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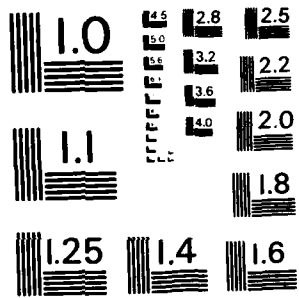
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Reactions of Mono(disilylamino)phosphines
with Carbon Tetrachloride

by

R.R. Ford, M.A. Goodman, R.H. Neilson
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A series of mono(disilylamino)phosphines $(\text{Me}_3\text{Si})_2\text{NPRR}'$ ($\text{R}, \text{R}' = \text{Me}, \text{Et}, \text{i-Pr}, \text{t-Bu}, \text{CH}_2\text{SiMe}_3, \text{CH}_2\text{CH}=\text{CH}_2, \text{CH}_2\text{Ph}, \text{Ph}, \text{NMe}_2, \text{OMe}, \text{OCH}_2\text{CF}_3$) and two related phosphines, $\text{Me}_2\text{SiCH}_2\text{CH}_2\text{Me}_2\text{SiNP}(\text{t-Bu})\text{CH}_2\text{SiMe}_3$ and $(\text{t-BuMe}_2\text{Si})_2\text{NPMe}_2$, were treated with CCl_4 either neat or in CH_2Cl_2 . The reactions proceeded with elimination of CHCl_3 and/or $\text{Me}_3\text{SiCCl}_3$ to form a variety of new P-chloro-N-silylphosphoranimines of general formula $\text{Me}_3\text{SiN}=\text{P}(\text{Cl})\text{R}'\text{R}''$. The preferential course of the reaction was dependent on solvent polarity and on the electronic and steric influence of the substituents at nitrogen and phosphorus. Complete physical and spectroscopic (^1H , ^{13}C , and ^{31}P NMR) characterization data are given for the new phosphines and P-chloro-N-silylphosphoranimines.

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

Reactions of Mono(disilylamino)phosphines with
Carbon Tetrachloride¹

Randal R. Ford, Mary A. Goodman, Robert H. Neilson,
Aroop K. Roy, Urszula G. Wettermark, and Patty Wisian-Neilson*

A series of mono(disilylamino)phosphines $(\text{Me}_3\text{Si})_2\text{NPRR}'$ ($\text{R}, \text{R}' = \text{Me}, \text{Et}, \text{i-Pr}, \text{t-Bu}, \text{CH}_2\text{SiMe}_3, \text{CH}_2\text{CH}=\text{CH}_2, \text{CH}_2\text{Ph}, \text{Ph}, \text{NMe}_2, \text{OMe}, \text{OCH}_2\text{CF}_3$) and two related phosphines, $\text{Me}_2\text{SiCH}_2\text{CH}_2\text{Me}_2\text{SiNP}(\text{t-Bu})\text{CH}_2\text{SiMe}_3$ and $(\text{t-BuMe}_2\text{Si})_2\text{NPMe}_2$, were treated with CCl_4 either neat or in CH_2Cl_2 . The reactions proceeded with elimination of CHCl_3 and/or $\text{Me}_3\text{SiCCl}_3$ to form a variety of new P-chloro-N-silylphosphoranimines of general formula $\text{Me}_3\text{SiN}=\text{P}(\text{Cl})\text{R}'\text{R}''$. The preferential course of the reaction was dependent on solvent polarity and on the electronic and steric influence of the substituents at nitrogen and phosphorus. Complete physical and spectroscopic (^1H , ^{13}C , and ^{31}P NMR) characterization data are given for the new phosphines and P-chloro-N-silylphosphoranimines.

Introduction

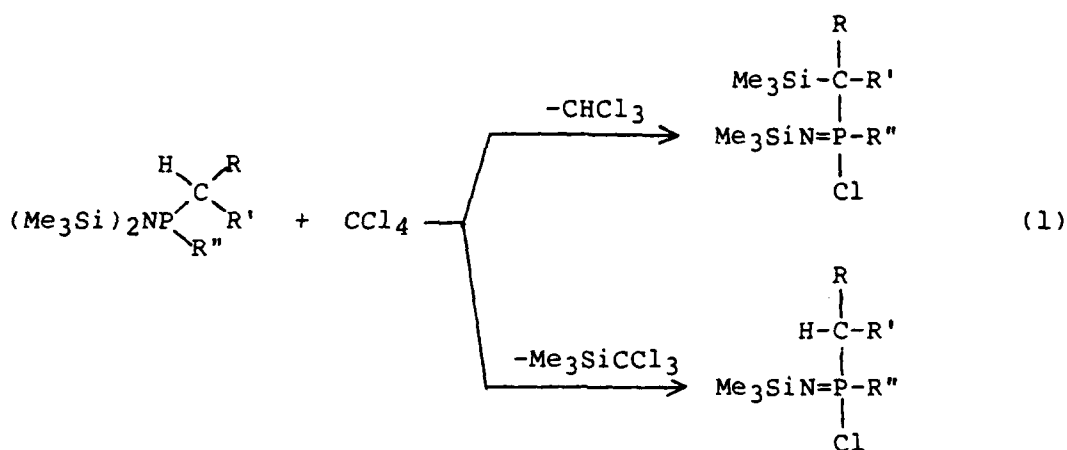
Due to the reactivity of the silicon-nitrogen bond, the chemistry of (disilylamino)phosphines, i.e. $(\text{Me}_3\text{Si})_2\text{NPRR}'$, often differs substantially from that of simple alkyl or aryl substituted phosphines.² As part of our continuing study of the reactivity of silicon-nitrogen-phosphorus compounds, we have investigated the oxidation reactions of a variety of bis(disilylamino)phosphines³ and mono(disilylamino)phosphines with CCl_4 .

The reaction of CCl_4 with tertiary phosphines which contain a CH proton α to phosphorus, but no disilylamino groups, produces CHCl_3 and phosphorus ylides.⁴ This presumably occurs via initial formation of an ion pair intermediate $[\text{R}_3\text{PCl}^+][\text{CCl}_3^-]$ ⁵ with subsequent attack at the hydrogen by the CCl_3^- anion.

It was shown earlier that an alternate reaction pathway also becomes important when CCl_4 interacts with phosphines containing both an α hydrogen and two disilylamino groups.³ In addition to proton abstraction by the CCl_3^- anion, attack at a silicon-nitrogen bond may occur with elimination of $\text{Me}_3\text{SiCCl}_3$. The competition between these two pathways is influenced by the steric bulk of the substituents at phosphorus and by solvent polarity.

In this paper, we report on the reactions of CCl_4 with mono(disilylamino)phosphines which contain α hydrogens. As in the reactions of CCl_4 with bis(disilylamino)phosphines, both the silicon-nitrogen bond and the α hydrogens are potentially

reactive sites. Two different types of N-silylphosphoranimine products may, therefore, be produced from these reactions (eq 1).

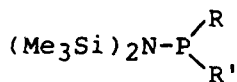


Our primary objectives were (a) to compare the CCl_4 reaction products with those obtained from bis(disilylamino)phosphines or from tertiary phosphines with no disilylamino substituents, (b) to better understand the influence of steric and electronic differences of substituents at phosphorus, i.e. R, R', and R'', and (c) to prepare various P-chloro-N-silylphosphoranimines which are potential precursors to polyphosphazenes and to novel three-coordinate phosphorus compounds.

Results and Discussion

Phosphine Synthesis. The various bis(disilylamino)-phosphines used in this study can be divided into four general categories: (1) simple dialkyl- or alkyl(phenyl)phosphines (1-7); (2) (trimethylsilylmethyl)phosphines (8-14); (3) phosphines with

benzyl or allyl substituents (15-18); and (4) systems with N-silyl groups other than Me₃Si (19-20).



1: R = R' = Me

2: R = R' = Et

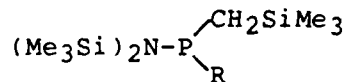
3: R = R' = *i*-Pr

4: R = *i*-Pr, R' = *t*-Bu

5: R = Ph, R' = Me

6: R = Ph, R' = Et

7: R = Ph, R' = *i*-Pr



8: R = Me

9: R = CH₂SiMe₃

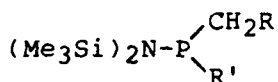
10: R = Ph

11: R = *t*-Bu

12: R = OMe

13: R = OCH₂CF₃

14: R = NMe₂

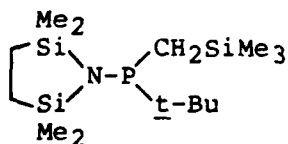


15: R = Ph, R' = Ph

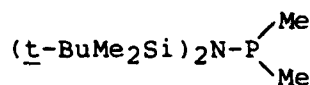
16: R = Ph, R' = CH₂Ph

17: R = CH=CH₂, R' = Ph

18: R = CH=CH₂, R' = CH₂CH=CH₂



19



20

Many of these phosphines were prepared as described previously using the Wilburn procedure⁶ or related methods.^{7,8}

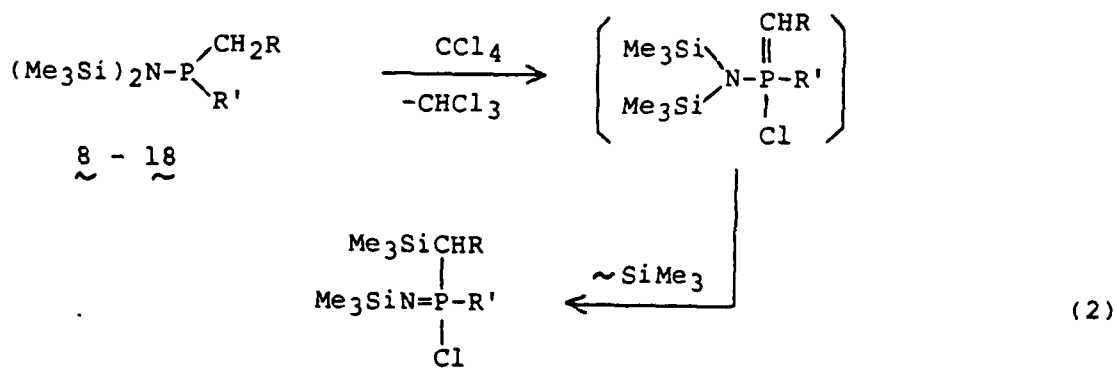
Of the compounds reported here for the first time, phosphines 8 and 13 were prepared by the nucleophilic substitution reactions of MeMgBr or CF₃CH₂OH with (Me₃Si)₂NP(Cl)CH₂SiMe₃.⁸ Compound 10 was made from (Me₃Si)₂NP(Cl)Ph⁶ and Me₃SiCH₂MgCl.⁹ Repeated distillations failed to give an analytically pure sample of 10, but a satisfactory analysis was obtained for 23, the P-chloro-N-silylphosphoranimine derivative obtained from its reaction with CCl₄. The preparation of the dimethylamino compound 14¹⁰ involved the sequential reaction of Me₃SiCH₂PCl₂ with Me₃SiNMe₂ and LiN(SiMe₃)₂. Allyl and benzyl Grignard reagents were used in the Wilburn synthesis⁶ to prepare phosphines 15-18. Compounds 15, 16, and 17, each had broad boiling point ranges and failed to give satisfactory elemental analysis. As in the case of 10, however, the trace impurities in these phosphines were not detectable in their NMR spectra. Moreover, good analytical data were obtained for the P-chloro-phosphoranimine derivatives 28 and 29, the decomposition product of 31, and several other derivatives¹¹. Compounds 19 and 20 were made by procedures similar to those above using (t-BuMe₂Si)₂NH¹² and Me₂SiCH₂CH₂SiMe₂NH¹³ in place of (Me₃Si)₂NH.

Preparative and ³¹P NMR spectral data for these new compounds are listed in Table II. The ¹H and ¹³C NMR data for selected compounds is given in Table I with complete spectral and analytical data included as Supplementary Material. The ¹H NMR spectra of several compounds (8, 10, 13, 15, and 16) show that the CH₂ protons of the CH₂SiMe₃ and CH₂Ph groups are

diastereotopic. The splitting pattern of these protons is a typical AB portion of an ABX spectrum ($X = {}^3\text{1p}$). Standard procedures for analysis of an ABX spectrum¹⁴ were used to determine the chemical shifts and coupling constants. The ${}^1\text{H}$ NMR spectra of phosphines 17-19 could not be analyzed in detail since the patterns were significantly complicated by the signals of other CH and/or CH_2 protons.

CCl_4 Reactions. The reactions of mono(disilylamino)-phosphines with carbon tetrachloride are grouped into two general categories: (a) those which result only in elimination of CHCl_3 and (b) those which proceed with elimination of both CHCl_3 and $\text{Me}_3\text{SiCCl}_3$. These groups are discussed independently below.

a) CHCl_3 Elimination. Despite the presence of the disilylamino group on phosphorus, a large number of phosphines with α hydrogens were found to react with CCl_4 in the same manner as tertiary alkyl phosphines⁴ giving only CHCl_3 elimination (eq 2). Unlike simple tertiary phosphines, however, the products



21: $\text{R} = \text{SiMe}_3$, $\text{R}' = \text{Me}$

22: $\text{R} = \text{SiMe}_3$, $\text{R}' = \text{CH}_2\text{SiMe}_3$

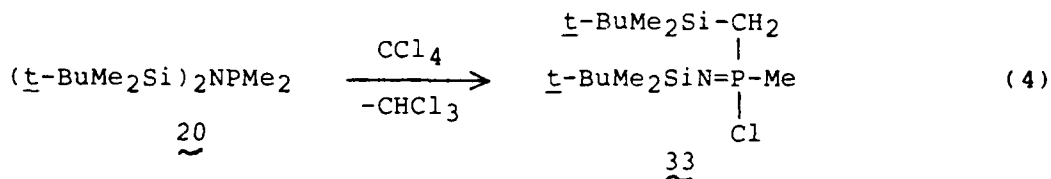
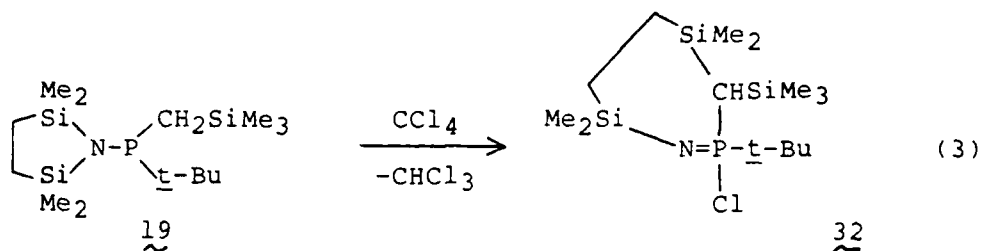
- \sim 23: R = SiMe₃, R' = Ph
 \sim 24: R = SiMe₃, R' = t-Bu
 \sim 25: R = SiMe₃, R' = OMe
 \sim 26: R = SiMe₃, R' = OCH₂CF₃
 \sim 27: R = SiMe₃, R' = NMe₂
 \sim 28: R = R' = Ph
 \sim 29: R = Ph, R' = CH₂Ph
 \sim 30: R = CH=CH₂, R' = Ph
 \sim 31: R = CH=CH₂, R' = CH₂CH=CH₂

are P-chloro-N-silylphosphoranimines and not phosphorus ylides. The ylides are presumably intermediates which undergo a rapid [1,3] silyl shift from nitrogen to carbon to form the N-silylphosphoranimines \sim 21- \sim 31. There is precedence for such a silyl shift in a number of related systems.^{3,15} Several features of the ¹H and ¹³C NMR spectra of the products indicated that the phosphoranimines, rather than the ylides, were indeed obtained. In fact, none of these compounds exhibited the upfield chemical shifts typical of ylides in either the ¹H or ¹³C NMR spectra (¹H, ca. -0.8 ppm and ¹³C, ca. -7.0 ppm).¹⁶ The presence of a (Me₃Si)₂CH group in compounds \sim 21- \sim 27 is indicated by the observation of three Me₃Si signals in the ¹H NMR. One signal is the imino group, Me₃SiN=, and the others are the C-bonded diastereotopic Me₃Si groups adjacent to a chiral phosphorus. Evidence for the non-equivalence of the two Me₃Si groups on carbon is provided by the chemical shift changes of these signals which occur upon changing the solvent from benzene to CH₂Cl₂.

The observation of two distinct Me₃Si signals in the ¹H and ¹³C NMR spectra as well as the lack of typical ylide signals is consistent with the phosphoranimine structures for 28 and 29. In addition, the P-C-H signals in the ¹H and ¹³C NMR spectra of 30 and 31 had large J_{PH} (13-18 Hz) and J_{PC} (80-83 Hz) couplings as well as ¹H NMR chemical shifts indicative of allylic (2-3 ppm), rather than vinylic (5-6 ppm) protons¹⁷. Two signals were observed in the ³¹P NMR spectra of 28-31 due to the diastereomers which result from the presence of two chiral centers in these molecules.

With the exception of compound 30, derived from the allyl(phenyl)phosphine 17, these new phosphoranimines were isolated and purified by vacuum distillation. They were identified by NMR spectroscopy and also characterized by elemental analysis. Compound 30 was a high boiling material which was best purified by recrystallization, after which NMR spectra indicated that very little impurity remained. Attempted distillation of the purified material resulted in decomposition via elimination of Me₃SiCl. The residue after heating was identified as $\{[\text{CH}_2=\text{CH}-\text{C}(\text{SiMe}_3)\text{H}]\text{P}(\text{Ph})=\text{N}\}_n$ by elemental analysis and ³¹P NMR (see Experimental Section).

Two related phosphines, 19 and 20, with different silyl substituents at nitrogen also reacted with CCl₄ to produce only CHCl₃ elimination products (eq 3 and 4). The seven-membered ring compound 32 is analogous to that obtained from a similar [1,3]

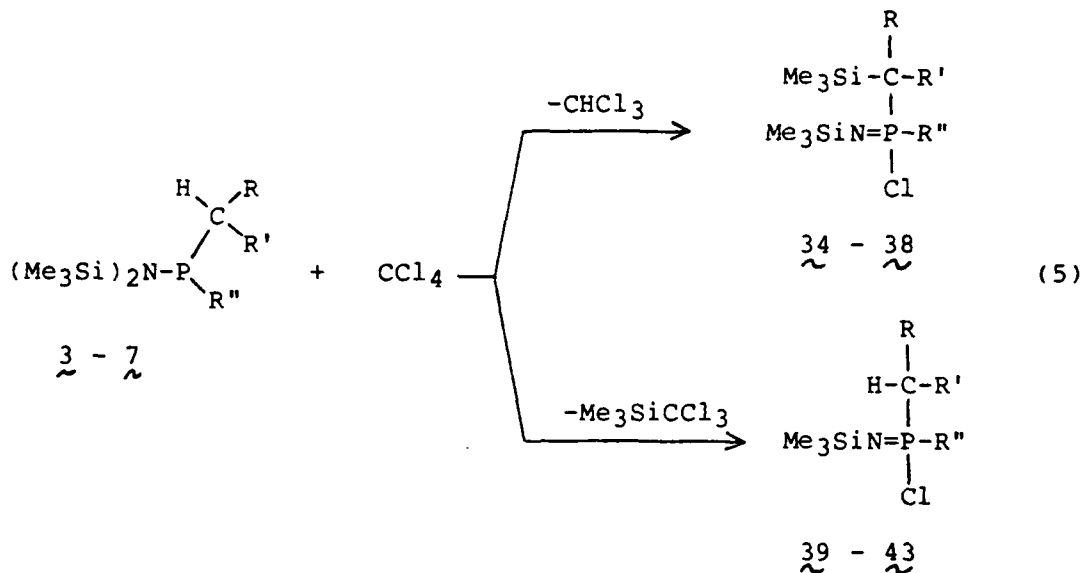


silyl shift upon treatment of $\text{Me}_2\text{SiCH}_2\text{CH}_2\text{Me}_2\text{SiNPMe}_3^+ \text{I}^-$ with $n\text{-BuLi}$.¹⁵ As noted in this earlier case, the formation of the cyclic compound strongly suggests that the silyl shift from nitrogen to carbon is an intramolecular process. The reaction of 20 with CCl_4 (eq 4) is also consistent with the process being intramolecular. In contrast to $(\text{Me}_3\text{Si})_2\text{NPMe}_2$ (1), which is discussed later, 20 gives exclusively the CHCl_3 elimination product 33 either with CH_2Cl_2 as a solvent or in excess CCl_4 . Presumably the conformation of the bulky t -butyl group prevents the external attack of the CCl_3^- anion at silicon [which readily occurs with less hindered groups in $(\text{Me}_3\text{Si})_2\text{NPMe}_2$], but does not interfere with an internal attack at silicon by an ylidic carbon within the same molecule.

A common feature in most of the phosphines involved in these reactions is the acidic character of the α protons. Attack of the CCl_3^- anion on these protons is likely because the resulting ylide intermediates are resonance stabilized by the adjacent

SiMe₃, CH=CH₂, or Ph groups. Once formed, the ylides may then easily rearrange via a [1,3] silyl shift. We have noted only a few exceptions to this generalization. As reported previously,³ [(Me₃Si)₂N]₂PCH₂R (R = SiMe₃, Ph) reacted with CCl₄ to give both CHCl₃ and Me₃SiCCl₃ elimination products. Formation of Me₃SiCCl₃ in these cases is not surprising since there are a large number of Me₃Si groups available for attack by the CCl₃⁻ anion. Another exception occurred in this series. The reaction of (Me₃Si)₂NP(CH₂SiMe₃)Me (8) in CH₂Cl₂ produced only the CHCl₃ elimination product 21, but in excess CCl₄ with no other solvent, another phosphorus compound was also formed as indicated by ³¹P NMR (δ 25.5). Although it was not possible to separate this second product from 21, NMR analysis indicated that the CCl₃⁻ anion may also have attacked the hydrogens on the P-Me group.

(b) CHCl₃ and Me₃SiCCl₃ Elimination. The reactions of mono(disilylamino)phosphines containing simple alkyl groups (i.e. Me, Et, i-Pr) with CCl₄ were often more complicated. Generally, both CHCl₃ and Me₃SiCCl₃ elimination products were formed (eq 5) with a change in solvent having a profound effect on which products were predominant. This is in contrast to most of the reactions described above where only CHCl₃ elimination was observed in either CH₂Cl₂ or in excess CCl₄. Table III summarizes the yields of each type of product obtained when these reactions were done in CH₂Cl₂ and in excess CCl₄.

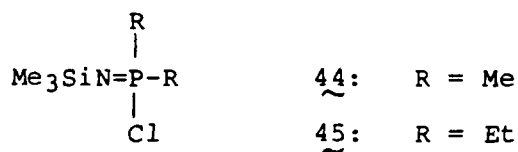


When these reactions were carried out neat (i.e. excess CCl_4), the favored products were always those resulting from the elimination of CHCl_3 (34-38). For reasons similar to those discussed above, these products were identified by NMR spectroscopy as the P-chloro-N-silylphosphoranimines and not the ylides. Unlike many of the previous reactions, at least trace amounts of the $\text{Me}_3\text{SiCCl}_3$ elimination products were observed in each reaction mixture.

When the same phosphines were treated with CCl_4 in CH_2Cl_2 , the product distribution was influenced by the nature of the phosphorus substituent. The *iso*-propylphosphines (3, 4, and 7) produced small amounts of the CHCl_3 elimination products and large yields of the $\text{Me}_3\text{SiCCl}_3$ elimination products, 41-43. In these cases the CCl_3^- anion which is relatively free in the polar

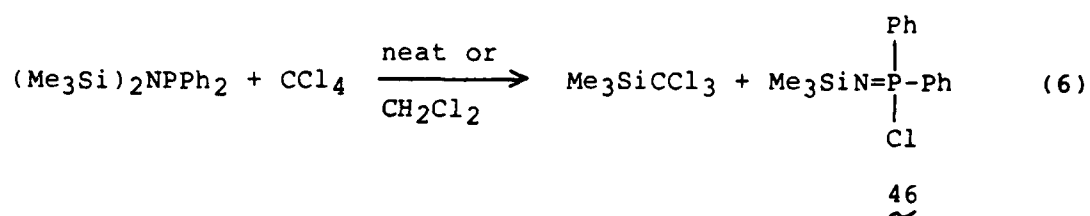
solvent CH_2Cl_2 , preferentially attacks the silicon rather than the sterically hindered hydrogens in the iso-propyl group. The Ph/Me and Ph/Et phosphines 5 and 6, on the other hand, produced primarily the CHCl_3 elimination products, 34 and 35. Here the hydrogens of the methyl and ethyl groups are less sterically crowded so there is less competition by the Me_3Si group for the CCl_3^- anion.

The reactions of the simplest phosphines $(\text{Me}_3\text{Si})_2\text{NPR}_2$ (1: R = Me, 2: R = Et) gave complex mixtures of products either in CH_2Cl_2 or CCl_4 . Typically, as many as four major signals were observed in the ^{31}P NMR spectra of the reaction mixtures. When each reaction was carried out under very dilute conditions ($<0.5\text{M}$ in CH_2Cl_2), low yields of the $\text{Me}_3\text{SiCCl}_3$ elimination products, 44 and 45 were isolated by distillation. No other pure compounds



could be isolated from any of the reaction mixtures. In view of the clean reaction (eq 4) observed for the analogous (t-BuMe₂Si)₂N substituted phosphine 20, these results show that the nature of the silicon substituents can also significantly influence the course of such reactions.

One reaction of CCl_4 with a mono(disilylamino)phosphine with no α hydrogens was also investigated (eq 6). As expected, the



$\text{Me}_3\text{SiCCl}_3$ elimination product 46 was obtained. On heating in a sealed glass ampoule, 46 eliminated Me_3SiCl forming $(\text{Ph}_2\text{PN})_3$. This is analogous to the thermal decomposition of $\text{Me}_3\text{SiN}=\text{P}(\text{X})\text{Ph}_2$ ($\text{X} = \text{Fl}8, \text{Br}19$).

Conclusion. Several trends become evident from the results of this series of reactions as well as those involving bis(disilylamino)phosphines. Both the elimination of CHCl_3 and $\text{Me}_3\text{SiCCl}_3$ are reasonable pathways for these reactions to follow. The elimination of CHCl_3 is favored by (a) non-polar solvents which promote a "tighter" intermediate ion pair $[\text{R}_3\text{P}^+\text{Cl}][\text{CCl}_3^-]$, resulting in preferential attack of the CCl_3^- anion on the nearby α hydrogen; (b) substituents at the α carbon (e.g. $\text{SiMe}_3, \text{Ph}, \text{CH}=\text{CH}_2$) which tend to resonance stabilize the ylide intermediate; and (c) α hydrogens which are not sterically hindered by other substituents on the α carbon. The elimination of $\text{Me}_3\text{SiCCl}_3$ is favored by (a) polar solvents which allow for a relatively "loose" ion pair and a CCl_3^- anion which is free to attack a peripheral Me_3Si group; (b) an abundance of $(\text{Me}_3\text{Si})_2\text{N}$ groups³ so there is a greater chance for attack at silicon; and (c) sterically hindered α hydrogens which limit their accessibility by the CCl_3^- anion.

Experimental Section

General Procedures. The following reagents were purchased from commercial sources and used without further purification: MeMgBr(Et₂O), PhCH₂MgCl(THF), *t*-BuLi(pentane), CH₂=CHCH₂MgCl(Et₂O), CF₃CH₂OH, and PhPCl₂. Spectroscopic grade CCl₄ was stored over molecular sieves. Dichloromethane, Et₂O, and Et₃N were distilled from CaH₂ prior to use. Published procedures were used to prepare Me₂SiCH₂CH₂Me₂SiNH¹³, Me₃SiCH₂MgCl⁹, (Me₃Si)₂NLi⁶, and (*t*-BuMe₂Si)₂NH¹². The mono(disilylamino)phosphines, 1-7, 9, 11 and 12 were also prepared by published procedures.⁶⁻⁸ Proton NMR spectra were recorded on a Varian-EM390 spectrometer, while a JEOL FX-60 spectrometer was used to record ¹³C{¹H} and ³¹P{¹H} NMR spectra. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Table I contains ¹H and ¹³C NMR data for representative compounds. Physical, preparative, and ³¹P NMR data for all the compounds reported here are listed in Table II.

All reactions and manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. Typical procedures used in the preparation of the new compounds in this report are described below.

Preparation of (Me₃Si)₂NP(Me)CH₂SiMe₃, 8. The chlorophosphine (Me₃Si)₂NP(Cl)CH₂SiMe₃⁸ (31.08 g, 99 mmol) and Et₂O (100 mL) were placed in a three-necked, round bottom flask equipped with a magnetic stir bar, a nitrogen inlet, and an addition funnel. The reaction flask was cooled to 0°C and MeMgBr (36.7

ml, 2.7 M, 99 mmol) was added dropwise via the addition funnel. The mixture was allowed to warm to room temperature and to stir overnight. The Grignard salts were removed from the mixture by filtration under nitrogen and solvent was removed from the filtrate under reduced pressure. Distillation of the yellow liquid residue through a 10 cm Vigreux column yielded 19.0 g of a colorless liquid which was identified as 8.

Preparation of $(\text{Me}_3\text{Si})_2\text{NP}(\text{OCH}_2\text{CF}_3)\text{CH}_2\text{SiMe}_3$, 13. A three-necked round bottom flask equipped with a magnetic stir bar, a nitrogen inlet, and a septum was charged with $(\text{Me}_3\text{Si})_2\text{NP}(\text{Cl})\text{CH}_2\text{SiMe}_3^8$ (18.4 g, 58.6 mmol), Et_3N (8.2 mL, 58.8 mmol), and Et_2O (50 mL). The mixture was cooled to 0°C and $\text{CF}_3\text{CH}_2\text{OH}$ (4.6 mL, 58.6 mmol) was added slowly via syringe. This mixture was warmed to room temperature and stirred for ca. 2 h. Filtration under nitrogen removed $\text{Et}_3\text{N}\cdot\text{HCl}$. Solvent was removed from the filtrate affording a colorless residue which was distilled under vacuum through a 10 cm Vigreux column to give 16.1 g of 13 as a colorless liquid.

Preparation of $(\text{Me}_3\text{Si})_2\text{NP}(\text{Ph})\text{CH}_2\text{SiMe}_3$, 10. A three-necked, round bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and an addition funnel was charged with PhPCl_2 (27.2 mL, 0.20 mol) and Et_2O (100 mL) and the mixture was cooled to -78°C . A solution of $(\text{Me}_3\text{Si})_2\text{NLi}$ (0.20 mol in ca. 200 mL of hexane⁶) was added dropwise via the addition funnel. The mixture was then warmed to 0°C ; stirred at that temperature for 2 h; then warmed to room temperature and stirred overnight. This mixture was

cooled to 0° and $\text{Me}_3\text{SiCH}_2\text{MgCl}^9$ (0.20 mol in ca. 200 mL of Et_2O) was added dropwise. After warming to room temperature and stirring for ca. 5 h, the mixture was filtered under nitrogen. Solvent removal at reduced pressure gave a yellow residue which was distilled through a 10 cm Vigreux column to give 43.3 g of a colorless liquid which solidified on standing (mp 30-31°C) and was identified as 10.

Preparation of $\text{Me}_2\text{SiCH}_2\text{CH}_2\text{Me}_2\text{SiNP}(\text{t-Bu})\text{CH}_2\text{SiMe}_3$, 19. A procedure similar to that used to prepare $(\text{Me}_3\text{Si})_2\text{NP}(\text{Cl})\text{CH}_2\text{SiMe}_3^8$ was used to prepare $\text{Me}_2\text{SiCH}_2\text{CH}_2\text{Me}_2\text{SiNP}(\text{Cl})\text{CH}_2\text{SiMe}_3^{10}$. This chlorophosphine (19.8 g, 63.5 mmol) and Et_2O (50 mL) were placed in a three-necked, round bottom flask equipped with a nitrogen inlet, a magnetic stir bar, and a septum. After cooling the solution to 0°C, t-BuLi (32.0 mL, 2M) was added via syringe. The mixture was warmed to room temperature and stirred overnight. Filtration, solvent removal from the filtrate, and distillation of the residue gave 19.

Synthesis of 15, 16, 17, 18, and 20 by the Wilburn Method. Typically 250 to 350 mmol of 15-18 were prepared according to the Wilburn⁶ procedure using PhCH_2MgCl or $\text{CH}_2=\text{CHCH}_2\text{MgCl}$. Compound 20 was also prepared by the Wilburn procedure using $(\text{t-BuMe}_2\text{Si})_2\text{NH}$ in place of $(\text{Me}_3\text{Si})_2\text{NH}$.

Reactions of (Disilylamino)phosphines with CCl_4 . Unless otherwise noted, the following procedures are typical of those used to prepare the P-chloro-N-silylphosphoranimines 21-46.

a) Neat Reactions. The (disilylamino)phosphine 3 (6.60 g, 23.8 mmol) was placed in a 100-mL round bottom flask equipped with a magnetic stir bar, nitrogen inlet, and septum. After cooling to 0°C, a five-fold excess (11.5 mL, 118.9 mmol) of CCl₄ was added to the phosphine via syringe. The mixture was stirred overnight at room temperature and a yellow solution formed. Excess CCl₄ and other volatiles were removed under reduced pressure. Vacuum distillation of the residue afforded 37.

b) Reactions in CH₂Cl₂. In a similar set-up, the phosphine 3 (4.86 g, 17.5 mmol) and CH₂Cl₂ (18 mL) were placed in the flask and cooled to 0°C. One molar equivalent (1.7 mL, 17.5 mmol) of CCl₄ was then added via syringe. Solvent removal at reduced pressure and distillation of the yellow liquid residue gave 42.

Reaction of 17 with CCl₄. The reaction was carried out as described in a and b above, but upon attempted distillation only a few drops distilled. When the reaction was repeated, the crude product was recrystallized from CH₂Cl₂ by adding hexane (Tables I and II). An attempt to further purify this material by vacuum distillation resulted in decomposition. The residue in the flask was identified as oligomeric $\{[\text{CH}_2=\text{CHCH}(\text{SiMe}_3)]\text{P}(\text{Ph})=\text{N}\}_n$ by ³¹P NMR (δ - 5.42) and elemental analysis: Calc. C, 61.24; H, 7.71. Found: C, 61.62; H, 6.70.

Reaction of 1 and 2 with CCl₄. The reaction of 1 with CCl₄ was carried out as described in a and b above and also according

to procedure b with freshly distilled hexane as a solvent. In each case as many as 4 major signals and several smaller signals were observed in the ^{31}P NMR spectra of the reaction mixtures. Vacuum distillation did not give any fractions containing a single pure compound. However, low yields of pure samples of 44 and 45 were obtained in dilute CH_2Cl_2 solutions. Typically, the phosphine 1 (7.23 g, 32.7 mmol) and CH_2Cl_2 (32 mL) were placed in a 250 mL round bottom flask equipped with a magnetic stirrer, nitrogen inlet, and addition funnel. After cooling the solution to 0°C , CCl_4 (3.2 mL, 32.7 mmol) in CH_2Cl_2 (32 mL) was added dropwise. The mixture was warmed to room temperature and stirred for ca. one h. Solvent removal and distillation afforded 44. A similar procedure using ca. twice as much CH_2Cl_2 was used to obtain 45.

Thermal decomposition of 46. A sample (3.95 g, 12.8 mmol) of 46 was placed in a heavy-walled glass ampoule which was sealed under vacuum. Light brown solids formed after heating in an oven at 180°C for 67 h. The ampoule was opened and Me_3SiCl (1.38 g, yield 97%) was removed under vacuum. A ^{31}P NMR spectrum of the crude material contained a large signal at 15.24 and a small one at δ 6.12. Recrystallization from hot CH_3CN gave pure crystals of the trimer $(\text{Ph}_2\text{P}=\text{N})_3$ (mp $228-230^\circ\text{C}$, $^{31}\text{P}(\text{THF}) \delta$ 15.9) 20 .

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Supplementary Material Available. Tables of ^1H and ^{13}C NMR spectroscopic data and analytical data for all new compounds. Ordering information is given on any current masthead page.

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Table I: ^1H and ^{13}C NMR Spectroscopic Data
for Selected Compounds.^a

compd	signal	^1H NMR			^{13}C NMR		
		δ	J_{PH}	J_{HH}	δ	J_{PC}	
$(\text{Me}_3\text{Si})_2\text{NP} \begin{cases} \text{CH}_2\text{SiMe}_3 \\ \text{OCH}_2\text{CF}_3 \end{cases}$ 13	$(\text{Me}_3\text{Si})_2\text{N}$	0.32	1.5		4.55	8.6	
	Me_3SiCH_2	0.15	0.9		0	4.9	
	Me_3SiCH_2	0.88	7.3	13.8	27.41	39.1	
			1.75	1.8	13.8		
	OCH_2CF_3	3.93	7.2 ^c		65.50	23.2 ^c	
	OCH_2CF_3				124.38	13.4 ^d	
$(\text{Me}_3\text{Si})_2\text{NP} \begin{cases} \text{CH}_2\text{CH}=\text{CH}_2 \\ \text{CH}_2\text{CH}=\text{CH}_2 \end{cases}$ 18	$(\text{Me}_3\text{Si})_2\text{N}$	0.37 ^e	1.2		4.79	7.3	
	$-\text{CH}_2\text{CH}=\text{CH}_2$	2.27- 2.91 ^{b,e}			38.03	23.8	
	$-\text{CH}_2\text{CH}=\text{CH}_2$	5.63- 6.17 ^{b,e}			134.23	12.8	
	$-\text{CH}_2\text{CH}=\text{CH}_2$	4.94- 5.27 ^{b,e}			116.44	10.4	
$\begin{array}{c} \text{Cl} \\ \\ \text{Me}_3\text{SiN}=\text{P}-\text{CH}(\text{SiMe}_3)_2 \\ \\ \text{OCH}_2\text{CF}_3 \end{array}$ 26	Me_3SiN	0.08			2.90	5.5	
	$(\text{Me}_3\text{Si})_2\text{CH}$	0.24			1.81	4.3	
		0.31					
	$(\text{Me}_3\text{Si})_2\text{CH}$	1.31	27.0		27.71	100.7	
	OCH_2CF_3	4.20	8.4 ^f		60.69	7.3 ^g	
	OCH_2CF_3				123.48	14.7 ^h	

Table I. continued

compd	signal	¹ H NMR			¹³ C NMR	
		δ	J _{PH}	J _{HH}	δ	J _{PC}
$ \begin{array}{c} \text{Cl} \quad \text{SiMe}_3 \\ \quad \\ \text{Me}_3\text{SiN}=\text{P}-\text{CHCH}=\text{CH}_2 \\ \\ \text{CH}_2\text{CH}=\text{CH}_2 \end{array} $	Me ₃ SiN	-0.02	0.6		3.29	4.9
	Me ₃ SiCH	0.21			0.69	2.4
		0.22			0.85	2.4
	Me ₃ SiCH	2.3-3.0 ^b			45.87	80.0
					43.17	80.6
	SiCHCH=CH ₂	4.7-5.4 ^{b,e}			132.22	7.3
					131.82	8.5
	SiCHCH=CH ₂	5.5-6.1 ^{b,e}			120.81	14.7
					120.63	14.0
	PCH ₂ CH=CH ₂	2.3-3.0 ^b			44.37	70.2
				44.13	70.2	
PCH ₂ CH=CH ₂	4.7-5.4 ^{b,e}			128.93	10.4	
				128.53	9.8	
PCH ₂ CH=CH ₂	5.5-6.1 ^{b,e}			117.80	17.1	
				118.21	15.9	
$ \begin{array}{c} \text{SiMe}_2 \\ \\ \text{Me}_2\text{Si} \quad \text{CHSiMe}_3 \\ \quad \\ \text{N}=\text{P}-\text{t-Bu} \\ \\ \text{Cl} \end{array} $	MeSi	0.01-0.38 ^b			1.17-5.52 ^b	
	Me ₃ SiCH	1.56	13.8		25.24	32.2
	SiCH ₂	0.64-0.97 ^b			11.50	
					12.93	
	Me ₃ C	1.19	19.2		25.40	
	Me ₃ C				40.45	88.9

Table I. continued

compd	signal	¹ H NMR			¹³ C NMR	
		δ	J _{PH}	J _{HH}	δ	J _{PC}
$ \begin{array}{c} \text{Cl} \\ \\ \text{Me}_3\text{SiN}-\text{P}-\text{CMe}_2\text{SiMe}_3 \\ \\ \text{i-Pr} \end{array} $	Me ₃ SiN	0.18			3.43	4.3
	Me ₃ SiC	0.03			-1.46	
	Me ₃ SiC				32.04	65.9
	Me ₂ C	1.08-1.41 ^b			20.99	4.9
					20.79	1.3
	Me ₂ CH	1.08-1.41 ^b			19.51	3.1
					18.76	3.7
	Me ₂ CH	2.05-2.41 ^b			34.90	71.4
$ \begin{array}{c} \text{Cl} \\ \\ \text{Me}_3\text{SiN}=\text{P}-\text{i-Pr} \\ \\ \text{i-Pr} \end{array} $	Me ₃ SiN	0.02			3.37	4.9
	Me ₂ CH	1.20	19.2	6.8	16.43	3.1
					16.00	3.7
	Me ₂ CH	2.19	6.9	6.9	32.45	78.1

^a Chemical shifts downfield from Me₄Si for ¹H and ¹³C spectra, coupling constants in Hz. Solvents: ¹H, CH₂Cl₂; ¹³C, CDCl₃, unless noted otherwise.

^b Multiplet. ^c J_{HF} = 9.0 Hz; J_{FC} = 35.4 Hz. ^d J_{FC} = 278.3 Hz. ^e Solvent: benzene. ^f Couplings in benzene; J_{FH} = 8.4 Hz. ^g J_{FC} = 37.2 Hz.

^h J_{FC} = 277.7 Hz.

Table II. Preparative and ^{31}P NMR Spectroscopic Data

compd	preparative		^{31}P NMR
	% yield ^a	bp °C(mm)	δ^b
8	66	37-38(0.01)	36.29
10	61	98-100(0.01)	41.95
13	73	40-42(0.01)	165.49
15	78	115-150(0.05)	54.36
16	62	133-143(0.10)	62.53
17	65	73-90(0.02)	46.96
18	65	71-73(0.03)	49.61
19	56	65-69(0.01)	56.66
20	75	70-76(0.05)	31.21
21	76	51(0.01)	26.97
22	(71)	69-75(0.01) mp 38-41°C	29.06
23	(61)	82-86(0.01)	19.66
24	84	75-80(0.03)	49.71
25	(82)	48(0.01)	15.16
26	(78)	66-68(0.01)	12.13
27	(75)	61-62(0.01)	21.80
28	84	124-126(0.05)	18.58, 16.93 ϵ
29	(87)	130-137(0.05)	22.62, 24.03 ϵ
30	75 d	104(0.05) ϵ	17.72, 16.48 ϵ
31	(84)	70-78(0.15)	25.53, 23.40 ϵ
32	(62)	80-80.5(0.01)	52.14, 44.17 ϵ

Table II. continued

33	(72)	80-82(0.03)	23.53
34	(80)	77-81(0.10)	16.63
35	(82)	118(0.10)	25.80, 27.04 ^c
36	(33)	92(0.03)	35.94
37	(75)	62(0.07)	54.01
38	(52)	70-72(0.07)	57.42
40	8	87-96(1.3)	24.03
41	82	68-70(0.01)	30.63
42	77	38(0.15)	50.77
43	95	38-40(0.05)	54.55
44	28	46-47(4.7)	23.05
45	42	60-61(1.2)	39.07
46	(74)	110(0.05)	11.30

^a Values in parentheses are yields from neat CCl₄ reactions. Other yields for 21-46 are from CCl₄ reactions in CH₂Cl₂. ^b Chemical shifts downfield from H₃PO₄. Solvent: CDCl₃. ^c Diastereomers. ^d Estimated yield from recrystallization. ^e Only a few drops distilled before decomposition.

Table III. Percent Yields of Products Obtained via Equation 5^a

R	R'	R''	<u>CHCl₃ elimination</u>			<u>Me₃SiCCl₃ elimination</u>		
			No.	neat	CH ₂ Cl ₂	No.	neat	CH ₂ Cl ₂
H	H	Ph	<u>34</u>	80	79	<u>39</u>	t	t
Me	H	Ph	<u>35</u>	82	25	<u>40</u>	t	8
Me	Me	Ph	<u>36</u>	33	t	<u>41</u>	12	82
Me	Me	<u>i</u> -Pr	<u>37</u>	75	t	<u>42</u>	t	77
Me	Me	<u>t</u> -Bu	<u>38</u>	52	t	<u>43</u>	31	95

^a Isolated yields, based on starting phosphine, of products obtained by fractional distillation. t = trace (i.e. product not isolated by distillation but detected by ³¹P NMR in the reaction mixture).

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