yellow color even when freshly distilled (bp 52°C/0.4 mm). The 2-coordinate nature of 4 is confirmed by the very low-field position of the ^{31}P resonance (δ309.9) as well as by elemental analysis. The ^{31}P shift is, in fact, farther downfield than other methylenephosphines which range from ca. 150 to 275 ppm[2]. Our value is in good agreement, however, with that of the isoelectronic iminophosphine $(Me_3Si)_2N\text{-}P{=}NSiMe_3$ which occurs at 325 ppm.[3a]

The alternative structure 4a which could result from a [1,3]N→C silyl shift (eq 6) was also considered because



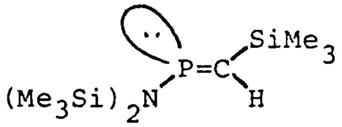
(6)

4

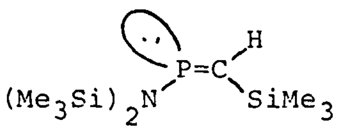
4a

such silyl migrations are well documented in Si-N-P systems.[8] The iminophosphine structure 4a can be rejected, however, on the basis of ^{1}H and ^{13}C NMR evidence. Both the ^{1}H (δ7.09) and the ^{13}C (δ148.3) signals for the CH moiety occur at low field as would be expected for an sp^2 rather than an sp^3 hybridized carbon.

At least three other features of the methylenephosphine 4 are worthy of note. First, compound 4 appears to be the first stable methylenephosphine that contains a C-H substituent as a site for potential derivatization. Second, there exists the possibility of cis-trans isomerism about the P=C π bond. All of the NMR (^{1}H, ^{13}C, and ^{31}P) data,



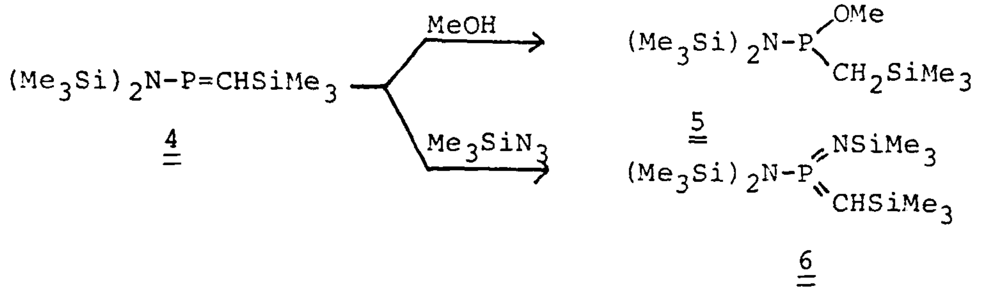
trans



cis

however, indicate the presence of only one isomer which, on steric grounds, is probably the *trans* form. The alternative possibility that there is a rapid *cis*-*trans* equilibrium would be inconsistent with a recently reported methylenephosphine $ClP{=}C(Ph)SiMe_3$ which, in fact, does show both isomers.[2d] Third, compound **4** can be viewed as an isoelectronic but neutral analogue of the aminophosphinium cations $(R_2N)_2P^+$. These ionic species exhibit some interesting features, including phosphorus-metal double bonds[5d], when employed as ligands. Amino(methylene)phosphines such as **4** , with the advantage of being neutral compounds which can be isolated and purified, should also have a rich transition metal derivative chemistry. All of these aspects of the chemistry of **4** are under investigation in our laboratory and will be reported in future papers.

Preliminary study of the chemistry of the methylenephosphine **4** reveals two types of reactions: (1) addition of polar reagents across the P=C bond, and (2) oxidation to give 3-coordinate P^V derivatives. These are illustrated, respectively, by the reaction of **4** with methanol (eq 7) to yield the methoxyphosphine **5** and with trimethylsilyl azide (eq 8) to yield [bis(trimethylsilyl)amino](trimethylsilylimino)(trimethylsilylmethylene)phosphorane **6**. As discussed above for compound **4**, the possibility of structural isomerism

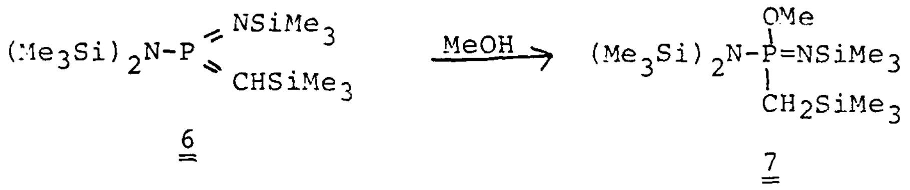


$$(Me_3Si)_2N\text{-}P{=}CHSiMe_3 \ (\mathbf{4}) \xrightarrow{MeOH} (Me_3Si)_2N\text{-}P(OMe)(CH_2SiMe_3) \ (\mathbf{5}) \quad (7)$$

$$(Me_3Si)_2N\text{-}P{=}CHSiMe_3 \ (\mathbf{4}) \xrightarrow{Me_3SiN_3} (Me_3Si)_2N\text{-}P({=}NSiMe_3)({=}CHSiMe_3) \ (\mathbf{6}) \quad (8)$$

of 6 to $(Me_3Si)_2CH\text{-}P({=}NSiMe_3)_2$ was discounted on the basis of NMR spectral data. Particularly diagnostic were the observation of three Me_3Si signals in the ^1H and ^{13}C NMR and the marked similarity of the ^{31}P and ^{13}C NMR data for 6 with that reported by Niecke[9] for the related compounds $(Me_3Si)_2N\text{-}P({=}NSiMe_3){=}CRR''$.

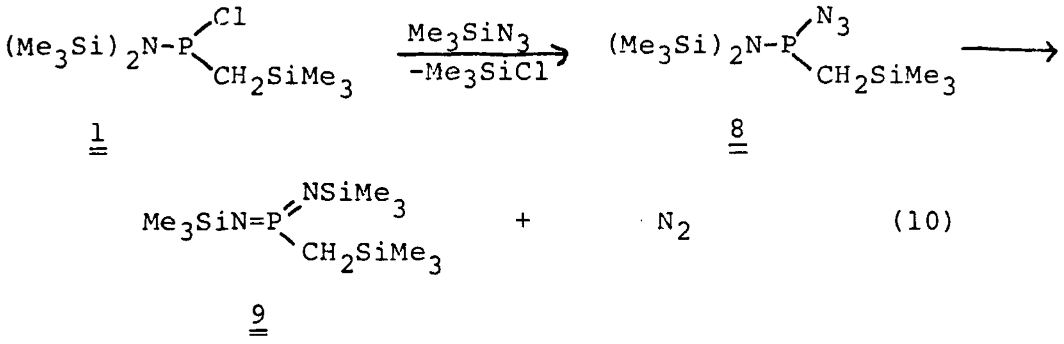
Further characterization of 6 results from its addition reaction with MeOH (eq 9) which gave the P-methoxyphosphinimine 7 in high yield. As observed for other compounds



$$(Me_3Si)_2N\text{-}P({=}NSiMe_3)({=}CHSiMe_3) \ (\mathbf{6}) \xrightarrow{MeOH} (Me_3Si)_2N\text{-}P(OMe)(CH_2SiMe_3){=}NSiMe_3 \ (\mathbf{7}) \quad (9)$$

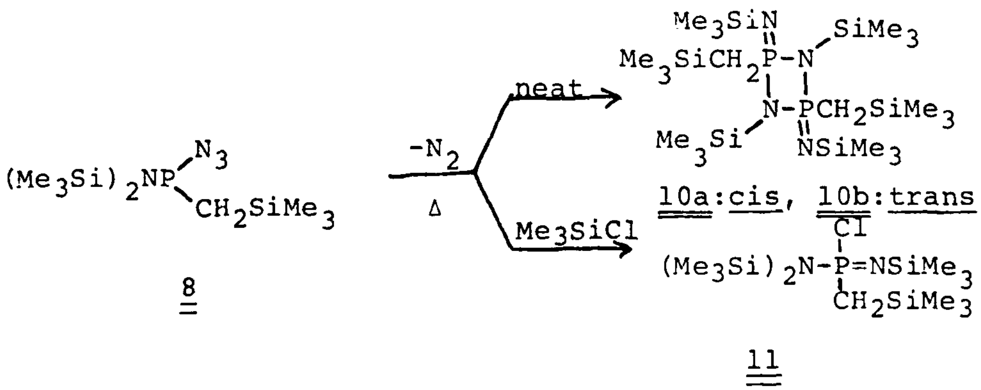
of this type[10], the ^1H NMR spectrum of 7 shows equivalence of the $(Me_3Si)_2N\text{-}$ and $Me_3SiN{=}$ protons of room temperature due to a rapid [1,3] silyl exchange between the two nitrogens. The variable temperature NMR study of 7 and several related compounds will be reported elsewhere[11].

We have also studied the reaction of trimethylsilyl azide with the chlorophosphine 1 with the hope of obtaining another type of 3-coordinate P^V compound 9 according to eq 10. The first step does, in fact, proceed smoothly at


$$\mathrm{(Me_3Si)_2N{-}P(Cl)(CH_2SiMe_3)} \xrightarrow[\mathrm{-Me_3SiCl}]{\mathrm{Me_3SiN_3}} \mathrm{(Me_3Si)_2N{-}P(N_3)(CH_2SiMe_3)} \longrightarrow \mathrm{Me_3SiN{=}P({=}NSiMe_3)(CH_2SiMe_3)} + \mathrm{N_2} \qquad (10)$$

1 8 9

room temperature either neat or in solution (CH_2Cl_2 or C_6H_6) to afford the azidophosphine 8 in virtually quantitative yield. Compound 8 is stable at room temperature and was characterized by NMR (Table I) and IR (ν_{N_3} = 2075 cm^{-1}) spectroscopy. Furthermore, moderate heating of 8 did cause elimination of N_2, but in no case was it possible to isolate the bis(trimethylsilylimino)phosphorane 9. Instead, the isolated products from such reactions were dependent upon whether or not chlorotrimethylsilane was present during the decomposition of the azidophosphise 8. Specifically, when 8 was heated alone at <u>ca</u>. 65°C for 18 hours (eq 11), the product was a solid which appears to be a mixture of the <u>cis</u> and <u>trans</u> isomers (10a and 10b) of the dimer of compound 9. When 8 was heated in refluxing benzene which also



(11)

8

10a:<u>cis</u>, 10b:<u>trans</u>

(12)

11

contained one equivalent of Me_3SiCl(eq 12), the major product was the P-chlorophosphinimine 11. Compound 11 most likely results from addition of Me_3SiCl across one of the P=N bonds of the 3-coordinate intermediate 9. These results clearly suggest that, by using azidophosphines such as 8, it is possible to generate reactive di(imino)phosphoranes (e.g. 9) in solution. The synthetic implications of this reaction certainly merit further investigation.

A final point concerns the ^1H NMR spectra of compounds 1, 2, 5, and 8 which show the CH_2 protons of the CH_2SiMe_3 group to be diastereotopic. The splitting pattern of these protons, therefore, is an 8-line AB portion of a typical ABX ($X={}^{31}P$) spectrum. The chemical shifts and coupling constants (Table I) were determined from the line spacings according to standard procedures for the analysis of an ABX spectrum.[12]

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without further purfication: $(Me_3Si)_2NH$, Me_3SiN_3, Me_3SiCH_2Cl, PCl_3, MeOH, *n*-BuLi (hexane solution), and *t*-BuLi (pentane solution). The Grignard reagent Me_3SiCH_2MgCl was prepared in Et_2O solution from Me_3SiCH_2Cl and Mg according to the published procedure[13]. Ether, THF, and benzene were distilled from CaH_2 prior to use. Dichloromethane was distilled from P_4O_{10} and stored over molecular sieves. Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P

NMR, both with ^1H decoupling, were obtained in the FT mode on a JEOL FX-60 instrument. Infrared spectra were obtained on a Beckman 4250 spectrophotometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The procedures described are typical of those used for the preparation of the new compounds in this study.

[Bis(trimethylsilyl)amino](chloro)(trimethylsilylmethyl)-phosphine (1). A 2-L, 3-necked flask, equipped with a paddle stirrer, N_2 inlet, and a 500-mL addition funnel, was charged with Et_2O (500 mL) and $(Me_3Si)_2NH$ (122 mL, 0.583 mol). After the solution was cooled to 0°C, n-BuLi (375 mL, 1.6 M in hexane) was added (over ca. 15 min) with stirring. The mixture was stirred at room temperature for 2h and then cooled to -78°C. Phosphorus trichloride (50.9 mL, 0.583 mmol) was added slowly via syringe and the mixture was allowed to warm to room temperature and was stirred for 1h. The mixture, now containing $(Me_3Si)_2NPCl_2$, was cooled to 0°C and a solution of Me_3SiCH_2MgCl (ca. 0.58 mol) in Et_2O (400 mL) was added from the addition funnel over ca. 30 min. The mixture was then stirred overnight at room temperature. After allowing the solids to settle, the supernatant solution was decanted and the solids were washed 3 times with ca. 50-ml portions of Et_2O. Solvent removal from the combined decantate and washings gave a yellow liquid residue from which 1 was distilled as a colorless liquid (107g, 58% yield, bp 78-79°C/0.30 mm). Anal. Calcd: C, 38.25; H, 9.31. Found: C, 38.49; H, 9.42.

[Bis(trimethylsilyl)amino]bis(trimethylsilylmethyl)phosphine(2). In the same manner, $(Me_3Si)_2NPCl_2$ (ca. 0.225 mol) was prepared in solution and treated with 2 equiv of Me_3SiCH_2MgCl (ca. 0.450 mol). Compound 2 was isolated by distillation as a colorless liquid (53.4g, 65% yield, bp 80-85°C/0.30 mm). Anal. Calcd: C, 45.97; H, 11.02. Found: C, 45.92, H, 10.85.

[Bis(trimethylsily)amino](tert-butyl)(trimethylsilylmethyl)phosphine (3). A 250-mL, 2-necked flask, equipped with a magnetic stirrer and an addition funnel, was charged with Et_2O (50 mL) and the chlorophosphine 1 (10.60g, 33.8 mmol). tert-Butyllithium (17.6 ml, 2.1 M pentane solution) was added (over ca. 10 min) to the stirred solution at 0°C. The mixture was then warmed to room temperature and stirred for 30 min. Filtration, solvent removal, and distillation gave the t-butylphosphine 3 as a colorless liquid (8.05g, 71% yield, bp 79-85°C/0.07 mm). Anal. Calcd: C, 50.09; H, 11.41. Found: C, 49.94; H, 11.26.

[Bis(trimethylsilyl)amino](trimethylsilylmethylene)-phosphine (4). The chlorophosphine 1 (19.4g, 20.0 mL, 61.8 mmol) was added via syringe to a stirred solution of $(Me_3Si)_2NLi$, prepared from $(Me_3Si)_2NH$ (13.1 mL, 63 mmol) and n-BuLi (41.9 mL, 1.6 M in hexane), in THF (125 mL). After ca. 30 min, a white solid was beginning to precipitate.

The mixture was stirred at room temperature for 48h to complete the reaction.[14] Filtration and solvent removal left a yellow liquid/white solid residue from which **4** was distilled as a pale straw-colored liquid (12.5g, 73% yield, bp 52°C/0.4 mm). The product retained its color even after a redistillation. *Anal*. Calcd: C, 43.27; H, 10.17. Found: C, 43.16; H, 10.45.

[Bis(trimethylsilyl)amino](methoxy)(trimethylsilylmethyl)-phosphine (**5**). Anhydrous methanol (0.69 mL, 17.0 mmol) was added via syringe to the methylenephosphine **4** (4.60 g, 16.6 mmol) with stirring at room temperature. The reaction was not exothermic but the mixture became somewhat cloudy. After stirring for 30 min, the mixture was clear and colorless. A ^{1}H NMR spectrum showed only the product **5** and some excess MeOH. Distillation gave the methoxyphosphine **5** as a colorless liquid (3.35g, 65% yield, bp 39°C/0.05 mm). *Anal*. Calcd: C, 42.67; H, 10.34. Found: C, 42.63; H, 10.09.

[Bis(trimethylsilyl)amino](trimethylsilylimino)(trimethylsilylmethylene)phosphorane (**6**). Trimethylsilyl azide (1.55 mL, 11.7 mmol) was added via syringe with stirring to the methylenephosphine **4** (2.94g, 10.6 mmol) at 0°C. After the mixture was warmed to room temperature, an exothermic reaction with gas evolution occurred. The mixture was recooled with an ice bath to moderate the reaction. After *ca*. 10 min, the mixture was again warmed to room temperature and was stirred for 1h. A ^{1}H NMR spectrum showed the reaction to be complete and free of byproducts. Distillation gave **6** as a colorless liquid (2.80g, 73% yield, bp 63-64°C/0.05 mm). *Anal*. Calcd: C, 42.81; H, 10.22. Found: C, 42.51; H, 10.31.

P-[Bis(trimethylsilyl)amino]-P-methoxy-P-(trimethylsilylmethyl)-N-(trimethylsilyl)phosphinimine (7). Compound 6 (26.5 mmol) was prepared as described above but was not purified by distillation. Excess Me_3SiN_3 was removed under vacuum. Anhydrous methanol (1.17 mL, 29 mmol) was then added via syringe to compound 6 with stirring at 0°C. The reaction was quite exothermic. After stirring for 30 min at room temperature, distillation gave the phosphinimine 7 as a colorless liquid (7.75g, 74% yield, bp 91-94°C/0.10 mm). Anal. Calcd: C, 42.38, H. 10.41. Found: C, 42.54; H, 10.41.

Azido[bis(trimethylsilyl)amino](trimethylsilyl)phosphine (8). Trimethylsilyl azide (1.26 mL, 9.5 mmol) was added via syringe to a stirred sample of the chlorophosphine 1 (2.70g, 8.60 mmol) at room temperature. The reaction was not exothermic but, after stirring for 1h, NMR spectral analysis showed complete conversion to the azidophosphine 8. Chlorotrimethylsilane and excess Me_3SiN_3 were removed under vacuum leaving 8 as a colorless liquid. The IR spectrum of the neat liquid contained a strong N_3 stretching band at 2075 cm^{-1}. Attempted distillation brought about decomposition as described below. Separate experiments also showed that 8 could be similarly prepared in CH_2Cl_2 or C_6H_6 solution.

Thermal decomposition of the azidophosphine 8. In the absence of Me_3SiCl. A neat sample of the azidophosphine 8 (ca. 10 mmol) was prepared as described above in a 50 mL-flask equipped with a reflux condenser attached to a vacuum system. The system was evacuated and the flask was heated with an oil bath at 65°C. The evolved nitrogen was collected in the vacuum system at the rate of *ca*. 1 mmol/h . After 18h, heating was discontinued leaving a wax-like solid which sublimed (*ca*. 110°C/0.03mm) to yield a white powdery solid. The NMR spectral data indicate the formation of a mixture of the dimers **10a** and **10b**: ^{1}H NMR (CDCl$_3$): δ0.03, 0.13, 0.28 (Me$_3$Si); δ1.50 (d, J_{PH}=20.4 Hz), 1.60 (d, J_{PH}= 20.4 Hz)(CH$_2$). ^{31}P NMR (CDCl$_3$): δ-12.3, -22.0 (*cis* and *trans*).

In the presence of Me$_3$SiCl. Trimethylsilyl azide (4.51 mL, 34 mmol) was added to a stirred solution of the chlorophosphine **1** (9.70g, 30.9 mmol) in benzene (30 mL). After stirring 1h, the ^{1}H NMR spectrum shows complete formation of the azidophosphine **8** and Me$_3$SiCl. The mixture was then heated at 85°C in an oil bath for 18h. Gas evolution was observed during this time. A ^{31}P NMR spectrum of the mixture showed the major product to be the phosphinimine **11** along with small amounts of the dimers **10a** and **10b**. Solvent removal left a viscous liquid from which **11** was distilled as a colorless liquid (*ca*. 20% yield, bp 75-76°C/ 0.20 mm). *Anal*. Calcd: C, 38.92; H, 9.55. Found: C, 38.36; H, 9.60. The solid remaining in the distillation flask was shown by ^{31}P NMR to contain the dimers **10a** and **10b**.

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Table I. NMR Spectroscopic Data[a]

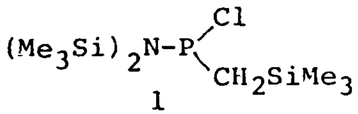
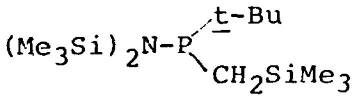
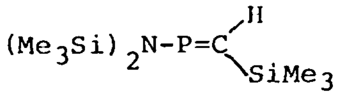
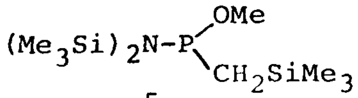
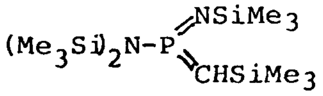
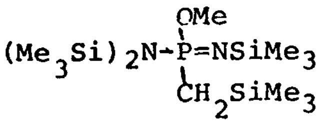
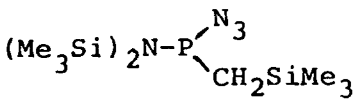
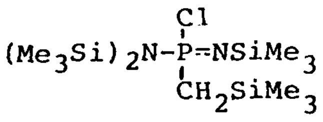
Compd	Signal	^{1}H δ	^{1}H J_{PH}	^{13}C δ	^{13}C J_{PH}	^{31}P δ
 $(Me_3Si)_2N{-}P(Cl)CH_2SiMe_3$ 1	Me$_3$SiN	0.39	1.5	4.57	5.5	164.1
	Me$_3$SiC	0.25	0.5	0.18	9.2	
	CH$_2$[b]	1.63	10.6	31.39	61.0	
		1.95	10.3			
$(Me_3Si)_2NP(CH_2SiMe_3)_2$ 2	Me$_3$SiN	0.38	0.5	5.66	17.7	42.9
	Me$_3$SiC	0.24	0.0	0.47	5.5	
	CH$_2$[b]	0.98	2.1			
		1.27	1.3			
 $(Me_3Si)_2N{-}P(t{-}Bu)CH_2SiMe_3$ 3	Me$_3$SiN[c]	0.36	1.6	5.34	15.3	66.6
		0.38	0.0	6.94	0.0	
	Me$_3$SiC	0.22	0.8	0.59	5.5	
	$\underline{\mathrm{Me}}_3$C	1.11	12.0	28.16	17.7	
	Me$_3\underline{\mathrm{C}}$			33.03	31.3	
	CH$_2$[d]	∼1.2	-	14.92	48.2	
 $(Me_3Si)_2N{-}P{=}C(H)SiMe_3$ 4	Me$_3$SiN	0.27	0.7	3.84	6.7	309.9
	Me$_3$SiC	0.09	1.4	1.03	9.2	
	CH [e]	7.09	18.5	148.32	70.2	
 $(Me_3Si)_2N{-}P(OMe)CH_2SiMe_3$ 5	Me$_3$SiN	0.23	1.2	4.69	7.9	157.4
	Me$_3$SiC	0.08	0.6	0.20	4.9	
	OMe	3.39	14.1	54.31	20.1	
	CH$_2$[b]	0.79	7.7	27.41	39.0	
		1.54	3.5			
 $(Me_3Si)_2N{-}P({=}NSiMe_3){=}CHSiMe_3$ 6	(Me$_3$Si)$_2$N	0.35	0.0	2.49	1.8	102.6
	Me$_3$SiN=	0.11	0.6	3.22	3.9	
	Me$_3$SiC	0.08	0.5	1.08	6.7	
	CH [f]	2.25	8.3	58.27	148.9	

Table I. (continued)

Compd	Signal	^1H δ	^1H J_{PH}	^{13}C δ	^{13}C J_{PH}	^{31}P δ
 $(Me_3Si)_2N-\overset{OMe}{\underset{CH_2SiMe_3}{P}}=NSiMe_3$	Me_3SiN [g]	0.22	-	4.87	-	19.2
	Me_3SiC	0.12	0.0	0.77	3.7	
	OMe	3.45	12.3	49.22	6.1	
	CH_2	1.28	20.4	25.05	114.8	
7						
	Me_3SiN	0.31	1.5	4.57	7.9	131.5
	Me_3SiC	0.13	0.8	0.00	4.9	
	CH_2 [b]	0.94	7.6	25.48	42.1	
		1.58	3.6			
8						
 $(Me_3Si)_2N-\overset{Cl}{\underset{CH_2SiMe_3}{P}}=NSiMe_3$	$(Me_3Si)_2N$	0.45	0.0	5.32	2.5	20.1
	$Me_3SiN=$	0.12	0.0	2.92	4.9	
	Me_3SiC	0.25	0.0	0.67	4.3	
	CH_2 [h]	~1.6-2.2	-	34.80	94.0	
11						

[a] Chemical shifts in ppm downfield from Me_4Si for ^1H and ^{13}C spectra and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^1H, CH_2Cl_2; ^{13}C and ^{31}P, $CDCl_3$. [b] The diastereotopic CH_2 protons were analyzed as the AB part of an ABX spectrum.[14] In each case, J_{AB} = 13.8 Hz. [c] Nonequivalence of Me_3Si groups on nitrogen due to hindered P-N bond rotation. [d] Multiplet (^1H) obscured by t-butyl signal. [e] J_{CH}=23.5 Hz. [f] J_{CH}=14.4 Hz. [g] Exchanging Me_3Si groups on nitrogens (see text). [h] Broad multiplet (^1H).

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