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Synthesis and Characterization of Mixed-Substituent *N*-Silylphosphoranimines

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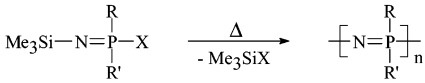
The preparation of a large series of new *N*-silyl-*P*-alkylphosphoranimines and their (silylamino)phosphine precursors is reported. Oxidative bromination of the P-functional (silylamino)phosphines, $(Me_3Si)_2NP(R)X$ [R = *n*-Pr, *n*-Bu, *i*-Pr, *t*-Bu; X = Br, OR′ (R′ = CH_2CF_3, Ph)], occurred smoothly at 0 °C and afforded the desired *P*-bromophosphoranimines, $Me_3SiN{=}P(R)(X)Br$. Nucleophilic substitution reactions of the *P*-dibromo members of this series with LiOR′ gave the corresponding *P*-trifluoroethoxy- and *P*-phenoxyphosphoranimines, $Me_3SiN{=}P(R)(OR')_2$ (R′ = CH_2CF_3, Ph). All of these *N*-silylphosphoranimines, which are potential precursors to new cyclic and/or polymeric phosphazenes, were obtained as thermally stable, distillable liquids and were characterized by NMR (^1H, ^{13}C, and ^{31}P) spectroscopy and elemental analysis.

Introduction

Depending on the substituents attached to phosphorus along the P−N backbone, poly(phosphazenes), $[R_2P{=}N]_n$, can have a very wide range of physical and chemical properties as well as potential applications.[1] The structural and chemical diversity of poly(phosphazenes) is made possible by the two general and complementary methods employed for their synthesis. The very well-studied ring-opening/substitution approach, developed by Allcock and co-workers,[2] is best suited to the preparation of phosphazenes bearing alkoxy, aryloxy, or amino substituents. In contrast, the condensation polymerization of *N*-silylphosphoranimines (eq 1), developed by Wisian-Neilson and Neilson[3] and recently extended by others,[4,5] is commonly used for the synthesis of poly(alkyl/arylphosphazenes) in which all of the side groups are attached directly by carbon−phosphorus bonds.



(1)

R, R' = alkyl, aryl; X = Cl, Br, OCH_2CF_3, OPh

In the condensation method (eq 1), the substituents on phosphorus are introduced prior to polymerization beginning with the synthesis of suitable [bis(trimethylsilyl)amino]-phosphines, $(Me_3Si)_2NPRR'$, via the Wilburn method (eqs 2−4).[6] Subsequent oxidative halogenation (e.g., with Br_2 or C_2Cl_6), followed by nucleophilic substitution at phosphorus (e.g., with $LiOCH_2CF_3$ or LiOPh) affords the typical phosphazene precursors such as $Me_3SiN{=}P(X)Me_2$ and $Me_3SiN{=}P(X)(Ph)Me$ (X = OCH_2CF_3, OPh).[7]

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(5) Another type of condensation polymerization, based on elimination of $Cl_3P(O)$ from the *N*-phosphorylphosphoranimine, $Cl_2P(O)N{=}PCl_3$, is an efficient, alternate route to poly(dichlorophosphazene): D'Halluin, G.; De Jaeger, R.; Chambrette, J. P.; Potin, P. *Macromolecules* **1992**, *25*, 1254.

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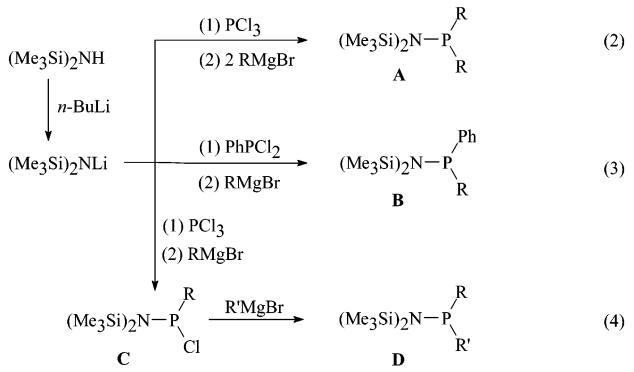
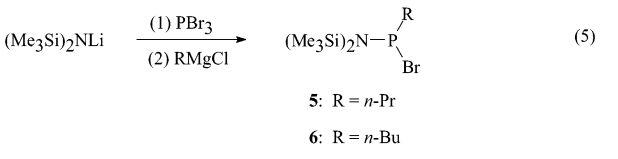
The Wilburn method has been used to prepare a wide variety of symmetrical dialkyl (**A**), unsymmetrical alkylphenyl (**B**), or unsymmetrical dialkyl (**D**) derivatives.[8] The monosubstituted chlorophosphines (**C**) can be isolated only with relatively bulky groups on phosphorus (e.g., R = *n*-Pr, Ph, *t*-Bu, CH_2SiMe_3).[9,10] In addition to their use as intermediates in the synthesis of dialkylphosphines (**D**), these chlorophosphines (**C**) have a rich derivative chemistry, some of which forms the basis for the present study.



Specifically, we report here on the synthesis and characterization of several new "mixed substituent" (disilylamino)-phosphines, $(Me_3Si)_2NP(R)X$, and their conversion to a large series of similarly functionalized *N*-silylphosphoranimines, $Me_3SiN{=}P(R)XY$, (X, Y = Cl, Br, OCH_2CF_3, OPh). Condensation reactions of the latter compounds to afford new cyclic and polymeric phosphazenes[11] will be reported separately.

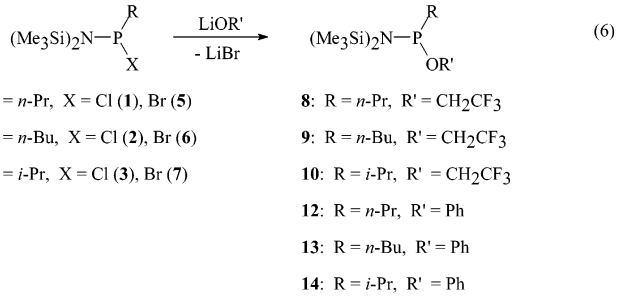
Results and Discussion

(Silylamino)phosphines. Some of the new compounds described herein were prepared from the monochlorophosphines, $(Me_3Si)_2NP(R)Cl$ (**1**, R = *n*-Pr; **2**, R = *n*-Bu; **3**, R = *i*-Pr; and **4**, R = *t*-Bu),[10,12] obtained via the Wilburn method (variation **C**). In this study, we also investigated the extension of this method for the preparation of some analogous bromophosphines (eq 5) by using PBr_3 in place of PCl_3.



The bromophosphines **5**−**7** were obtained as air-sensitive, distillable liquids that were characterized by NMR (^1H, ^{13}C, and ^{31}P) spectroscopy. They did not, however, provide satisfactory elemental analyses because of the presence of small amounts of the dialkylphosphines, $(Me_3Si)_2NPR_2$, and/or hydrolysis products. In the case of the *n*-propyl derivative **5**, as with its P−Cl analogue **1**, a 10−20% impurity of $(Me_3Si)_2NP(n\text{-}Pr)_2$ could not be removed by fractional distillation. Nevertheless, all of these *P*-halophosphines **1**−**7** were useful for further derivative chemistry. Most importantly, all of the resulting *N*-silylphosphoranimines (see later), intended as phosphazene precursors, were obtained in an analytically pure form after a single redistillation.

The nucleophilic displacement of chlorine (in **1**−**3**) or bromine (in **5**−**7**) occurred readily when these halophosphines were treated with either lithium trifluoroethoxide or lithium phenoxide (eq 6). The mixed substituent (silylamino)-phosphines **8**−**10** and **12**−**14** were obtained in good yields (ca. 70−80%), from either the P−Cl or P−Br precursors, and were fully characterized by NMR spectroscopy and elemental analyses.



With the *n*-alkyl derivatives (**8**, **9**, **12**, and **13**), these reactions proceeded smoothly in Et_2O solution. In the case of the more sterically crowded *i*-propyl compounds **10** and **14**, however, THF was found to be the best solvent. Several attempts were made to prepare the *t*-butyl analogue, $(Me_3Si)_2N(t\text{-}Bu)OCH_2CF_3$ (**11**), from the corresponding P−Cl precursor **4** without success. In either Et_2O or THF solution (even at reflux), almost no reaction occurred, presumably because of steric hindrance by the *t*-Bu group on phosphorus. Similar difficulties with other nucleophilic substitution reactions involving **4** have been observed.[10] At best, we were able to isolate only small amounts of **11** mixed with unidentified and inseparable impurities. Reversing the order of addition of nucleophiles in the Wilburn synthesis (i.e., treating the intermediate dichlorophosphine $(Me_3Si)_2NPCl_2$, with 1 equi of $LiOCH_2CF_3$ followed by *t*-BuMgCl) was also investigated without success. Therefore, **11** was characterized only by NMR spectroscopy, and no attempts were made to prepare the *P*-phenoxy analogue.

The NMR spectral data obtained for the new (silylamino)-phosphines are all consistent with the proposed structures. The ^{31}P NMR chemical shifts (Table 1) are characteristically downfield (>150 ppm) for the deshielded phosphorus(III) center bearing an electronegative P−X (X = Cl, Br, OCH_2-

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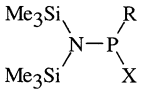
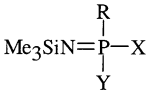
Table 1. ^{31}P NMR Chemical Shifts (ppm) of Mixed Substituent (Silylamino)Phosphines



R	X = Cl	X = Br	X = OR_f[a]	X = OPh
n-Pr	159.8	168.4	166.0	154.0
n-Bu	160.0	169.3	166.4	154.3
i-Pr	163.7	171.6	172.0	172.0
t-Bu	164.8	172.5[b]	175.7[b]	*c*

[a] $OR_f = OCH_2CF_3$. [b] Compound not isolated from impurities. [c] Unknown compound.

Table 2. ^{31}P NMR Chemical Shifts (ppm) of Mixed Substituent *N*-Silylphosphoranimines



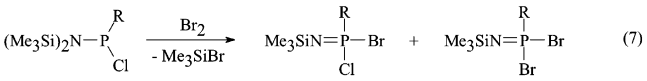
R	X = Cl Y = Cl	X = Br Y = Cl	X = Br Y = Br	X = OPh Y = Br	X = OR_f[a] Y = Br	X = OPh Y = OPh	X = OR_f[a] Y = OR_f[a]
n-Pr	2.8	−18.0	−40.5	−0.4	4.4	9.9	21.0
n-Bu	*c*	−7.2	−39.5	0.1	5.0	10.5	21.5
i-Pr	14.3	−1.1	−18.7	11.4	15.9	13.0	24.5
t-Bu	19.7[b]	8.7	−5.8	*c*	22.0	*c*	*c*

[a] $OR_f = OCH_2CF_3$. [b] Published data.[14] [c] Unknown compound.

CF_3, OPh) group. For a given substituent (X), the ^{31}P NMR signal shifts steadily downfield (by ca. 6 ppm) as the steric bulk of the alkyl group increases from *n*-propyl to *i*-propyl to *t*-butyl. The ^{1}H and ^{13}C NMR spectra contained the expected peak multiplicities and intensities. For example, with the exception of the terminal CH_3 group in the *n*-Bu derivatives **6**, **9**, and **13**, all of the alkyl carbon signals appeared as doublets in the ^{13}C NMR spectra because of spin-coupling to phosphorus. The methyl groups within the *i*-propyl substituents of compounds **3**, **10**, and **14** are diastereotopic because of the asymmetric arrangement at phosphorus. Accordingly, the methyl groups give rise to two doublets (P−C coupling) in the ^{13}C NMR spectra and two sets of doubled doublets (P−H and H−H coupling) in the ^{1}H NMR spectra.

***N*-Silylphosphoranimines.** To prepare useful precursors to phosphazenes, it is necessary to oxidize the (silylamino)-phosphines to the phosphorus(V) state. This is normally accomplished by reactions with either bromine or hexachloroethane which routinely afford high yields of the *P*-bromo- or *P*-chloro-*N*-silylphosphoranimines,[7] respectively. Initially, we attempted to prepare the dichlorophosphoranimine $Me_3SiN{=}P(i\text{-Pr})Cl_2$ (**15**) by treating the chlorophosphine, $(Me_3Si)_2NP(i\text{-Pr})Cl$ (**1**), with C_2Cl_6. This reaction, however, was much slower than that of the dialkylphosphines, $(Me_3Si)_2NPR_2$, with C_2Cl_6, probably because of the electron withdrawing effect of the P−Cl group, and it failed to go to completion even at elevated temperatures. Although the desired product could be identified by NMR spectroscopy (Table 2), it was impossible to separate it from unreacted hexachloroethane. Thus, it was concluded that this was not a feasible synthetic route to compounds such as **15**. Very recently, however, Manners et al.[13] have used SO_2Cl_2 to cleanly prepare the trichlorophosphoranimine, $Me_3SiN{=}PCl_3$, from the dichlorophosphine, $(Me_3Si)_2NPCl_2$. It is likely that the same oxidative chlorination procedure will be used to advantage in our future studies with chlorophosphines such as **1**−**4**.

We then studied the direct bromination of the P−Cl phosphines (**1**−**4**). As expected, these reactions (eq 7) occurred rapidly at 0 °C, but in all cases, inseparable mixtures of bromochloro- (**16**−**19**) and dibromophosphoranimines (**20**−**23**) were obtained. Typically, after removal of solvent and the halosilane byproducts, Me_3SiX (X = Cl, Br), the remaining liquid was found to be about a 3:1 mixture, with the dibromophosphoranimine being the major product. The ^{31}P NMR signals (Table 2) of the dibromo derivatives **20**−**23** are generally shifted upfield by ca. 20 ppm compared to the analogous mixed halo derivatives **16**−**19**. The reasons for the predominance of the dibromophosphoranimines in the product mixtures are uncertain. Clearly, however, halogen exchange at phosphorus is occurring during the reaction. The equilibrium product distribution may simply reflect the greater volatility and ease of removal of Me_3SiCl versus Me_3SiBr.



(7)

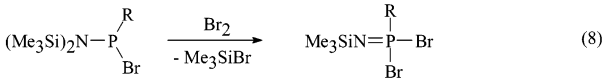
1: R = *n*-Pr **16**: R = *n*-Pr **20**: R = *n*-Pr

2: R = *n*-Bu **17**: R = *n*-Bu **21**: R = *n*-Bu

3: R = *i*-Pr **18**: R = *i*-Pr **22**: R = *i*-Pr

4: R = *t*-Bu **19**: R = *t*-Bu **23**: R = *t*-Bu

On the other hand, direct bromination (eq 8) of the P−Br phosphines **5**−**7** readily afforded the pure dibromophosphoranimines **20**−**23** in high yield. These products were extremely moisture sensitive, but they were thermally stable to distillation at moderate temperatures (ca. 50 °C) under vacuum. They were fully characterized by NMR (^{1}H, ^{13}C, and ^{31}P) spectroscopy and, for **21** and **22**, elemental analysis. The failure of the *n*-propyl compound **20** to give a satisfactory elemental analysis is due the presence of small amounts (ca. 10%) of the dialkylphosphine in the starting material rather than any problem with the bromination reaction itself.



(8)

5: R = *n*-Pr **20**: R = *n*-Pr

6: R = *n*-Bu **21**: R = *n*-Bu

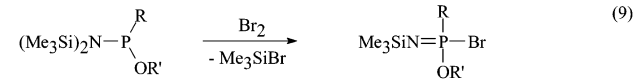
7: R = *i*-Pr **22**: R = *i*-Pr

The NMR spectra of these dibromophosphoranimines were easily assigned on the basis of the proposed structures. In addition to the integrated peak intensities in the ^{1}H NMR spectra and the dramatic upfield shifts in the ^{31}P NMR spectra, a very clear indication of oxidation at phosphorus is the observation of the characteristically large one-bond ($J_{PC} \sim 100$ Hz) P−C coupling constants in the ^{13}C NMR

(13) Wang, B.; Rivard, E.; Manners, I. *Inorg. Chem.* **2002**, *41*, 1690.
(14) Gololobov, Y. G.; Gusaà, N. I.; Randina, L. V. *Zh. Obshch. Khim.* **1982**, *52*, 1260.

spectra.[7] In contrast to the starting phosphine **7**, the *i*-propyl Me groups in the phosphoranimine **22** are magnetically equivalent because of the loss of the asymmetric arrangement at phosphorus. They appear as a doubled doublet (J_{HH} = 7.0 Hz, J_{PH} = 30.8 Hz) and a simple doublet (J_{PC} = 4.5 Hz) in the ^{1}H and ^{13}C NMR spectra, respectively.

Bromination of the *P*-trifluoroethoxy- (**8**−**11**) and the *P*-phenoxyphosphines (**12**−**14**) also occurred smoothly at 0 °C (eq 9). The desired *N*-silyl-*P*-bromophosphoranimines, that is, the *P*-trifluoroethoxy (**24**−**27**) and the *P*-phenoxy derivatives (**28**−**30**), were obtained in high yields as colorless, moisture-sensitive, but thermally stable, distillable liquids. They all gave satisfactory elemental analyses and NMR spectra in full accord with the proposed structures. Notably, the ^{31}P NMR signals (Table 2) are shifted downfield by 30−40 ppm relative to the corresponding dibromo analogues described previously. Such shifts are consistent with the presence of an electron withdrawing OR′ substituent on phosphorus. As with their phosphine precursors and the analogous dibromophosphoranimines, there is again a steady downfield trend in the ^{31}P NMR chemical shifts as the steric bulk of the alkyl substituent increases. The asymmetric structural arrangement at phosphorus in **24**−**30** is reflected in the observation of nonequivalent C−Me groups in the *i*-propyl derivatives **26** and **30**. For example, compound **30** exhibits two clear sets of doubled doublets in the ^{1}H NMR spectrum, centered at δ 1.28 (J_{HH} = 6.9, J_{PH} = 2.2) and δ 1.36 (J_{HH} = 7.0, J_{PH} = 3.0).

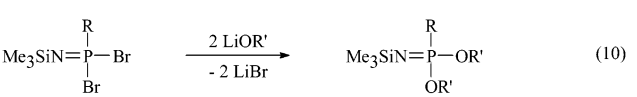


(9)

8: R = *n*-Pr, R' = CH_2CF_3
9: R = *n*-Bu, R' = CH_2CF_3
10: R = *i*-Pr, R' = CH_2CF_3
11: R = *t*-Bu, R' = CH_2CF_3
12: R = *n*-Pr, R' = Ph
13: R = *n*-Bu, R' = Ph
14: R = *i*-Pr, R' = Ph

24: R = *n*-Pr, R' = CH_2CF_3
25: R = *n*-Bu, R' = CH_2CF_3
26: R = *i*-Pr, R' = CH_2CF_3
27: R = *t*-Bu, R' = CH_2CF_3
28: R = *n*-Pr, R' = Ph
29: R = *n*-Bu, R' = Ph
30: R = *i*-Pr, R' = Ph

In addition to their potential as precursors to new cyclic and/or linear phosphazenes of general formula [R(Br)P=N]$_n$,[11] the *N*-silyl-*P*,*P*-dibromophosphoranimines **20**−**22** were found to be useful for further derivative chemistry. Specifically, treatment with 2 equiv of either lithium phenoxide or lithium trifluoroethoxide (eq 10) easily converted them to the disubstituted derivatives **31**−**36**. These new phosphazeneprecursors were obtained in high yields as thermally stable, distillable liquids that were readily characterized by multinuclear NMR spectroscopy and elemental analysis. Their ^{31}P NMR chemical shifts are summarized in Table 2.



(10)

20: R = *n*-Pr
21: R = *n*-Bu
22: R = *i*-Pr

31: R = *n*-Pr, R' = Ph
32: R = *n*-Bu, R' = Ph
33: R = *i*-Pr, R' = Ph
34: R = *n*-Pr, R' = CH_2CF_3
35: R = *n*-Bu, R' = CH_2CF_3
36: R = *i*-Pr, R' = CH_2CF_3

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without further purification: $(Me_3Si)_2NH$, PBr_3, PCl_3, *n*-PrMgCl (2.0 M in ether), *n*-BuMgCl (2.0 M in ether), *i*-PrMgCl (2.0 M in ether), *t*-BuMgCl (2.0 in ether), *n*-BuLi (2.5 in hexane), Br_2, CF_3CH_2OH, and PhOH. Solvents such as diethyl ether, benzene, and hexane were freshly distilled under nitrogen from CaH_2 before use. Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone. Proton, ^{13}C-{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Varian XL-300 spectrometer. Proton and ^{13}C{^{1}H} NMR spectra of selected compounds were recorded on a Varian INOVA-400 spectrometer. Chemical shifts (δ) are reported in ppm relative to Me_4Si (^{1}H and ^{13}C NMR) or H_3PO_4 (^{31}P NMR), and coupling constants (*J* values) are in hertz. Elemental analysis was performed by E&R Microanalytical Laboratory, Inc., Parsippany, NJ.

Preparation of *P*-Bromo(silylamino)phosphines, $(Me_3Si)_2NP(Br)R$. 5: R= *n*-Pr. In a typical preparation, a 500 mL three-neck flask, equipped with a N_2 inlet, a 125 mL addition funnel, a magnetic stir bar, and a rubber septum, was charged with $(Me_3Si)_2NH$ (20.9 mL, 0.10 mol) and ether (100 mL). The solution was cooled to 0 °C, and *n*-BuLi (40 mL, 2.5 M in hexane, 0.10 mol) was added to the addition funnel via syringe. The *n*-BuLi was then slowly added to the cooled solution, and the addition funnel was washed with ether (30 mL). The ice bath was removed, and the mixture was allowed to warm to room temperature and was stirred for 1 h. The mixture was then cooled to −78 °C, and PBr_3 (9.4 mL, 0.100 mole) was added via syringe to the addition funnel and then slowly added to the cooled reaction mixture. Dry ether (30 mL) was again used to wash the addition funnel. The cold bath was removed, and the mixture was allowed to warm to room temperature while stirring for 1.5 h. The mixture was then cooled to 0 °C, and *n*-PrMgCl (50 mL, 2.0 M in ether, 0.10 mol) was added slowly via the addition funnel. The mixture was allowed to warm to room temperature and then stirred overnight. Most of the ether was removed under reduced pressure, leaving a thick slurry that was washed three times with hexane (200 mL total) to help precipitate the salts. The supernatant was decanted into a N_2-purged flask, and the solvent was removed under reduced pressure, leaving an oily residue. Fractional distillation through a 10-cm column gave **5** as a colorless liquid. Yield: 85%. Bp: 80−83 °C (0.8 mmHg). ^{1}H NMR: δ 0.56 (s, Me_3Si), 1.28 (t, CH_2CH_3, J_{HH} = 7.3), 1.68−1.82 (m, CH_2CH_3), 2.48−2.60 (m, PCH_2). ^{13}C NMR: δ 4.0 (d, Me_3Si, J_{PC} = 8.7), 15.2 (d, CH_2CH_3, J_{PC} = 14.5), 18.6 (d, CH_2CH_3, J_{PC} = 25.7), 41.5 (d, PCH_2, J_{PC} = 43.9). ^{31}P NMR: δ 168.4. A satisfactory elemental analysis was not obtained because of the presence of small amounts of the di(*n*-propyl)phosphine.

6: R = *n*-Bu. The same procedure, using *n*-BuMgCl, gave **6** as a colorless liquid. Yield: 71%. Bp: 85 °C (0.3 mmHg). ^{1}H NMR: δ 0.55 (s, Me_3Si), 1.16 (t, CH_2CH_3, J_{HH} = 6.9), 1.64−1.74 (m, CH_2CH_3), 1.64−1.74 (m, $CH_2CH_2CH_3$), 2.49−2.60 (m, PCH_2). ^{13}C NMR: δ 4.0 (d, Me_3Si, J_{PC} = 8.7), 13.8 (s, CH_2CH_3), 27.2 (d, CH_2CH_3, J_{PC} = 24.4), 23.6 (d, $CH_2CH_2CH_3$, J_{PC} = 14.3), 39.0 (d, PCH_2, J_{PC} = 43.8). ^{31}P NMR: δ 169.3. A satisfactory elemental analysis was not obtained because of the presence of small amounts of unidentified impurities, possibly resulting from hydrolysis.

7: R = *i*-Pr. The same procedure, using *i*-PrMgCl, gave **7** as a colorless liquid. Yield: 82%. Bp: 85 °C (0.9 mmHg). ^{1}H NMR:

δ 0.32 (s, Me_3Si), 1.04 (dd, CHCH_3, J_{HH} = 7.3, J_{PH} = 16.2), 1.11 (dd, CHCH_3, J_{HH} = 7.0, J_{PH} = 20.7), 2.71 (ds, PCH, J_{HH} = 7.2, J_{PH} = 1.3). ^{13}C NMR: δ 4.0 (d, Me_3Si, J_{PC} = 7.4), 17.8 (d, CHCH_3, J_{PC} = 22.6), 18.0 (d, CHCH$_3$, J_{PC} = 33.4), 34.3 (d, PCH, J_{PC} = 40.7). ^{31}P NMR: δ 171.6. A satisfactory elemental analysis was not obtained because of the presence of small amounts of unidentified impurities, possibly resulting from hydrolysis.

Preparation of *P*-Trifluoroethoxy(silylamino)phosphines, $(Me_3Si)_2NP(OCH_2CF_3)$R. 8: R = *n*-Pr. In a typical preparation, a 100 mL three-neck flask, equipped with a N_2 inlet, a 25 mL addition funnel, a rubber septum, and a magnetic stir bar, was charged with CF_3CH_2OH (1.8 mL, 0.025 mol) and ether (60 mL). The solution was cooled to 0 °C, and *n*-BuLi (2.5M in hexane, 10 mL, 0.025 mol) was added slowly from the addition funnel. The mixture was warmed to room temperature and stirred for 1 h. A separate 250 mL three-neck flask, equipped as described, was charged with the *P*-bromophosphine **5** (0.025 mol) and ether (100 mL). This solution was cooled to 0 °C, and the $LiOCH_2CF_3$ solution was slowly transferred to the stirred solution of **5** through a cannula via N_2 pressure. After the mixture was warmed to room temperature and stirred overnight, most of the ether was removed under reduced pressure leaving a thick slurry. The slurry was washed three times with hexane (100 mL) to help precipitate the salts. The supernatant was decanted into a N_2-purged flask, and the solvent was removed under reduced pressure, leaving an oily residue. Fractional distillation through a 10-cm column gave **8** as a colorless liquid. Yield: 71%. Bp: 85 °C (0.3 mmHg). ^{1}H NMR: δ 0.24 (s, Me_3Si), 1.02 (t, CH_2CH_3, J_{HH} = 7.2), 1.37−1.54 (m, CH_2CH_3), 1.55−1.96 (m, PCH_2), 3.96 (q, OCH_2, J_{HH} = J_{PH} = 8.8). ^{13}C NMR: δ 4.0 (d, Me_3Si, J_{PC} = 8.7), 15.2 (d, CH_2CH_3, J_{PC} = 14.5), 18.6 (d, CH_2CH_3, J_{PC} = 25.7), 36.2 (d, PCH_2, J_{PC} = 19.5), 66.0 (dq, OCH_2, J_{PC} = 24.0, J_{FC} = 35.3), 124.1 (dq, CF_3, J_{PC} = 11.4, J_{FC} = 278.4). ^{31}P NMR: δ 166.0. Anal. Calcd for $C_{11}H_{27}F_3NOPSi_2$: C, 39.62; H, 8.16. Found: C, 39.69; H, 8.15.

9: R = *n*-Bu. The same procedure using *P*-bromophosphine **6** gave compound **9** as a colorless liquid. Yield: 71%. Bp: 70−75 °C (0.8 mmHg). ^{1}H NMR: δ 0.24 (d, Me_3Si, J_{PH} = 1.1), 0.92 (t, CH_2CH_3, J_{HH} = 6.9), 1.34−1.46 (m, CH_2CH_3), 1.34−1.46 (m, $CH_2CH_2CH_3$), 1.55−1.97 (m, PCH_2), 3.96 (q, OCH_2, J_{HH} = J_{PH} = 8.7). ^{13}C NMR: δ 4.2 (d, Me_3Si, J_{PC} = 7.5), 13.8 (s, CH_2CH_3), 24.0 (d, CH_2CH_3, J_{PC} = 13.9), 26.0 (d, $CH_2CH_2CH_3$, J_{PC} = 20.7), 36.2 (d, PCH_2, J_{PC} = 19.5), 66.0 (dq, OCH_2, J_{PC} = 24.0, J_{FC} = 35.3), 124.1 (dq, CF_3, J_{PC} = 11.4, J_{FC} = 278.4). ^{31}P NMR: δ 166.4. Anal. Calcd for $C_{12}H_{29}F_3NOPSi_2$: C, 41.48; H, 8.41. Found: C, 41.71; H, 8.26. The same procedure using *P*-bromophosphine **7** and THF as the solvent instead of ether gave compound **10** as a colorless liquid.

10: R = *i*-Pr. Yield: 82%. Bp: 55−70 °C (1.3 mmHg). ^{1}H NMR: δ 0.25 (s, Me_3Si), 0.97 (dd, CHCH_3, J_{HH} = 7.3, J_{PH} = 29.8), 1.02 (dd, CHCH_3, J_{HH} = 7.2, J_{PH} = 29.6), 2.71 (ds, PCH, J_{HH} = J_{PH} = 7.2), 3.96 (q, OCH_2, J_{HH} = J_{PH} = 8.7). ^{13}C NMR: δ 4.2 (d, Me_3Si, J_{PC} = 6.4), 16.8 (d, CHCH_3, J_{PC} = 24.4), 17.4 (d, CHCH$_3$, J_{PC} = 23.9), 31.6 (d, PCH, J_{PC} = 15.1), 66.0 (dq, OCH_2, J_{PC} = 23.4, J_{FC} = 35.0), 124.0 (dq, CF_3, J_{PC} = 11.4, J_{FC} = 278.4). ^{31}P NMR: δ 154.0. Anal. Calcd for $C_{11}H_{27}F_3NOPSi_2$: C, 39.62; H, 8.16. Found: C, 39.74; H, 7.99.

11: R = *t*-Bu. The same procedure and various modifications thereof, starting from either $(Me_3Si)_2NP(t\text{-Bu})Cl$[10] or $(Me_3Si)_2NPCl_2$,[6] gave low yields of highly impure samples of compound **11**. Consequently, it was characterized only by NMR spectral data. ^{1}H NMR: δ 0.27 (s, Me_3Si), 0.29 (s, Me_3Si), 1.02 (d, CCH_3, J_{PH} = 29.6), 3.95−4.07 (m, OCH_2). ^{13}C NMR: δ 4.3 (d, Me_3Si, J_{PC} = 14.6), 5.5 (d, Me_3Si, J_{PC} = 6.4), 26.1 (d, CCH_3, J_{PC} = 18.7), 35.6 (d, PC, J_{PC} = 25.8), 66.0−67.9 (m, OCH_2), CF_3 (not observed). ^{31}P NMR: δ 175.7.

Preparation of *P*-Phenoxy(silylamino)phosphines ($Me_3Si)_2NP(OPh)$R. The same apparatus and procedure as described for the preparation of **5** were employed except that phenol (2.3 g, 0.025 mole) was used instead of CF_3CH_2OH. Compounds **12**−**14** were obtained as colorless liquids with the following characterization data.

12: R = *n*-Pr. Yield: 78%. Bp: 90−115 °C (0.8 mmHg). ^{1}H NMR: δ 0.31 (d, Me_3Si, J_{PH} = 1.4), 1.32 (t, CH_2CH_3, J_{HH} = 7.2), 1.55−1.67 (m, CH_2CH_3), 1.75−2.16 (m, PCH_2), 7.03−7.36 (m, OPh). ^{13}C NMR: δ 4.4 (d, Me_3Si, J_{PC} = 7.4), 15.8 (d, CH_2CH_3, J_{PC} = 14.4), 17.6 (d, CH_2CH_3, J_{PC} = 22.4), 39.0 (d, PCH_2, J_{PC} = 20.9), 119.4 (d, *o*-Ph, J_{PC} = 10.3), 122.0 (s, Ph), 129.3 (s, Ph), 157.2 (d, *ipso*-Ph, J_{PC} = 7.8). ^{31}P NMR: δ 154.0. Anal. Calcd for $C_{15}H_{30}NOPSi_2$: C, 55.00; H, 9.23. Found: C, 54.74; H, 9.46.

13: R = *n*-Bu. Yield: 70%. Bp: 100−120 °C (0.9 mmHg). ^{1}H NMR: δ 0.26 (d, Me_3Si, J_{PH} = 1.2), 0.96 (t, CH_2CH_3, J_{HH} = 7.3), 1.34−2.53 (m, CH_2CH_3, $CH_2CH_2CH_3$), 1.68−2.12 (m, PCH_2), 7.00−7.27 (m, OPh). ^{13}C NMR: δ 4.4 (d, Me_3Si, J_{PC} = 7.6), 14.3 (s, CH_2CH_3), 24.1 (d, CH_2CH_3, J_{PC} = 13.9), 26.2 (d, $CH_2CH_2CH_3$, J_{PC} = 21.5), 36.4 (d, PCH_2, J_{PC} = 20.6), 119.5 (d, *o*-Ph, J_{PC} = 10.1), 122.0 (s, Ph), 129.4 (s, Ph), 157.2 (s, *ipso*-Ph). ^{31}P NMR: δ 154.3. Anal. Calcd for $C_{16}H_{32}NOPSi_2$: C, 56.26; H, 9.44. Found: C, 56.47; H, 9.43.

14: R = *i*-Pr. As in the preparation of **10**, THF was used as the solvent instead of ether. Yield: 70%. Bp: 110−113 °C (0.9 mmHg). ^{1}H NMR: δ 0.26 (s, Me_3Si), 0.97 (dd, CHCH_3, J_{HH} = 7.2, J_{PH} = 17.2), 1.02 (dd, CHCH_3, J_{HH} = 7.0, J_{PH} = 17.1), 2.28 (ds, PCH, J_{HH} = J_{PH} = 7.0), 7.00−7.27 (m, OPh). ^{13}C NMR: δ 4.5 (d, Me_3Si, J_{PC} = 7.2), 17.0 (d, CHCH_3, J_{PC} = 25.7), 17.1 (d, CHCH$_3$, J_{PC} = 24.6), 31.8 (d, PCH, J_{PC} = 16.6), 119.5 (d, *o*-Ph, J_{PC} = 10.0), 122.0 (s, Ph), 129.3 (s, Ph), 151.0 (s, *ipso*-Ph). ^{31}P NMR: δ 159.5. Anal. Calcd for $C_{15}H_{30}NOPSi_2$: C, 55.00; H, 9.23. Found: C, 55.01; H, 9.33.

Preparation of *N*-Silyl-*P,P*-dibromophosphoranimines $Me_3SiN{=}PRBr_2$R. 20: R = *n*-Pr. In a typical preparation, a 250 mL three-neck flask, equipped with a N_2 inlet, a 60 mL addition funnel, a magnetic stir bar, and a rubber septum, was charged with the *P*-bromophosphine **5** (0.050 mol) and benzene (70 mL). The solution was cooled to 0 °C. A solution of bromine (2.8 mL, 0.055 mole) in benzene (10 mL) was added to the addition funnel via syringe. The bromine solution was then added slowly to the phosphine solution with constant stirring. The addition was stopped when a slight red-brown color persisted in the reaction mixture. The mixture was allowed to warm to room temperature and was stirred for 1 h. Solvent and the Me_3SiBr byproduct were removed under reduced pressure leaving a red-brown viscous liquid. Fractional distillation through a 10-cm column gave **20** as a colorless, very moisture-sensitive liquid. A satisfactory elemental analysis was not obtained because of the presence of small amounts of unidentified impurities. Yield: 80%. Bp: 30−32 °C (0.03 mmHg). ^{1}H NMR: δ 0.36 (s, Me_3Si), 1.32 (t, CH_2CH_3, J_{HH} = 7.2), 1.98−2.17 (m, CH_2CH_3), 2.86−2.96 (m, PCH_2). ^{13}C NMR: δ 1.5 (d, Me_3Si, J_{PC} = 8.1), 13.9 (d, CH_2CH_3, J_{PC} = 25.0), 18.0 (d, CH_2CH_3, J_{PC} = 8.0), 52.8 (d, PCH_2, J_{PC} = 103.0). ^{31}P NMR: δ −40.5. The same procedure using *P*-bromophosphine **6** gave compound **21** as a colorless liquid. Yield: 72%. Bp: 55−60 °C (0.03 mmHg). ^{1}H NMR: δ 0.36 (s, Me_3Si), 1.20 (t, CH_2CH_3, J_{HH} = 7.4), 1.72 (sextet, CH_2CH_3, J_{HH} = 7.4), 1.93−2.10 (m, $CH_2CH_2CH_3$), 2.86−2.97 (m, PCH_2). ^{13}C NMR: δ 1.4 (d, Me_3Si, J_{PC} = 8.2), 13.5 (s, CH_2CH_3), 22.3 (d, CH_2CH_3, J_{PC} = 24.8), 26.0 (d, $CH_2CH_2CH_3$, J_{PC} = 8.3), 50.5 (d, PCH_2, J_{PC} = 103.1). ^{31}P NMR: δ −39.2. Anal.

Calcd for $C_7H_{18}Br_2NPSi$: C, 25.09; H, 5.41. Found: C, 26.04; H, 5.02. The same procedure using *P*-bromophosphine **7** gave compound **22** as a colorless liquid. Yield: 90%. Bp: 35−40 °C (0.03 mmHg). ^{1}H NMR: δ 0.12 (s, Me_3Si), 1.31 (dd, CHCH_3, J_{HH} = 7.0, J_{PH} = 30.8), 2.58 (ds, PCH, J_{HH} = 6.9, J_{PH} = 10.4). ^{13}C NMR: δ 1.4 (d, Me_3Si, J_{PC} = 7.0), 16.9 (d, CHCH_3, J_{PC} = 4.5), 47.8 (d, PCH, J_{PC} = 99.2). ^{31}P NMR: δ −18.7. Anal. Calcd for $C_6H_{16}Br_2NPSi$: C, 22.45; H, 5.02. Found: C, 22.76; H, 5.10.

Preparation of *N*-Silyl-*P*-bromo-*P*-trifluoroethoxyphosphoranimines, $Me_3SiN{=}P(Br)(OCH_2CF_3)R$. Using the same apparatus and procedure as described for the preparation of **20**, the *P*-trifluoroethoxyphosphines **8**−**11** were treated with Br_2. Compounds **24**−**27** were obtained as colorless liquids with the following characterization data.

24: R = *n*-Pr. Yield: 80%. Bp: 30−32 °C (0.03 mmHg). ^{1}H NMR: δ 0.08 (s, Me_3Si), 1.06 (t, CH_2CH_3, J_{HH} = 7.3), 1.73 (sextet, CH_2CH_3, 8.0), 2.12−2.26 (m, PCH_2), 4.11−4.43 (m, OCH_2). ^{13}C NMR: δ 2.4 (d, Me_3Si, J_{PC} = 5.2), 14.6 (d, CH_2CH_3, J_{PC} = 21.9), 16.8 (d, CH_2CH_3, J_{PC} = 6.0), 41.5 (d, PCH_2, J_{PC} = 122.7), 60.9 (dq, OCH_2, J_{PC} = 7.5, J_{FC} = 37.6), 124.1 (dq, CF_3, J_{PC} = 12.6, J_{FC} = 277.3). ^{31}P NMR: δ 4.4. Anal. Calcd for $C_8H_{18}BrF_3NOPSi$: C, 28.25; H, 5.33. Found: C, 28.48; H, 5.51.

25: R = *n*-Bu. Yield: 86%. Bp: 35−40 °C (0.03 mmHg). ^{1}H NMR: δ 0.09 (d, Me_3Si, J_{PH} = 1.1), 0.94 (t, CH_2CH_3, J_{HH} = 7.3), 1.45 (sextet, CH_2CH_3, J_{HH} = 7.5), 1.67 (q, $CH_2CH_2CH_3$, J_{HH} = 8.0), 2.15−2.27 (m, PCH_2), 4.14−4.43 (m, OCH_2). ^{13}C NMR: δ 2.2 (d, Me_3Si, J_{PC} = 5.1), 13.5 (s, CH_2CH_3), 22.9 (d, CH_2CH_3, J_{PC} = 21.7), 24.8 (d, $CH_2CH_2CH_3$, J_{PC} = 6.0), 39.1 (d, PCH_2, J_{PC} = 122.9), 60.7 (dq, OCH_2, J_{PC} = 7.7, J_{FC} = 37.7), 124.1 (dq, CF_3, J_{PC} = 12.6, J_{FC} = 277.6). ^{31}P NMR: δ 5.0. Anal. Calcd for $C_9H_{20}F_3NOPSi$: C, 30.52; H, 5.69. Found: C, 30.34; H, 5.43.

26: R = *i*-Pr. Yield: 88%. Bp: 32−41 °C (1.0 mmHg). ^{1}H NMR: δ 0.09 (s, Me_3Si), 1.24 (dd, CHCH_3, J_{HH} = 7.0, J_{PH} = 24.9), 1.25 (dd, CHCH_3, J_{HH} = 7.2, J_{PH} = 25.7), 2.26 (ds, PCH, J_{HH} = J_{PH} = 7.2), 4.11−4.44 (m, OCH_2). ^{13}C NMR: δ 2.2 (d, Me_3Si, J_{PC} = 4.8), 16.8 (d, CHCH_3, J_{PC} = 4.2), 17.4 (d, $CH$$CH_3$, J_{PC} = 3.6), 37.6 (d, PCH, J_{PC} = 121.9), 60.7 (dq, OCH_2, J_{PC} = 8.0, J_{FC} = 37.5), 123.0 (dq, CF_3, J_{PC} = 12.3, J_{FC} = 277.3). ^{31}P NMR: δ 15.9. Anal. Calcd for $C_8H_{18}F_3NOPSi$: C, 28.25; H, 5.33. Found: C, 28.19; H, 5.32.

27: R = *t*-Bu. ^{1}H NMR: δ 0.07 (s, Me_3Si), 1.24 (d, CCH_3, J_{PH} = 22.6), 4.07−4.42 (m, OCH_2). ^{13}C NMR: δ 2.2 (d, Me_3Si, J_{PC} = 5.0), 41.1 (d, CCH_3, J_{PC} = 117.9), 60.7 (dq, OCH_2, J_{PC} = 8.0, J_{FC} = 37.5), 123.0 (dq, CF_3, J_{PC} = 12.3, J_{FC} = 277.3). ^{31}P NMR: δ 22.0. Because **27** was prepared from the highly impure phosphine **11**, analytical data were not obtained.

Preparation of *N*-Silyl-*P*-bromo-*P*-phenoxyphosphoranimines, $Me_3SiN{=}P(Br)(OPh)R$. Using the same apparatus and procedure as described above for the preparation of **20**, the *P*-phenoxyphosphines **12**−**14** were treated with Br_2. Compounds **28**−**30** were obtained as colorless liquids with the following characterization data.

28: R = *n*-Pr. Yield: 73%. Bp: 85−88 °C (0.03 mmHg). ^{1}H NMR: δ 0.10 (d, Me_3Si, J_{PH} = 1.4), 1.11 (dt, CH_2CH_3, J_{HH} = 7.2, J_{PH} = 2.2), 1.83 (ds, CH_2CH_3, J_{HH} = J_{PH} = 7.7), 2.23−2.40 (m, PCH_2), 7.18−7.36 (m, OPh). ^{13}C NMR: δ 2.1 (d, Me_3Si, J_{PC} = 5.3), 14.6 (d, CH_2CH_3, J_{PC} = 22.5), 16.8 (d, CH_2CH_3, J_{PC} = 5.9), 41.5 (d, PCH_2, J_{PC} = 128.0), 121.7 (d, *o*-Ph, J_{PC} = 4.9), 125.4 (s, Ph), 129.3 (s, Ph), 150.1 (d, *ipso*-Ph, J_{PC} = 12.7). ^{31}P NMR: δ −0.4. Anal. Calcd for $C_{12}H_{21}BrNOPSi$: C, 43.12 H, 6.33. Found: C, 43.17; H, 6.65.

29: R = *n*-Bu. Yield: 61%. Bp: 103−110 °C (0.02 mmHg). ^{1}H NMR: δ 0.10 (d, Me_3Si, J_{PH} = 1.2), 0.98 (t, CH_2CH_3, J_{HH} = 7.3), 1.49 (sextet, CH_2CH_3, J_{HH} = J_{PH} = 7.3), 1.78 (dq, $CH_2CH_2CH_3$, J_{HH} = 7.3, J_{PH} = 7.7), 2.26−2.39 (m, PCH_2), 7.18−7.35 (m, OPh). ^{13}C NMR: δ 2.1 (d, Me_3Si, J_{PC} = 5.5), 13.7 (s, CH_2CH_3), 23.0 (d, CH_2CH_3, J_{PC} = 21.7), 25.1 (d, $CH_2CH_2CH_3$, J_{PC} = 5.8), 39.3 (d, PCH_2, J_{PC} = 128.4), 121.7 (d, *o*-Ph, J_{PC} = 5.0), 125.3 (s, Ph), 129.3 (s, Ph), 150.2 (d, *ipso*-Ph, J_{PC} = 12.0). ^{31}P NMR: δ 0.1. Anal. Calcd for $C_{13}H_{23}BrNOPSi$: C, 44.83; H, 6.66. Found: C, 44.84; H, 6.66.

30: R = *i*-Pr. Yield: 70%. Bp: 110−113 °C (0.9 mmHg). ^{1}H NMR: δ 0.11 (s, Me_3Si), 1.28 (dd, CHCH_3, J_{HH} = 6.9, J_{PH} = 2.2), 1.36 (dd, CHCH_3, J_{HH} = 7.0, J_{PH} = 3.0), 2.38 (ds, PCH, J_{HH} = 7.0, J_{PH} = 15.9), 7.22−7.36 (m, OPh). ^{13}C NMR: δ 2.1 (d, Me_3Si, J_{PC} = 5.2), 16.2 (d, CHCH_3, J_{PC} = 4.5), 16.8 (d, $CH$$CH_3$, J_{PC} = 3.9), 37.6 (d, PCH, J_{PC} = 127.3), 121.6 (d, *o*-Ph, J_{PC} = 5.2), 125.2 (s, Ph), 129.3 (s, Ph), 150.3 (d, *ipso*-Ph, J_{PC} = 13.3). ^{31}P NMR: δ 11.4. Anal. Calcd for $C_{12}H_{21}BrNOPSi$: C, 43.12; H, 6.33. Found: C, 43.20; H, 6.54.

Preparation of *N*-Silyl-*P,P*-diphenoxyphosphoranimines, $Me_3SiN{=}P(OPh)_2R$. 31: R = *n*-Pr. In a typical preparation, a 250 mL, three-neck flask, equipped with a N_2 inlet, a 25 mL addition funnel, a magnetic stir bar, and a rubber septum, was charged with phenol (4.7 g, 0.050 mol) and ether (100 mL). The solution was cooled to 0 °C, and *n*-BuLi (20 mL, 2.5M in hexane, 0.050 mol) was added slowly via the addition funnel. The mixture was allowed to warm to room temperature and was stirred for 1 h. A separate 250 mL, three-neck flask, equipped in a similar fashion, was charged with the dibromophosphoranimines **20** (0.025 mole) and ether (100 mL). The lithium phenoxide solution was transferred to the solution containing **20** at 0 °C through a cannula via N_2 pressure. After warming to room temperature and stirring overnight, most of the ether was removed under reduced pressure leaving a thick slurry. The slurry was washed three times with hexane (100 mL) to help precipitate the salts. The supernatant was decanted into a N_2-purged flask, and the solvent was removed under reduced pressure leaving an oily residue. Fractional distillation through a 10-cm column gave **31** as a colorless liquid. Yield: 12.2 g (70%). Bp: 110−125 °C (0.03 mmHg). ^{1}H NMR: δ 0.05 (s, Me_3Si), 1.32 (dt, CH_2CH_3, J_{HH} = 7.2, J_{PH} = 1.7), 1.95−2.12 (m, CH_2CH_3), 2.19−2.30 (m, PCH_2), 7.39−7.57 (m, OPh). ^{13}C NMR: δ 3.2 (d, Me_3Si, J_{PC} = 3.2), 15.6 (d, CH_2CH_3, J_{PC} = 19.3), 17.0 (d, CH_2CH_3, J_{PC} = 5.1), 31.4 (d, PCH_2, J_{PC} = 144.3), 121.6 (d, *o*-Ph, J_{PC} = 4.1), 124.7 (s, Ph), 129.7 (s, Ph), 151.6 (d, *ipso*-Ph, J_{PC} = 9.3). ^{31}P NMR: δ 9.9. Anal. Calcd for $C_{18}H_{26}NO_2PSi$: C, 62.22; H, 7.54. Found: C, 62.37; H, 7.40.

32: R = *n*-Bu. The same procedure using dibromophosphine **21** gave compound **32** as a colorless liquid. Yield: 70%. Bp: 125−138 °C (0.03 mmHg). ^{1}H NMR: δ 0.02 (s, Me_3Si), 1.19 (t, CH_2CH_3, J_{HH} = 7.3), 1.69 (t, CH_2CH_3, J_{HH} = 7.4), 1.89−2.03 (m, $CH_2CH_2CH_3$), 2.17−2.29 (m, PCH_2), 7.36−7.55 (m, OPh). ^{13}C NMR: δ 2.8 (d, Me_3Si, J_{PC} = 3.4), 13.6 (s, CH_2CH_3), 23.6 (d, CH_2CH_3, J_{PC} = 18.5), 25.0 (d, $CH_2CH_2CH_3$, J_{PC} = 5.2), 28.6 (d, PCH_2, J_{PC} = 144.5), 121.2 (d, *o*-Ph, J_{PC} = 4.6), 124.2 (s, Ph), 129.3 (s, Ph), 151.3 (d, *ipso*-Ph, J_{PC} = 9.2). ^{31}P NMR: δ 10.5. Anal. Calcd for $C_{19}H_{28}NO_2PSi$: C, 63.13; H, 7.81. Found: C, 63.12; H, 7.73.

33: R = *i*-Pr. The same procedure using dibromophosphine **22** and THF as the solvent instead of ether gave compound **33** as a colorless liquid. Yield: 72%. Bp: 55−60 °C (0.03 mmHg). ^{1}H NMR: δ 0.24 (s, Me_3Si), 1.35 (dd, CHCH_3, J_{HH} = 7.1, J_{PH} = 20.1), 2.24 (ds, PCH, J_{HH} = 7.1, J_{PH} = 18.4), 7.11−7.31 (m, OPh). ^{13}C NMR: δ 3.1 (d, Me_3Si, J_{PC} = 4.4), 16.8 (d, CHCH_3, J_{PC} = 4.4), 28.5 (d, PCH, J_{PC} = 148.9), 121.6 (d, *o*-Ph, J_{PC} = 4.3), 124.4 (s, Ph), 129.5 (s, Ph), 151.7 (d, *ipso*-Ph, J_{PC} = 9.8). ^{31}P NMR: δ 13.0.

Anal. Calcd for $C_{18}H_{26}NO_2PSi$: C, 62.22; H, 7.54. Found: C, 62.38; H, 7.42.

Preparation of *N*-Silyl-*P,P*-bis(trifluoroethoxy)phosphoranimines, $Me_3SiN{=}P(OCH_2CF_3)_2R$. The same apparatus and procedure as described for the preparation of **31** was employed except that CF_3CH_2OH (3.6 mL, 0.050 mol) was used instead of phenol. As in the synthesis of the *P*-*i*-propyl derivative **33**, THF was used as the solvent instead of ether in the preparation of **36**. Compounds **34**−**36** were obtained as colorless liquids with the following characterization data.

34: R = *n*-Pr. Yield: 85%. Bp: 40−44 °C (1.2 mmHg). ^{1}H NMR: δ 0.06 (s, Me_3Si), 1.01 (dt, CH_2CH_3, J_{HH} = 7.3, J_{PH} = 1.6), 1.55−1.67 (m, CH_2CH_3), 1.73−1.84 (m, PCH_2), 4.13−4.32 (m, OCH_2). ^{13}C NMR: δ 3.0 (d, Me_3Si, J_{PC} = 2.7), 15.1 (d, CH_2CH_3, J_{PC} = 19.1), 16.2 (d, CH_2CH_3, J_{PC} = 5.3), 30.7 (d, PCH_2, J_{PC} = 139.6), 61.0 (dq, OCH_2, J_{PC} = 6.4, J_{FC} = 37.2), 123.3 (dq, CF_3, J_{PC} = 8.7, J_{FC} = 277.3). ^{31}P NMR: δ 21.0. Anal. Calcd for $C_{10}H_{20}F_6NO_2PSi$: C, 33.43; H, 5.61. Found: C, 33.68; H, 5.51.

35: R = *n*-Bu. Yield: 51%. Bp: 52−54 °C (1.2 mmHg). ^{1}H NMR: δ 0.05 (s, Me_3Si), 0.92 (t, CH_2CH_3, J_{HH} = 7.3), 1.39 (sextet, CH_2CH_3, J_{HH} = 7.4), 1.47−1.61 (m, $CH_2CH_2CH_3$), 1.73−1.85 (m, PCH_2), 4.10−4.35 (m, OCH_2). ^{13}C NMR: δ 3.0 (d, Me_3Si, J_{PC} = 2.9), 13.4 (s, CH_2CH_3), 23.5 (d, CH_2CH_3, J_{PC} = 18.8), 24.4 (d, $CH_2CH_2CH_3$, J_{PC} = 5.2), 28.3 (d, PCH_2, J_{PC} = 140.0), 60.9 (dq, OCH_2, J_{PC} = 6.5, J_{FC} = 37.1), 123.1 (dq, CF_3, J_{PC} = 8.2, J_{FC} = 277.5). ^{31}P NMR: δ 21.5. Anal. Calcd for $C_{11}H_{22}F_6NO_2PSi$: C, 35.39; H, 5.94. Found: C, 34.95; H, 5.77.

36: R = *i*-Pr. Yield: 50%. Bp: 40−44 °C (1.2 mmHg). ^{1}H NMR: δ 0.09 (s, Me_3Si), 1.14 (dd, $CHCH_3$, J_{HH} = 7.0, J_{PH} = 20.2), 2.00 (ds, PCH, J_{HH} = 7.2, J_{PH} = 18.9), 4.14−4.30 (m, OCH_2). ^{13}C NMR: δ 3.1 (d, Me_3Si, J_{PC} = 2.8), 15.9 (d, $CHCH_3$, J_{PC} = 4.3), 28.0 (d, PCH, J_{PC} = 144.1), 60.7 (dq, OCH_2, J_{PC} = 7.0, J_{FC} = 37.2), 123.2 (dq, CF_3, J_{PC} = 8.2, J_{FC} = 277.4). ^{31}P NMR: δ 24.5. Anal. Calcd for $C_{10}H_{20}F_6NO_2PSi$: C, 33.43; H, 5.61. Found: C, 33.10; H, 5.46.

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