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Synthesis, Structure, and Reactivity of Some Sterically Hindered (Silylamino)phosphines

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A series of new (silylamino)phosphines that contain sterically bulky silyl groups on nitrogen were prepared by deprotonation/substitution reactions of the hindered disilylamines *t*-BuR_2Si(Me_3Si)NH (**1**, R = Me; **2**, R = Ph) and (Et_3Si)$_2$NH (**3**). Sequential treatment of the *N*-lithio derivatives of **1**–**3** with PCl_3 or $PhPCl_2$ and MeLi gave the corresponding (silylamino)phosphines *t*-BuR_2Si(Me_3Si)NP(R′)Me (**5**, R = Me, R′ = Ph; **6**, R = Ph, R′ = Me) and (Et_3Si)$_2$NP(R)Me (**11**, R = Me; **12**, R = Ph) in high yields. Two of the *P*-chloro intermediates *t*-BuR_2Si(Me_3Si)-NP(Ph)Cl (**7**, R = Ph; **9**, R = Me) were also isolated and fully characterized. Hydrolysis of **7** afforded the crystalline PH-substituted aminophosphine oxide *t*-BuPh_2SiN(H)P(Ph)(=O)H (**10**). Thermal decomposition of **7** occurred with elimination of Me_3SiCl and formation of a novel P_2N_2 four-membered ring system (**36**) that contains both P(III) and P(V) centers. Reactions of the *N*-lithio derivatives of amines **1** and **2** with phosphorus trihalides afforded the thermally stable –PF_2 derivatives *t*-BuR_2Si(Me_3Si)NPF_2 (**13**, R = Me; **14**, R = Ph) and the unstable –PCl_2 analogue **17** (R = Ph). Reduction (using $LiAlH_4$) of the SiPh-substituted dihalophosphines **14** and **17** gave the unstable parent phosphine *t*-BuPh_2Si(Me_3Si)NPH_2 (**15**). The *P*-organo-substituted (silylamino)phosphines underwent oxidative bromination to afford high yields of the corresponding *N*-silyl-*P*-bromophosphoranimines *t*-BuR_2SiN=P(R′)(Me)Br (**18**, R = R′ = Me; **19**, R = Me, R′ = Ph; **20**, R = Ph, R′ = Me) and Et_3SiN=P(R)(Me)Br (**23**, R = Me; **24**, R = Ph). Subsequent treatment of these reactive PBr compounds with lithium trifluoroethoxide or phenoxide produced the corresponding PO derivatives *t*-BuR_2SiN=P(R′)(Me)OR″ (**25** and **26**, R″ = CH_2CF_3; **28**–**30**, R″ = Ph) and Et_3SiN=P(R)(Me)OR′ (**31** and **33**, R′ = CH_2CF_3; **32** and **34**, R = Ph), respectively. Many of the new compounds containing the bulky *tert*-butyl*diphenyl*silyl group, *t*-BuPh_2Si, were solids that gave crystals suitable for X-ray diffraction studies. Consequently, the crystal structures of three (silylamino)phosphines (**6**, **7**, and **14**), one (silylamino)phosphine oxide (**10**), one *N*-silylphosphoranimine (**30**), and the cyclic compound **36** were determined. Among the (silylamino)-phosphines, the P–N bond distances [**6**, N–PMe_2, 1.725(3) Å; **7**, N–P(Ph)Cl, 1.68(1) Å, **14**, N–PF_2, 1.652(4) Å] decreased significantly as the electron-withdrawing nature of the phosphorus substituents increased. The *N*-silylphosphoranimine *t*-BuPh_2SiN=PMe_2OPh (**30**), which is a model system for poly(phosphazene) precursors, had a much shorter P=N distance of 1.512(6) Å and a wide Si–N–P bond angle of 166.4(3)°. A similar P=N bond distance [1.514(7) Å] and Si–N–P angle [169.9(6)°] were observed for the exocyclic P=N—Si linkage in the ring compound **36**, while the phosphine oxide **10** had P–N and P=O distances of 1.637(4) and 1.496(3) Å, respectively, and a Si–N–P angle of 134.3(2)°.

Introduction

During the last two decades, the chemistry of compounds containing the Si—N—P linkage has been extensively developed.[1] Depending on the substituent pattern and the oxidation state or coordination number at phosphorus, such compounds are useful precursors to cyclic and polymeric poly(phosphazenes) as well as various low-coordinate phosphorus systems. The most useful synthetic entry to Si—N—P systems is the Wilburn method[2] (eqs 1—3) in which phosphorus halides are successively substituted with silyl-

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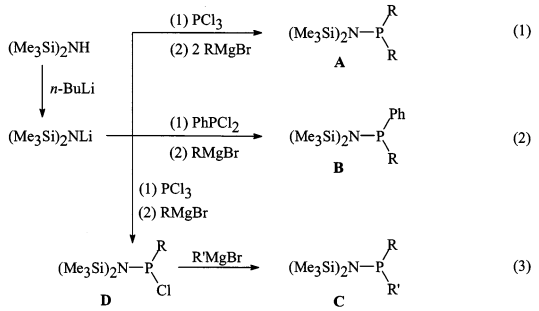
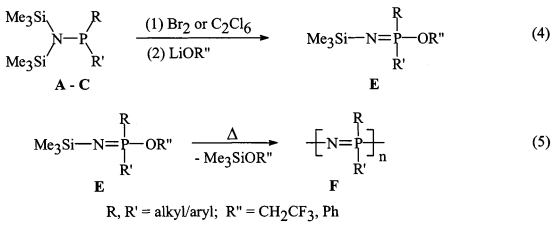


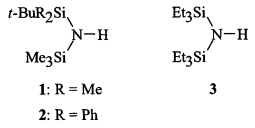
amides and organometallic reagents. This is generally a convenient, one-pot synthesis of a wide variety of both symmetrical (**A**) and unsymmetrical (**B** and **C**) diorganosubstituted (silylamino)phosphines. In cases with R groups more sterically demanding than methyl or ethyl, it is possible to isolate the monosubstituted chlorophosphines **D**.[3]

Within the realm of phosphazene chemistry, the (silylamino)phosphines **A**−**C** are routinely converted to *N*-silylphosphoranimines **E** by sequential oxidative halogenation and substitution reactions (eq 4).[4] Subsequent thermolysis of these *N*-silylphosphoranimines **E** readily affords poly(alkyl/arylphosphazenes) **F** via a condensation polymerization process (eq 5).[5] This general process complements other synthetic routes to poly(phosphazenes)[6] and significantly extends the overall scope of phosphazene chemistry.



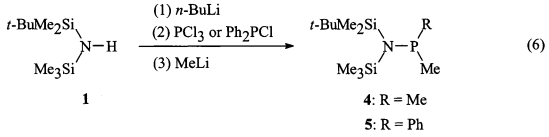
The steric and electronic effects of varying the substituents (R, R′) and the leaving groups (e.g., OR″) on phosphorus have been studied both for the polymerization process and also in the fundamental reactivity of the Si−N−P precursors.[7]

In contrast, relatively little is known about the effects of changing the nature of the silyl group on nitrogen. Toward that end, we report here on the synthesis and reactivity of a variety of new (silylamino)phosphines derived from the more sterically demanding silylamines **1**−**3**. During the course of this study, a number of crystalline Si−N−P derivatives were obtained and studied by X-ray diffraction as well, thus providing valuable structural and stereochemical information about these important classes of phosphazene precursors.



Results and Discussion

Synthesis of (Silylamino)phosphines. In the initial phase of this study, the general Wilburn method (eqs 1−3) was used to prepare a series of new (silylamino)phosphines derived from the sterically crowded disilylamines **1**−**3**. One such compound, the dimethylphosphine **4**, containing the *tert*-butyldimethylsilyl group, had been previously prepared by this method.[8] We found, however, that the reaction occurs faster and affords higher yields upon changing the solvent from Et_2O to THF and using MeLi instead of MeMgBr in the final step of the process (eq 6). In the case of the *P*-phenyl analogue **5**, these reaction conditions are, in fact, required to replace the PCl group.



Phosphines **4** and **5** were obtained in good yields (ca. 75%) as colorless, thermally stable, distillable liquids that were fully characterized by multinuclear (^{1}H, ^{13}C, and ^{31}P) NMR spectroscopy and elemental analysis. The asymmetric center at phosphorus in **5** (^{31}P NMR δ 39.9) is evident from the observation of two sets of doublets for the diastereotopic SiMe groups in both the ^{1}H [δ 0.26 (d, J_{PH} = 1.8 Hz), 0.44 (d, J_{PH} = 1.8 Hz)] and ^{13}C [δ ∠0.14 (d, J_{PC} = 5.4 Hz), 0.08 (d, J_{PC} = 6.1 Hz)] NMR spectra.

A similar strategy, starting with *tert*-butyl*diphenyl*silyl-(trimethylsilyl)amine (**2**), was employed in attempts to prepare the analogous (silylamino)phosphines **6** and **8** (eqs 7−9). The dimethylphosphine **6** was obtained in ca. 50% yield as a very high boiling point liquid that solidified on standing. Recrystallization from hexane/CH_2Cl_2 afforded X-ray-quality crystals (see below). Synthesis of the *P*-phenyl analogue **8**, however, was not successful. The reaction always stopped at the chlorophosphine stage (i.e., **7**) as indicated by the downfield signal (δ 143) in the ^{31}P NMR spectrum. The use of MeLi, TMEDA, and prolonged stirring under reflux did not bring about methylation of the intermediate chlorophosphine **7**. Compound **7** decomposed during distillation, producing Me_3SiCl as a volatile byproduct. A more

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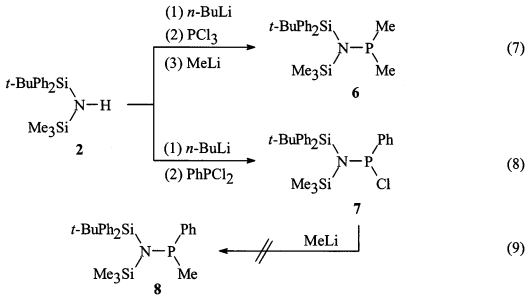
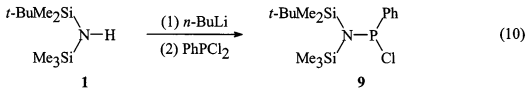


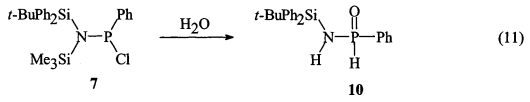
controlled thermolysis of **7** was also carried out, and the results are discussed below. Prior to distillation, recrystallization of the chlorophosphine **7** gave analytically pure crystals that were suitable for X-ray diffraction (see below).

For comparative purposes, after chlorophosphine **7** was prepared as above, we repeated the Wilburn process with *tert*-butyl*dimethyl*silyl(trimethylsilyl)amine (**1**) and $PhPCl_2$, stopping at the PCl stage (eq 10). In this way, the analogous



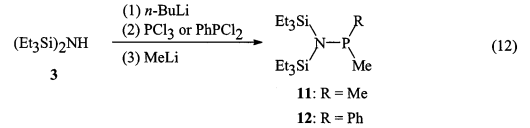
chlorophosphine **9** was obtained in 83% yield as a thermally stable, distillable liquid that had a characteristically low field signal (δ 146) in the ^{31}P NMR spectrum. Like the *P*-methyl derivative **5**, compound **9** exhibited diastereotopic SiMe groups in its ^{1}H and ^{13}C NMR spectra.

As expected, the chlorophosphines **7** and **9** were sensitive to atmospheric moisture, and some hydrolysis was evident during initial attempts to recrystallize **7**. In a separate experiment, a sample of **7** was stirred at room temperature overnight in THF solution containing a small amount of water (eq 11). Solvent removal left a gummy white solid which, after recrystallization, was identified as the PH-substituted phosphine oxide **10**.



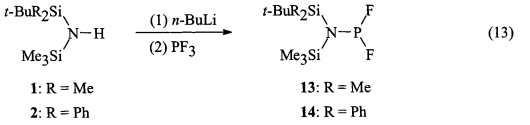
The hydrolysis product **10** was conclusively identified by NMR spectroscopy and a single-crystal X-ray diffraction study. The NH (δ 4.42, br) and PH (δ 8.08) groups were clearly observed in the ^{1}H NMR spectrum, with the latter occurring as a doublet of doublets ($^{1}J_{PH}$ = 528 Hz, $^{3}J_{HH}$ = 9.2 Hz). The same large, one-bond P−H coupling constant ($^{1}J_{PH}$ = 528 Hz) was observed in the ^{1}H-coupled ^{31}P NMR spectrum (δ 16.0) along with a three-bond coupling to the NH proton ($^{3}J_{PH}$ = 11.5 Hz).

We also used the Wilburn method for the synthesis of (silylamino)phosphines derived from the symmetrical disilylamine **3** (eq 12). These reactions proceeded smoothly and



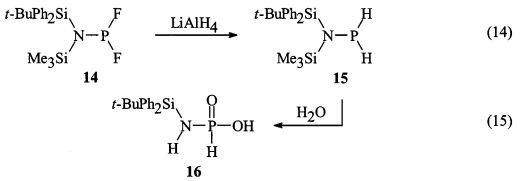
afforded ca. 70% yields of phosphines **11** and **12** as distillable liquids that were readily characterized by NMR spectroscopy and elemental analysis. The increased steric hindrance of the triethylsilyl groups (as compared to Me_3Si) required the use of MeLi (instead of MeMgBr) to effect substitution at phosphorus. In these cases, however, the reactions proceeded to completion in Et_2O solution rather than THF as was required for the *tert*-butyl-substituted silylamines **1** and **2**.

Since the stabilizing influence of these bulky silylamino groups was apparent from some of the reactions described above, we decided to investigate the possible synthesis of other, potentially more reactive, (silylamino)phosphine derivatives. As had been reported previously in the case of the bis(trimethylsilyl)amino analogue $(Me_3Si)_2NPF_2$,[9] we found that the *N*-lithio derivatives of silylamines **1** and **2** reacted smoothly with phosphorus trifluoride to give the desired $-PF_2$ phosphines **13** and **14** (eq 13).



The difluorophosphines **13** and **14** were obtained in good yields (ca. 70%) and were readily identified by NMR spectroscopy. In particular, their ^{31}P NMR spectra consisted of triplets with characteristically large one-bond P−F coupling constants of ca. 1200 Hz. While **13** was a distillable liquid, the *tert*-butyldiphenylsilyl analogue **14** was a crystalline solid that was studied by X-ray diffraction.

The fact that **14** readily crystallized led to the question of whether it might be possible to obtain stable, crystalline $-PH_2$ or $-PCl_2$ analogues. Neither of these derivatives are stable enough to distill when simple Me_3Si groups are present on nitrogen.[10] A number of attempts were made to prepare the $-PH_2$ derivative **15** by reducing the difluorophosphine **14** with lithium aluminum hydride (eq 14). The reaction, however, always gave an inseparable mixture of products including the desired $-PH_2$ derivative **15** (^{31}P NMR δ −21, J_{PH} = 191 Hz) and unreacted starting material **14** (^{31}P NMR δ 165, J_{PF} = 1,228 Hz). Attempts to isolate **15** in pure form by recrystallization led, instead, to formation of a hydrolysis product that was subsequently identified as the phosphorus-(V) derivative **16** (eq 15). Although it was isolated in low



yield (ca. 10%) and its crystals were not suitable for X-ray diffraction, the structure of **16** was readily apparent from NMR spectral data. For example, the phosphorus(V) oxidation state was confirmed by the relatively high field ^{31}P NMR

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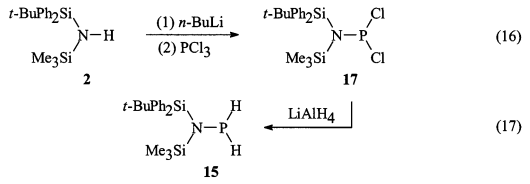
Table 1. Crystallographic Data for the (Silylamino)Phosphines *t*-$BuPh_2Si(Me_3Si)NPMe_2$ (**6**), *t*-$BuPh_2Si(Me_3Si)NP(Ph)Cl$ (**7**), and *t*-$BuPh_2Si(Me_3Si)NPF_2$ (**14**)

	6	**7**	**14**
empirical formula	$C_{21}H_{34}PSi_2$	$C_{25}H_{33}NPSi_2Cl$	$C_{19}H_{28}NPSi_2F_2$
fw	373.65	470.14	395.58
cryst size (mm)	0.450 × 0.350 × 0.225	0.380 × 0.330 × 0.280	0.430 × 0.400 × 0.330
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/a$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	10.880(6)	16.500(8)	9.484(2)
b (Å)	9.438(5)	15.021(6)	14.106(2)
c (Å)	22.930(19)	22.638(8)	17.054(2)
α (deg)	90.00	90.00	90.00
β (deg)	104.47	111.10	105.31
γ (deg)	90.00	90.00	90.00
V (Å^3)	2280(3)	5235(7)	2200.4(6)
Z	4	8	4
μ (cm^{-1})	2.24	3.06	2.46
λ (Å)	0.71069	0.71069	0.71069
D_c (g/cm^3)	1.130	1.193	1.194
T (K)	298	298	298
R[a]	0.0533	0.088	0.058
R_w[b]	0.0495	0.114	0.068

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

chemical shift (δ 1.2) and the large one-bond P−H coupling constant (652 Hz) observed in both the ^{1}H and ^{31}P NMR spectra.

An alternate route to the $-PH_2$ derivative **15** via the $-PCl_2$ intermediate **17** (eqs 16 and 17) was also investigated. In this case, the dichlorophosphine **17** was obtained in crude



form as a yellow liquid. Although **17** decomposed upon attempted distillation, it was of sufficient purity for subsequent reactions and was characterized by NMR spectroscopy. The ^{31}P NMR signal was far downfield (δ 189), and the ^{1}H and ^{13}C NMR spectra contained the expected peaks for the *t*-$BuPh_2Si$ and Me_3Si groups.

Subsequent treatment of **17** with $LiAlH_4$ produced the $-PH_2$ derivative **15**, isolated as a gummy white solid after solvent removal, that was easily identified by NMR spectroscopy as noted above. Unfortunately, compound **15** could not be purified by distillation without thermal decomposition or by recrystallization without significant hydrolysis (to yield **16**).

Structures of (Silylamino)phosphines. The molecular structure and stereochemistry of aminophosphines[1] have been studied by various techniques including X-ray and electron diffraction and IR and NMR spectroscopy.[11,12] The possibility of (p−d)π bonding between the lone pair orbital on nitrogen and the vacant 3d orbitals of phosphorus and, in the case of the (silylamino)phosphines,[13] also silicon has been proposed. For example, electron diffraction studies conducted on various SiN compounds have shown that nitrogen has a planar geometry.[14] Similarly, X-ray[15] and electron diffraction[16] studies of R_2NPF_2 (R = H, Me) have shown the geometry at nitrogen to be planar, with the R_2N plane bisecting the PF_2 angle. This gauche relationship of the lone pair orbitals of nitrogen and phosphorus is favored from Coulombic considerations. The P−N bond distances were found to be 1.684 Å (R = Me) and 1.661 Å (R = H) in the vapor phase. These distances are much shorter than the generally cited P−N single bond distance of 1.77 Å.[17] Furthermore, electron diffraction and IR studies of (silylamino)difluorophosphine, $H_3SiN(H)PF_2$,[18] indicated a planar geometry at nitrogen with P−N and Si−N bond distances of 1.657 and 1.720 Å, respectively. Such studies have conclusively shown that the nitrogen atom is planar, and thus sp^2 hybridized, with some degree of multiple bond character in the P−N linkage.

Within this context, it is interesting to examine the structural data obtained here on the new (silylamino)-phosphines **6**, **7**, and **14**. All three compounds crystallized in the monoclinic crystal system (Table 1) and exhibited planar geometries at the nitrogen center (Table 3). In comparing the structural data (Table 3) for the (silylamino)-phosphines **6** (Figure 1), **7** (Figure 2), and **14** (Figure 3),

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Table 2. Crystallographic Data for the (Silylamino)phosphine Oxide **10**, the *N*-Silylphosphoranimine **30**, and the Cyclic Compound **36**

	10	**30**	**36**
empirical formula	$C_{22}H_{26}NPSiO$	$C_{24}H_{30}NPSiO$	$C_{61}H_{69}N_3P_2Si_3Cl_2$[c]
fw	379.51	407.57	1061.35*c*
cryst size (mm)	0.200 × 0.200 × 0.300	0.500 × 0.325 × 0.275	0.200 × 0.150 × 0.120
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/a$ (No. 14)
a (Å)	12.65(2)	12.12(3)	19.361(4)
b (Å)	10.09(3)	9.72 (1)	13.943(2)
c (Å)	16.11(3)	19.38(3)	23.638(2)
α (deg)	90.00	90.00	90.00
β (deg)	99.8(1)	101.9(1)	113.656(9)
γ (deg)	90.00	90.00	90.00
V (Å^3)	2026(3)	2235(5)	5845(3)
Z	4	4	4
μ (cm^{-1})	1.99	1.90	24.58
λ (Å)	0.71069	0.71069	1.54178
D_c (g/cm^3)	1.244	1.220	1.224
T (K)	298	298	298
R[a]	0.051	0.092	0.078
R_w[b]	0.050	0.124	0.071

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. [c] Includes one molecule of CH_2Cl_2.

Table 3. Selected Bond Distances (Å) and Angles (deg) for the (Silylamino)phosphines *t*-$BuPh_2Si(Me_3Si)NPMe_2$ (**6**), *t*-$BuPh_2Si(Me_3Si)NP(Ph)Cl$ (**7**), and *t*-$BuPh_2Si(Me_3Si)NPF_2$ (**14**)

atoms	distance	atoms	angle
	Compound **6**		
Si(1)−N	1.756(2)	Si(1)−N−Si(2)	124.5(1)
Si(2)−N	1.758(3)	Si(1)−N−P	110.8(1)
P−N	1.725(3)	Si(2)−N−P	124.7(1)
P−C(20)	1.822(5)	N−P−C(20)	107.5(2)
P−C(21)	1.823(4)	N−P−C(21)	104.3(2)
Si(1)−C(13)	1.920(4)	C(20)−P−C(21)	99.5(2)
	Compound **7**		
Si(1)−N	1.77(1)	Si(1)−N−Si(2)	122.6(8)
Si(2)−N	1.80(1)	Si(1)−N−P	112.0(7)
P−N	1.68(1)	Si(2)−N−P	125.0(8)
P−Cl	2.110(8)	N−P−Cl	107.4(5)
P−C(20)	1.85(2)	N−P−C(20)	105.6(8)
Si(1)−C(13)	1.94(2)	C(20)−P−Cl	98.8(7)
	Compound **14**		
Si(1)−N	1.788(4)	Si(1)−N−Si(2)	120.9(2)
Si(2)−N	1.796(5)	Si(1)−N−P	117.0(3)
P−N	1.652(4)	Si(2)−N−P	122.1(2)
P−F(1)	1.542(5)	N−P−F(1)	101.1(3)
P−F(2)	1.585(5)	N−P−F(2)	101.6(3)
Si(1)−C(13)	1.889(6)	F(1)−P−F(2)	91.0(3)

two trends are readily apparent. First, the P−N bond distances decrease markedly and systematically [**6**, N−PMe_2, 1.725(3) Å; **7**, N−P(Ph)Cl, 1.68(1) Å, **14**, N−PF_2, 1.652(4) Å]. Second, the bond angles at phosphorus decrease correspondingly in the same order [**6**, C−P−C, 99.5(2)°; **7**, C−P−Cl, 98.8(7)°; **14**, F−P−F, 91.0(3)°]. Both trends are consistent with an increase in P−N bond order due to the increasing electron-withdrawing nature of the groups on phosphorus.

An X-ray structural analysis of the phosphine oxide **10** (Figure 4) was also obtained. Like the (silylamino)-phosphines **6**, **7**, and **14**, this compound crystallized in the monoclinic system (Table 2), and its molecular structure revealed a planar geometry at nitrogen (Table 4). It exhibited a P−N bond distance of 1.637(4) Å and P−H, N−H, and P═O distances of 1.37(3), 0.85(3), and 1.496(3) Å, respectively. The possibility of intermolecular H-bonding (e.g., N−H····O═P) in this structure was ruled out by examination of the crystal packing diagram and the intermolecular distances.

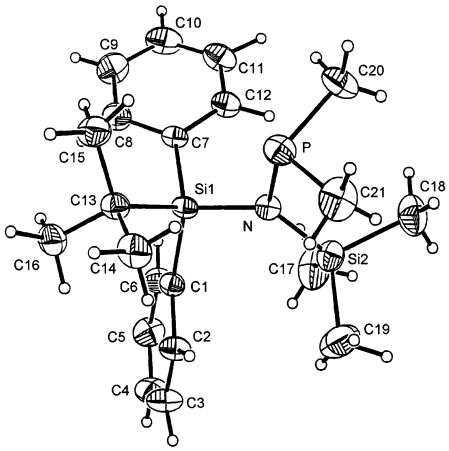


Figure 1. ORTEP representation of compound **6**. Thermal ellipsoids are drawn at the 50% probability level.

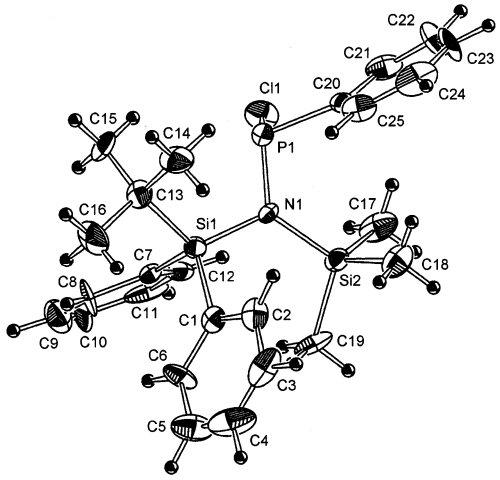


Figure 2. ORTEP representation of compound **7**. Thermal ellipsoids are drawn at the 50% probability level.

Synthesis of N-Silylphosphoranimines. In this phase of the study, the objective was to convert some of the (silylamino)phosphines described above to new *N*-silylphos-

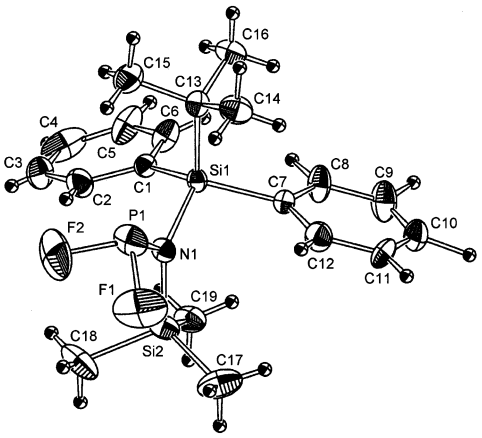


Figure 3. ORTEP representation of compound **14**. Thermal ellipsoids are drawn at the 50% probability level.

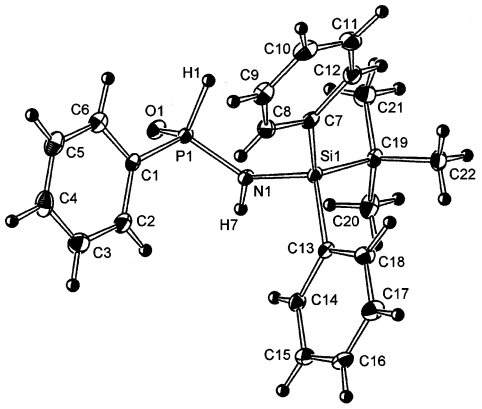
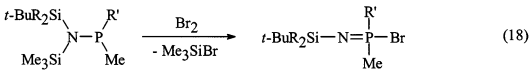


Figure 4. ORTEP representation of compound **10**. Thermal ellipsoids are drawn at the 50% probability level.

phoranimines of type **E** (eq 4). Such compounds not only are potential phosphazene precursors but are also of interest as mechanistic probes for the polymerization process and other reactions. Thus, we initiated a study of the oxidative bromination reactions of these sterically hindered *N*-silylphosphoranimines.

The bromination reactions of the unsymmetrically substituted (silylamino)phosphines **4**−**6** (eq 18) proceeded smoothly in benzene solution at 0 °C. Proton NMR spectra of the volatile components indicated that the less sterically hindered Me_3Si group was selectively eliminated as Me_3SiBr, leaving the bulky *t*-BuR_2Si group on the imino nitrogen.



4: R = R' = Me
5: R = Me, R' = Ph
6: R = Ph, R' = Me

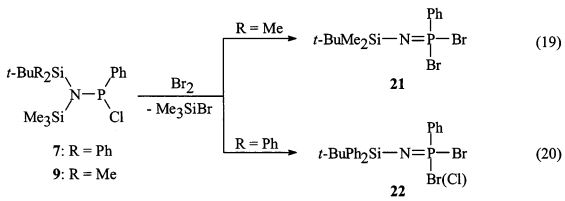
18: R = R' = Me
19: R = Me, R' = Ph
20: R = Ph, R' = Me

Phosphoranimines **18** and **19** were obtained in high yields as thermally stable, distillable liquids and were fully characterized by NMR (^1H, ^{13}C, and ^{31}P) spectroscopy and elemental analysis. The diphenylsilyl analogue **20**, however, was a gummy solid that decomposed on attempted distillation and could not be completely purified by recrystallization. All three compounds were subsequently converted to more stable derivatives as described below.

Table 4. Selected Bond Distances (Å) and Angles (deg) for the (Silylamino)phosphine Oxide **10**, the *N*-Silylphosphoranimine **30**, and the Cyclic Compound **36**

atoms	distance	atoms	angle
	Compound **10**		
Si−N	1.746(4)	Si−N−P	134.3(2)
N−H(7)	0.85(3)	Si−N−H(7)	114(2)
P−N	1.637(4)	P−N−H(7)	111(2)
P−O	1.496(3)	N−P−O	113.9(2)
P−H(1)	1.37(3)	N−P−H(1)	102(1)
P−C(1)	1.788(4)	N−P−C(1)	109.4(2)
Si−C(19)	1.883(5)	O−P−H(1)	111(1)
Si−C(13)	1.889(5)	O−P−C(1)	111.0(2)
Si−C(7)	1.875(7)	C(1)−P−H(1)	109(1)
	Compound **30**		
Si−N	1.686(6)	Si−N−P	166.4(3)
P−N	1.512(6)	N−P−O	115.1(3)
P−O	1.584(4)	N−P−C(17)	116.4(4)
P−C(17)	1.784(7)	N−P−C(18)	116.1(3)
P−C(18)	1.765(8)	O−P−C(17)	98.2(3)
Si(1)−C(13)	1.844(5)	O−P−C(18)	103.5(3)
O−C(19)	1.413(7)	C(17)−P−C(18)	105.2(4)
	Compound **36**		
P(1)−N(1)	1.765(6)	N(1)−P(1)−N(2)	84.0(3)
P(1)−N(2)	1.752(7)	N(1)−P(2)−N(2)	87.0(3)
P(2)−N(1)	1.689(7)	P(1)−N(1)−P(2)	95.0(3)
P(2)−N(2)	1.730(6)	P(1)−N(2)−P(2)	94.0(3)
P(1)−C(17)	1.83(1)	P(2)−N(3)−Si(3)	169.9(6)
P(2)−N(3)	1.514(7)	P(1)−N(1)−Si(1)	126.3(4)
P(2)−C(55)	1.81(1)	P(2)−N(1)−Si(1)	138.7(4)
N(1)−Si(1)	1.752(7)	N(1)−P(2)−N(3)	118.8(4)
N(2)−Si(2)	1.751(7)	N(2)−P(2)−N(3)	120.8(4)
N(3)−Si(3)	1.681(8)	P(1)−N(2)−Si(2)	128.1(4)
Si(1)−C(13)	1.91(1)	P(2)−N(2)−Si(2)	137.2(4)
Si(2)−C(35)	1.91(1)	N(2)−P(2)−C(55)	105.9(4)
Si(3)−C(51)	1.89(1)	N(1)−P(1)−C(17)	102.3(4)
		N(2)−P(1)−C(17)	106.6(4)
		N(1)−P(2)−C(55)	105.7(4)
		N(2)−P(2)−C(55)	114.7(4)

Bromination reactions of the *P*-chlorophosphines **7** and **9** were also studied (eqs 19 and 20). In the case of the dimethylsilyl-substituted (silylamino)phosphine **9**, the prod-

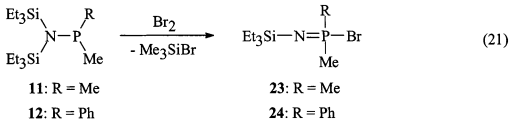


uct was a fully characterized, distillable liquid that was identified as the dibromophosphoranimine **21** by NMR and mass spectroscopy. For example, the mass spectrum of **21** contained a weak molecular ion peak at *m*/*e* 397 and several more intense fragmentation peaks that showed intensity patterns consistent with the presence of two bromine atoms.

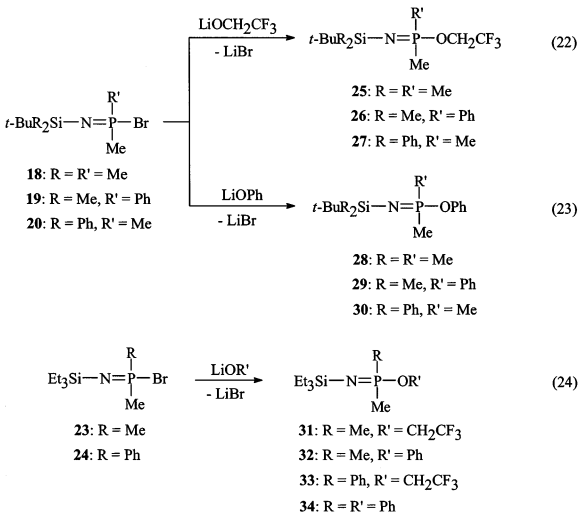
In contrast, the diphenylsilyl analogue **7**, upon bromination, appeared to give a mixture of the dibromo- and bromochlorophosphoranimines **22** as indicated by the presence of two signals (δ −35.3 and −59.3) in the ^{31}P NMR spectrum of the crude product. Rather than attempts to separate the mixture, **22** was converted directly to the bis(trifluoroethoxy)phosphoranimine derivative as described below.

The bis(triethylsilyl)aminophosphines **11** and **12** reacted smoothly with bromine under similar conditions to afford

the expected bromophosphoranimines **23** and **24**, respectively (eq 21). These products were distillable liquids, characterized by NMR spectroscopy. Like all of the *P*-bromophosphoranimines reported here, their ^{31}P NMR chemical shifts occur ca. 25−35 ppm upfield from those of the parent (silylamino)-phosphines.

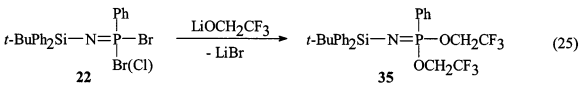


All of these *P*-bromophosphoranimines exhibited reactivity toward nucleophiles similar to those of their *N*-$SiMe_3$ counterparts. For example, when the *tert*-butylsilyl-substituted compounds **18**−**20** were treated with $LiOCH_2CF_3$ or LiOPh (eqs 22 and 23), the desired *P*-trifluoroethoxy (**25**−**27**) and *P*-phenoxy (**28**−**30**) derivatives were formed in good yields. Similarly, the *N*-$SiEt_3$ analogues **31**−**34** were also prepared (eq 24) as part of this study.



Compounds **25**, **26**, and **28**−**34** were all obtained in high yields (70−95%) as thermally stable, distillable liquids and were fully characterized by NMR (^{1}H, ^{13}C, and ^{31}P) spectroscopy and elemental analysis. The ^{31}P NMR chemical shifts were ca. 20−30 ppm for the trifluoroethoxy derivatives and ca. 14−25 ppm for the phenoxy analogues. The *Si*-phenyl derivative **27**, however, could not be purified by distillation due to some thermal decomposition. The silyl ether byproduct *t*-$BuPh_2SiOCH_2CF_3$ was detected by NMR spectroscopy in the distillate obtained from that reaction. Consequently, no further attempts were made to purify **27**. The *N*-*tert*-butyldiphenylsilyl-*P*-phenoxy analogue **30**, however, solidified on standing and was recrystallized to give X-ray-quality crystals (see below).

The dihalophosphoranimine **22** was treated with 2 equiv of $LiOCH_2CF_3$ to give the bis(trifluoroethoxy) derivative **35** (eq 25). The crude product from this reaction was contaminated with other, unidentified materials, and fractional distillation gave **35** only in low yield (ca. 20%). Although the distilled product was readily identified as **35** by NMR spectroscopy, a satisfactory elemental analysis could not be obtained. This compound also showed some tendency to crystallize on standing, but crystals suitable for X-ray analysis were not formed.



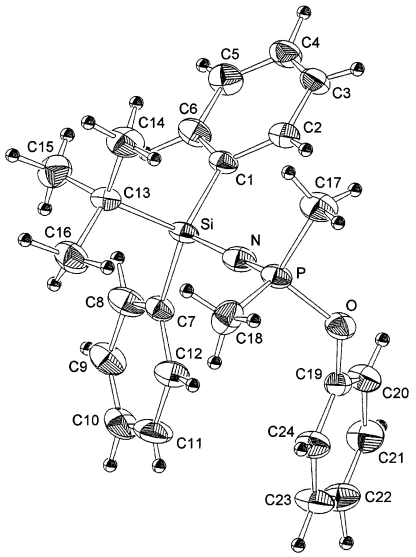


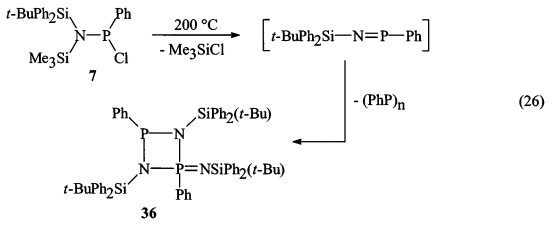
Figure 5. ORTEP representation of compound **30**. Thermal ellipsoids are drawn at the 50% probability level.

Structure of an N-Silylphosphoranimine. Among the new *N*-silylphosphoranimines prepared in this study, compound **30** (Figure 5) is probably the most significant. This *t*-$BuPh_2SiN$-substituted *P*,*P*-dimethyl-*P*-phenoxyphosphoranimine was obtained in 60% yield as a colorless, high-boiling-point liquid that crystallized on standing. The X-ray diffraction study of **30** (Tables 2 and 4) is the first for an *N*-silylphosphoranimine that is suitably functionalized to be a phosphazene polymer precursor (eq 5). Moreover, compound **30** is a rare example of a simple acyclic P═N compound that crystallized without the assistance of metal complexation.[11,13]

The X-ray analysis of **30** revealed a very short P═N bond distance of 1.512(6) Å, a Si−N distance of 1.686(6) Å, and a P−O distance of 1.584(4) Å. The Si−N−P bond angle of 166.4(3)°, while far from linear, is considerably larger than that expected for a formally sp^2 hybridized nitrogen center. The average N−P−C(17,18) bond angle was 116.25°, with the N−P−O and P−O−C19 bond angles being 115.1(3)° and 121.6(4)°, respectively. Many of these distances and angles are markedly different from those in the precursor (silylamino)phosphine **6**. For example, the P−N distance is dramatically shortened from 1.725(3) Å (**6**) to 1.512(6) Å (**30**), the Si−N distance is shortened from 1.756(2) Å (**6**) to 1.686(6) Å (**30**), the Si−N−P angle is opened from 110.8-(1)° (**6**) to 166.4(3)° (**30**), and the C−P−C angle is widened from 99.5(2)° (**6**) to 105.2(4)° (**30**). Such differences are consistent with the absence of lone-pair repulsions in going from the P(III) to the P(V) oxidation state and with the relief of steric crowding due to loss of the $SiMe_3$ group from nitrogen. Stereochemical changes are also noted within the

bulky *t*-BuPh$_2$Si group itself. In the phosphine **6**, the planes of the phenyl rings are nearly orthogonal to each other, whereas, in the less sterically congested phosphoranimine **30**, such twisting of the rings is not observed.

Thermolysis of a P-Chlorophosphine. Since the crystalline chlorophosphine **7** (Figure 2) decomposed upon attempted distillation, a more controlled thermolysis was carried out to identify the decomposition products (eq 26).



(26)

Thus, a neat sample of **7** was heated in a sealed ampule at 200 °C for several days. After the sample was cooled to room temperature, three distinct products were observed in the reaction tube: a colorless liquid, a waxy brown solid, and a powdery orange solid. The liquid was easily removed under reduced pressure and was identified as Me_3SiCl by ^1H and ^{13}C NMR spectroscopy. The orange product was insoluble in all common solvents and, on the basis of its physical appearance and insolubility, was presumed to be the cyclic polyphosphines $(PhP)_n$ (n = 5, 6).[19] This also accounts for the apparent stoichiometry of the thermolysis reaction.

The brown solid was readily soluble in CH_2Cl_2, which facilitated its complete separation from the orange powder. The ^{31}P NMR spectrum of the soluble product was strongly suggestive of the cyclic structure **36** since two doublets for the P(III) and P(V) centers[20] were observed at 96.8 and 1.66 ppm, respectively, with a P−P coupling constant of 48.9 Hz. Although the ^1H and ^{13}C NMR spectra contained complex multiplets in the phenyl and *t*-Bu regions, the relative peak intensities were consistent with the proposed structure. Recrystallization from a minimal amount of hexane/CH_2Cl_2 afforded white crystals that were suitable for X-ray diffraction. The analysis (Tables 2 and 4) confirmed the cyclic structure of **36** and the P(III)−P(V) arrangement (Figure 6).

The average endocyclic P−N bond distance in **36** is 1.734 Å, while the exocyclic P═N bond distance is only 1.514(7) Å, similar to the formal double bond in the phosphoranimine **30**. The Si−N bonds for the Si atoms attached directly to the ring have an average length of 1.752 Å, while the Si−N distance in the exocyclic P═N−Si linkage is 1.689 Å. The P−N−Si bond angle within the same moiety is quite large [169.9(6)°] and also comparable to that in the acyclic analogue **30**. The P-bonded phenyl groups are arranged on opposite sides of the four-membered ring in a *trans* relationship to each other with an average P−C bond distance of 1.82 Å. The X-ray analysis also revealed the presence of one molecule of the crystallization solvent CH_2Cl_2 (not shown in Figure 6) per ring molecule.

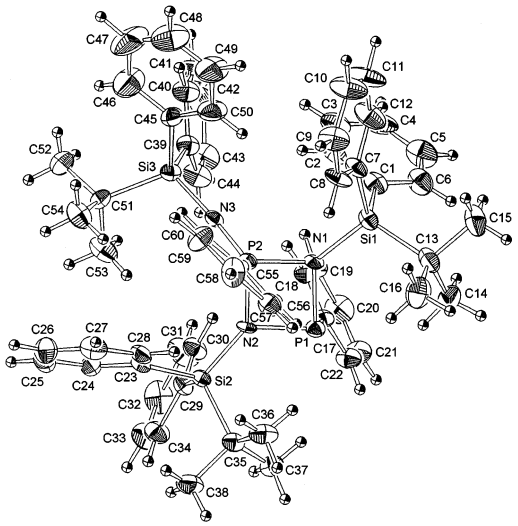


Figure 6. ORTEP representation of compound **36**. Thermal ellipsoids are drawn at the 50% probability level.

Conclusion. A series of new (silylamino)phosphines containing the sterically bulky disilylamino groups *t*-BuR_2Si(Me_3Si)N− (R = Me, Ph) or $(Et_3Si)_2$N− have been prepared and characterized. In addition to several *P*-alkyl/aryl derivatives, two −PF_2 phosphines were isolated as stable products, and evidence for a −PH_2 derivative was also obtained. Oxidative bromination of the *t*-BuR_2Si(Me_3Si)N-substituted aminophosphines occurred with selective cleavage of the $SiMe_3$ group, giving exclusively the *t*-BuR_2SiN-substituted *N*-silylphosphoranimines. In addition to providing enhanced thermal stability relative to the Me_3Si analogues, the bulky *t*-BuPh$_2$Si group, in particular, imparted crystallinity to many of the products. Consequently, X-ray crystal structures were obtained on a series of three of the title compounds as well as some of their oxidation and thermolysis products. The results of a more systematic study of the thermal decomposition of the new *N*-silylphosphoranimines, as possible phosphazene precursors, will be reported elsewhere.

Experimental Section

Materials and General Procedures. The starting disilylamines *t*-BuR_2Si(Me_3Si)NH (**1**, R = Me; **2**, R = Ph) and $(Et_3Si)_2$NH (**3**) were prepared according to published procedures.[21,22] The reagents PCl_3, PF_3, $PhPCl_2$, CF_3CH_2OH, PhOH, $LiAlH_4$ (1.0 M in Et_2O), MeLi (1.4 M in Et_2O), and *n*-BuLi (2.5 M in hexane) were used as received from commercial sources. Hexane, Et_2O, CH_2CI_2, and TMEDA were distilled under N_2 from CaH_2 and either used immediately or stored over molecular sieves. Tetrahydrofuran (THF) was distilled under N_2 from Na/benzophenone immediately prior to use. Proton, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian XL-300 spectrometer using $CDC1_3$ or C_6D_6 as a lock solvent. Positive ^1H and ^{13}C NMR chemical shifts and ^{31}P NMR shifts are downfield from the external references Me_4Si and H_3PO_4, respectively, with coupling constants (J) given in hertz. Elemental analyses were performed by E&R Microanalytical Laboratory, Inc., Corona, NY. GC/mass spectrometry was done

(19) Cowley, A. H. *Chem. Rev.* **1965**, *65*, 617.
(20) Appel, R.; Halstenberg, M. *J. Organomet. Chem.* **1975**, *99*, C25.
(21) Bowser, J. R.; Neilson, R. H.; Wells, R. L. *Inorg. Chem.* **1978**, *17*, 1882.
(22) Fessenden, R.; Fessenden, J. S. *Chem. Rev.* **1961**, *61*, 361.

using a Hewlett-Packard 5890 gas chromatograph and 5989A mass spectrometer system. All reactions and manipulations were carried out under a nitrogen atmosphere and/or by using standard vacuum line techniques.

X-ray Crystallography. Diffraction data of compounds **6**, **7**, **10**, **14**, **30**, and **36** were collected at room temperature on a Rigaku AFC6S diffractometer. Crystallographic data are summarized in Tables 1 and 2. The structures (Figures 1−6) were solved using direct methods[23] and refined using the Texsan program package.[24] All non-hydrogen atoms were refined anisotropically, while H atoms were constrained with a riding model. Selected bond distances and angles are listed in Tables 3 and 4. Further details regarding the crystal data and refinement as well as full tables of bond lengths and angles for these structures have been deposited with the Cambridge Crystallographic Data Center.[25]

Preparation of (Disilylamino)phosphines *t*-BuR_2Si(Me_3Si)NP(R′)Me (5, 6) and (Et_3Si)$_2$NP(R)Me (11, 12). 5 (R = Me, R′ = Ph). A 1 L, three-neck flask, equipped with a magnetic stir bar, N_2 inlet, and 250 mL addition funnel, was charged with the disilazane **1** (50.8 g, 0.250 mol) and THF (250 mL). The flask was cooled to 0 °C, and *n*-BuLi (0.250 mol, 100 mL, 2.5 M solution in hexane) was added dropwise from the addition funnel. Following the addition, the funnel was rinsed with THF (ca. 10 mL) that was added to the reaction mixture. The reaction was allowed to warm to room temperature while it was stirred for ca. 1.5 h. The flask was then cooled to −78 °C, and $PhPCl_2$ (0.250 mol, 33.9 mL) was added dropwise to the stirred reaction mixture. The mixture was allowed to warm to room temperature while it was stirred for ca. 2 h. The addition funnel was again rinsed with THF (ca. 10 mL) that was added to the reaction mixture. The flask was cooled to 0 °C, and MeLi (0.250 mol, 179 mL, 1.4 M solution in Et_2O) was added dropwise to the stirred reaction mixture at 0 °C. The mixture was then allowed to warm to room temperature and stirred overnight. Solvents were removed under reduced pressure, and hexane (ca. 600 mL) was added to extract the product from the salts. The mixture was filtered under reduced pressure, the salts were washed with hexane (4 × 50 mL), and the washings were combined with the filtrate. Solvent was removed under reduced pressure, leaving a viscous, oily residue. Fractional distillation gave **5** as a colorless liquid. Yield: 73%. Bp: 100−104 °C (0.01 mmHg). ^{1}H NMR: δ −0.02 (s, *Me*$_3$Si), 0.26 (d, *Me*$_2$Si, J_{PH} = 1.8), 0.44 (d, *Me*$_2$Si, J_{PH} = 1.8), 0.97 (s, *Me*$_3$C), 1.64 (d, P*Me*, J_{PH} = 6.6), 7.1−7.4 (m, *Ph*). ^{13}C NMR: δ 6.00 (s, *Me*$_3$Si), −0.14 (d, *Me*$_2$Si, J_{PC} = 5.4), 0.08 (d, *Me*$_2$Si, J_{PC} = 6.1), 17.3 (d, P*Me*, J_{PC} = 27.2), 20.5 (s, Me$_3$*C*), 28.3 (d, *Me*$_3$C, J_{PC} = 6.3), 147.3 (d, P*Ph*, J_{PC} = 23.6), 128.7 (d, *o-Ph*, J_{PC} = 15.4), 128.2 (d, *m-Ph*, J_{PC} = 2.4), 126.8 (s, *p-Ph*). ^{31}P NMR: δ 39.9. Anal. Calcd for $C_{16}H_{32}NPSi_2$: C, 59.03; H, 9.91. Found: C, 58.71; H, 9.91.

6 (R = Ph, R′ = Me). The same procedure (0.250 mol scale), using the disilylamine **2**, PCl_3 instead of $PhPCl_2$, and MeLi (2 equiv) gave product **6** as a colorless liquid that solidified on standing. Yield: 50%. Bp: 140−160 °C (0.01 mmHg). ^{1}H NMR: δ −0.18 (s, *Me*$_3$Si), 1.06 (s, *Me*$_3$C), 1.45 (d, P*Me*, J_{PH} = 7.1), 7.2−7.6 (m, *Ph*). ^{13}C NMR: δ 6.43 (s, *Me*$_3$Si), 19.8 (d, P*Me*, J_{PC} = 24.0), 21.6 (d, Me$_3$*C*, J_{PC} = 5.7), 29.4 (d, *Me*$_3$C, J_{PC} = 11.9), 138.3 (d, Si*Ph*, J_{PC} = 6.4), 136.3 (s, *o-Ph*), 127.5 (s, *m-Ph*), 129.2 (s, *p-Ph*). ^{31}P NMR: δ 35.4. Anal. Calcd for $C_{21}H_{34}NPSi_2$: C, 65.07; H, 8.84. Found: C, 64.82; H, 9.05. Crystals of **6** suitable for X-ray diffraction were obtained by recrystallization from a minimal amount of hexane/CH_2Cl_2 (1:1 by volume).

11 (R = Me). The same procedure (0.250 mol scale), using the disilylamine **3**, PCl_3 instead of $PhPCl_2$, and MeLi (2 equiv) gave product **11** as a colorless liquid. Yield: 73%. Bp: 79−80 °C (0.01 mmHg). ^{1}H NMR: δ 0.63 (q, Me*CH*$_2$Si, J_{HH} = 7.7), 0.83 (t, *Me*CH$_2$Si, J_{HH} = 7.8), 1.24 (d, P*Me*, J_{PH} = 6.3). ^{13}C NMR: δ 7.60 (d, Me*CH*$_2$Si, J_{PC} = 8.3), 7.93 (s, *Me*CH$_2$Si), 20.6 (d, P*Me*, J_{PC} = 22.8). ^{31}P NMR: δ 31.1. Anal. Calcd for $C_{14}H_{36}NPSi_2$: C, 55.03; H, 11.87. Found: C, 54.55; H, 11.75.

12 (R = Ph). The same procedure (0.250 mol scale), using the disilylamine **3**, $PhPCl_2$, and MeLi (1 equiv) gave product **12** as a colorless liquid. Yield: 70%. Bp: 108−117 °C (0.01 mmHg). ^{1}H NMR: δ 0.62 (q, Me*CH*$_2$Si, J_{HH} = 7.7), 0.86 (t, *Me*CH$_2$Si, J_{HH} = 7.7), 1.60 (d, P*Me*, J_{PH} = 6.5), 7.1−7.3 (m, *Ph*). ^{13}C NMR: δ 7.82 (d, Me*CH*$_2$Si, J_{PC} = 7.5), 8.15 (s, *Me*CH$_2$Si), 18.2 (d, P*Me*, J_{PC} = 27.2), 147.5 (d, P*Ph*, J_{PC} = 22.7), 128.9 (d, *o-Ph*, J_{PC} = 16.0), 128.1 (d, *m-Ph*, J_{PC} = 3.0), 126.9 (d, *p-Ph*, J_{PC} = 2.0). ^{31}P NMR: δ 36.2. Anal. Calcd for $C_{19}H_{38}NPSi_2$: C, 62.07; H, 10.42. Found: C, 61.84; H, 10.30.

In the preparations of compounds **11** and **12**, Et_2O could be used as the solvent instead of THF with no significant difference in product yield.

Preparation of Phenyl(chloro)phosphines *t*-BuR_2Si(Me_3Si)NP(Ph)Cl (7, 9) and the Hydrolysis Product *t*-BuPh_2Si(H)NP(=O)(Ph)H (10). 7 (R = Ph). A 250 mL, three-neck flask, equipped with a magnetic stir bar, N_2 inlet, and 50 mL addition funnel, was charged with the disilazane **2** (16.4 g, 0.050 mol) and THF (125 mL). The flask was cooled to 0 °C, and *n*-BuLi (0.050 mol, 20.0 mL, 2.5 M solution in hexane) was added dropwise from the addition funnel. Following the addition, the funnel was rinsed with THF (ca. 10 mL) that was added to the reaction mixture. The reaction was allowed to warm to room temperature while it was stirred for ca. 1.5 h. The flask was then cooled to −78 °C, and $PhPCl_2$ (0.050 mol, 6.8 mL) was added dropwise to the stirred reaction mixture. The mixture was then allowed to warm to room temperature and stirred overnight. Solvents were removed under reduced pressure, and hexane (ca. 100 mL) was added to extract the product from the salts. The mixture was filtered under reduced pressure, the salts were washed with hexane (4 × 15 mL), and the washings were combined with the filtrate. Solvent was removed under reduced pressure, leaving a white solid. Recrystallization from hexane/CH_2Cl_2 (1:1 by volume) gave product **7** as white crystals that were suitable for X-ray diffraction. Yield: 65%. ^{1}H NMR: δ −0.07 (s, *Me*$_3$Si), 1.48 (s, *Me*$_3$C), 7.7−8.4 (m, *Ph*). ^{13}C NMR: δ 5.13 (s, *Me*$_3$Si), 22.0 (d, Me$_3$*C*, J_{PC} = 7.0), 28.8 (d, *Me*$_3$C, J_{PC} = 9.3), 127.8−142.5 (m, *Ph*). ^{31}P NMR: δ 143.4. Anal. Calcd for $C_{25}H_{33}ClNPSi_2$: C, 63.87; H, 7.08. Found: C, 64.03; H, 6.94.

9 (R = Me). The same procedure (0.050 mol scale), using the disilylamine **1** and $PhPCl_2$, gave product **9** as a colorless, distillable liquid. Yield: 83%. Bp: 107−110 °C (0.01 mmHg). ^{1}H NMR: δ 0.09 (s, *Me*$_3$Si), 0.04 (d, *Me*$_2$Si, J_{PH} = 2.9), −0.42 (d, *Me*$_2$Si, J_{PH} = 2.2), 1.07 (d, *Me*$_3$C, J_{PH} = 1.3), 7.3−7.7 (m, *Ph*). ^{13}C NMR: δ 5.41 (s, *Me*$_3$Si), −0.07 (d, *Me*$_2$Si, J_{PC} = 14.7), −0.82 (d, *Me*$_2$Si, J_{PC} = 19.9), 20.4 (s, Me$_3$*C*), 27.8 (d, *Me*$_3$C, J_{PC} = 6.6), 128.5−145.4 (m, *Ph*). ^{31}P NMR: δ 145.9. Anal. Calcd for $C_{15}H_{29}ClNPSi_2$: C, 52.07; H, 8.45. Found: C, 51.94; H, 8.73.

Hydrolysis of 7. Some hydrolysis was observed during the initial attempts to recrystallize the phenyl(chloro)phosphine **7**. In a separate experiment, a small sample of **7** (0.010 mol) was stirred at room temperature overnight in THF (10 mL) solution containing about

(23) Sheldrick, G. M. *SHELX86. Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1986.

(24) *Texsan-Texray Structure Analysis Package*, Version 1.701; Molecular Structure Corp., March 1995.

(25) X-ray crystallographic data for compounds **6**, **7**, **10**, **14**, **30**, and **36** have been deposited with the Cambridge Crystallographic Data Center and are available as Deposit Numbers 158350 (**6**), 158353 (**7**), 158352 (**10**), 158354 (**14**), 158351 (**30**), and 157316 (**36**).

0.5 mL of water. Solvent was removed under reduced pressure, leaving a gummy white solid. Recrystallization from hexane/CH_2Cl_2 (1:1 by volume) gave product **10** as white crystals that were suitable for X-ray diffraction. Yield: 15%. ^{1}H NMR: δ 1.15 (s, *Me*$_3$C), 4.42 (br, N*H*), 7.2−7.7 (m, *Ph*), 8.08 (dd, $^1J_{PH}$ = 528, $^3J_{HH}$ = 9.2). ^{13}C NMR: δ 19.1 (d, Me$_3$*C*, J_{PC} = 3.2), 27.1 (s, *Me*$_3$C), 127.9−136.1 (m, *Ph*). ^{31}P NMR: δ 16.0 (dd, *P*H, $^1J_{PH}$ = 528, $^3J_{PH}$ = 11.5).

Preparation of Difluorophosphines *t*-BuR$_2$Si(Me$_3$Si)NPF$_2$ (13, 14). 13 (R = Me). A 250 mL, three-neck flask, equipped with a magnetic stir bar, N_2 inlet, and 25 mL addition funnel, was charged with the disilylamine **1** (7.73 g, 0.038 mol) and Et_2O (50 mL). The center neck of the flask was attached to a standard glass vacuum line by way of a Teflon stopcock. The flask was cooled to 0 °C, and *n*-BuLi (0.038 mol, 15.3 mL of a 2.5 M solution in hexane) was added dropwise from the addition funnel. The reaction mixture was allowed to warm to room temperature and stirred for ca. 1 h. The addition funnel was replaced by a glass stopper, and the flask was cooled to −78 °C and degassed. Gaseous PF_3 (0.040 mol) was measured on the vacuum line and condensed at −196 °C in one of the U-traps of the vacuum manifold. The reaction mixture was then cooled to −196 °C, and the PF_3 was allowed to warm and recondense into the reaction flask. The flask was warmed to −78 °C, allowing the contents to melt. The mixture was then allowed to warm slowly to room temperature with stirring. As the reaction mixture warmed, a green, gel-like precipitate formed. The reaction mixture was then stirred overnight. Solvents were removed under reduced pressure, and hexane (ca. 100 mL) was added to extract the product from the salts. The mixture was filtered under reduced pressure, the salts were washed with hexane (4 × 15 mL), and the washings were combined with the filtrate. Solvent was removed under reduced pressure, leaving a thick yellow liquid. Fractional distillation gave **13** as a colorless liquid. Yield: 76%. Bp: 50−70 °C (0.01 mmHg). ^{1}H NMR: δ 0.31 (s, *Me*$_3$Si), 0.32 (s, *Me*$_2$Si), 0.95 (s, *Me*$_3$C). ^{13}C NMR: δ −0.48 (br, *Me*$_2$Si), −0.24 (br, *Me*$_2$Si), 4.47 (d, *Me*$_3$Si, J_{PC} = 2.2), 19.4 (s, Me$_3$*C*), 27.2 (d, *Me*$_3$C, J_{PC} = 4.8). ^{31}P NMR: δ 165.8 (t, *P*F$_2$, J_{PF} = 1238). Anal. Calcd for $C_9H_{24}F_2NPSi_2$: C, 39.82; H, 8.91. Found: C, 39.82; H, 9.35.

14 (R = Ph). The same procedure (0.038 mol scale), using the disilylamine **2**, gave product **14** as a white solid after solvent removal. Recrystallization from hexane/CH_2Cl_2 (1:1 by volume) gave product **14** as white crystals that were suitable for X-ray diffraction. Yield: 70%. ^{1}H NMR: δ −0.03 (s, *Me*$_3$Si), 1.07 (s, *Me*$_3$C), 7.5−7.9 (m, *Ph*). ^{13}C NMR: δ 4.1 (s, *Me*$_3$Si), 20.9 (d, Me$_3$*C*, J_{PC} = 5.1), 28.2 (d, *Me*$_3$C, J_{PC} = 13.5), 135.2 (d, Si*Ph*, J_{PC} = 3.9), 136.1 (s, *o-Ph*), 128.0 (s, *m-Ph*), 130.0 (s, *p-Ph*). ^{31}P NMR: δ 164.8 (t, *P*F$_2$, J_{PF} = 1228).

Preparation of Dichlorophosphine *t*-BuPh$_2$Si(Me$_3$Si)NPCl$_2$ (17), the −PH$_2$ Derivative 15, and the Hydrolysis Product 16. −PCl$_2$ Compound 17. A 250 mL, three-neck flask, equipped with a magnetic stir bar, N_2 inlet, and 50 mL addition funnel, was charged with the disilazane **2** (12.8 g, 0.039 mol) and Et_2O (100 mL). The flask was cooled to 0 °C, and *n*-BuLi (0.039 mol, 15.6 mL, 2.5 M solution in hexane) was added dropwise from the addition funnel. Following the addition, the funnel was rinsed with Et_2O (ca. 10 mL) that was added to the reaction mixture. The reaction was allowed to warm to room temperature while it was stirred for ca. 1.5 h. The flask was then cooled to −78 °C, and PCl_3 (0.039 mol, 3.4 mL) was added dropwise to the stirred reaction mixture. The mixture was then allowed to warm to room temperature and stirred overnight. Solvents were removed under reduced pressure, and hexane (ca. 100 mL) was added to extract the product from the salts. The mixture was filtered under reduced pressure, the salts were washed with hexane (3 × 20 mL), and the washings were combined with the filtrate. Solvent removal left **17** as a viscous liquid that decomposed upon attempted distillation. ^{1}H NMR: δ 0.17 (s, *Me*$_3$Si), 1.13 (s, *Me*$_3$C), 7.5−7.9 (m, *Ph*). ^{13}C NMR: δ 5.33 (s, *Me*$_3$Si), 21.6 (d, Me$_3$*C*, J_{PC} = 7.5), 28.4 (d, *Me*$_3$C, J_{PC} = 14.8), 134.2 (d, Si*Ph*, J_{PC} = 6.6), 136.3 (s, *o-Ph*), 128.0 (s, *m-Ph*), 130.3 (s, *p-Ph*). ^{31}P NMR: δ 188.8.

−PH$_2$ Compound 15. The dichlorophosphine **17** (0.039 mol), prepared as just described, was dissolved in Et_2O (50 mL) in a 100 mL, three-neck flask that had been purged with N_2. The flask was equipped with a gas inlet, magnetic stir bar, and 25 mL addition funnel. The flask was cooled to 0 °C, and $LiAlH_4$ (0.020 mol, 19.5 mL of a 1.0 M solution in Et_2O) was added dropwise to the stirred reaction mixture. The mixture, which became turbid during the addition, was allowed to warm to room temperature and stirred overnight. Solvents were removed under reduced pressure, and hexane (ca. 100 mL) was added to extract the product from the salts. The mixture was filtered under reduced pressure, the salts were washed with hexane (3 × 20 mL), and the washings were combined with the filtrate. Solvent removal left **15** as a gummy white solid that decomposed upon attempted distillation. ^{1}H NMR: δ −0.06 (s, *Me*$_3$Si), 1.18 (s, *Me*$_3$C), 5.17 (d, P*H*, J_{PH} = 191), 7.3−7.8 (m, *Ph*). ^{13}C NMR: δ 1.44 (s, *Me*$_3$Si), 20.9 (d, Me$_3$*C*, J_{PC} = 5.5), 28.8 (d, *Me*$_3$C, J_{PC} = 9.1), 137.4 (d, Si*Ph*, J_{PC} = 3.9), 135.8 (s, *o-Ph*), 127.7 (s, *m-Ph*), 129.4 (s, *p-Ph*). ^{31}P NMR: δ −21.0 (t, *P*H$_2$, J_{PH} = 191).

Hydrolysis of 15. Attempts to recrystallize product **15** from hexane/CH_2Cl_2 resulted in the formation of small amounts of a white solid, subsequently identified as the hydrolysis product **16**. Yield: 10%. ^{1}H NMR: δ 1.00 (d, *Me*$_3$C, J_{PH} = 10.6), 2.97 (d, N*H*, J_{PH} = 6.4), 7.2−7.7 (m, *Ph*), 7.06 (dd, P*H*, $^1J_{PH}$ = 652, $^3J_{HH}$ = 1.8). ^{13}C NMR: δ 18.8 (d, Me$_3$*C*, J_{PC} = 4.3), 26.8 (d, *Me*$_3$C, J_{PC} = 39.3), 128.0−136.1 (m, *Ph*). ^{31}P NMR: δ 1.2 (dd, *P*H, $^1J_{PH}$ = 652, $^3J_{PH}$ = 7.3).

Preparation of P-Bromophosphoranimines *t*-BuR$_2$SiN=P(R′)(Me)Br (18−20), *t*-BuR$_2$SiN=P(Ph)Br$_2$ (21, 22), and Et$_3$SiN=P(R)(Me)Br (23, 24). 18 (R = R′ = Me). A 250 mL, three-neck flask, equipped with a magnetic stir bar, N_2 inlet, and 50 mL addition funnel, was charged with the (silylamino)phosphine **4** (13.2 g, 0.050 mol) and benzene (100 mL). The flask was cooled to 0 °C, and a solution of Br_2 (0.050 mol) in benzene (30 mL) was added slowly to the stirred reaction mixture. The addition of Br_2 was stopped when a faint yellow color persisted in the solution. The mixture was then allowed to warm to room temperature. The solvent and Me_3SiBr were removed under reduced pressure. The residual liquid was then stirred under a dynamic vacuum for ca. 2 h to completely remove any Me_3SiBr. Distillation gave product **18** as a colorless liquid. Yield: 87%. Bp: 40−48 °C (0.1 mmHg). ^{1}H NMR: δ −0.09 (s, *Me*$_2$Si), 0.75 (s, *Me*$_3$C), 2.00 (d, P*Me*, J_{PH} = 13.6). ^{13}C NMR: δ 2.30 (d, *Me*$_2$Si, J_{PC} = 4.8), 18.3 (d, Me$_3$*C*, J_{PC} = 6.2), 26.4 (s, *Me*$_3$C), 29.3 (d, P*Me*, J_{PC} = 80.0). ^{31}P NMR: δ 6.4. Anal. Calcd for $C_8H_{21}BrNPSi$: C, 35.56; H, 7.83. Found: C, 35.58; H, 7.80.

19 (R = Me, R′ = Ph). The same procedure, using (silylamino)-phosphine **5**, gave product **19** as a colorless, distillable liquid. Yield: 71%. Bp: 88−94 °C (0.01 mmHg). ^{1}H NMR: δ −0.09 (d, *Me*$_2$Si, J_{PH} = 4.7), 0.93 (s, *Me*$_3$C), 2.27 (d, P*Me*, J_{PH} = 13.9), 7.4−7.9 (m, *Ph*). ^{13}C NMR: δ 2.10 (d, *Me*$_2$Si, J_{PC} = 4.3), 18.5 (s, Me$_3$*C*), 26.6 (s, *Me*$_3$C), 29.5 (d, P*Me*, J_{PC} = 81.1), 137.8 (d, P*Ph*, J_{PC} = 121), 128.6 (d, *o-Ph*, J_{PC} = 14.6), 130.4 (d, *m-Ph*, J_{PC} = 12.0), 132.1 (d, *p-Ph*, J_{PC} = 3.1). ^{31}P NMR: δ 0.2. Anal. Calcd for $C_{13}H_{23}BrNPSi$: C, 46.99; H, 6.98. Found: C, 46.72; H, 6.87.

20 (R = Ph, R′ = Me). The same procedure, using (silylamino)-phosphine **6**, afforded a gummy yellow solid after removal of benzene and Me_3SiBr. This material decomposed upon attempted distillation. Further purification and characterization was not attempted. Instead, it was used directly for the synthesis of the *P*-OCH_2CF_3 (**27**) or *P*-OPh (**30**) derivative as described below.

21 (R = Me). The same procedure, using the *P*-chloro-(silylamino)phosphine **9**, gave product **21** as a colorless, distillable liquid. Yield: 68%. Bp: 105−110 °C (0.01 mmHg). ^{1}H NMR: δ 0.12 (d, *Me*$_2$Si, J_{PH} = 1.2), 0.89 (d, *Me*$_3$C, J_{PH} = 1.4), 7.4−7.9 (m, *Ph*). ^{13}C NMR: δ −3.16 (d, *Me*$_2$Si, J_{PC} = 6.2), 18.4 (d, Me$_3$*C*, J_{PC} = 8.8), 26.3 (s, *Me*$_3$C), 140.4 (d, P*Ph*, J_{PC} = 159), 128.6 (d, *o-Ph*, J_{PC} = 18.9), 130.3 (d, *m-Ph*, J_{PC} = 13.3), 133.2 (d, *p-Ph*, J_{PC} = 4.2). ^{31}P NMR: δ −10.9.

22 (R = Ph). The same procedure, using *P*-chloro(silylamino)-phosphine **7**, afforded a yellow solid after removal of benzene and Me_3SiBr. This material decomposed upon attempted distillation. Further purification and characterization was not attempted. Instead, it was used directly for the synthesis of the *P*-OCH_2CF_3 derivative **35** as described below.

23 (R = Me). The same procedure, using the (silylamino)-phosphine **11**, gave product **23** as a colorless, distillable liquid. Yield: 76%. Bp: 40−42 °C (0.01 mmHg). ^{1}H NMR: δ 0.41 (q, Me*CH*$_2$Si, J_{HH} = 7.9), 0.84 (t, *Me*CH$_2$Si, J_{HH} = 7.9), 2.00 (d, P*Me*, J_{PH} = 13.6). ^{13}C NMR: δ 6.75 (d, Me*CH*$_2$Si, J_{PC} = 5.4), 7.53 (s, *Me*CH$_2$Si), 29.6 (d, P*Me*, J_{PC} = 80.7). ^{31}P NMR: δ 5.8. Anal. Calcd for $C_8H_{21}BrNPSi$: C, 35.56; H, 7.83. Found: C, 35.36; H, 7.64.

24 (R = Ph). The same procedure, using the (silylamino)-phosphine **12**, gave product **24** as a colorless liquid that decomposed slightly during distillation. Yield: 75%. Bp: 107−115 °C (0.01 mmHg). ^{1}H NMR: δ 0.52 (q, Me*CH*$_2$Si, J_{HH} = 7.9), 0.91 (t, *Me*CH$_2$Si, J_{HH} = 7.7), 2.22 (d, P*Me*, J_{PH} = 13.9), 7.4−7.8 (m, *Ph*). ^{13}C NMR: δ 6.98 (d, Me*CH*$_2$Si, J_{PC} = 5.2), 7.65 (s, *Me*CH$_2$Si), 29.6 (d, P*Me*, J_{PC} = 82.0), 137.8 (d, P*Ph*, J_{PC} = 119.7), 128.5 (d, *o-Ph*, J_{PC} = 14.6), 130.4 (d, *m-Ph*, J_{PC} = 11.9), 132.1 (d, *p-Ph*, J_{PC} = 3.0). ^{31}P NMR: δ −2.8.

Preparation of P-Trifluoroethoxy- and P-Phenoxyphosphoranimines *t*-BuR$_2$SiN=P(R′)(Me)OCH$_2$CF$_3$ (25, 26), t-BuR$_2$SiN=P(R′)(Me)OPh (28−30), Et$_3$SiN=P(R)(Me)OR′ (31−34), and t-BuPh$_2$SiN=P(Ph)(OCH$_2$CF$_3$)$_2$ (35). 25 (R = R′ = Me). A 250 mL, three-neck flask, equipped with a magnetic stir bar, N_2 inlet, and 125 mL addition funnel, was charged with the *P*-bromophosphoranimine **18** (13.5 g, 0.050 mol), freshly prepared as described above, and THF (100 mL). The solution was cooled to 0 °C. Another 250 mL, three-neck flask, equipped with a magnetic stir bar, N_2 inlet, and 50 mL addition funnel, was charged with CF_3CH_2OH (3.6 mL, 0.050 mol) and THF (50 mL). From the addition funnel, *n*-BuLi (0.050 mL, 20.0 mL, 2.5 M solution in hexane) was added slowly to the stirred solution at 0 °C. The mixture was allowed to warm to room temperature while it was stirred for ca. 1 h. This solution of $LiOCH_2CF_3$ was transferred via cannula to the addition funnel on the other flask and was then added slowly to the stirred solution of **18** at 0 °C. The mixture was then allowed to warm to room temperature and stirred overnight. Solvents were removed under reduced pressure, and hexane (ca. 125 mL) was added to extract the product from the salts. The mixture was filtered under reduced pressure, the salts were washed with hexane (3 × 20 mL), and the washings were combined with the filtrate. Solvent removal, followed by fractional distillation, afforded product **25** as a colorless liquid. Yield: 90%. Bp: 40−47 °C (0.8 mmHg). ^{1}H NMR: δ −0.09 (s, *Me*$_2$Si), 0.80 (s, *Me*$_3$C), 1.41 (d, P*Me*, J_{PH} = 13.9), 4.17 (dq, O*CH*$_2$, J_{PH} = 10.0, J_{FH} = 8.7). ^{13}C NMR: δ −1.33 (d, *Me*$_2$Si, J_{PC} = 24.3), 18.5 (d, Me$_3$*C*, J_{PC} = 4.9), 26.5 (s, *Me*$_3$C), 19.4 (d, P*Me*, J_{PC} = 93.8), 59.4 (dq, O*CH*$_2$, J_{PC} = 5.2, J_{FC} = 36.6), 123.9 (dq, *CF*$_3$, J_{PC} = 7.4, J_{FC} = 278). ^{31}P NMR: δ 30.0. Anal. Calcd for $C_{10}H_{23}F_3NOPSi$: C, 41.51; H, 8.01. Found: C, 41.63; H, 8.00.

26 (R = Me, R′ = Ph). The same procedure, using the *P*-bromophosphoranimine **19**, gave product **26** as a colorless, distillable liquid. Yield: 56%. Bp: 66−70 °C (0.01 mmHg). ^{1}H NMR: δ −0.05 (s, *Me*$_2$Si), 0.84 (s, *Me*$_3$C), 1.59 (d, P*Me*, J_{PH} = 14.3), 3.7−4.3 (m, O*CH*$_2$), 7.3−7.7 (m, *Ph*). ^{13}C NMR: δ −1.18 (d, *Me*$_2$Si, J_{PC} = 4.5), 18.7 (d, Me$_3$*C*, J_{PC} = 5.1), 26.6 (s, *Me*$_3$C), 18.9 (d, P*Me*, J_{PC} = 95.2), 59.6 (m, O*CH*$_2$, J_{PC} = 4.9), 123.9 (m, *CF*$_3$, J_{FC} = 272), 133.9 (d, P*Ph*, J_{PC} = 134), 128.7 (d, *o-Ph*, J_{PC} = 13.2), 131.4 (d, *m-Ph*, J_{PC} = 10.7), 131.9 (d, *p-Ph*, J_{PC} = 2.6). ^{31}P NMR: δ 20.9. Anal. Calcd for $C_{15}H_{25}F_3NOPSi$: C, 51.27; H, 7.17. Found: C, 51.22; H, 7.20.

28 (R = R′ = Me). The same procedure, using the *P*-bromophosphoranimine **18** and LiOPh (prepared from PhOH and *n*-BuLi as described above) instead of $LiOCH_2CF_3$, gave product **28** as a colorless, distillable liquid. Yield: 85%. Bp: 55−58 °C (0.01 mmHg). ^{1}H NMR: δ −0.21 (s, *Me*$_2$Si), 0.74 (s, *Me*$_3$C), 1.49 (d, P*Me*, J_{PH} = 13.6), 7.0−7.2 (m, *Ph*). ^{13}C NMR: δ −1.42 (d, *Me*$_2$-Si, J_{PC} = 2.7), ca. 19 (Me$_3$*C*, obscured by P*Me* signal), 26.6 (s, *Me*$_3$C), 19.3 (d, P*Me*, J_{PC} = 95.7), 151.8 (d, O*Ph*, J_{PC} = 9.4), 121.6 (d, *o-Ph*, J_{PC} = 4.5), 129.5 (s, *m-Ph*), 124.2 (s, *p-Ph*). ^{31}P NMR: δ 24.8. Anal. Calcd for $C_{14}H_{26}NOPSi$: C, 59.33; H, 9.25. Found: C, 59.39; H, 9.40.

29 (R = Me, R′ = Ph). The same procedure, using the *P*-bromophosphoranimine **19** and LiOPh (prepared from PhOH and *n*-BuLi as described above) instead of $LiOCH_2CF_3$, gave product **29** as a colorless, distillable liquid. Yield: 92%. Bp: 100−115 °C (0.01 mmHg). ^{1}H NMR: δ −0.13 (d, *Me*$_2$Si, J_{PH} = 1.3), −0.14 (d, *Me*$_2$Si, J_{PH} = 1.2), 0.81 (d, *Me*$_3$C, J_{PH} = 1.3), 1.70 (d, P*Me*, J_{PH} = 13.9), 6.9−7.9 (m, *Ph*). ^{13}C NMR: δ −1.22 (d, *Me*$_2$Si, J_{PC} = 1.8), −1.34 (d, *Me*$_2$Si, J_{PC} = 2.1), 18.7 (d, Me$_3$*C*, J_{PC} = 5.6), 26.7 (s, *Me*$_3$C), 19.8 (d, P*Me*, J_{PC} = 97.4), 135.2 (d, P*Ph*, J_{PC} = 138), 128.5 (d, P-*o-Ph*, J_{PC} = 13.2), 131.5 (d, P-*m-Ph*, J_{PC} = 10.6), 131.5 (s, P-*p-Ph*), 152.0 (d, O*Ph*, J_{PC} = 8.6), 121.3 (d, O-*o-Ph*, J_{PC} = 5.1), 129.4 (s, O-*m-Ph*), 123.9 (s, O-*p-Ph*). ^{31}P NMR: δ 15.6. Anal. Calcd for $C_{19}H_{28}NOPSi$: C, 66.05; H, 8.17. Found: C, 65.96; H, 7.94.

30 (R = Ph, R′ = Me). The same procedure, using the *P*-bromophosphoranimine **20** and LiOPh (prepared from PhOH and *n*-BuLi as described above) instead of $LiOCH_2CF_3$, gave product **30** as a colorless, distillable liquid that solidified on standing. Recrystallization from hexane/CH_2Cl_2 (1:1 by volume) gave crystals of **30** that were suitable for X-ray diffraction. Yield: 71%. Bp: 140−162 °C (0.01 mmHg). ^{1}H NMR: δ 0.97 (s, *Me*$_3$C), 1.47 (d, P*Me*, J_{PH} = 13.8), 7.0−7.6 (m, *Ph*). ^{13}C NMR: δ 19.7 (d, Me$_3$*C*, J_{PC} = 4.4), 27.7 (s, *Me*$_3$C), 19.2 (d, P*Me*, J_{PC} = 96.0), 139.8 (d, Si*Ph*, J_{PC} = 2.1), 135.6 (s, Si-*o-Ph*), 129.6 (s, Si-*m-Ph*), 127.2 (s, Si-*p-Ph*), 151.6 (d, O*Ph*, J_{PC} = 9.2), 121.7 (d, O-*o-Ph*, J_{PC} = 4.3), 124.3 (d, O-*m-Ph*, J_{PC} = 1.5), 128.4 (s, O-*p-Ph*). ^{31}P NMR: δ 25.0. Anal. Calcd for $C_{24}H_{30}NOPSi$: C, 70.73; H, 7.42. Found: C, 68.08; H, 7.35.

31 (R = Me, R′ = CH$_2$CF$_3$). The same procedure, using the *P*-bromophosphoranimine **23**, gave product **31** as a colorless, distillable liquid. Yield: 95%. Bp: 48−55 °C (0.1 mmHg). ^{1}H NMR: δ 0.36 (q, Me*CH*$_2$Si, J_{HH} = 7.9), 0.82 (t, *Me*CH$_2$Si, J_{HH} = 7.9), 1.38 (d, P*Me*, J_{PH} = 13.9), 4.12 (m, O*CH*$_2$, J_{FH} = 9.0). ^{13}C NMR: δ 7.68 (s, Me*CH*$_2$Si), 7.71 (s, *Me*CH$_2$Si), 19.5 (d, P*Me*, J_{PC} = 93.7), 59.4 (m, O*CH*$_2$, J_{PC} = 5.2), 123.9 (dq, *CF*$_3$, J_{PC} = 7.8, J_{FC} = 278). ^{31}P NMR: δ 30.3. Anal. Calcd for $C_{10}H_{23}F_3NOPSi$: C, 41.51; H, 8.01. Found: C, 41.63; H, 7.88.

32 (R = Me, R′ = Ph). The same procedure, using the *P*-bromophosphoranimine **23** and LiOPh (prepared from PhOH and *n*-BuLi as described above) instead of $LiOCH_2CF_3$, gave product **32** as a colorless, distillable liquid. Yield: 60%. Bp: 63−64 °C (0.01 mmHg). ^{1}H NMR: δ 0.32 (q, Me*C*H_2Si, J_{HH} = 7.8), 0.78 (t, *Me*CH_2Si, J_{HH} = 7.9), 1.49 (d, P*Me*, J_{PH} = 13.8), 7.0−7.2 (m, *Ph*). ^{13}C NMR: δ 7.61 (d, Me*C*H_2Si, J_{PC} = 3.3), 7.69 (s, *Me*CH_2Si), 19.4 (d, P*Me*, J_{PC} = 95.7), 151.9 (d, O*Ph*, J_{PC} = 9.0), 121.4 (d, *o-Ph*, J_{PC} = 4.5), 124.1 (d, *m-Ph*, J_{PC} = 1.5), 129.5 (s, *p-Ph*). ^{31}P NMR: δ 24.8. Anal. Calcd for $C_{14}H_{26}NOPSi$: C, 59.33; H, 9.25. Found: C, 59.25; H, 9.62.

33 (R = Me, R′ = CH_2CF_3). The same procedure, using the *P*-bromophosphoranimine **24**, gave product **33** as a colorless, distillable liquid. Yield: 89%. Bp: 64−67 °C (0.01 mmHg). ^{1}H NMR: δ 0.48 (q, Me*C*H_2Si, J_{HH} = 7.8), 0.91 (t, *Me*CH_2Si, J_{HH} = 7.8), 1.62 (d, P*Me*, J_{PH} = 14.3), 3.7−3.9 (m, O*C*H_2, J_{FH} = 8.4), 4.1−4.3 (m, O*C*H_2, J_{FH} = 8.5), 7.5−7.8 (m, *Ph*). ^{13}C NMR: δ 7.86 (d, Me*C*H_2Si, J_{PC} = 2.8), 7.75 (s, *Me*CH_2Si), 19.1 (d, P*Me*, J_{PC} = 96.0), 59.6 (m, O*C*H_2, J_{PC} = 4.9), 123.9 (dq, *C*F_3, J_{PC} = 10.4, J_{FC} = 278), 134.1 (d, P*Ph*, J_{PC} = 135), 128.6 (d, *o-Ph*, J_{PC} = 13.3), 131.4 (d, *m-Ph*, J_{PC} = 10.7), 131.8 (d, *p-Ph*, J_{PC} = 2.8). ^{31}P NMR: δ 20.1. Anal. Calcd for $C_{15}H_{25}F_3NOPSi$: C, 51.27; H, 7.17. Found: C, 51.14; H, 7.35.

34 (R = Me, R′ = Ph). The same procedure, using the *P*-bromophosphoranimine **24** and LiOPh (prepared from PhOH and *n*-BuLi as described above) instead of $LiOCH_2CF_3$, gave product **34** as a colorless, distillable liquid. Yield: 81%. Bp: 118−119 °C (0.01 mmHg). ^{1}H NMR: δ 0.42 (q, Me*C*H_2Si, J_{HH} = 7.9), 0.86 (t, *Me*CH_2Si, J_{HH} = 7.9), 1.72 (d, P*Me*, J_{PH} = 13.6), 6.9−7.9 (m, *Ph*). ^{13}C NMR: δ 7.68 (d, Me*C*H_2Si, J_{PC} = 3.3), 7.76 (s, *Me*CH_2Si), 19.9 (d, P*Me*, J_{PC} = 98.3), 135.2 (d, P*Ph*, J_{PC} = 136), 128.5 (d, P-*o-Ph*, J_{PC} = 13.3), 131.5 (d, P-*m-Ph*, J_{PC} = 10.6), 131.5 (s, P-*p-Ph*), 152.0 (d, O*Ph*, J_{PC} = 8.8), 121.2 (d, O-*o-Ph*, J_{PC} = 4.9), 129.3 (s, O-*m-Ph*), 123.8 (s, O-*p-Ph*). ^{31}P NMR: δ 14.3. Anal. Calcd for $C_{19}H_{28}NOPSi$: C, 66.05; H, 8.17. Found: C, 65.81; H, 8.55.

Compound 35. The same procedure, using the *P*-bromophosphoranimine **22** and $LiOCH_2CF_3$ in a 1:2 mole ratio, gave product **35** as a colorless, distillable liquid. The product contained small amounts of unidentified impurities. Yield: 20%. Bp: 110−130 °C (0.01 mmHg). ^{1}H NMR: δ 1.35 (d, *Me*$_3$C, J_{PH} = 2.1), 4.42 (m, O*C*H_2, J_{FH} = 8.2), 7.5−8.2 (m, *Ph*). ^{13}C NMR: δ 19.8 (d, Me_3C, J_{PC} = 4.4), 27.6 (s, *Me*$_3$C), 62.0 (dq, O*C*H_2, J_{PC} = 5.2, J_{FC} = 37.4), 125.0 (dq, *C*F_3, J_{PC} = 10.7, J_{FC} = 278), ca. 135 (obscured by other signals, P*Ph*), 128.8 (d, P-*o-Ph*, J_{PC} = 16.2), 131.8 (d, P-*m-Ph*, J_{PC} = 10.8), 132.8 (s, P-*p-Ph*), 138.1 (d, Si*Ph*, J_{PC} = 2.2), 135.4 (s, Si-*o-Ph*), 129.1 (s, Si-*m-Ph*), 127.7 (s, Si-*p-Ph*). ^{31}P NMR: δ 5.9.

Preparation of the Cyclic Compound 36. A freshly prepared sample of the *P*-chlorophosphine **7** (9.4 g, 0.020 mol) was transferred under N_2 to a heavy-walled glass ampule (ca. 25 mL) that was then evacuated and sealed. The tube was placed in a protective metal pipe and then heated in an oven at 200 °C for 7 days. After being cooled to room temperature, the pipe was opened. The ampule contained a colorless liquid, a waxy brown solid, and an orange, powdery solid. The tube was cooled to −196 °C, opened, and quickly attached to a standard vacuum line. As the contents warmed to room temperature, the volatile product was collected in a U-trap and subsequently identified as Me_3SiCl (2.05 g, 94% yield) by ^{1}H and ^{13}C NMR spectroscopy. After the tube was filled with N_2, CH_2Cl_2 (5 mL) was added and appeared to dissolve all except the orange solid. The CH_2Cl_2 solution was removed via syringe and added to a large volume (ca. 300 mL) of hexane. After the insoluble material was allowed to settle, the supernatant liquid was decanted and the solvent was removed under reduced pressure, leaving a white solid (ca. 50% yield). Recrystallization from a minimal amount of hexane/CH_2Cl_2 (1:1 by volume) gave product **36** as white crystals that were suitable for X-ray diffraction. ^{1}H NMR: δ 0.75 (s, *Me*$_3$C), 0.97 (s, *Me*$_3$C), 6.4−8.3 (m, *Ph*). ^{13}C NMR: δ 20.1 (m, Me_3C), 28.5 (m, *Me*$_3$C), 126.8−145.0 (m, *Ph*). ^{31}P NMR: δ 1.6 [d, *P*(V), J_{PP} = 48.9], 96.8 [d, *P*(III), J_{PP} = 48.9].

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