trans-[$\mathrm{PtCl_2\{CH_2{=}CHCHMe_2\}L}$] (L = 2,6-$\mathrm{Me_2C_5H_3N}$), 74909-83-4; *trans*-[$\mathrm{PtCl_2\{CH_2{=}CHCHMe_2\}L}$] (L = MeCN), 107270-93-9; *trans*-[$\mathrm{PtCl_2\{CH(L)CH_2CH_2Ph\}L}$] (L = 2-$\mathrm{MeC_5H_4N}$), 74889-88-6; *trans*-[$\mathrm{PtCl_2\{CH(L)CH_2CH_2C_6H_4Me\}L}$] (L = 2-$\mathrm{MeC_5H_4N}$), 107246-60-6; *trans*-[$\mathrm{PtCl_2(CH_2{=}CMeEt)L}$] (L = 2-$\mathrm{MeC_5H_4N}$), 82942-41-4; *trans*-[$\mathrm{PtCl_2(CH_2{=}CMeEt)L}$] (L = MeCN), 107246-61-7; *trans*-[$\mathrm{PtCl_2(CH_2{=}CMe}$-*i*-Pr)L] (L = $\mathrm{C_5H_5N}$), 67235-52-3; *trans*-[$\mathrm{PtCl_2(CH_2{=}CMe}$-*i*-Pr)L] (L = 2-$\mathrm{MeC_5H_4N}$), 107246-62-8; $\mathrm{Ph\overline{CHCD_2C}H_2}$, 88377-58-6; $\mathrm{Ph\overline{CHCBr_2C}H_2}$, 3234-51-3; $\mathrm{Bu_3SnD}$, 6180-99-0; $\mathrm{Me_2\overline{CCD_2C}H_2}$, 107270-86-0; $\mathrm{Me_2\overline{CCBr_2C}H_2}$, 32264-50-9; *trans*-[$\mathrm{\overline{CHMeCHMeC}D_2}$], 107270-87-1; *trans*-[$\mathrm{\overline{CHMeCHMeC}Br_2}$], 3591-58-0; *trans*-[$\mathrm{PtCl_2\{CH(L)CH_2CHMe_2\}L}$] (L = $\mathrm{C_5H_5N}$), 77629-79-9; $\mathrm{\overline{PtCl_2\{CH_2CH(4\text{-}MeC_6H_4)C}H_2\}}$, 38922-12-2; *trans*-[$\mathrm{PtCl_2(CH_2{=}CHCH_2\text{-}4\text{-}MeC_6H_4)(2,6\text{-}Me_2(py))}$], 107246-63-9; $\mathrm{CD_3CN}$, 2206-26-0; *trans*-[$\mathrm{PtCl_2(CH_2{=}CMeEt)(CD_3CN)}$], 77629-76-6; *trans*-[$\mathrm{PtCl_2(CH_2{=}CHCHMe_2)(CD_3CN)}$], 77629-75-5; *trans*-[$\mathrm{PtCl_2(CH_2{=}CMeEt)py}$], 77629-80-2; *trans*-$\mathrm{PtCl_2py_2}$, 14024-97-6; $\mathrm{Pt_2Cl_4(C_2H_4)_2}$, 12073-36-8; $\mathrm{CH_2{=}CHCHMe_2}$, 563-45-1; $\mathrm{Pt_2Cl_4(CH_2{=}CHCHMe_2)_2}$, 88760-38-7; *trans*-[$\mathrm{PtCl_2(CH_2{=}CHCHMe_2)(2\text{-}Me(py))}$], 107246-64-0; $\mathrm{\overline{PtCl_2(CD_2CHMeC}HMe}$, 107270-88-2; $\mathrm{\overline{PtCl_2(CD_2CHMeC}HMe)py_2}$, 107246-65-1; *trans*-[$\mathrm{PtCl_2(CHD{=}CMeCHDMe)(2\text{-}Me(py))}$], 82942-32-3; $\mathrm{CHD{=}CMeCHDMe}$, 82945-14-0; $\mathrm{CHD{=}CMeCDMe_2}$, 82948-82-1; *trans*-$\mathrm{PtCl_2(CHD{=}CMeCDMe_2)(py)}$, 107246-66-2; *trans*-[$\mathrm{PtCl_2\{CH(L)CH_2CH_2Me\}L}$] (L = $\mathrm{C_5H_5N}$), 77629-77-7; PrCHO, 123-72-8; $\mathrm{\overline{PtCl_2(CHPhCH_2C}H_2)L_2}$ (L = 2-$\mathrm{MeC_5H_4N}$), 107246-67-3; $\mathrm{\overline{PtCl_2(CH_2CHPhC}H_2)L_2}$ (L = 2-$\mathrm{MeC_5H_4N}$), 107246-68-4; $\mathrm{\overline{PtCl_2(CH_2CMe_2C}H_2)L_2}$ (L = 2-$\mathrm{MeC_5H_4N}$), 107246-69-5; $\mathrm{\overline{PtCl_2(CH_2CMe_2C}H_2)L_2}$ (L = 2,6-$\mathrm{Me_2C_5H_3N}$), 107246-70-8; *trans*-[$\mathrm{PtCl_2\{CH(L)CH_2CHMe_2\}L}$] (L = 2,6-$\mathrm{Me_2C_5H_3N}$), 74889-90-0; $\mathrm{\overline{PtCl_2(CH_2CD_2C}HPh)}$, 107270-89-3; $\mathrm{\overline{PtCl_2(CD_2CH_2C}HPh)}$, 107270-90-6; *trans*-[$\mathrm{PtCl_2\{CH(L)CD_2CH_2Ph\}L}$] (L = 2-$\mathrm{MeC_5H_4N}$), 74889-89-7; *trans*-[$\mathrm{PtCl_2\{CH(L)CD_2CHMe_2\}L}$] (L = 2-$\mathrm{MeC_5H_4N}$), 107246-71-9; $\mathrm{\overline{PtCl_2(CH_2CD_2C}Me_2)}$, 107270-91-7; $\mathrm{\overline{PtCl_2(CH_2CMe_2C}D_2)}$, 107270-92-8; *trans*-[$\mathrm{PtCl_2\{CD(L)CH_2CHDPh\}L}$] (L = 2-$\mathrm{MeC_5H_4N}$), 107246-72-0; *trans*-[$\mathrm{PtCl_2\{CD(L)CH_2CDMe_2\}L}$] (L = 2-$\mathrm{MeC_5H_4N}$), 107246-73-1; *trans*-[$\mathrm{PtCl_2\{CH(L)CD_2CHMe_2\}L}$] (L = 2,6-$\mathrm{Me_2C_5H_3N}$), 107246-74-2.

Synthesis of C-Silylated Phosphoranimines[1]

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The title compounds are derived from the phosphazene precursors $\mathrm{Me_3SiN{=}P(OCH_2CF_3)R^1R^2}$ (**1**, $\mathrm{R^1 = R^2 = Me}$; **2**, $\mathrm{R^1 = Ph}$, $\mathrm{R^2 = CH_2CH{=}CH_2}$; **3**, $\mathrm{R^1 = R^2 = CH_2CH{=}CH_2}$) by a deprotonation/silylation process. Thus, treatment of **1** with *n*-BuLi at −78 °C in $\mathrm{Et_2O}$ solution generates the reactive intermediate $\mathrm{Me_3SiN{=}P(OCH_2CF_3)(Me)CH_2^-Li^+}$ (**1a**) which, after quenching with appropriate chlorosilanes, affords the silylated phosphoranimines $\mathrm{Me_3SiN{=}P(OCH_2CF_3)(Me)CH_2SiMe_2R}$ [**4**, R = Me; **5**, R = Ph; **6**, $\mathrm{R = CH{=}CH_2}$; **7**, R = H; **8**, $\mathrm{R = (CH_2)_3CN}$]. Similarly, the reaction of **1a** with $\mathrm{Me_2SiCl_2}$ or $\mathrm{(ClMe_2SiCH_2)_2}$ in a 2:1 ratio yields the bis((phosphoranimino)silanes) $\mathrm{[Me_3SiN{=}P(OCH_2CF_3)(Me)CH_2]_2E}$ (**9**, $\mathrm{E = SiMe_2}$; **10**, $\mathrm{E = SiMe_2CH_2CH_2SiMe_2}$). Addition of MeLi to the crude Si–Cl product of the 1:1 reaction of **1a** and $\mathrm{Me_2SiCl_2}$ leads to the formation of **4**. The deprotonation/silylation reactions of the allyl-substituted phosphoranimines **2** and **3** give the 3-silylpropenyl derivatives $\mathrm{Me_3SiN{=}P(OCH_2CF_3)(R)CH{=}CHCH_2SiMe_3}$ (**11**, R = Ph; **12**, $\mathrm{R = CH_2CH{=}CH_2}$) with the *E* configuration about the C=C double bond. Application of a second silylation reaction to products **4** and **12** affords the disilylated derivatives $\mathrm{Me_3SiN{=}P(OCH_2CF_3)(Me)CH(SiMe_3)_2}$ (**13**) and $\mathrm{Me_3SiN{=}P(OCH_2CF_3)(CH{=}CHCH_2SiMe_3)_2}$ (**14**), respectively. Although the analogous reactions of the phosphoranimine anions with dichlorosiloxanes are generally unsatisfactory, the sequential treatment of $\mathrm{(ClSiMe_2)_2O}$ with **1a** and MeLi does yield the siloxy compound $\mathrm{Me_3SiN{=}P(OCH_2CF_3)(Me)CH_2SiMe_2OSiMe_3}$ (**15**). These new silylated phosphoranimines are found to be much more thermally stable (to ca. 200–220 °C) than their unsubstituted precursors, and they do not yield poly(phosphazenes) upon decomposition under extreme conditions. Detailed characterization data, including multinuclear (^{1}H, ^{13}C, ^{31}P, and ^{29}Si) NMR spectra, of the silyl derivatives **4**–**15** are presented.

Introduction

The *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines such as $\mathrm{Me_3SiN{=}P(OCH_2CF_3)Me_2}$ (**1**) are useful as precursors to poly(alkyl/arylphosphazenes) via a thermally induced condensation polymerization reaction.[3] In order to extend the scope and utility of this process, we are investigating various methods of introducing functional groups into both the phosphoranimine "monomers" as well as the preformed polymers. As reported recently, we have found that both the precursors (e.g., **1**) and the polymers (e.g., $\mathrm{[Ph(Me)PN]_n}$) undergo facile deprotonation/substitution reactions in which phosphine-functionalized precursors[4] or silylated polymers,[5] respectively, are produced.

In this paper, we report the results of a more complete study of the deprotonation/silylation reactions of phos-

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(1) Taken in part from: Wettermark, U. G. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1986.

(2) Department of Chemistry, Southern Methodist University, Dallas, TX, 75275.

(3) (a) Wisian-Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 2848. (b) Neilson, R. H.; Wisian-Neilson, P. *J. Macromol. Sci., Chem.* **1981**, *A16*, 425. (c) Neilson, R. H.; Hani, R.; Wisian-Neilson, P.; Meister, J. J.; Roy, A. K.; Hagnauer, G. L. *Macromolecules*, in press.

(4) (a) Roy, A. K. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1984. (b) Roy, A. K.; Hani, R.; Neilson, R. H.; Wisian-Neilson, P. *Organometallics* **1987**, *6*, 378.

(5) Wisian-Neilson, P.; Ford, R. R.; Neilson, R. H.; Roy, A. K. *Macromolecules* **1986**, *19*, 2089.

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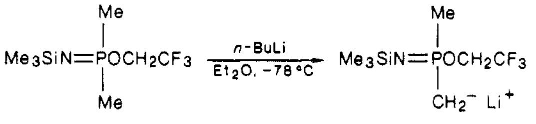
phoranimine 1 and the allyl-substituted analogues $Me_3SiN{=}P(OCH_2CF_3)(CH_2CH{=}CH_2)R$ (**2**, R = Ph; **3**, R = $CH_2CH{=}CH_2$). The major objectives of this work were (1) to determine the optimum reaction conditions for the deprotonation of **1**–**3**, (2) to prepare a wide variety of silylated derivatives of **1**, (3) to determine the site(s) of deprotonation/silylation of the allyl compounds **2** and **3**, and (4) to investigate the potential of the silylated derivatives as precursors to new poly(alkyl/arylphosphazenes).

Results and Discussion

In an earlier report, Schmidbaur[6] showed that the permethylated *N*-silylphosphoranimine $Me_3SiN{=}PMe_3$ could be converted to the silyl derivative $Me_3SiN{=}P(CH_2SiMe_3)Me_2$ by treatment with *n*-BuLi followed by Me_3SiCl. Similar deprotonation/substitution reactions have been carried out on methyl-substituted cyclic phosphazenes (e.g., $[Me_2PN]_3$) by Paddock and co-workers.[7] Allcock[8] has reported, however, that phosphazenes bearing *trifluoroethoxy* groups undergo facile dehydrofluorination upon reaction with *n*-BuLi and various electrophiles. In the light of these prior findings, therefore, our initial goal was to determine reaction conditions in which deprotonation of the *P–Me but not the P–OCH_2CF_3* substituent of phosphoranimines such as **1** could be accomplished.

The Deprotonation Reaction. We find that, when the dimethylphosphoranimine **1** is treated with 1 equiv of *n*-BuLi in ether at −78 °C (eq 1), the carbanion intermediate **1a** is formed quantitatively. With use of ^{31}P NMR spectroscopy to monitor the reaction, two important observations concerning the formation and the reactivity of the anionic intermediate **1a** were made. First, the ^{31}P NMR signal of **1** (27.5 ppm in ether) is immediately replaced by that of the anion **1a** (64.5 ppm) upon addition of the *n*-BuLi. As the temperature of the solution is raised, the signal for **1a** persists as the only peak in the spectrum up to ca. −50 °C. Above that temperature, the signal due to the starting material **1** begins to reappear, and, above ca. 0 °C, **1** becomes the predominant species in the solution. A second product, with a ^{31}P NMR chemical shift of −9.8 ppm, is also observed as the temperature is increased to ca. 20 °C. When this experiment is carried out on a preparative scale, compound **1** is obtained in 10–30% yield as the only distillable product. The product corresponding to the −9.8 ppm signal could not be isolated and identified. Since these reactions were done under rigorously anhydrous conditions, the regeneration of **1** is thought to be due to the thermal decomposition of the anion **1a** accompanied by some degree of self-protonation.



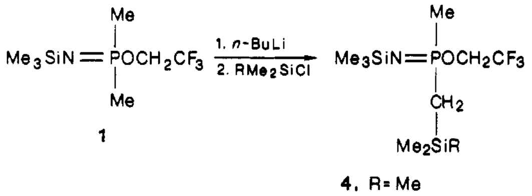
$$Me_3SiN{=}\overset{Me}{\underset{Me}{P}}OCH_2CF_3 \xrightarrow[Et_2O,\ -78\,°C]{n\text{-BuLi}} Me_3SiN{=}\overset{Me}{\underset{CH_2^-\ Li^+}{P}}OCH_2CF_3 \qquad (1)$$

1 **1a**

Second, addition of Me_3SiCl to the anion solution at −78 °C results in the immediate and quantitative formation of the silylated derivative (see below). When less reactive electrophiles such as $PhCH_2Cl$ are used as the quenching agent, the ^{31}P NMR signal of the anion **1a** remains undiminished and no product is observed until the temperature is raised above ca. 0 °C.[1] In this case, a significant amount of the starting material **1** is produced along with the benzyl substituted product.

From these "NMR tube" experiments, it is concluded that **1** is deprotonated smoothly by *n*-BuLi at −78 °C and that the anionic intermediate **1a**, while stable only at low temperature, does undergo facile substitution reactions with highly reactive electrophiles. Thus, it seemed reasonable to investigate the preparative scale reactions of **1a** with a series of chlorosilanes.

Reactions with Monochlorosilanes. When solutions of **1a** are treated with various monochlorosilanes RMe_2SiCl (eq 2), the corresponding (silylmethyl)phosphoranimines **4**–**8** are obtained as colorless, distillable liquids. These products are fully characterized by NMR spectroscopy (^1H, ^{13}C, and ^{31}P) and elemental analysis (Tables I and II). Also, ^{29}Si NMR spectral data for some representative compounds are summarized in Table III. The asymmetry of the structures of these silylation products is reflected by the NMR spectroscopic data. The methylene protons of both the $SiCH_2P$ and the OCH_2CF_3 groups are diastereotopic and give rise to ABX and $ABXY_3$ patterns, respectively. The complete assignments of the chemical shifts and coupling constants can be accomplished by means of two-dimensional homonuclear *J*-resolved ^1H NMR spectra (HOM2DJ) on a 300-MHz instrument. Illustrative data obtained in this fashion for compound **4** is listed in Table I. Very similar patterns are observed for the corresponding protons in the spectra of compounds **5**–**8**.



$$\underset{\mathbf{1}}{Me_3SiN{=}\overset{Me}{\underset{Me}{P}}OCH_2CF_3} \xrightarrow[2.\ RMe_2SiCl]{1.\ n\text{-BuLi}} Me_3SiN{=}\overset{Me}{\underset{CH_2SiMe_2R}{P}}OCH_2CF_3 \qquad (2)$$

4, R = Me
5, R = Ph
6, R = $CH{=}CH_2$
7, R = H
8, R = $CH_2CH_2CH_2CN$

In the early stages of this work, we were concerned about the possibility of Me_3Si group rearrangements in these reactions. For example, on the basis of some previous studies[9] of phosphorus ylides containing *N*-silyl substituents, a [1,3]-Me_3Si shift from nitrogen to carbon in **1a** to give $[Me_3SiCH_2(Me)(OCH_2CF_3)P{=}N]^-Li^+$ seemed feasible. Such isomerizations are precluded, however, by the NMR spectral data for these compounds, with the ^{29}Si NMR spectra (Table III) being especially diagnostic. For example, the ^{29}Si chemical shift and the P–Si coupling constant of the *C-bonded* $PhMe_2Si$ group in **5** are quite different from those observed for the *N-bonded* $PhMe_2Si$ group in the transsilylation[10] product $PhMe_2SiN{=}P(OCH_2CF_3)Me_2$.

From a synthetic viewpoint, it is noteworthy that, even when potentially reactive groups are present on silicon (e.g., **6**–**8**), the $Me_3SiN{=}POCH_2CF_3$ backbone of the molecule remains intact. Thus, in addition to producing some novel compounds, these reactions can serve as useful models for similar deprotonation/silylation processes on the preformed poly(alkyl/arylphosphazenes). Indeed, some of the polymeric analogues have already been reported in a recent communication.[5]

Reactions with Dichlorosilanes. When Me_2SiCl_2 was treated with 2 equiv of the anion **1a** (eq 3), both chlorine atoms were replaced, giving the bis((phosphoranimino)-

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[6] Schmidbaur, H.; Jonas, G. *Chem. Ber.* **1967**, *100*, 1120.

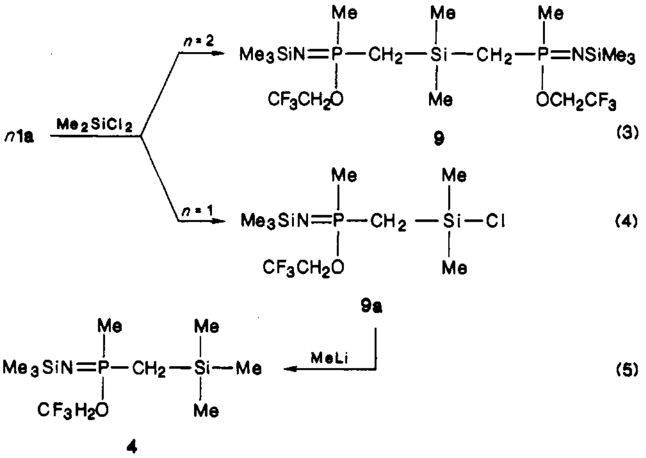
[7] Gallicano, K. D.; Oakley, R. T.; Paddock, N. L.; Sharma, R. D. *Can. J. Chem.* **1981**, *59*, 2654.

[8] Allcock, H. R.; Suszko, P. R.; Evans, T. L. *Organometallics* **1982**, *1*, 1443.

[9] Wilburn, J. C.; Neilson, R. H. *Inorg. Chem.* **1979**, *18*, 347 and references cited therein.

[10] Wettermark, U. G.; Neilson, R. H. *Inorg. Chem.*, in press.

silane) 9 in good yield. The symmetrical structure of 9 is readily apparent from its NMR spectral data. While the ^{31}P NMR spectrum consists of a singlet, the ^{29}Si NMR spectrum contains a triplet (J_{PSi} = 6.4 Hz) for the Me_2Si silicon due to coupling to two equivalent phosphorus nuclei. Moreover, in the ^{13}C spectrum, the equivalent CH_2 carbons are found as a doublet of doublets with a large one-bond coupling (93.6 Hz) to the adjacent phosphorus and a small three-bond coupling (3.6 Hz) to the remote phosphorus.



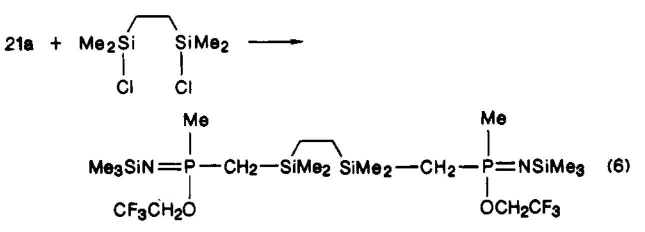
9 (3)

9a (4)

4 (5)

We also attempted to prepare the product of the 1:1 stoichiometric reaction of **1a** and Me_2SiCl_2 (eq 4). In this case, the (chlorodimethylsilyl)methyl derivative **9a** was obtained as a distillable, but very reactive liquid. The ^{31}P NMR spectrum of this product contained one signal at 39.0 ppm. The ^1H NMR spectrum displayed two Me–Si doublets in a 3:2 ratio, a P–Me doublet, and a PCH_2Si multiplet. Further characterization data for **9a** was not obtained; instead, a derivative was prepared by the addition of 1 equiv of MeLi (eq 5). The expected substitution product **4** was formed in high yield and was identified by NMR spectroscopy.

Similarly, when 0.5 equiv of 1,2-bis(chlorodimethylsilyl)ethane was used as the electrophile, both chlorines were displaced by the phosphoranimine anion **1a** (eq 6).

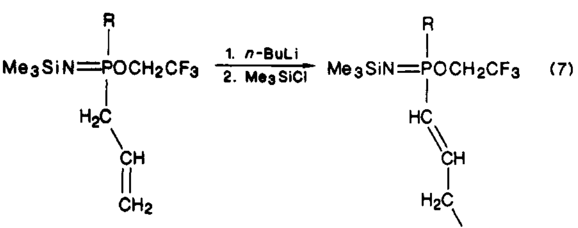


(6)

10

The disubstituted product **10** is a thermally stable, high boiling liquid that was characterized by NMR spectroscopy and elemental analysis. An attempt was also made to prepare the 1:1 substitution product; however, none of the desired product could be isolated. Only a low yield of the doubly substituted derivative **10** was obtained in this case.

Silyl Derivatives of Allylphosphoranimines. Like the dimethyl analogue **1**, both of the allyl-substituted phosphoranimines **2** and **3** also undergo the deprotonation/silylation process (eq 7). These reactions produce high yields of phosphoranimines **11** and **12** in which the Me_3Si group is attached exclusively to the terminal carbon of the allyl substituent. No indication of the formation of the $P-CH(SiMe_3)CH{=}CH_2$ isomer was evident in the NMR spectra of the products. A similar selectivity has been noted when the anions from these allylphosphoranimines were treated with Ph_2PCl.[4] The ^1H



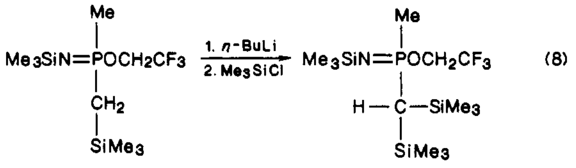
(7)

2, R = Ph
3, R = CH2CH=CH2

11, R = Ph
12, R = CH2CH=CH2

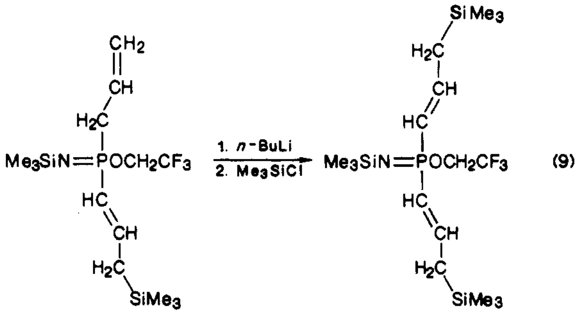
NMR spectra (Table I) of these compounds, particularly **12**, are quite complex, but complete assignment is possible at 300 MHz. The differentiation of some P–H and H–H couplings was made by again using the HOM2DJ technique. In such spectra, the P–H couplings are resolved along the chemical shift axis, leaving the simplified H–H multiplets in the second dimension. The data clearly show that both compounds exist as the *E* isomer with a large trans coupling (ca. 17 Hz) between the vinylic protons of the silylated allyl groups. In the case of **12**, the assignments of the signals in the vinylic region of the ^{13}C NMR spectrum were confirmed by a two-dimensional heteronuclear $^{13}C/^1H$ chemical shift correlation (HETCOR) experiment.

Disilyl Derivatives. As part of this work, we were also interested in the possibility of carrying out a second deprotonation/silylation reaction on the silylated phosphoranimines such as **4** and **12**. In a preliminary study, Roy[4a] was unable to generate the dianion by treating **1** with 2 equiv of *n*-BuLi. We find, however, that disilylated derivatives can be prepared if the reactions are done in a stepwise manner. Thus, treatment of the monosilylated compounds **4** and **12** with 1 equiv of *n*-BuLi, followed by quenching with Me_3SiCl, affords the disilyl derivatives **13** (eq 8) and **14** (eq 9), respectively.



(8)

4 13



(9)

12 14

The NMR spectra of compounds **13** and **14** are in complete agreement with the assigned structures. In particular, the ^1H NMR spectrum of **13** contains doublets for the P–Me and P–CH protons in the correct 3:1 intensity ratio. Furthermore, nonequivalence of the diastereotopic Me_3Si groups of the $(Me_3Si)_2CH$ moiety is clearly evident in the ^{29}Si as well as the ^1H and ^{13}C NMR spectra of **13**. The symmetrical structure of **14**, on the other hand, is easily discerned from the relative simplicity of its ^1H and ^{13}C NMR spectra.

An interesting feature of these reactions (eq 8 and 9) is the difference in the regioselectivity of the second de-

Table I. NMR Spectroscopic Data[a,b]

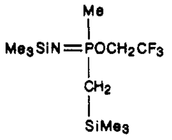
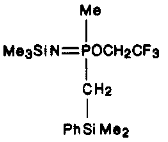
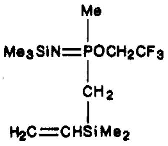
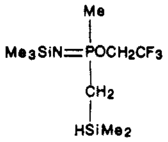
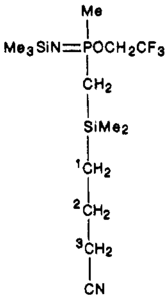
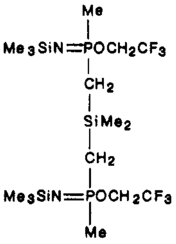
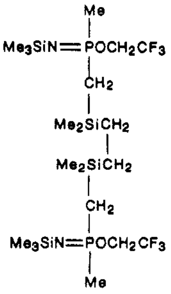
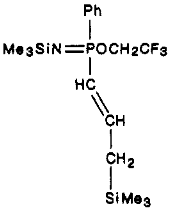
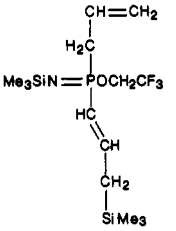
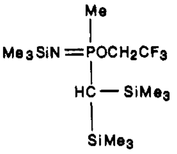
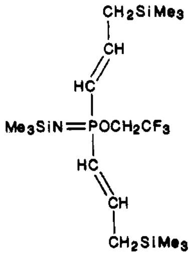
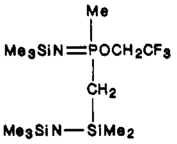
compd	signal	^1H NMR		^{13}C NMR		^{31}P NMR
		δ	J_{PH}	δ	J_{PC}	δ
 $Me_3SiN{=}P(Me)(OCH_2CF_3)CH_2SiMe_3$ **4**	Me_3SiN	0.09		3.60	3.1	32.80
	Me_3SiC	-0.03		0.06	3.0	
	PMe	1.39	14.0	20.51	85.4	
	PCH_2[c]	1.05	18.6	22.70	89.3	
		1.17	20.4			
			(15.1)[d]			
	OCH_2[c]	4.02	9.0	59.18	4.6	
		4.17	9.0		(36.7)[e]	
			(12.8)[d]			
			(9.0)[f]			
	CF_3			123.98	8.5	
					(277.7)[e]	
 $Me_3SiN{=}P(Me)(OCH_2CF_3)CH_2SiMe_2Ph$ **5**	Me_3Si	0.09		3.66	3.7	32.65
	Me_2Si	0.51		2.18	1.8	
		0.52				
	PMe	1.32	13.8	19.73	85.4	
	PCH_2	1.5[g]		22.11	89.7	
 $Me_3SiN{=}P(Me)(OCH_2CF_3)CH_2SiMe_2CH{=}CH_2$ **6**	Me_3Si	0.02		3.57	3.9	32.55
	Me_2Si	0.22		-1.95	1.8	
		0.24				
	PMe	1.44	13.5	20.07	85.9	
	PCH_2	1.3[g]		21.79	88.9	
	CH=	6.1-6.2[h]		138.39	3.9	
	$=CH_2$	5.6-6.0[h]		132.48		
 $Me_3SiN{=}P(Me)(OCH_2CF_3)CH_2SiMe_2H$ **7**	Me_3Si	-0.04		3.57	3.7	32.15
	Me_2Si	0.19	(3.5)[d]	-3.04	3.8	
		0.20	(3.5)[d]			
	PMe	1.45	13.7	19.46	87.7	
	PCH_2	1.2[g]		20.80	86.2	
	SiH	4.06	(3.5)[d]			
 $Me_3SiN{=}P(Me)(OCH_2CF_3)CH_2SiMe_2{}^1CH_2{}^2CH_2{}^3CH_2CN$ **8**	Me_3Si	0.09		3.43	3.1	32.25
	Me_2Si	0.05		2.17	3.1	
	PMe	1.37	14.0	20.02	84.23	
	PCH_2	1.1[g]		20.75	91.55	
	$^1CH_2$	0.5-0.8[h]		15.83	3.7	
	$^2CH_2$	1.4-1.7[h]		20.30		
	$^3CH_2$	2.23	(7.0)[d]	20.59		
	CN			119.55		
 $[Me_3SiN{=}P(Me)(OCH_2CF_3)CH_2]_2SiMe_2$ **9**	Me_3Si	-0.07		3.65	3.7	32.17
	Me_2Si	0.21		0.20	3.7	
	PMe	1.40	13.8	20.44	84.6	
	PCH_2	1.3[g]		21.77	93.6	
					3.6	
 $[Me_3SiN{=}P(Me)(OCH_2CF_3)CH_2SiMe_2CH_2]_2$ **10**	Me_3Si	-0.02		3.70	3.1	33.03
	Me_2Si	0.09		-2.39	3.1	
	PMe	1.40	14.0	20.21	84.3	
	PCH_2	1.1[g]		20.90	90.8	
	$SiCH_2$	0.46		8.48	3.8	

Table I (Continued)

		^{1}H NMR		^{13}C NMR		^{31}P NMR
compd	signal	δ	J_{PH}	δ	J_{PC}	δ
 **11**	Me_3SiN	0.12		3.80	2.8	13.14
	Me_3SiC	0.06		−1.74		
	$SiCH_2$	1.77	(8.5)[d] (1.3)[d]	26.87	19.1	
	P*CH*=CH[c]	5.70	24.2 (16.4, 1.3)[d]	120.64	137.4	
	PCH=*CH*[c]	6.62	21.2 (16.4, 8.5)[d]	128.43	14.0	
 **12**	Me_3SiN	0.10		3.84	2.8	20.59
	Me_3SiC	0.08		−1.75		
	$SiCH_2$	1.73	(8.5)[d] (1.4)[d]	26.86	18.2	
	PCH_2	2.51	18.3 (10.4, 7.3, 1.4)[d]	38.68	92.9	
	CH=CH_2[c]	5.72	5.8 (18.0, 10.4, 7.3)[d]	128.91	8.2	
	CH=*CH_2*[c]	5.09	5.8 (18.0, 1.4)[d]	119.55	12.6	
		5.12	5.3 (10.4, 1.4)[d]			
	P*CH*=CH[c]	5.47	25.7 (16.6, 1.4)[d]	118.76	132.9	
	PCH=*CH*[c]	6.65	20.2 (16.6, 8.5)[d]	150.96	3.8	
 **13**	Me_3SiN	0.01		3.83	3.2	33.31
	Me_3SiC	0.20		2.11		
		0.21		2.18		
	PMe	1.45	13.4	21.54	83.4	
	PCH	0.71	20.2	23.27	79.1	
 **14**	Me_3SiN	0.03		3.99	3.8	15.03
	Me_3SiC	0.05		−1.65		
	$SiCH_2$	1.73	(8.4)[d]	26.74	17.7	
	P*CH*=CH	5.52	23.3 (16.6)[d]	121.12	138.6	
	PCH=*CH*	6.54	21.3 (16.6, 8.4)[d]	148.47	4.3	
 **15**	Me_3SiN	0.06		3.67	4.9	32.53
	Me_2Si	0.18		2.19	5.3	
		0.21				
	Me_3SiO	0.00		2.01		
	PMe	1.45	13.6	19.79	87.7	
	PCH_2	1.2[g]		24.77	86.6	

[a] Chemical shifts relative to Me_4Si for ^{1}H and ^{13}C spectra and to H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^{31}P, CH_2Cl_2; ^{1}H and ^{13}C, $CDCl_3$. [b] The ^{1}H and ^{13}C NMR spectra data for the OCH_2CF_3 group showed very little variation throughout the series 4–15. The complete data are given for 4 as a representative example. [c] Assignments of ^{1}H/^{13}C chemical shifts and coupling constants based in part on HOM2DJ and/or HETCOR spectra. [d] J_{HH} values in parentheses. [e] J_{PC} values in parentheses. [f] J_{PH} values in parentheses. [g] Center of ABX multiplet. See 4 for typical data. [h] Complex multiplet.

protonation/silylation process in the two cases. The introduction of the second silyl group on the same carbon as the first in **13** was not surprising due to the expected stability of the α-silyl anion of **4**. In fact, the ability to generate such an intermediate has opened up a broad range of further derivative chemistry.[11] Our observation that the second silylation of the allyl compound **12** occurs at the opposite end of the molecule is somewhat surprising. It is possible that the initial deprotonation of **12** occurs at the PCH_2 site due to preferential stabilization if the α anion by P(V) (rather than by Si at the $SiCH_2$ site).

Reactions with Dichlorosiloxanes. With the intention of possibly preparing phosphazene precursors containing siloxane (i.e., $[Me_2SiO]_n$) cross-linking units, we also studied some reactions of the anion **1a** with chlorine-terminated dimethylsiloxanes. These reactions, however, were found to be much less satisfactory than those with the chlorosilanes. For example, when the disiloxane $(ClSiMe_2)_2O$ was added to a solution of 2 equiv of the anion

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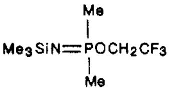
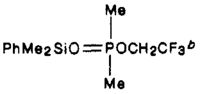
[11] Scheide, G. M.; Neilson, R. H., unpublished results.

Table II. Preparative and Analytical Data

compd	yield, %	bp, °C (p, mmHg)	anal.[a] C	anal.[a] H
4	86	65 (2.5)	37.91 (37.60)	7.85 (7.89)
5	61	65–80 (0.1)	47.61 (47.22)	7.08 (7.08)
6	65	41 (0.1)	40.31 (39.66)	7.68 (7.54)
7	90	40 (0.2)	36.03 (35.39)	7.84 (7.59)
8	68	95 (0.1)	42.17 (41.92)	7.79 (7.58)
9	50	87 (0.7)	35.08 (34.90)	6.99 (6.95)
10	31	110–120 (0.1)	37.89 (37.72)	7.74 (7.54)
11	89	85 (0.1)	50.52 (50.10)	7.45 (7.17)
12	84	59 (0.1)	45.44 (45.32)	7.77 (7.88)
13	40	88 (0.8)	40.12 (39.80)	8.42 (8.43)
14	71	94 (0.1)	45.30 (46.02)	8.63 (8.41)
15	51	57 (0.1)	37.02 (36.64)	7.89 (7.88)

[a] Calculated values in parentheses.

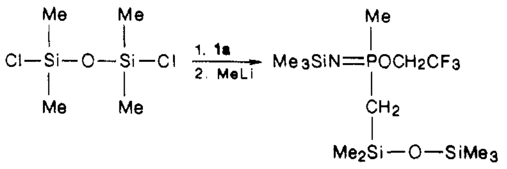
Table III. Silicon-29 NMR Spectroscopic Data[a]

compd	signal	$\delta(^{29}Si)$	J_{PSi}
 $Me_3SiN{=}P(Me)_2OCH_2CF_3$ 1	Me_3Si	−10.72	19.5
 $PhMe_2SiO{=}P(Me)_2OCH_2CF_3$[b]	$PhMe_2Si$	−17.36	22.3
4	Me_3SiN	−12.05	20.8
	Me_3SiC	−1.03	5.1
5	Me_3Si	−11.83	20.8
	$PhMe_2Si$	−6.23	6.1
7	Me_3Si	−11.71	20.1
	HMe_2Si	−17.61	5.9
9	Me_3Si	−11.77	21.1
	Me_2Si	−2.36	6.4
11	Me_3SiN	−10.93	18.1
	Me_3SiC	2.03	3.9
12	Me_3SiN	−11.97	22.6
	Me_3SiC	1.65	3.9
13	Me_3SiN	−13.71	21.9
	Me_3SiC	1.30	3.8
	Me_3SiC	0.41	7.0
14	Me_3SiN	−11.75	22.0
	Me_3SiC	1.67	3.3

[a] Chemical shifts downfield from Me_4Si; coupling constants in Hz; $CDCl_3$ solution. See Experimental Section for spectral parameters. [b] For preparative details and additional characterization data see ref 1 and 10.

1a, the ^{31}P NMR spectrum of the mixture indicated that a single phosphorus species was present. Upon attempted distillation, however, this compound decomposed into at least three phosphorus-containing products that could not be separated and identified. Similar difficulties were encountered when an oligomeric siloxane $Cl-(SiMe_2O)_nSiMe_2-Cl$ (n = 5) was used in place of the disiloxane.

A somewhat modified siloxane derivative was prepared (eq 10) by means of the reaction of **1a** with $(ClSiMe_2)_2O$ in a 1:1 ratio. In this case, we did not attempt to isolate the initial product but rather prepared the $-OSiMe_3$ derivative **15** by adding 1 equiv of MeLi to the reaction mixture. Compound **15**, a distillable liquid, was characterized by NMR spectroscopy and elemental analysis. Although most of these siloxane/anion reactions were not straightforward, the successful synthesis of **15** suggests that further study of such systems may be worthwhile.



$$ClMe_2Si{-}O{-}SiMe_2Cl \xrightarrow[2.\ MeLi]{1.\ \mathbf{1a}} Me_3SiN{=}P(Me)(OCH_2CF_3)CH_2Me_2Si{-}O{-}SiMe_3 \qquad (10)$$

15

Thermolysis Reactions. The thermal decomposition of N-silyl-P-(trifluoroethoxy)phosphoranimines (e.g., **1**) normally proceeds smoothly via the elimination of $Me_3SiOCH_2CF_3$ to give poly(alkyl/arylphosphazenes).[3] We anticipated, therefore, that the silyl derivatives would also undergo this condensation/polymerization process to provide an alternate route to silylated poly(alkyl/arylphosphazenes).[5] We find, however, that *the silylated compounds (e.g., **4–8**) are much more thermally stable than their precursors and that, when extreme conditions are used, they decompose to form intractable residues rather than linear poly(phosphazenes).*

For example, when the phosphoranimines **4–8** and **11** were heated in sealed ampules at 185 °C for 6 days [typical conditions for the synthesis of other poly(alkyl/arylphosphazenes)[3]], the silylated precursors were recovered unchanged. After prolonged periods (up to 21 days) at 200–220 °C, the reaction mixtures still did not contain phosphazene products or the $Me_3SiOCH_2CF_3$ byproduct. The contents of the ampules consisted of black liquid/solid mixtures. The liquid materials were isolated by distillation and identified as unchanged starting materials (ca. 50% recovery) by NMR spectroscopy. The black solid residues were insoluble in all common solvents and were not further investigated.

Numerous attempts were also made to copolymerize the phosphoranimines **4–8** with **1**, but, again, no silylated poly(alkyl/arylphosphazenes) were formed. In a typical experiment, **1** and **4** were combined in a 5:1 molar ratio and heated at 185 °C for 6 days without change. Thus, not only does **4** resist polymerization itself, but also its presence in the mixture appears to inhibit the homopolymerization of the dimethyl compound **1**. Continued heating at 200–220 °C for 14 days caused some decomposition to occur. The silyl ether $Me_3SiOCH_2CF_3$ was removed under vacuum and identified by NMR spectroscopy. The remaining material in the ampule consisted of a light brown solid and an insoluble black deposit on the walls of the vessel. The light colored solid, removed by extraction with CH_2Cl_2, showed a major signal at 6.5 ppm in the ^{31}P NMR spectrum that corresponds to poly(dimethylphosphazene) $[Me_2PN]_n$.[3] Much smaller peaks at 24.0 and 15.0 ppm, indicative of cyclic phosphazenes $[Me_2PN]_{4,5}$, were also present. No evidence for CH_2SiMe_3 substituents on the polymer backbone was found in the ^1H NMR spectrum of the material. Very similar results were obtained when copolymerizations of **1** and the potential cross-linking units **9** and **10** were attempted. Again, the only nonvolatile product that could be isolated and identified was $[Me_2PN]_n$.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without further purification: RMe_2SiCl (R = Me, Ph, H, $CH{=}CH_2$, $CH_2CH_2CH_2CN$), Me_2SiCl_2, $(ClMe_2SiCH_2)_2$, $Cl-(SiMe_2O)_nSiMe_2-Cl$, MeLi (ether solution), and n-BuLi (hexane solution). Dichlorotetramethyldisiloxane was obtained commercially and was distilled prior to use. Ether and hexane were distilled from CaH_2 and stored over molecular sieves prior to use. The N-silyl-P-(trifluoroethoxy)phosphoranimines[4,12] **1**, **2**, and **3** were prepared according to the published procedures. Some ^1H NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P NMR spectra, both with ^1H decoupling, were obtained on a JEOL FX-60 instrument. Other ^1H and ^{13}C NMR spectra,

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(12) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1980**, *19*, 1875.

including several two-dimensional spectra (HOM2DJ and HETCOR), were obtained on a Varian XL-300 spectrometer. Silicon-29 NMR spectra were recorded on the Varian XL-300 instrument under the following conditions: typically 10–15-min acquisition times (15-s delay time) on $CDCl_3$ solutions (ca. 30–50% v/v) in 5-mm tubes with suppressed Overhauser decoupling. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. The following procedures are typical of those used for the preparation of the new compounds in this study. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum.

Preparation of the Silylated Phosphoranimines 4–8. A 250-mL, three-necked flask, equipped with a N_2 inlet, a magnetic stirrer, and a septum, was charged with the *N*-silyl-*P*-(trifluoroethoxy)phosphoranimine **1** (typically, 25 mmol) and ether (60 mL). The solution was cooled to −78 °C, and an equimolar quantity of *n*-BuLi was added via syringe. After the mixture (now containing the anion **1a**) was stirred for ca. 30 min at −78 °C, the appropriate chlorosilane RMe_2SiCl (25 mmol) was added and the mixture was allowed to warm to room temperature and was stirred overnight. After the addition of hexane (ca. 50 mL), the mixture was filtered and the solids were washed with hexane. Following solvent removal, distillation through a 10-cm column gave **4–8** as colorless liquids (Tables I–III).

Preparation of the Phosphoranimines 9 and 4 (via 9a). Solutions of the anion **1a** (typically, 30 mmol) were prepared by the same procedure. Addition of 0.5 equiv of Me_2SiCl_2 (15 mmol) at −78 °C, followed by product isolation as described above, gave **9** as a colorless, distillable liquid. Addition of 1 equiv of Me_2SiCl_2 at −78 °C afforded the reactive chlorosilyl derivative **9a**, obtained by distillation as an impure and very air-sensitive liquid (^{31}P NMR 39.0 ppm). Therefore, in a separate experiment, a solution of **9a** (ca. 15 mmol) was treated with MeLi (15 mmol, ether solution) at −78 °C. The mixture was allowed to warm to room temperature. After filtration and solvent removal, distillation gave the Me_3Si derivative **4** in ca. 50% yield.

Preparation of Phosphoranimine 10. A solution of $(ClMe_2SiCH_2)_2$ (15 mmol) in ether (ca. 10 mL) was added via syringe to a stirred solution of the anion **1a** (30 mmol), prepared as described above, at −78 °C. The mixture was allowed to warm to room temperature. After filtration and solvent removal, distillation afforded **10** as a colorless liquid.

Preparation of the Allyl Derivatives 11 and 12. By means of the procedure described above for the preparation of **4–8**, the allyl phosphoranimines **2** and **3** were treated with *n*-BuLi to give solutions of the corresponding anions **2a** and **3a**, respectively. In a typical experiment, the diallylphosphoranimine **3** (30.0 g, 100 mmol) was dissolved in ether (250 mL) and cooled to −78 °C. One equivalent of *n*-BuLi (40.0 mL, 2.5 M solution in hexane) was added via syringe to the stirred solution over ca. 10 min. After the mixture was stirred for 1 h, Me_3SiCl (12.7 mL, 100 mmol) was added via syringe and the mixture was allowed to warm to room temperature. The salts were allowed to settle, the supernatant solution was decanted, and the salts were washed with hexane. Solvent removal from the combined decantate and washings, followed by distillation through a 10-cm column, afforded **12** as a colorless liquid. Compound **11** was similarly prepared from the phenyl/allyl precursor **2**.

Preparation of the Disilyl Derivatives 13 and 14. By means of the same procedure, the monosilylated allyl compound **12** (12.3 g, 33.1 mmol) was treated with *n*-BuLi (12.8 mL, 2.6 M hexane solution) followed by Me_3SiCl (4.2 mL, 33.1 mmol). Product isolation as above gave **14** as a colorless liquid. Compound **13** was similarly prepared from the monosilylated precursor **4**.

Preparation of the Siloxane Derivative 15. Two equivalents of the anion **1a** (30 mmol) were allowed to react with 1 equiv of the siloxane $(ClMe_2Si)_2O$ (15 mmol) in the usual manner, and then MeLi (15 mmol) was added to the reaction mixture at −78 °C. Product isolation as above gave **15** as a colorless liquid.

Thermolysis Reactions. In a typical experiment, the precursors **1** and **4** were combined in a 5:1 mole ratio (ca. 4 g total) in a heavy-walled glass ampule under nitrogen. The contents of the ampule were degassed by the freeze–pump–thaw technique and sealed under vacuum. The ampule was heated first at 185 °C and then, since no change was observed, at 200 °C for an additional 15 days. At this point, the contents of the ampule consisted of a black liquid/solid mixture and light brown solid. The ampule was opened, attached to a vacuum system, and the volatile product was collected in a cold (196 °C) flask. This product was identified as $Me_3SiOCH_2CF_3$ by comparison of its ^1H NMR spectrum to that of an authentic sample. The soluble polymer was isolated by extraction with CH_2Cl_2 followed by precipitation into hexane and was identified as $[Me_2PN]_n$ by ^1H and ^{31}P NMR spectroscopy. The remaining black solid was insoluble in all common solvents and was not further characterized. All other thermolysis reactions and the associated product analyses were carried out according to similar procedures.

Acknowledgment. We thank the U.S. Army Research Office and The Robert A. Welch Foundation for generous financial support of this research.

Registry No. **1**, 73296-44-3; **2**, 106162-31-6; **3**, 106162-32-7; **4**, 106821-78-7; **5**, 106821-79-8; **6**, 106821-80-1; **7**, 106835-95-4; **8**, 106821-81-2; **9**, 106835-96-5; **9a**, 106821-87-8; **10**, 106821-82-3; **11**, 106821-83-4; **12**, 106821-84-5; **13**, 102537-44-0; **14**, 106821-85-6; **15**, 106821-86-7; Me_3SiCl, 75-77-4; $PhMe_2S$-Cl, 768-33-2; $(CH_2{=}CH)Me_2SiCl$, 1719-58-0; HMe_2SiCl, 1066-35-9; $(NC(CH_2)_3)Me_2SiCl$, 18156-15-5; Me_2SiCl_2, 75-78-5; $(ClMeSiCH_2)_2$, 13528-93-3; $(ClMe_2Si)_2O$, 2401-73-2.