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# Transsilylation Reactions of Phosphazene Precursors[1]

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The transsilylation reactions of the phosphazene precursor $Me_3SiN{=}P(OCH_2CF_3)Me_2$ (**1**) with a variety of chlorosilanes, dichlorosilanes, and dichlorosiloxanes were studied. Thus, treatment of **1** with chlorosilanes $RMe_2SiCl$ at 0 °C in $CH_2Cl_2$ solution affords the transsilylation products $RMe_2SiN{=}P(OCH_2CF_3)Me_2$ (**2**, R = Ph; **3**, R = CH=$CH_2$; **4**, R = $CH_2Cl$; **5**, R = $CH_2CH_2CH_2CN$; **6**, R = $CH_2CH_2OC(O)Me$). Compound **1** reacts with the dichlorosilanes $Me_2SiCl_2$ and $(ClMe_2SiCH_2)_2$ in both 2:1 and 1:1 stoichiometry to give the novel phosphoranimines $[Me_2(CF_3CH_2O)P{=}N]_nECl_{2-n}$ (**7**, $n$ = 2, E = $SiMe_2$; **8**, $n$ = 2, E = $SiMe_2CH_2CH_2SiMe_2$; **9**, $n$ = 1, E = $SiMe_2$; **10**, $n$ = 1, E = $SiMe_2CH_2CH_2SiMe_2$). The chlorosilyl derivatives **9** and **10** react with PhLi and RLi (R = Me, *n*-Bu) to form respectively **2** and the seven-membered ring compound $Me_2SiCH_2CH_2SiMe_2CH_2P(Me)(OCH_2CF_3){=}N$ (**11**). Reactions of the chlorine-terminated siloxanes $Cl(SiMe_2O)_nSiMe_2Cl$ ($n$ = 1, 2, 3, 5) with 2 equiv of **1** yield the corresponding series of siloxane–phosphoranimine oligomers $E(SiMe_2O)_nSiMe_2E$, where E = $N{=}P(OCH_2CF_3)Me_2$ (**12**, $n$ = 1; **13**, $n$ = 2; **14**, $n$ = 3; **15**, $n$ = 5). In a 1:1 ratio, **1** reacts with $(ClMe_2Si)_2O$ to form the chlorosiloxane $Me_2(CF_3CH_2O)P{=}NSiMe_2OSiMe_2Cl$ (**16**), which, upon treatment with RLi, is converted to the $-OSiMe_2R$ derivatives **17** (R = Me) and **18** (R = *n*-Bu). The thermal decomposition reactions of the siloxane–phosphoranimine products were also studied, but siloxane–phosphazene copolymers were not formed. Instead, for example, **15** decomposes to yield poly(dimethylphosphazene) and the trifluoroethoxy-terminated siloxane $CF_3CH_2O(SiMe_2O)_nSiMe_2OCH_2CF_3$ (**19**).

## Introduction

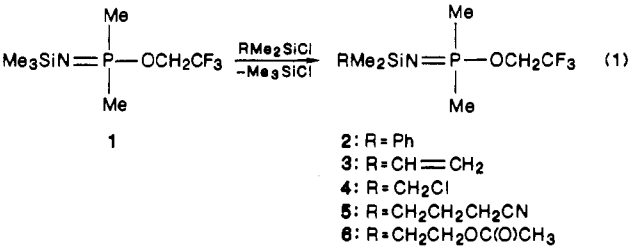
The *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines such as $Me_3SiN{=}P(OCH_2CF_3)Me_2$ (**1**) are useful precursors to poly(alkyl/arylphosphazenes) via a thermally induced condensation polymerization process.[2] Aside from this important thermolysis reaction, however, the chemistry of these phosphazene precursors has not been studied in a systematic fashion. At least two major areas probably merit attention in this context: (1) deprotonation/substitution reactions of the *P*-alkyl side groups and (2) silicon–nitrogen bond cleavage (e.g., transsilylation) reactions.

We have recently shown that the first of these two modes of reactivity can lead to a variety of phosphinyl-[3] and silyl-substituted[1,4] phosphazene precursors. In this paper, we report our initial results related to the second of the above areas. Specifically, a series of transsilylation reactions of **1** with a variety of chlorosilanes and siloxanes is described along with the results of thermolysis reactions of some of the transsilylated products.

## Results and Discussion

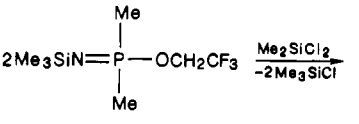
The reactions of *N*-(trimethylsilyl)-*P*,*P*-dimethyl-*P*-(trifluoroethoxy)phosphoranimine (**1**) with various mono- and dichlorosilanes and some dichlorosiloxanes were studied in this work. Research in other laboratories[5] has shown that *triorgano*-substituted *N*-silylphosphoranimines such as $Me_3SiN{=}PMe_3$ undergo a variety of transsilylation reactions. Little is known, however, about the influence that functional groups on phosphorus (e.g., $OCH_2CF_3$) have on such reactions.

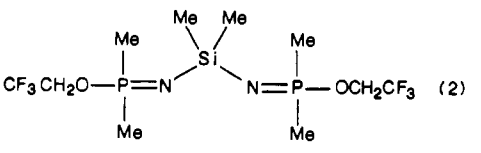
**Reactions with Chlorosilanes.** The phosphoranimine **1** was treated with various monochlorosilanes (eq 1) at 0 °C in $CH_2Cl_2$ solution. After the mixtures were allowed to warm to room temperature, the reactions were complete as indicated by $^{31}P$ NMR spectroscopy. The transsilylation products **2–6** were obtained as colorless, distillable liquids and were identified by NMR spectroscopy and elemental analysis (Tables I and II).



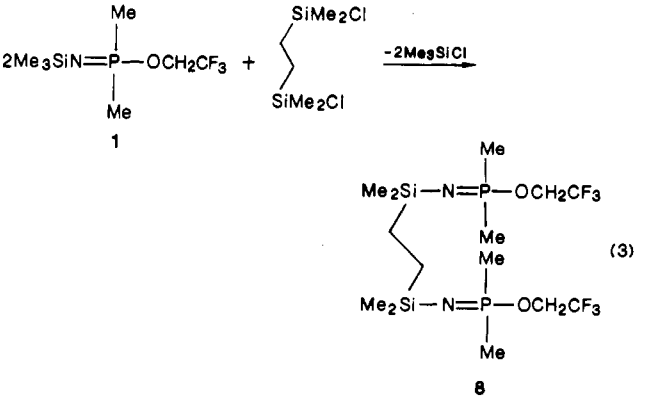
(1)

Silanes containing two Si–Cl bonds were also used in the transsilylation reactions. These reactions were carried out with both 1 and 2 equiv of the phosphoranimine **1**/equiv of the silyl reagent. When the phosphoranimine **1** was allowed to react with dimethyldichlorosilane in a 2:1 mole ratio, 2 equiv of $Me_3SiCl$ was eliminated, with the formation of the bis(phosphoranimino)silane **7** (eq 2). Similarly, 1,2-bis(chlorodimethylsilyl)ethane gave the transsilylation product **8** when treated with 2 equiv of **1** (eq 3).



(2)



(3)

(1) Taken in part from: Wettermark, U. G. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1986.
(2) (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.
(3) (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*, in press.
(4) Wettermark, U. G.; Scheide, G. M.; Neilson, R. H.; Wisian-Neilson, P., submitted for publication in *Organometallics*.
(5) See for example: (a) Wolfsberger, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1975**, *30B*, 900, 904, 907. (b) *Ibid.* **1977**, *32B*, 967. (c) Wolfsberger, W. *Chem.-Ztg.* **1979**, *103*, 345. (d) Wolfsberger, W. *J. Organomet. Chem.* **1979**, *173*, 277.

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**Table I.** NMR Spectroscopic Data[a,b]

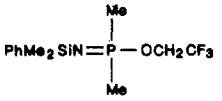
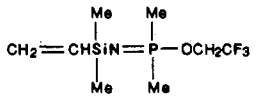
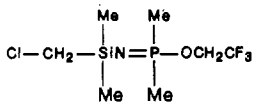
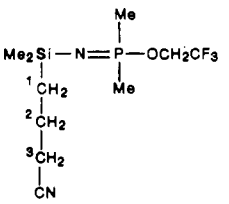
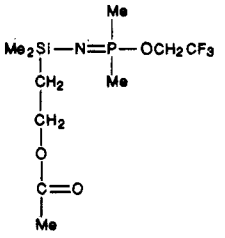
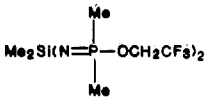
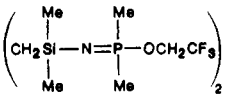
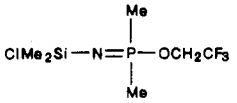
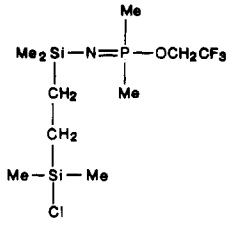
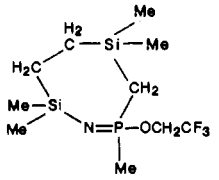
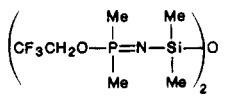
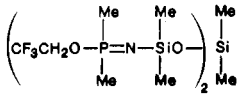
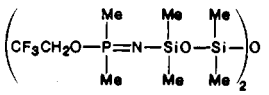
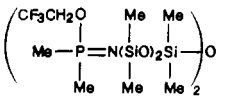
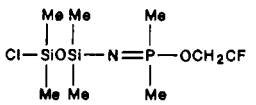
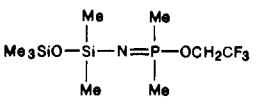
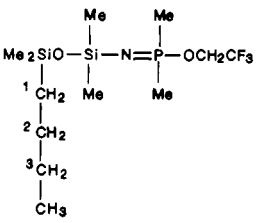
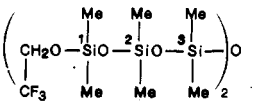
| compd | signal | $^1$H, $\delta$ ($J_{PH}$) | $^{13}$C, $\delta$ ($J_{PC}$) | $^{31}$P, $\delta$ |
|---|---|---|---|---|
|  | $Me_2Si$ | 0.33 | 2.38 (4.1) | 34.39 |
| | PMe | 1.48 (13.7) | 18.42 (92.5) | |
| | Ph | 7.4–7.6[c] | 127.75 | |
| | | | 128.56 | |
| | | | 133.21 | |
| 2 | | | | |
|  | $Me_2Si$ | 0.08 | 1.92 (4.0) | 34.02 |
| | PMe | 1.47 (14.2) | 18.95 (93.7) | |
| | =CHSi | 6.1–6.2[c] | 142.97 (4.0) | |
| | $CH_2$= | 5.6–5.8[c] | 129.66 | |
| 3 | | | | |
|  | $Me_2Si$ | 0.01 | 0.18 (3.0) | 34.72 |
| | $ClCH_2$ | 2.63 | 33.80 (5.0) | |
| | PMe | 1.40 (14.0) | 18.86 (93.4) | |
| 4 | | | | |
|  | $Me_2Si$ | −0.08 | 1.49 (3.4) | 32.83 |
| | PMe | 1.39 (14.4) | 20.18 (93.6) | |
| | 1-$CH_2$ | 0.5–0.6[c] | 19.15 (5.2) | |
| | 2-$CH_2$ | 1.6–1.7[c] | 20.47 | |
| | 3-$CH_2$ | 2.27 (6.7)[d] | 20.81 | |
| | CN | | 120.10 | |
| 5 | | | | |
|  | $Me_2Si$ | 0.01 | 2.21 (3.4) | 32.85 |
| | PMe | 1.46 (13.7) | 18.95 (92.7) | |
| | $SiCH_2$ | 0.93 (8.8)[d] | 21.37 (4.0) | |
| | $CH_2OC(O)$ | 4.14 (8.8)[d] | 20.55 | |
| | CMe | 1.98 | 63.36 | |
| | C=O | | 171.33 | |
| 6 | | | | |
|  | $Me_2Si$ | −0.02 | 5.50 (3.0) | 30.98 |
| | PMe | 1.41 (14.2) | 18.44 (93.7) | |
| 7 | | | | |
|  | $Me_2Si$ | −0.04 | 1.03 (3.0) | 32.60 |
| | $CH_2Si$ | 0.35 | 12.13 (4.0) | |
| | PMe | 1.43 (13.7) | 18.98 (92.7) | |
| 8 | | | | |
|  | $Me_2Si$ | 0.30 | 6.18 | 38.84 |
| | PMe | 1.46 (13.5) | 18.41 (94.7) | |
| 9 | | | | |
|  | $Me_2SiN$ | 0.30 | 1.00 (3.4) | 33.89 |
| | $Me_2SiCl$ | 0.70 | 10.93 | |
| | PMe | 1.63 (14.0) | 18.53 (90.6) | |
| | $CH_2SiN$ | 0.1–0.6[c] | 0.62 | |
| | $CH_2SiCl$ | 0.1–0.6[c] | 10.76 | |
| 10 | | | | |

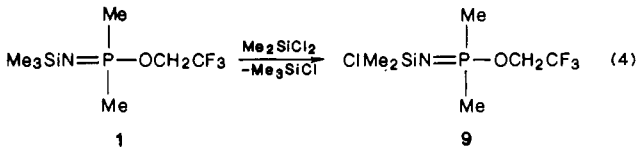
**Table I** (Continued)

| compd | signal | $^1$H, $\delta$ ($J_{PH}$) | $^{13}$C, $\delta$ ($J_{PC}$) | $^{31}$P, $\delta$ |
|---|---|---|---|---|
|  | $Me_2SiN$ | −0.05 | −1.16 (4.0) | 39.58 |
| | $Me_2SiC$ | 0.04 | 1.50 (3.8) | |
| | $H_2CSi$ | 0.6–0.8[b] | 9.11 | |
| | | | 12.25 | |
| | $PCH_2$ | 1.23 (13.7) | 22.32 (69.4) | |
| | PMe | 1.42 (13.5) | 19.94 (104.2) | |
| 11 | | | | |
|  | $Me_2SiN$ | −0.03 | 3.36 (3.7) | 32.83 |
| | PMe | 1.42 (14.0) | 18.41 (94.0) | |
| 12 | | | | |
|  | $Me_2SiN$ | −0.03 | 3.16 (3.7) | 33.84 |
| | $OSiMe_2O$ | −0.05 | 1.26 | |
| | PMe | 1.42 (13.8) | 18.30 (93.4) | |
| 13 | | | | |
|  | $NSiMe_2$ | −0.03 | 3.16 (3.7) | 33.05 |
| | $OSiMe_2O$ | −0.06 | 1.13 | |
| | PMe | 1.40 (13.0) | 18.31 (93.4) | |
| 14 | | | | |
|  | $NSiMe_2$ | 0.02 | 3.16 (3.7) | 33.15 |
| | $OSiMe_2O$ | −0.01 | 1.05 | |
| | | −0.06 | 0.93 | |
| | PMe | 1.40 (13.5) | 18.43 (94.0) | |
| 15 | | | | |
|  | $SiMe_2N$ | 0.08 | 3.33 (3.7) | 34.34 |
| | $ClSiMe_2$ | 0.40 | 4.46 | |
| | PMe | 1.51 (13.3) | 18.69 (83.8) | |
| 16 | | | | |
|  | $SiMe_2N$ | 0.05 | 3.60 (3.9) | 34.62 |
| | $Me_3Si$ | 0.01 | 2.10 | |
| | P-Me | 1.48 (13.5) | 18.73 (93.7) | |
| 17 | | | | |
|  | $SiMe_2N$ | 0.10 | 3.59 (3.6) | 33.94 |
| | $Me_2SiO$ | 0.01 | 0.41 | |
| | PMe | 1.46 (13.8) | 18.69 (94.2) | |
| | 1-$CH_2$ | 0.48–0.52[c] | 13.92 | |
| | 2-$CH_2$ | 1.25–1.30[c] | 25.78 | |
| | 3-$CH_2$ | 1.25–1.30[c] | 26.61 | |
| | $CH_3$ | 0.82–0.86[c] | 18.37 | |
| 18 | | | | |
|  | 1-$SiMe_2$ | 0.16 | 1.21 | |
| | 2-$SiMe_2$ | 0.09 | 1.13 | |
| | 3-$SiMe_2$ | 0.08 | 1.01 | |
| | $OCH_2$ | 3.98 [8.8][e] | 60.95 [36.3][e] | |
| | $CF_3$ | | 124.43 [279.0][e] | |
| 19 | | | | |

[a] Chemical shifts relative to $Me_4Si$ for $^1$H and $^{13}$C spectra and to $H_3PO_4$ for $^{31}$P NMR spectra; coupling constants in Hz. Solvents: $CDCl_3$ for $^1$H and $^{13}$C NMR spectra, $CH_2Cl_2$ for $^{13}$P NMR spectra unless noted otherwise. [b] The $^1$H and $^{13}$C data for the $OCH_2CF_3$ groups showed very little variation throughout the series **2–18**. Typical data for **3**: $^1$H NMR 4.18 ppm (quintet, $J_{PH} = J_{FH} = 8.8$ Hz); $^{13}$C NMR 59.62 ppm (quartet of doublets, $J_{FC} = 36.2$ Hz, $J_{PC} = 5.0$ Hz), 123.73 ppm (quartet of doublets, $J_{FC} = 278.0$ Hz, $J_{PC} = 8.1$ Hz). [c] Complex multiplet. [d] $J_{HH}$. [e] $J_{FH}$ and/or $J_{FC}$.

Compounds **7** and **8** are colorless liquids that were purified by vacuum distillation and characterized by the techniques mentioned above. In both reactions, small amounts of monosubstituted products were also observed by $^{31}$P NMR spectroscopy prior to distillation. Therefore, we performed the same reactions using equimolar amounts of the reactants in order to obtain the compounds containing one chlorine atom on silicon.

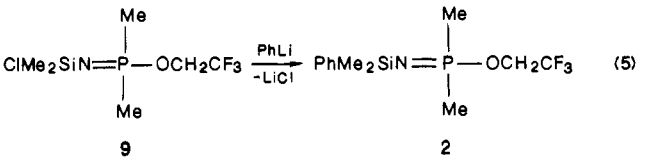
The phosphoranimine **1** reacted smoothly with $Me_2SiCl_2$ in a 1:1 ratio, giving a high yield of product **9** (eq 4). Compound **9** was isolated by vacuum distillation, as a colorless liquid that fumed



(4)

when exposed to air. It displayed one resonance at 38.84 ppm in the $^{31}P$ NMR spectrum and gave the expected $^{1}H$ NMR and $^{13}C$ NMR spectra, recorded soon after distillation. When it stood in a closed flask under nitrogen at room temperature for several days, however, the phosphoranimine **9** changed from a colorless liquid into a white solid. This material displayed several $^{31}P$ NMR shifts between 10.0 and 55.7 ppm, indicating that extensive decomposition had occurred.

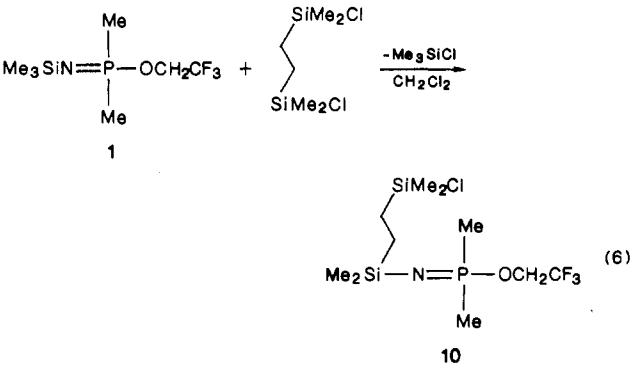
A derivatization reaction was therefore conducted on a freshly prepared sample of phosphoranimine **9** (eq 5). The chlorine atom



(5)

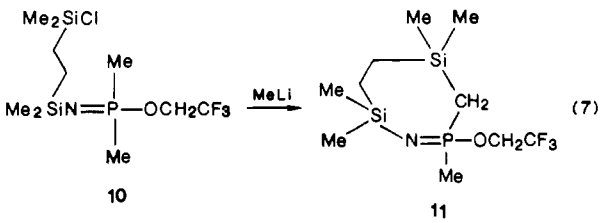
on silicon was replaced with a phenyl group by treatment of **9** with PhLi, yielding the previously prepared compound **2**.

The transsilylation reaction between the phosphoranimine **1** and 1 equiv of the dichlorodisilylethane also led to the formation of the monosubstituted silane **10** (eq 6). The colorless liquid **10**



(6)

was characterized by NMR spectroscopy and elemental analysis and then used in a derivatization reaction in order to verify its structure. Originally, we intended to conduct a simple replacement of the chlorine atom on the terminal silicon of the phosphoranimine **10** with a methyl group. Instead, a deprotonation of a P–Me group and a ring closure (eq 7) occurred when 1 equiv of MeLi was added to **10** at −78 °C.



(7)

The seven-membered ring compound **11** is a colorless, distillable liquid that was purified by a vacuum distillation and characterized by NMR spectroscopy and elemental analysis. When compound **10** was treated with *n*-BuLi, instead of MeLi, under similar conditions, **11** was obtained in approximately the same yield.

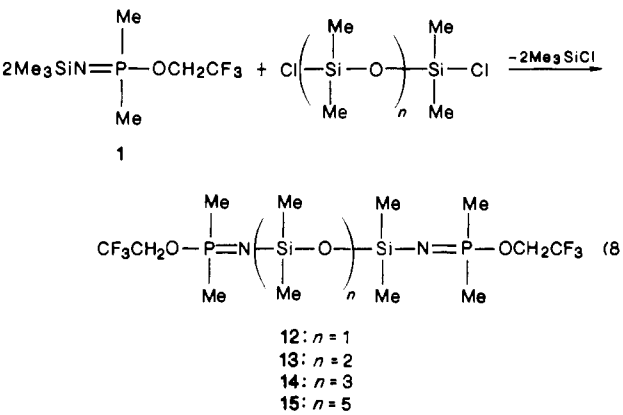
The cyclic compound **11** is a phosphoranimine derived from **1** by the results of the two main modes of reactivity of these *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines. First, the transsilylation reaction enabled us to place the chlorosilyl group on nitrogen (eq 6). Second, the deprotonation[1,4] of the methyl group on phosphorus presumably generated a reactive anionic intermediate, which then displaced the terminal chlorine atom in the same molecule to give the cyclic product **11** (eq 7).

**Table II.** Preparative and Analytical Data

| compd | % yield | bp, °C (mm) | anal.[a] % C | anal.[a] % H |
|---|---|---|---|---|
| **2** | 84 | 72 (2.0) | 46.78 (46.59) | 6.27 (6.19) |
| **3** | 85 | 58–60 (4.5) | 36.92 (37.06) | 6.75 (6.56) |
| **4** | 79 | 66 (4.0) | 29.83 (29.84) | 5.56 (5.72) |
| **5** | 64 | 77 (0.1) | 40.26 (40.04) | 6.82 (6.67) |
| **6** | 80 | 65–68 (0.1) | 37.44 (37.62) | 6.61 (6.63) |
| **7** | 43 | 58 (0.3) | 29.93 (29.56) | 5.74 (5.45) |
| **8** | 65 | 91 (0.2) | 34.33 (34.14) | 6.63 (6.50) |
| **9** | 72 | 55–59 (2.0) | 26.39 (26.92) | 5.60 (5.27) |
| **10** | 62 | 75–85 (0.1) | 34.22 (33.93) | 7.10 (6.78) |
| **11** | 47 | 83 (3.5) | 38.51 (37.81) | 7.39 (7.24) |
| **12** | 51 | 80 (0.1) | 30.62 (30.00) | 5.88 (5.87) |
| **13** | 41 | 91–95 (0.1) | 30.38 (30.32) | 6.33 (6.18) |
| **14** | 50 | 85–100 (0.1) | 30.95 (30.56) | 6.70 (6.41) |
| **15** | 48 | 120 (0.15) | 30.20 (30.88) | 6.44 (6.74) |
| **16** | 45 | 61 (1.0) | 28.35 (28.08) | 5.86 (5.85) |
| **17** | 46 | 52 (0.15) | | |
| **18** | 50 | 52 (0.1) | 39.76 (39.67) | 8.07 (7.99) |
| **19** | 84 | 98–105 (0.1) | 30.92 (30.66) | 6.47 (6.43) |

[a] Calculated values in parentheses.

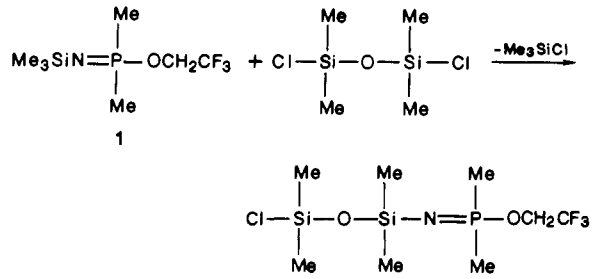
**Reactions with Dichlorosiloxanes.** In order to further investigate the scope of the transsilylation process, a series of reactions between the phosphoranimine **1** and chlorine-terminated siloxanes was conducted in $CH_2Cl_2$ solution (eq 8). When carried out in



(8)

2:1 stoichiometry, all of these reactions led to the formation of bis(phosphoranimino)siloxanes in good yields via the elimination of $Me_3SiCl$. The products **12–15** are colorless liquids that were purified by distillation and characterized by NMR spectroscopy and elemental analysis.

When equimolar amounts of **1** and dichlorotetramethyldisiloxane were mixed, the chlorosiloxane–phosphoranimine compound **16** was formed (eq 9) as a reactive liquid that fumed on exposure to air. After characterization of **16** by NMR spectroscopy and elemental analysis, a derivatization was attempted, as was done with the chlorosilyl–phosphoranimines **9** and **10** in eq 5 and 7. We expected that the deprotonation of a P–Me group of **16** and a ring closure would take place, giving a six-membered siloxane–phosphoranimine, analogous to **11** (eq 7).

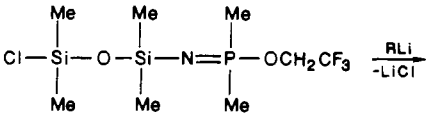


1

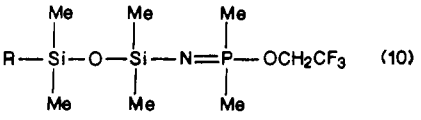


16

Instead, when 1 equiv of MeLi or *n*-BuLi was added to **16**, a simple nucleophilic displacement at the Si–Cl bond took place (eq 10).



16



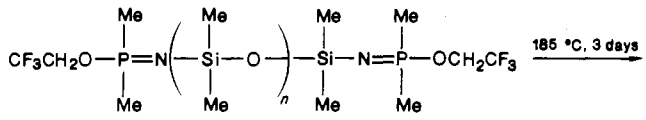
17: R = Me
18: R = *n*-Bu

The substitution products **17** and **18** were isolated by fractional distillation as colorless liquids and were identified by NMR spectroscopy. An elemental analysis of **18** was obtained.

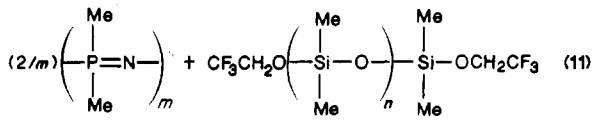
It is possible that the difference in the RLi reactions of **10** and **16** lies in the relative reactivity of the Si–Cl bond in the two compounds. The more electronegative oxygen substituent on silicon in **16** would tend to enhance the electrophilicity of the silicon center, thus making it more susceptible to attack by RLi.

**Thermolysis Reactions.** The siloxane–phosphoranimine compounds **12–18**, synthesized by the transsilylation reactions, contain the monomeric units of both polyphosphazenes and polysiloxanes. Thus, it was thought that they might be useful as precursors for the synthesis of some novel copolymers. In order to investigate this possibility, several thermolysis reactions of the siloxane–phosphoranimine transsilylation products, both alone and in mixtures with **1**, were conducted. Two representative experiments are described here.

First, a sample of the pure compound **15** was placed in a heavy-walled glass ampule and heated at 185 °C for 3 days. When the ampule was cooled, the contents separated into two fractions: one a light brown solid and the other a clear liquid. When the products of the thermolysis were examined, it became evident that the bis(phosphoranimino)siloxane **15** had undergone a decomposition reaction (eq 11) with the formation of poly(dimethyl-



15: *n* = 5

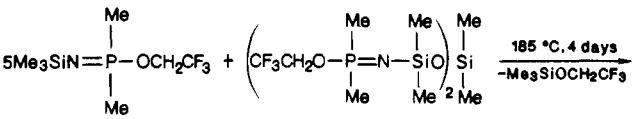


19

phosphazene) and the new siloxane **19**. The $^{31}P$ NMR spectrum of the crude solid product of this reaction displayed an intense peak at 6.4 ppm, a value typical for the $(NPMe_2)_n$ polymer,[2] and a small peak at 24.0 ppm, most probably the cyclic tetramer $(N{=}PMe_2)_4$.[6] No evidence for the incorporation of siloxane units into the $(Me_2PN)_n$ chains or rings was found. The liquid bis(trifluoroethoxy)siloxane compound **19** was identified by NMR and elemental analysis.

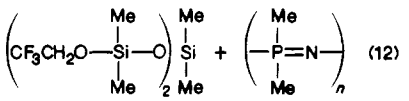
The results of this reaction (eq 11) indicate that the Si–N bond connecting the phosphazene and siloxane units of compound **15** is unstable under the thermolysis conditions. Indeed, the siloxane part of **15**, along with the $-OCH_2CF_3$ group, is eliminated from the P=N unit in the same manner as $Me_3SiOCH_2CF_3$ is formed in the condensation/polymerization of $Me_3SiN{=}P(OCH_2CF_3)Me_2$.[2]

In a second experiment, when 5 equiv of **1** was heated with 1 equiv of the phosphoranimine–siloxane **13**, poly(dimethylphosphazene) was again the major product (eq 12). The solid



1

13



19a

material formed in the ampule as a result of the thermolysis consisted of two products. This material was washed with hexane and, when dried, contained only the poly(dimethylphosphazene) ($^{31}P$ NMR: 6.2 ppm). The portion that dissolved in hexane contained a cyclic phosphazene ($^{31}P$ NMR: 25.7 ppm) and the (trifluoroethoxy)siloxane **19a**. Again, no indication of the formation of a siloxane–phosphazene copolymer was observed.

## Experimental Section

**Materials and General Procedures.** Phosphoranimine **1** was prepared according to the published procedure.[6] The Si–Cl compounds and the organolithium reagents were obtained from commercial sources and used without further purification. Hexane, $CH_2Cl_2$, and $Et_2O$ were distilled from $CaH_2$ and stored over molecular sieves. Proton and $^{13}C$ NMR spectra were recorded on a Varian XL-300 spectrometer; $^{31}P$ NMR spectra were obtained on a JEOL FX-60 instrument. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

**Preparation of Transsilylation Products 2–6.** Typically 20–30 mmol (5.0–7.4 g) of the phosphoranimine **1** was weighed into a flask equipped with a $N_2$ inlet, stirring bar, and a septum. Methylene chloride (25–35 mL) was added, and the flask was cooled to 0 °C. One equivalent of the appropriate chlorosilane was added to the reaction mixture via syringe. The mixture was allowed to warm to room temperature while being stirred. The $^{31}P$ NMR spectrum of the reaction mixture generally indicated the formation of one product. Solvent and $Me_3SiCl$ were removed under reduced pressure. The remaining product was purified by vacuum distillation and characterized by NMR spectroscopy and elemental analysis (Tables I and II).

**Preparation of 7 and 9.** The phosphoranimine **1** (4.5 g, 18.2 mmol) was dissolved in $CH_2Cl_2$ (30 mL) in a similar apparatus and cooled to 0 °C. Either 1 (**9**) or $^1/_2$ (**7**) equiv of $Me_2SiCl_2$ was added to the reaction mixture via syringe. After the mixture was warmed to room temperature, the $^{31}P$ NMR spectrum in each case indicated the formation of one major product. Solvent and $Me_3SiCl$ were removed as before. Reaction products were purified by vacuum distillation. Compound **9** was obtained in a high yield (72%) as a colorless liquid that gave satisfactory NMR spectra and elemental analysis. After standing for several days at room temperature in a closed flask under nitrogen, it decomposed into a white solid whose $^{31}P$ NMR spectrum displayed many peaks (see text).

**Preparation of 2 from 9.** One equivalent of PhLi (3.9 mL, 1.8 M solution in benzene) was added via syringe to a solution of freshly prepared **9** (1.8 g, 7.1 mmol) in $Et_2O$ (25 mL) at −78 °C in a flask equipped with a $N_2$ inlet, septum, and stirring bar. The solution was stirred for 30 min and then allowed to warm to room temperature. A white precipitate (LiCl) formed. The mixture was filtered, the solvent was removed under vacuum, and the product was distilled. The boiling point of the product and the NMR spectral data were identical with the data obtained for compound **2**, synthesized by the transsilylation reaction.

**Preparation of 8.** The phosphoranimine **1** (4.5 g, 18.2 mmol) was dissolved in $CH_2Cl_2$ (40 mL) and cooled to 0 °C. The solid silane $(CH_2SiMe_2Cl)_2$ (2.0 g, 9.1 mmol) was dissolved in $CH_2Cl_2$ (ca. 5 mL)

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

and added slowly to the reaction mixture via syringe. The ice bath was removed, and the solution was allowed to warm to room temperature. The $^{31}P$ NMR spectrum of the solution showed that two phosphorus compounds were present (**8** and **10**). The products were separated by vacuum distillation. Compound **8** was obtained as the major product with a $^{31}P$ NMR signal at 32.8 ppm. It was characterized by NMR spectroscopy and elemental analysis.

**Preparation of 10.** The silane $(CH_2SiMe_2Cl)_2$ (3.48 g, 16.2 mmol) was dissolved in $CH_2Cl_2$ (40 mL). The solution was cooled to 0 °C, and 1 equiv of the phosphoranimine **1** was added slowly via syringe. The solution was allowed to warm to room temperature. Solvent was removed and the product **10**, formed together with **8**, was purified by distillation. Compound **10**, an unstable, reactive liquid, was difficult to obtain in high purity. Therefore, **10** was used to synthesize the derivative **11**.

**Preparation of 11.** A fresh sample of compound **10** (3.5 g, 10 mmol) was dissolved in $Et_2O$ (25 mL) in a flask equipped with a $N_2$ inlet, septum, and stirring bar. The solution of **10** was cooled to -78 °C, and 1 equiv of MeLi (7.1 mL, 1.4 M solution in $Et_2O$) was added slowly via syringe. The reaction mixture was stirred while the cold bath was allowed to slowly warm to room temperature. Hexane (25 mL) was added to help precipitate the solids, the mixture was filtered, and the solvent was removed. Vacuum distillation afforded **11**, as a colorless liquid that was characterized by NMR spectroscopy and elemental analysis.

**Preparation of the Siloxane Derivatives 12-15.** In a typical experiment, compound **1** (4.5 g, 18.2 mmol) was dissolved in $CH_2Cl_2$ (35-40 mL), in a flask equipped with a magnetic stirrer, a nitrogen inlet, and a rubber septum. The solution of **1** was cooled to 0 °C, and the corresponding dichlorosiloxane (9.1 mmol) was added slowly via syringe. The mixture was stirred for 1 h and then allowed to warm to room temperature. The solvent and $Me_3SiCl$ were removed under reduced pressure. The remaining product was purified by distillation.

**Preparation of 16.** Although compound **16** could be prepared by the above procedure, a higher yield was obtained when **1** was added to 1 equiv of dichlorotetramethyldisiloxane dissolved in $CH_2Cl_2$. Solvent removal and distillation gave **16** as a colorless, reactive liquid.

**Preparation of 17.** In a flask equipped with a magnetic stirrer, $N_2$ inlet, and septum, **16** (1.5 g, 4.8 mmol) was dissolved in $Et_2O$ (10 mL) and cooled to -78 °C. One equivalent of MeLi ($Et_2O$ solution) was added via syringe. The solution was stirred at -78 °C for 1 h and then allowed to warm slowly to room temperature. Hexane (25 mL) was added, the mixture was filtered, and the solvent was removed under reduced pressure. Compound **17** was isolated by vacuum distillation as a colorless liquid.

**Preparation of 18.** In the same manner, **16** (8.2 mmol) was treated with 1 equiv of *n*-BuLi to give **18** as a colorless, distillable liquid.

**Thermolysis of 15.** A sample of **15** (2.2 g) was transferred to a heavy-walled glass ampule and degassed by the freeze-pump-thaw method. The ampule was sealed under vacuum and then heated at 185 °C for 3 days. The ampule then contained a solid product and a clear liquid. No volatile products were obtained when the contents of the ampule were subjected to a high vacuum. The clear liquid was removed with a pipet, and the remaining solid was identified as $(Me_2PN)_n$ by $^{31}P$ NMR spectroscopy. The clear liquid was purified by distillation and was identified as **19** by NMR spectroscopy and elemental analysis.

**Cothermolysis of 13 with 1.** Compounds **1** (3.2 g, 13 mmol) and **13** (1.5 g, 2.6 mmol) were transferred into a heavy-walled glass ampule, degassed, and sealed as described above. The ampule was heated at 185 °C for 4 days and then opened and attached to the vacuum line. The volatile byproduct was condensed into a cooled flask (-196 °C) and identified as $CF_3CH_2OSiMe_3$ by $^1H$ NMR spectroscopy. The nonvolatile products of the thermolysis were dissolved in $CH_2Cl_2$. The $^{31}P$ NMR spectrum of this mixture showed peaks at 8.9, 16.9, and 25.0 ppm. Addition of hexane caused the precipitation of the phosphazenes $(Me_2PN)_n$ ($^{31}P$ NMR 7.0 ppm) and $(Me_2PN)_4$ ($^{31}P$ NMR 25.7 ppm). Proton NMR analysis of the solution indicated the presence of the siloxane byproduct **19a**.

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Contribution from the Department of Chemistry, University of Vermont, Burlington, Vermont 05405

# (Vinyloxy)chlorocyclotetraphosphazenes. The Use of Two-Dimensional $^{31}P$ NMR Spectroscopy in Phosphazene Chemistry†

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The reactions of the lithium enolate of acetaldehyde, $LiOCHCH_2$, with octachlorocyclotetraphosphazene, $N_4P_4Cl_8$, led to the series of (vinyloxy)chlorocyclotetraphosphazenes $N_4P_4Cl_{8-n}(OCH{=}CH_2)_n$ ($n$ = 1, 2). The qualitative and quantitative analysis of the $^{31}P$ NMR spectrum of the mixture of bis isomers, $N_4P_4Cl_6(OCH{=}CH_2)_2$, was accomplished by a combination of *J*-resolved homonuclear 2-D NMR, $^{31}P\{^1H\}$ homonuclear shift-correlated 2-D NMR spectroscopy, and mixture simulation techniques. This represents the first demonstration of the use of 2-D NMR methods to solve problems in phosphazene chemistry. The reaction of $LiOCHCH_2$ is unique in the reactions of $N_4P_4Cl_8$ in that the 2,4-$N_4P_4Cl_6(OCH{=}CH_2)_2$ isomers are the major products. The composition of the $N_3P_3Cl_3(OCH{=}CH_2)_3$ mixture was also determined in order to shed light on the stereochemical course of the lithium enolate reactions.

## Introduction

The reactions of oxygen-based nucleophiles with cyclophosphazenes have received increased attention recently. We have been particularly interested in the reactions of the enolate anion of acetaldehyde with cyclotriphosphazenes.[1-3] The reaction of the ambidentate enolate anion occurs exclusively at the oxygen end of the nucleophile, leading to (vinyloxy)cyclotriphosphazenes.[1] These materials represent a new class of organofunctional cyclophosphazene monomers, and certain of these may be transformed into novel polymeric materials.[4] The extension of these reactions to other enolate anions has been noted.[1,5] The stereochemical pathway followed in the formation of the series $N_3P_3Cl_{6-n}(OCH{=}CH_2)_n$ ($n$ = 1-6) is predominantly nongeminal[2] and is exclusively nongeminal for the series $N_3P_3F_{6-n}(OCH{=}CH_2)_n$ ($n$ = 1-5).[3] In this paper, we report the reactions of the enolate anion of acetaldehyde with octachlorocyclotetraphosphazene, $N_4P_4Cl_8$. These studies have allowed us to expand the range of available (vinyloxy)phosphazene polymer precursors and to explore the stereochemical pathway followed in the less widely studied tetrameric series. We also report, for the first time, the use of two-dimensional $^{31}P$ NMR spectroscopy

† The general term cyclotetraphosphazene is used in this paper to represent cyclotetra($\lambda^5$-phosphazene).

(1) Allen, C. W.; Ramachandran, K.; Bright, R. P.; Shaw, J. C. *Inorg. Chim. Acta* **1982**, *64*, L109.
(2) Ramachandran, K.; Allen, C. W. *Inorg. Chem.* **1983**, *22*, 1445.
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