# Synthesis of Some *P*-Trifluoromethyl-Substituted (Silylamino)phosphines, *N*-Silylphosphoranimines, and Phosphazenes

**Sakthivel Karthikeyan and Robert H. Neilson***

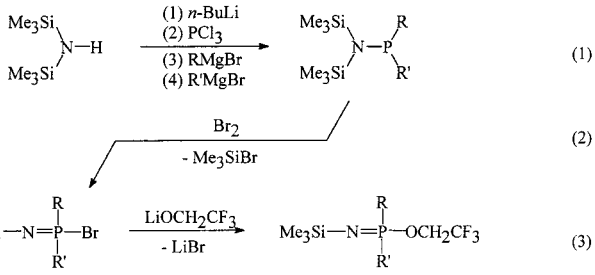
Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

*Received June 22, 1998*

Treatment of *P*-chloro-substituted (silylamino)phosphines, $(Me_3Si)_2NP(R)Cl$, with the trifluoromethylating agent, $[(Et_2N)_3PBr^+](CF_3^-)$ [generated *in situ* from $CF_3Br$ and $(Et_2N)_3P$], readily affords the corresponding *P*-trifluoromethylphosphines, $(Me_3Si)_2NP(R)CF_3$ (**4**, R = Ph; **5**, R = *n*-Pr). Subsequent oxidative halogenation of **4** and **5** with $X_2$ (X = Cl, Br, I) occurs with loss of $Me_3SiX$ to yield the *P*-halo-*P*-trifluoromethyl-*N*-silylphosphoranimines, $Me_3SiN{=}P(R)(CF_3)X$ (**6a**−**c**; R = Ph; **7a**−**c**, R = *n*-Pr). The P−Br compounds **6b** and **7b** were then converted to the *P*-trifluoroethoxy, $Me_3SiN{=}P(R)(CF_3)OCH_2CF_3$ (**8**, R = Ph; **9**, R = *n*-Pr), and *P*-phenoxy, $Me_3SiN{=}P(R)(CF_3)OPh$ (**10**, R = Ph; **11**, R = *n*-Pr), derivatives by nucleophilic substitution reactions with $LiOCH_2CF_3$ and LiOPh, respectively. Although these *P*-$CF_3$ systems are generally much more thermally stable than their *P*-alkyl analogs, the *P*-Br compounds **6b** and **7b** do thermally eliminate $Me_3SiBr$ to produce new *P*-trifluoromethyl substituted phosphazenes $[CF_3(R)P{=}N]_n$. The cyclic trimers ($n = 3$; **12**, R = Ph; **13**, R = *n*-Pr) were separated from the linear polymers ($n \sim 150-500$; **14**, R = Ph; **15**, R = *n*-Pr) by sublimation. These new compounds (4−15) were generally obtained in good yields and were fully characterized by NMR ($^1H$, $^{13}C$, $^{19}F$, and $^{31}P$) spectroscopy and elemental analysis.

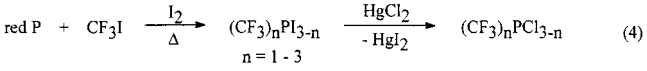
## Introduction

Certain types of Si−N−P compounds,[1] especially the [bis-(trimethylsilyl)amino]phosphines, $(Me_3Si)_2NPR_2$, and some of their oxidized derivatives, such as the *N*-silylphosphoranimines, $Me_3SiN{=}PR_2X$, are of considerable interest as precursors to polyphosphazenes, $[R_2P{=}N]_n$.[2] The synthesis of many of these Si−N−P compounds is readily accomplished by one or more of the reactions, or variations thereof, in the following three-step sequence (eqs 1−3).




As part of our ongoing efforts to greatly expand the scope of this synthetic methodology and, hence, the range of accessible phosphazene polymers, we have been investigating the prospects of incorporating perfluoroalkyl substituents (e.g., *P*-$CF_3$) into these systems. A long range objective is to prepare and characterize high molecular weight poly(phosphazenes) bearing *P*-$CF_3$ side groups which should enhance the thermal stability and surface properties of the polymers. A few prior studies in this area have dealt mainly with the $CF_3$-substituted *cyclic* phosphazenes, $[(CF_3)_2PN]_n$ ($n = 3, 4$).[3,4]

Methods of attaching perfluoroalkyl groups, especially $CF_3$, to phosphorus have traditionally been quite limited. Preparation of (trifluoromethyl)halophosphines, for example, involves tedious sealed-vessel reactions and multiple fractional condensations to obtain relatively small quantities of useful starting materials like $(CF_3)_2PCl$ (eq 4).[5] Once prepared, this reagent can be readily converted to (silylamino)phosphines (e.g., **1**, eq 5).[6] Nonetheless, this type of procedure is not only difficult, but it is also greatly limited in scope. For example, it does not provide access to mixed-substituent derivatives in which both fluoroalkyl and simple alkyl or aryl groups are attached to phosphorus.





More recently, however, Ruppert[7] has reported a much simpler and potentially very general method of incorporating

(1) For a general review of P−N compounds including Si−N−P systems, see: Neilson, R. H. In *Encyclopedia of Inorganic Chemisty*; King, R. B., Ed.; John Wiley & Sons; Chichester; England, 1994; Vol. 6, p 3180.

(2) (a) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice-Hall: Englewood Cliffs, NJ, 1992. (b) Wisian-Neilson, P. *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: England, 1994; Vol 7, p 3371. (c) Wisian-Neilson, P. *ACS Symp. Ser.* **1994**, *572*, 167. (d) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541. (e) Neilson, R. H.; Ford, R. R.; Hani, R.; Roy, A. K.; Scheide, G. M.; Wettermark, U. G.; Wisian-Neilson, P. *ACS Symp. Ser.* **1988**, *360*, 283. (f) Neilson, R. H.; Jinkerson, J. L.; Kucera, W. R.; Longlet, J. J.; Samuel, R. C.; Wood, C. E. *ACS Symp. Ser.* **1994**, *572*, 232. (g) Neilson, R. H.; Azimi, K.; Zhang, G.; Kucera, W. R.; Longlet, J. J. *Phosphorus, Sulfur, Silicon,* **1994**, *87*, 157.

(3) Tesi, G.; Douglas, C. M. *J. Am. Chem. Soc.* **1962**, *84*, 549.

(4) (a) Olms, P.; Roesky, H. W.; Keller, K.; Noltemeyer, M.; Bohra, R.; Schmidt, H.-G.; Stalke, D. *Chem. Ber.* **1991**, *124*, 2655. (b) Roesky, H. W.; Lucas, J.; Noltemeyer, M.; Sheldrick, G. M. *Chem. Ber.* **1984**, *117*, 1583.

10.1021/ic980707a CCC: $18.00 
Published on Web 04/07/1999

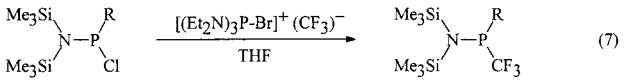
$CF_3$ groups into main group element compounds. The procedure, which is easily carried out in ordinary glassware, involves the *in situ* generation of a trifluoromethyl phosphonium species in solution (eq 6). Treatment of appropriate element halides with this reagent readily affords trifluoromethyl derivatives of phosphorus, boron, and silicon.[7,8]

$$(Et_2N)_3P + CF_3Br \rightarrow [(Et_2N)_3P\text{-}Br]^+(CF_3)^- \qquad (6)$$

We report here on the use of this reagent in the synthesis of a series of new trifluoromethyl substituted Si−N−P compounds as well as some preliminary studies of their conversion to cyclic and/or polymeric phosphazenes bearing $CF_3$ side groups.

## Results and Discussion

**(Silylamino)phosphines.** Addition of 1 equiv of $CF_3Br$ to a mixture of the appropriate chlorophosphine (**2** or **3**) and $(Et_2N)_3P$ in THF solution afforded the new trifluoromethyl derivatives **4** and **5**, respectively (eq 7). These new bis[(trimethylsilyl)amino]-(*trifluoromethyl*)phosphines were obtained in ca. 45−65% yields as thermally stable, distillable liquids that were fully characterized by multinuclear NMR spectroscopy and elemental analysis (Tables 1 and 2).



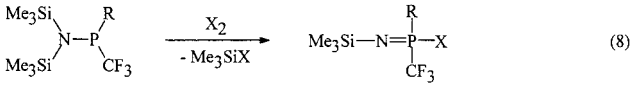

(7)

**2**: R = Ph
**3**: R = *n*-Pr

**4**: R = Ph
**5**: R = *n*-Pr

The presence of the $CF_3$ group in these compounds was readily confirmed by NMR spectroscopy. For example, the $^{31}P$ NMR signals, which are observed at ca. 55 ppm, are split into quartets due to spin coupling ($J_{PF} \sim 70-80$ Hz) to the three equivalent fluorines of the $CF_3$ group. Doublets with the same splittings were observed in the $^{19}F$ NMR spectra of these derivatives. Moreover, in the $^{13}C$ NMR spectra, the $CF_3$ carbon is found (ca. 131 ppm) as a quartet of doublets due to the one-bond C−F coupling ($J_{FC} \sim 325$ Hz) and the one-bond C−P coupling ($J_{PC} \sim 60$ Hz). Couplings to both fluorine and phosphorus are also readily seen for two of the phenyl carbons of **4** and for the *P*-$CH_2$ carbon of the *n*-propyl analog 5.

***N*-Silylphosphoranimines.** The highly electron-withdrawing ability of the *P*-$CF_3$ group in compounds like **4** and **5** greatly influences their derivative chemistry relative to that of their *P-methyl* analogs. For example, while the *alkyl*phosphines, $(Me_3Si)_2NP(R)Me$, react violently with chlorinating agents such as $CCl_4$ and $C_2Cl_6$, the *P*-$CF_3$ derivatives are inert to these reagents and actually require the use of molecular $Cl_2$ to affect oxidative chlorination (eq 8). Although there is good NMR spectroscopic evidence for the formation of the *P*-chlorophosphoranimines **6a** ($^{31}P$ NMR: $\delta$ −13.4 ppm, $J_{PF} = 109.7$ Hz) and **7a** ($^{31}P$ NMR: $\delta$ −3.5 ppm, $J_{PF} = 100.3$ Hz), neither compound could be isolated in pure form. Attempts to distill them under reduced pressure, resulted in thermal decomposition to inconclusively identified phosphazene oligomers. It seems unlikely that these chlorophosphoranimines are inherently unstable since their non-$CF_3$ analogs can be distilled and fully characterized. The inadvertent presence of small excesses of $Cl_2$ could be responsible for the thermal decomposition of these chlorophosphoranimines.




(8)

**4**: R = Ph
**5**: R = *n*-Pr

**6**: R = Ph; X = Cl(**a**), Br(**b**), I(**c**)
**7**: R = *n*-Pr; X = Cl(**a**), Br(**b**), I(**c**)

In contrast, the *bromination* of the same trifluoromethylphosphines was a much more straightforward process (eq 8). Treatment of **4** and **5** with an equimolar quantity of $Br_2$ in benzene solution afforded the desired *P-bromo-N*-silyl-phosphoranimines **6b** and **7b** in high yields (ca. 80−85%) as distillable liquids. Like their phosphine precursors, these new compounds were fully characterized by multinuclear NMR spectroscopy and elemental analysis (Tables 1 and 2). The expected upfield $^{31}P$ chemical shifts and increases in the P−C−F and P−C couplings were observed for these phosphoruse(V) derivatives relative to their P(III) precursors.[9] The thermal stability of the P-$CF_3$ derivatives **6b** and **7b** is significantly greater than that of their *P*-methyl analogs as evidenced by the fact that the *P*-$CH_3$ analog of **6b** cannot be distilled without extensive decomposition.[10]

The trifluoromethylphosphines **4** and **5** also react smoothly with iodine (eq 8) to afford the corresponding *P*-iodophosphoranimines **6c** and **7c**. Quite surprisingly, these derivatives were also thermally stable, *distillable* liquids that were readily characterized by NMR spectroscopy (e.g., **6c**, $^{31}P$ NMR, $\delta$ −19.7 ppm, $J_{PF} = 100.3$ Hz; and **7c**, $^{31}P$ NMR, $\delta$ −9.7 ppm, $J_{PF} = 90.6$ Hz). Unfortunately, these yellow liquids did not give satisfactory elemental analysis, possibly due the presence of small amounts of unreacted iodine. Further purification and complete characterization of these compounds was not pursued since the desired derivative chemistry and thermolysis reactions were accomplished satisfactorily with the *P-bromo* analogs **6b** and **7b**. Nonetheless, the fact that these *P*-iodo compounds could even be isolated is strong evidence of the stabilizing influence of the trifluoromethyl substituent.

The condensation polymerization route to polyphosphazenes has been most generally successful when the *P*-trifluoroethoxy or *P*-phenoxy substituted phosphoranmines are used as precursors. Accordingly, in the next phase of this effort, the *P*-bromo compounds **6b** and **7b** were derivatized by treatment with lithium trifluoroethoxide or phenoxide (eq 9). These reactions proceeded smoothly to afford the corresponding alkoxy (**8**, **9**) and phenoxy (**10**, **11**) derivatives. Compounds **8**−**11** were obtained in ca. 54−90% yields as distillable liquids that were fully characerized by NMR spectroscopy and elemental analysis (Tables 1 and 2).


(9)

**6b**: R = Ph
**7b**: R = *n*-Pr

**8**: R = Ph, R' = $CH_2CF_3$
**9**: R = *n*-Pr, R' = $CH_2CF_3$
**10**: R = Ph, R' = Ph
**11**: R = *n*-Pr, R' = Ph

The NMR spectra of these new phosphoranimines were generally straightforward and informative. For example, the

(5) Bennett, F. W.; Emeleus, H. J.; Haszeldine, *J. Chem. Soc.* **1953**, 1565.
(6) Neilson, R. H.; Lee, R. C.-Y.; Cowley, A. H. *Inorg. Chem.* **1977**, *16*, 1455.
(7) Volbach, W.; Ruppert, I. *Tetrahedron Lett.* **1983**, *24*, 5509.
(8) Ruppert, I.; Schlich, K.; Volbach, W. *Tetrahedron Lett.* **1984**, *25*, 2195.
(9) Wilburn, J. C.; Neilson, R. H. *Inorg. Chem.* **1977**, *16*, 2519.
(10) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1980**, *19*, 1975.

**Table 1.** NMR Spectral Data[a] for *P*-Trifluoromethyl Compounds

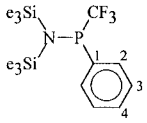
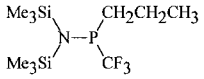
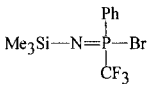
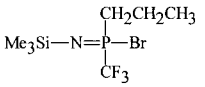
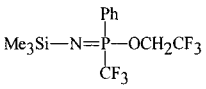
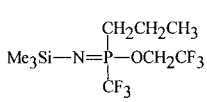
| | | $^1$H NMR | | $^{13}$C NMR | | | $^{31}$P NMR | $^{19}$F NMR | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | Signal | $\delta$ | $J_{PH}$ | $\delta$ | $J_{PC}$ | $J_{FC}$ | $\delta$ | $\delta$ | $J_{FP}$ |
|  **4** | $PCF_3$ | | | 130.83 | 59.8 | 324.9 | 55.7 | - 61.6 | 79.0[b] |
| | $Me_3Si$ | 0.12 | | 3.93 | 6.8 | | | | |
| | Ph | 7.2-7.4[c] | | | | | | | |
| | $C_1$ | | | 137.38 | 19.4 | 3.6 | | | |
| | $C_2$ | | | 129.32 | 17.1 | 1.8 | | | |
| | $C_3$ | | | 128.72 | 3.9 | | | | |
| | $C_4$ | | | 128.84 | 1.5 | | | | |
|  **5** | $PCF_3$ | | | 131.78 | 59.1 | 326.1 | 53.9 | - 62.0 | 69.0[b] |
| | $Me_3Si$ | 0.18 | | 4.34 | 6.0 | | | | |
| | $PCH_2$ | 1.5-2.0[c] | | 28.77 | 18.6 | 3.5 | | | |
| | $CH_2CH_3$ | 1.3-1.5[c] | | 18.42 | 21.8 | | | | |
| | $CH_2CH_3$ | 0.98 | (7.2)[d] | 15.67 | 15.1 | | | | |
|  **6b** | $PCF_3$ | | | 120.62 | 170.1 | 321.2 | - 23.7 | - 74.21 | 106.4[b] |
| | $Me_3Si$ | 0.10 | | 2.35 | 5.4 | | | | |
| | Ph | 7.4-8.0[c] | | | | | | | |
| | $C_1$ | | | 129.27 | 131.6 | | | | |
| | $C_2$ | | | 129.01 | 16.0 | | | | |
| | $C_3$ | | | 132.80 | 12.6 | | | | |
| | $C_4$ | | | 134.23 | 3.7 | | | | |
|  **7b** | $PCF_3$ | | | 120.15 | 147.5 | 321.7 | - 13.5 | - 74.6 | 96.0[b] |
| | $Me_3Si$ | - 0.02 | | 2.19 | 5.7 | | | | |
| | $PCH_2$ | 2.0-2.3[c] | | 37.95 | 87.1 | | | | |
| | $CH_2CH_3$ | 1.6-1.8[c] | | 15.83 | 6.5 | | | | |
| | $CH_2CH_3$ | 1.01 | 1.8 (7.4)[d] | 14.94 | 19.9 | | | | |
|  **8** | $PCF_3$ | | | 121.93 | 186.6 | 317.9 | - 6.4 | - 74.0 | 105.0[b] |
| | $Me_3Si$ | 0.07 | | 3.01 | 2.9 | | | | |
| | $OCH_2$ | 4.2-4.5[c] | | 60.97 | 5.4 | 38.0 | | | |
| | Ph | 7.4-8.0[c] | | | | | | | |
| | $C_1$ | | | 126.29 | 154.5 | | | | |
| | $C_2$ | | | 129.04 | 14.7 | | | | |
| | $C_3$ | | | 132.86 | 11.2 | | | | |
| | $C_4$ | | | 134.02 | 3.1 | | | | |
| | $CH_2CF_3$ | | | 123.09 | 9.0 | 277.5 | | - 75.4 | [8.3][e] |
|  **9** | $PCF_3$ | | | 121.85 | 165.3 | 318.7 | 7.1 | - 74.4 | 96.0[b] |
| | $Me_3Si$ | - 0.03 | | 2.95 | 2.7 | | | | |
| | $PCH_2$ | 1.7-1.8[c] | | 29.34 | 103.8 | | | | |
| | $CH_2CH_3$ | 1.5-1.7[c] | | 15.41 | 17.5 | | | | |
| | $CH_2CH_3$ | 0.96 | 1.4 (7.4)[d] | 14.86 | 4.9 | | | | |
| | $OCH_2$ | 4.0-4.5[c] | | 60.72 | 6.3 | 37.8 | | - 75.5 | [8.2][e] |
| | $CH_2CF_3$ | | | 123.16 | 8.7 | 277.5 | | | |

**Table 1** (Continued)

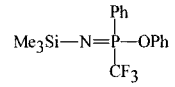
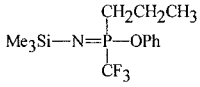
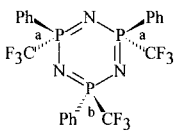
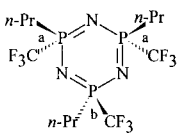
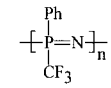
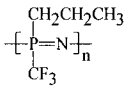
| Compound | Signal | $^1$H NMR $\delta$ | $^1$H NMR $J_{PH}$ | $^{13}$C NMR $\delta$ | $^{13}$C NMR $J_{PC}$ | $^{13}$C NMR $J_{FC}$ | $^{31}$P NMR $\delta$ | $^{19}$F NMR $\delta$ | $^{19}$F NMR $J_{FP}$ |
|---|---|---|---|---|---|---|---|---|---|
|  **10** | $PCF_3$ | | | 122.09 | 187.0 | 318.3 | - 11.6 | - 73.4 | 102.5[b] |
| | $Me_3Si$ | - 0.05 | 1.2 | 2.84 | 3.2 | | | | |
| | P-Ph | 7.4-8.0[c] | | | | | | | |
| | $C_1$ | | | 127.38 | 155.9 | | | | |
| | $C_2$ | | | 128.93 | 14.8 | | | | |
| | $C_3$ | | | 133.35 | 10.8 | | | | |
| | $C_4$ | | | 133.70 | 3.1 | | | | |
| | O-Ph | 7.0-7.5[c] | | | | | | | |
| | $C_1$ | | | 150.35 | 9.0 | | | | |
| | $C_2$ | | | 121.48 | 4.6 | | | | |
| | $C_3$ | | | 129.76 | | | | | |
| | $C_4$ | | | 125.36 | | | | | |
|  **11** | $PCF_3$ | | | 122.10 | 162.9 | 320.2 | 1.9 | - 73.1 | 93.4[b] |
| | $Me_3Si$ | - 0.19 | | 2.76 | 3.0 | | | | |
| | $PCH_2$ | 1.8-2.0[c] | | 29.89 | 109.2 | | | | |
| | $CH_2CH_3$ | 1.6-1.8[c] | | 15.54 | 17.8 | | | | |
| | $CH_2CH_3$ | 1.02 | (7.0)[d] | 15.16 | 4.8 | | | | |
| | O-Ph | 7.0-7.3[c] | | | | | | | |
| | $C_1$ | | | 150.43 | 10.3 | | | | |
| | $C_2$ | | | 121.72 | 4.1 | | | | |
| | $C_3$ | | | 129.66 | 1.5 | | | | |
| | $C_4$ | | | 125.32 | 1.7 | | | | |
|  **12** | $PCF_3$ (a). | | | 122[f] | 190 | 316 | 11.0 (a) | - 77.6 | 106.5[b] |
| | $PCF_3$ (b) | | | 122[f] | 190 | 316 | 11.7 (b) | - 78.2 | 104.5[b] |
| | P-Ph | 7.4-8.1[c] | | | | | | | |
| | $C_1$ (a) | | | 127.48 | 146.7 | | | | |
| | $C_1$ (b) | | | 126.90 | 145.6 | | | | |
| | $C_2$ (a) | | | 128.92 | 14.7 | | | | |
| | $C_2$ (b) | | | 129.00 | 14.6 | | | | |
| | $C_3$ (a) | | | 131.95 | 11.4 | | | | |
| | $C_3$ (b) | | | 132.01 | 11.4 | | | | |
| | $C_4$ (a) | | | 133.94 | 3.1 | | | | |
| | $C_4$ (b) | | | 134.12 | 3.1 | | | | |
|  **13** | $PCF_3$ (a) | | | 122.49 | 172.5 | 317.8 | 24.8[f] | - 77.11 | 97.2 |
| | $PCF_3$ (b) | | | 122.71 | 174.0 | 317.5 | | - 77.58 | 95.8 |
| | $PCH_2$ (a) | 1.7-1.9[c] | | 30.53 | 101.3 | | | | |
| | $PCH_2$ (b) | 1.7-1.9[c] | | 30.25 | 99.7 | | | | |
| | $CH_2CH_3$ (a) | 1.5-1.7[c] | | 15.52 | 18.9 | | | | |
| | $CH_2CH_3$ (b) | 1.5-1.7[c] | | 15.47 | 18.7 | | | | |
| | $CH_2CH_3$ (a) | 0.9-1.0[c] | | 13.57 | 5.0 | | | | |
| | $CH_2CH_3$ (b) | 0.9-1.0[c] | | 13.26 | 5.3 | | | | |

**Table 1** (Continued)

| Compound | Signal | $^1$H NMR $\delta$ | $^1$H NMR $J_{PH}$ | $^{13}$C NMR $\delta$ | $^{13}$C NMR $J_{PC}$ | $^{13}$C NMR $J_{FC}$ | $^{31}$P NMR $\delta$ | $^{19}$F NMR $\delta$ | $^{19}$F NMR $J_{FP}$ |
|---|---|---|---|---|---|---|---|---|---|
|  **14** | $PCF_3$ | | | 115-128[c] | | | - 15.8[f] | - 75[c] | 110 |
| | Ph | 7.0-8.3[c] | | | | | | | |
| | $C_1$ | | | 126-128[c] | | | | | |
| | $C_{2-4}$ | | | 128-134[c] | | | | | |
|  **15** | $PCF_3$ | | | 123[f] | 178 | 318 | 2.5[f] | - 76[c] | 96 |
| | $PCH_2$ | 1.7-1.8[c] | | 30-33[c] | | | | | |
| | $CH_2CH_3$ | 1.5-1.6[c] | | 14-16[c] | | | | | |
| | $CH_2CH_3$ | 0.8-1.0[c] | | 14-16[c] | | | | | |

[a] Proton and $^{13}$C chemical shifts downfield from $Me_4Si$; $^{31}$P shifts downfield from $H_3PO_4$; $^{19}$F shifts downfield from $CFCl_3$. Solvents: $CDCl_3$ for $^1$H, $^{13}$C, and $^{19}$F NMR; $CH_2Cl_2$ for $^{31}$P NMR. [b] $J_{FP}$ values obtained from $^{31}$P NMR spectrum. [c] Complex multiplet. [d] $J_{HH}$ values in parentheses. [e] $J_{HF}$ values in brackets. [f] Broad, overlapping signals.

**Table 2.** Preparative and Analytical Data for *P*-Trifluoromethyl Compounds

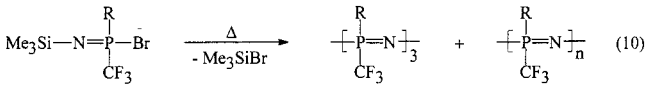
| compd | yield (%) | bp (°C/mmHg) | analysis[a] % C | analysis[a] % H |
|---|---|---|---|---|
| **4** | 45 | 66−67/0.03 | 46.37 (46.27) | 6.88 (6.87) |
| **5** | 64 | 50−52/0.7 | 39.69 (39.58) | 7.93 (8.30) |
| **6b** | 84 | 41−44/0.03 | 35.07 (34.90) | 4.37 (4.10) |
| **7b** | 80 | 54−55/4 | 27.65 (27.11) | 5.07 (5.20) |
| **8** | 88 | 54−56/0.6 | 39.79 (39.67) | 4.76 (4.44) |
| **9** | 54 | 51−54/8 | 32.98 (32.83) | 5.22 (5.51) |
| **10** | 90 | 76−79/0.05 | 53.95 (53.77) | 5.47 (5.36) |
| **11** | 72 | 50−52/0.07 | 48.22 (48.29) | 6.25 (6.55) |
| **12** | (40)[b] | (177−179)[c] | 44.39 (44.00) | 2.98 (2.64) |
| **13** | (80)[b] | | 30.79 (30.59) | 4.40 (4.49) |
| **14** | (60)[b] | | 43.94 (44.00) | 2.91 (2.64) |
| **15** | (20)[b] | | 31.16 (30.59) | 4.52 (4.49) |

[a] Calculated values in parentheses. [b] Relative percentages of cyclic trimer and linear polymer in product mixture (by $^{31}$P NMR). [c] Melting point in parentheses.

presence of two different $CF_3$ groups in the trifluoroethoxy systems **8** and **9** was clearly evident. While the $^{19}$F and $^{13}$C chemical shifts of the *P*-$CF_3$ group (e.g., **8**, $^{19}$F NMR, $\delta$ −74.0 ppm; $^{13}$C NMR, $\delta$ −121.9 ppm) and the *P*-$OCH_2CF_3$ group (e.g., **8**, $^{19}$F NMR, $\delta$ −75.4 ppm; $^{13}$C NMR, $\delta$ −123.1 ppm) are very close together, the P−C (P*C*$F_3$, $J_{PC}$ = 318 Hz; $POCH_2CF_3$, $J_{PC}$ = 278 Hz) and P−F (P*C*$F_3$, $J_{PF}$ = 104 Hz; $PCH_2CF_3$, $J_{PF} \approx 0$ Hz) coupling constants are distinctly different but consistent with the molecular structures.

**Phosphazenes.** Thermolysis studies of phosphoranimines **8**−**11** were conducted in evacuated, sealed ampules over the temperature range of 175−225 °C for periods of 2−12 days. Under such conditions, the *P-methyl* analogues of **8**−**11** readily and cleanly eliminate silyl ethers $Me_3SiOR'$ (R′ = $OCH_2CF_3$, Ph) to give the expected poly(alkyl/aryl)phosphazenes, $[Me(R)P{=}N]_n$ (R = alkyl, Ph). The *P-trifluoromethyl* derivatives (**8**−**11**) in this study, however, were found to be much more thermally robust and were generally recovered unchanged after such treatment. After prolonged heating at the highest temperatures (<220 °C), only small amounts of $Me_3SiF$ and some discoloration of the liquid material were observed. Still harsher conditions resulted in the production of more $Me_3SiF$ and unidentified black residues.

In contrast, the *P*-halophosphoranimines such as the *P*-bromo derivatives **6b** and **7b** readily eliminated the expected halosilanes to afford novel trifluoromethyl-substituted phosphazenes (**12**−**15**, eq 10). Upon removal of $Me_3SiBr$ under vacuum, the phosphazene products were isolated as off-white solids that were soluble in a variety of organic solvents including THF and $CH_2Cl_2$. Typically, the bromophosphoranimines were heated in sealed glass ampoules at ca. 180 °C for periods of 6 to 10 days to achieve complete thermolysis (ca. 94−98 % recovery of $Me_3SiBr$).



(10)

Analysis of the solid products of these reactions by $^{31}$P NMR spectroscopy indicated that mixtures of trimeric (**12**, **13**) and polymeric phosphazenes (**14**, **15**) were obtained in ratios of ca. 40/60 for **12**/**14** (R = Ph) and 80/20 for **13**/**15** (R = *n*-Pr). The respective trimers and polymers were separated from each other by multiple sublimations to yield fully-characterized samples of pure compounds (Tables 1 and 2). As observed previously for other phosphazene systems, the cyclic trimers have $^{31}$P chemical shifts that are ca. 20−30 ppm downfield from the corresponding polymers. Only trace amounts of the cyclic tetramers and higher homologs were discernible in the NMR spectra of the product mixtures. After purification by sublimation, the trimeric products were obtained as mixtures of cis and trans isomers, with the trans species (Table 1) greatly predominating.

The remaining polymeric portions of the product mixtures were isolated as pale yellow, amorphous solids that were readily soluble in THF. Size exclusion chromatography indicated that these new trifluoromethyl-substituted phosphazenes had moderate to high molecular weights (**14**, $M_w$ = 99 400 $M_w/M_n$ = 1.4; **15**, $M_w$ = 24 200; $M_w/M_n$ = 1.3) and narrow molecular weight distributions. Additional properties of these new polyphosphazenes will be reported as part of another study.

## Experimental Section

**Materials and General Procedures.** The following reagents were obtained from commercial sources and used as received: $(Me_3Si)_2NH$, $PCl_3$, $PhPCl_2$, *n*-BuLi, *n*-PrMgCl, $Cl_2$, $Br_2$, $I_2$, $CF_3Br$, $CF_3CH_2OH$, and PhOH. The solvents, $Et_2O$, THF, benzene, and hexane were dried using conventional procedures and stored under nitrogen atmosphere before

use. Hexaethyl phosphorus triamide, $(Et_2N)_3P$[11] and the chloro(silylamino)phosphines, $(Me_3Si)_2NP(R)Cl$ (R = Ph, *n*-Pr),[12] were prepared according to published procedures or minor variations thereof. All reactions and other manipulations were carried out under vacuum or dry nitrogen. Proton, carbon-13, and fluorine-19 NMR spectroscopic data were obtained on a Varian XL-300 NMR spectrometer. Phosphorus-31 NMR data were obtained on a JEOL FX-90 NMR spectrometer. Elemental analyses were obtained from Schwarzkopf Analytical Laboratory (Woodside, NY). Size exclusion chromatography was performed with a Waters GPC instrument using experimental conditions described earlier.[13]

**[Bis(trimethylsilyl)amino](phenyl)(trifluoromethyl)phosphine (4).** A nitrogen-filled, 100-mL, round-bottom flask, equipped with a magnetic stir bar and a Teflon stopcock side-arm, was charged with THF (10 mL), the chlorophosphine, $(Me_3Si)_2N(Ph)CI$ (**2**) (10.0 g, 33 mmol), and $(Et_2N)_3P$ (8.2 g, 33 mmol). The reaction flask was attached to a vacuum system and degassed by several freeze−pump−thaw cycles. One molar equivalent of $CF_3Br$ (33 mmol) was measured as a gas in the vacuum line and then condensed into a trap at −196 °C. The $CF_3Br$ was allowed to warm and then condense (through the side-arm) into the reaction vessel which was kept at −196 °C during the transfer. The side-arm of the flask was then closed and the contents were allowed to warm slowly to room temperature, followed by overnight stirring. The reaction flask was back-filled with dry nitrogen and hexane (ca. 50 mL) was added to help precipitate the phosphonium salt byproduct. The supernatant solution was decanted and the same extraction process was repeated 3 or 4 times. Solvents were removed under reduced pressure and fractional distillation through a 10-cm column afforded the desired product **4** as a colorless liquid (Tables 1 and 2).

**[Bis(trimethylsilyl)amino](*n*-propyl)(trifluoromethyl)phosphine (5)** was prepared on a 33-mmol scale according to the same procedure and was also isolated as a colorless, distillable liquid.

(***P*-Bromo-*P*-phenyl-*P*-trifluoromethyl-*N*-trimethylsilylphosphoranimine (6b).** A 250-mL, 3-necked, round-bottom flask, equipped with a magnetic stirring bar and an addition funnel, was charged with the phenyl(trifluoromethyl)phosphine **4** (14.3 g, 42 mmol) and dry benzene (100 mL), The solution was cooled to 0 °C and bromine (8.4 g, 52 mmol) was added dropwise from the addition funnel. When a pale yellow color persisted in the reaction mixture, the $Br_2$ addition was stopped. Analysis of the mixture by $^{31}P$ NMR spectroscopy confirmed' that the reaction was complete. Benzene and $Me_3SiBr$ were removed under reduced pressure. Fractional distillation then afforded the desired product 6b as a colorless, moisture-sensitive liquid (Tables 1 and 2).

***P*-Bromo-*P*-*n*-propyl-*P*-trifluoromethyl-*N*-trimethylsilylphosphoranimine (7b)** was prepared on a 54-mmol scale according to the same procedure and was isolated as a colorless, distillable liquid. The analogous *P*-chloro (**6a**, **7a**) and *P*-iodo (**6c**, **7c**) derivatives were prepared by treating the appropriate phosphines (**4**, **5**) with molecular chlorine ($Cl_2$) and iodine ($I_2$), respectively.

***P*-Phenyl-*P*-trifluoroethoxy-*P*-trifluoromethyl-*N*-trimethylsilylphosphoranimine (8).** The phenyl(trifluoromethyl)phosphine (**4**) was brominated in benzene to afford the *P*-bromophosphoranimine (**6b**) on a 54-mmol scale as described above. After solvent and $Me_3SiBr$ were removed under reduced pressure, THF (100 mL) was added to the reaction flask. In a separate flask, a solution of $LiOCH_2CF_3$ (54 mmol) in THF (75 mL) was prepared by slow addition of an equimolar amount of *n*-BuLi to $CF_3CH_2OH$ at −78 °C. The $LiOCH_2CF_3$ solution was transferred to the additional funnel and then added dropwise to the stirred solution of **5** at 0 °C.

The reaction mixture was warmed to room temperature and then stirred overnight. Solvent was removed under reduced pressure and hexane (200 nimL) added. The LiBr precipitate was removed by filtration and washed with hexane (50 mL). Solvents were removed under reduced pressure and fractional distillation through a 10-cm column afforded the desired product **8** as a colorless liquid (Tables 1 and 2). The other phosphoranimines (**9**−**11**) were prepared according to the same procedure by treating **7b** with $LiOCH_2CF_3$ (to give **9**) or by treating **6b** and **7b** with LiOPh (to give **10** and **11**, respectively). All of these new compounds were isolated by fractional distillation as colorless liquids (Tables 1 and 2).

**Thermolysis Reactions of Phosphoranimines 6−11.** In a typical procedure, the *P*- bromo-*P*-phenyl-phosphoranimine **6b** (ca. 20 mmol) was distilled directly into a heavy-walled glass ampule (ca. 10 mL volume). The ampule was sealed under vacuum, placed in a metal pipe for safety, and then heated in a thermo-regulated oven at 180 °C for 8−10 days. After cooling the contents of the ampule to −196 °C, the ampule was opened and quickly attached to a vacuum system. The volatile $Me_3SiBr$ byproduct was removed under vacuum, collected in a removable trap and weighed (typically greater than 90% recovery). The residual solid was dissolved in $CDCl_3$, analyzed by NMR spectroscopy (Table 1), and then freed of solvent. The cyclic phosphazene product **12** was removed from the residue by vacuum sublimation at ca. 100 °C. Subsequently, the solid residue was dissolved in $CH_2Cl_2$ and then precipitated by pouring this solution into a large quantity of hexane. This sublimation−precipitation procedure was repeated two times in order to obtain a pure sample of polyphosphazene **14** (Tables 1 and 2).

**Acknowledgment.** We thank the Robert A. Welch Foundation, the Texas Higher Education Coordinating Board (Advanced Technology Program), and the Texas Christian University Research Fund for financial support of this research.

IC980707A

(11) Stuebe, C.; Lankelma, H. P. *J. Am. Chem. Soc.* **1956**, *78*, 976.
(12) (a) Neilson, R. H.; Wisian-Neilson, P. *Inorg. Chem.* **1982**, *21*, 3568. (b) Neilson, R. H.; Jinkerson, D. L.; Karthikeyan, S.; Samuel, R.; Wood, C. E. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1991**, *32*, 483.
(13) Neilson, R. H.; Hani, R.; Wisian-Neilson, P.; Meister, J. J.; Roy, A. K.; Hagnauer, G. L. *Macromolecules*, **1987**, *20*, 910.