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Synthesis, Structure, and Reactivity of Some *N*-Phosphorylphosphoranimines

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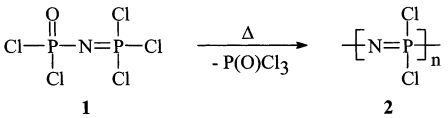
A large series of new *N*-phosphorylphosphoranimines that bear potentially reactive functional groups on both phosphorus centers were prepared by silicon–nitrogen bond cleavage reactions of *N*-silylphosphoranimines. Thus, treatment of the *N*-silylphosphoranimines, $Me_3SiN{=}P(Me)(R)X$ (R = Me, Ph; X = OCH_2CF_3 and R = Me, X = OPh), with phosphoryl chlorides, $RP(=O)Cl_2$ (R′ = Cl, Me, Ph), readily afforded the corresponding *N*-phosphoryl derivatives, $R'P(=O)(Cl){-}N{=}P(Me)(R)X$, in high yields. Subsequent reaction with 1 or 2 equiv of the silylamine, Me_3SiNMe_2, resulted in ligand exchange at the phosphoryl (P═O) group to give the *P*-dimethylamino analogues, $R'P(=O)(NMe_2)N{=}P(Me)(R)X$ (R′ = Cl, NMe_2, Me, Ph; R = Me, Ph; X = OCH_2CF_3, OPh). These new *N*-phosphorylphosphoranimines (and one thiophosphoryl analogue) were obtained as thermally stable, distillable liquids and were characterized by NMR (^1H, ^{13}C, and ^{31}P) spectroscopy and elemental analysis. One member of the series, $Cl_2P(=O)N{=}P(Me)(Ph)OCH_2CF_3$ (**4**), was also studied by single-crystal X-ray diffraction which revealed that the formal P(O)—N single bond [1.55(1) Å] is shorter than the formal $N{=}PR_2X$ double bond [1.60(1) Å]. Such structural features are compared to those of similar compounds and discussed in relationship to the unexpected thermolysis pathways observed for these *N*-phosphorylphosphoranimines, none of which produced poly(phosphazenes).

Introduction

The thermal condensation polymerization of many *N*-silylphosphoranimines, for example, $Me_3SiN{=}P(Me)(R)X$ (R = Me, Ph; X = OCH_2CF_3, OPh), is well-established as an efficient synthetic route to poly(alkyl/aryl-phosphazenes), $[N{=}P(Me)(R)]_n$.[1,2] In a related process, developed by De Jaeger,[3] poly(dichlorophosphazene) (**2**) can be prepared by condensation polymerization (eq 1) of the *N*-phosphoryl-phosphoranimine **1**.



1 **2** (1)

In this context, we were interested in the possibility of using this type of process to prepare substituted poly(phosphazenes) from suitable *N*-phosphorylphosphoranimines[4] bearing alkyl/aryl substituents. Some related *N*-phosphorylphosphoranimines have been reported and structurally characterized,[5,6] but generally, they do not contain the requisite functional groups on phosphorus. The reactivity of the Si—N bond in *N*-silylphosphoranimines toward nonmetal halides has been utilized to prepare many other Si—N═P[7] and B—N═P[8] derivatives. It seemed appropriate, therefore, to investigate the possible synthesis of P—N═P systems in a similar manner. We report here on the synthesis, structural characterization, and reactivity of a large series of new

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(1) (a) Wisian-Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 2848. (b) Neilson, R. H.; Hani, R.; Wisian-Neilson, P.; Meister, J. J.; Roy, A. K.; Hagnauer, G. L. *Macromolecules* **1987**, *20*, 910. (c) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541.

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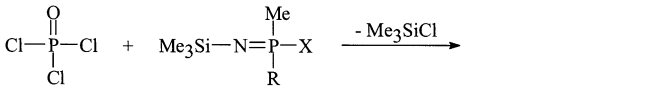
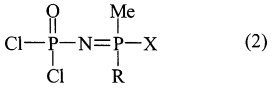
N-phosphorylphosphoranimines that bear useful functional groups on both phosphorus centers.

Results and Discussion

Synthesis of *N*-Phosphorylphosphoranimines. Phosphoryl chloride, $P(O)Cl_3$, reacted smoothly in a 1:1 mole ratio with appropriate *N*-silylphosphoranimines (eq 2) in Et_2O or CH_2Cl_2 solution at 0 °C to afford the new *N*-phosphorylphosphoranimines **3**−**5**. These P−N═P products were formed quantitatively (as indicated by ^{31}P NMR spectroscopy of the reaction mixtures) and were isolated in good yields as high boiling liquids by vacuum distillation. They were fully characterized by NMR spectroscopy and elemental analyses. Compounds **3** and **4** solidified on standing, and crystals of **4** suitable for X-ray diffraction analysis (see description later) were obtained.



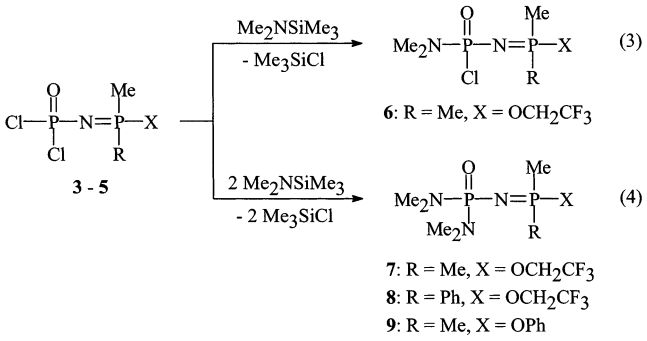


(2)

3: R = Me, X = OCH_2CF_3
4: R = Ph, X = OCH_2CF_3
5: R = Me, X = OPh

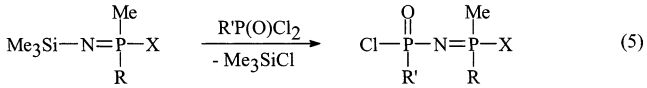
The structures of compounds **3**−**5** were easily confirmed by multinuclear NMR (^1H, ^{13}C, and ^{31}P) spectroscopy. They all exhibit two doublets in the ^{31}P NMR spectrum with a 2-bond P−P coupling constant of 16−18 Hz. The dichlorophosphoryl center [$Cl_2P(O)$—] appears as an upfield doublet (ca. −5 to −9 ppm) while the phosphoranimine center [—N═PR_2X] appears as a downfield doublet (ca. 40−54 ppm). The presence of two phosphorus atoms in each molecule is also readily apparent in the ^{13}C NMR spectra. For example, the *P*-methyl signals for **3** and **5** [e.g., **3**: δ 15.4 (dd, PCH_3, $^1J_{PC}$ = 92.0, $^3J_{PC}$ = 4.6)] and the aryl P−C signal in **4** [δ 124.1 (dd, P—C_{aryl}, $^1J_{PC}$ = 139.8, $^3J_{PC}$ = 10.1)] are observed as doubled doublets because of spin coupling to both the adjacent and remote phosphorus atoms. All other substituents, notably the trifluoroethoxy groups in **3** and **4**, were observed with the expected peak multiplicities and intensities in the ^1H and ^{13}C NMR spectra.

Interestingly, attempts to replace two chlorine atoms on the phosphoryl center by using 2 equiv of the *N*-silylphosphoranimines were unsuccessful and gave only the same monosubstituted products. The P−Cl bonds, however, were reactive toward other silicon−nitrogen reagents. The *N*-(dichlorophosphoryl)phosphoranimines **3**−**5** reacted smoothly at 0 °C with the simple silylamine, Me_3SiNMe_2, in either 1:1 (eq 3) or 2:1 (eq 4) stoichiometry to afford the respective *P*-dimethylamino derivatives **6**−**9**. The presence of the dimethylamino groups on the phosphoryl center served to decrease the boiling points and increase the thermal stability of these products relative to their *N*-(dichlorophosphoryl)-phosphoranimine analogues. A significant downfield shift ($\Delta\delta \sim 20-25$ ppm) for the phosphoryl signal and an increase in the P−P coupling constant ($\Delta^2J_{PP} \sim 3-9$ Hz) were observed in the ^{31}P NMR spectra of **6**−**9**. Additional signals in both the ^1H [e.g., **7**: δ 2.49 (d, N*Me*, J_{PH} = 14.2)] and ^{13}C [δ 16.4 (dd, N*Me*, $^2J_{PC}$ = 94.2, $^4J_{PC}$ = 4.0)] NMR spectra confirmed the presence of the dimethylamino groups.



The same *N*-silylphosphoranimines as used in eq 2 also reacted smoothly with methyl- and phenylphosphoryl chlorides to give the corresponding chloro(methyl) (**10**−**12**) and chloro(phenyl) (**13**−**14**) substituted *N*-phosphorylphosphoranimines (eq 5). The lower molecular weight compounds **10** and **11** were readily purified by fractional distillation and gave satisfactory elemental analyses. Some thermal decomposition occurred when compounds **12** and **13** were distilled at high temperature under vacuum. Accordingly, distillation of diphenyl substituted analogue **14** was not attempted. Nevertheless, all of these derivatives provided clean NMR spectra that were fully consistent with the proposed structures.

The ^{31}P NMR spectra revealed a marked downfield shift for the phosphoryl center ($\Delta\delta \sim 20-35$ ppm) in **10**−**14** relative to the dichlorophosphorylphosphoranimine analogues **3**−**5**. A noticeable decrease in the P−P coupling constants ($\Delta^2J_{PP} \sim 10$ Hz) was also apparent for compounds **10** and **11**, while no P−P coupling was observed for compound **12**. The ^1H and ^{13}C NMR spectra of compounds **10**−**12** contained doubled doublet patterns [e.g., **10**: ^1H NMR δ 1.79 (dd, CH_3P═O, $^2J_{PH}$ = 17.2, $^4J_{PH}$ = 2.2); ^{13}C NMR δ 24.7 (dd, CH_3P═O, $^1J_{PC}$ = 131.3, $^3J_{PC}$ = 9.0)] for the phosphoryl (P═O) methyl group, with spin coupling to two different phosphorus centers. Other NMR signals for the substituents attached to the P═N center were similar to those observed for analogous dichlorophosphoryl systems **3**−**5**.



10: R = Me, R' = Me, X = OCH_2CF_3
11: R = Ph, R' = Me, X = OCH_2CF_3
12: R = Me, R' = Me, X = OPh
13: R = Me, R' = Ph, X = OCH_2CF_3
14: R = Ph, R' = Ph, X = OCH_2CF_3

As was the case with the dichlorophosphoryl compounds (eqs 3 and 4), these monochloro analogues also reacted

(8) Shaw, Y. S.; Scheide, G. M.; Davis, C. E.; Mukherjee, P.; Neilson, R. H. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *41*, 141. (b) Neilson, R. H.; Azimi, K.; Zhang, G.; Kucera, W. R.; Longlet, J. L. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *87*, 157. (c) Azimi, K.; Neilson, R. H. *J. Cluster Sci.*, submitted for publication.

smoothly with the silylamine, Me_3SiNMe_2, to afford the corresponding $P-NMe_2$ derivatives (eq 6). In these reactions, the chloro(methyl)phosphorylphosphoranimines **10**−**13** were prepared as described and then treated with the silylamine in a one-pot procedure without distilling the P−Cl intermediates.

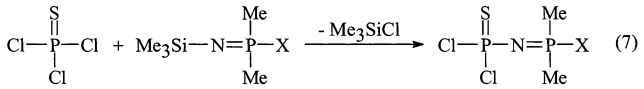
(6)

10 - 13

15: R = Me, R' = Me, X = OCH_2CF_3
16: R = Ph, R' = Me, X = OCH_2CF_3
17: R = Me, R' = Me, X = OPh
18: R = Me, R' = Ph, X = OCH_2CF_3

The desired dimethylamino derivatives **15**−**18** were obtained in good yields as thermally stable, distillable liquids (**18** solidified on standing) that were fully characterized by NMR spectroscopy and elemental analyses. The ^1H and ^{13}C NMR spectra showed the expected signals for the dimethylamino group as noted for the other $P-NMe_2$ compounds already described.

To investigate a possible extension of this type of chemistry to the thiophosphoryl (P═S) analogues, one reaction was studied. Treatment of the *N*-silylphosphoranimine, $Me_3SiN{=}PMe_2OCH_2CF_3$, with thiophosphoryl chloride, $P(S)C1_3$, (eq 7) readily gave *N*-(dichlorothiophosphoryl)-phosphoranimine **19** in good yield as a stable, distillable liquid. The ^{31}P NMR spectrum of this product contains two doublets at 38.9 (P═S) and 54.4 ppm (P═N) with a $^2J_{PP}$ value of 12.2 Hz. In further confirmation of the structure, the ^{13}C NMR contains a doubled doublet for the *P*-methyl carbons [δ 15.6 (dd, P*C*H_3, $^1J_{PC}$ = 91.8, $^3J_{PC}$ = 4.4)].



(7)

19: X = OCH_2CF_3

The NMR spectral data for several of these new *N*-phosphorylphosphoranimines provided additional information about their structures and stereochemistry. Compounds **11**, **14**, and **16** each have two asymmetric centers at the P═O and P═N phosphorus atoms, respectively. As a result, two sets of data, one for each diastereomer, are observed in the ^1H, ^{13}C, and ^{31}P NMR spectra. For example, the ^{31}P NMR spectrum of **11** consists of doublets at 42.2 (P═N) and 29.5 (P═O) ppm with a $^2J_{PP}$ value of 6.8 Hz for one isomer and doublets at 41.5 (P═N) and 29.3 (P═O) ppm with a $^2J_{PP}$ value of 7.1 Hz for the other diastereomer. Similar spectra were observed for compounds **14** and **16**. The two diastereomers of compounds **11**, **14**, and **16** were observed in approximately equal proportions by ^{31}P NMR spectroscopy. No attempts were made to separate the isomers.

In addition, several compounds (**6**, **10**, **12**, **13**, **15**, and **17**) that have asymmetry only at the phosphoryl (P═O) center exhibit magnetically nonequivalent N═P*Me*$_2$ groups. These diastereomeric groups are generally observed as two different signal patterns in the ^{13}C NMR spectrum and sometimes in the ^1H NMR spectrum. Similarly, as a result of asymmetry at the other phosphorus (P═N) center, compound **8** exhibits diastereotopic N*Me*$_2$ groups in the ^1H and ^{13}C NMR spectra.

Table 1. Crystal Data for *N*-Phosphorylphosphoranimine **4**

empirical formula	$C_9H_{10}O_2P_2Cl_2NF_3$
fw	353.03
crystal dimensions (mm^3)	0.35 × 0.35 × 0.40
crystal syst	monoclinic
space group	$P2_1/c$ (#14)
lattice parameters	a = 11.187(3) Å
	b = 10.955(2) Å
	c = 11.872(2) Å
	β = 90.135(3)°
	V = 1454.9(9) A^3
Z value	4
total obsd reflns	1045
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.119
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum wF_o^2]^{1/2}$	0.113
diffractometer	Rigaku AFC6S
radiation	Cu Kα (λ = 1.54178 Å)

Table 2. Intramolecular Distances[a] Involving the Non-Hydrogen Atoms for Compound **4**

atom	atom	distance	atom	atom	distance
Cl1	P1	2.016(7)	F3	C2	1.12(3)
Cl2	P1	2.035(8)	O2	C1	1.45(3)
P1	O1	1.45(1)	C1	C2	1.57(3)
P1	N1	1.55(1)	C4	C5	1.38(3)
P2	O2	1.59(1)	C4	C9	1.36(4)
P2	N1	1.60(1)	C5	C6	1.37(3)
P2	C3	1.79(3)	C6	C7	1.34(4)
P2	C4	1.79(2)	C7	C8	1.35(3)
F1	C2	1.19(4)	C8	C9	1.37(3)
F2	C2	1.41(5)			

[a] Distances are in angstroms (Å) with standard deviations in the least significant figure given in parentheses.

Table 3. Intramolecular Bond Angles[a] Involving the Non-Hydrogen Atoms for Compound **4**

atom	atom	atom	angle	atom	atom	atom	angle
Cl1	P1	C12	100.3(3)	F1	C2	F2	111(3)
Cl1	P1	O1	110.4(7)	F1	C2	F3	116(5)
Cl1	P1	N1	108.1(6)	F1	C2	C1	109(3)
C12	P1	O1	108.4(7)	F2	C2	F3	110(4)
C12	P1	N1	110.6(9)	F2	C2	C1	101(3)
O1	P1	N1	117.7(7)	F3	C2	C1	109(2)
O2	P2	N1	113.2(8)	P2	C4	C5	119(2)
O2	P2	C3	101.3(7)	P2	C4	C9	121(1)
O2	P2	C4	106.6(7)	C5	C4	C9	120(2)
N1	P2	C3	117.9(9)	C4	C5	C6	119(3)
N1	P2	C4	106.8(8)	C5	C6	C7	120(2)
C3	P2	C4	110(1)	C6	C7	C8	121(2)
P2	O2	C1	121(2)	C7	C8	C9	119(3)
P1	N1	P2	137(1)	C4	C9	C8	120(2)
O2	C1	C2	106(2)				

[a] Angles are in degrees with estimated standard deviations in the least significant figure given in parentheses.

Structure of *N*-Phosphorylphosphoranimines. While most of the new phosphoranimines reported here are liquids, compounds **3**, **4**, **13**, and **18** were obtained as low-melting solids. In the case of $Cl_2P(=O)$-N═P(Ph)(Me)OCH_2CF_3 (**4**), recrystallization from Et_2O afforded crystals suitable for X-ray diffraction. The resulting crystallographic data, selected bond lengths, and bond angles are summarized in Tables 1, 2, and 3, respectively, and the molecular structure is depicted in Figure 1.

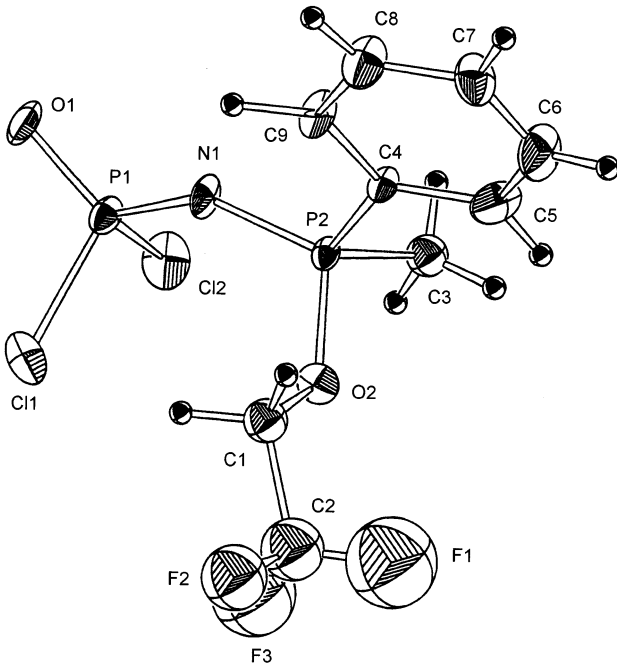
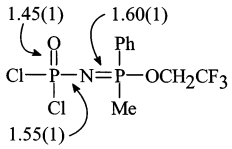
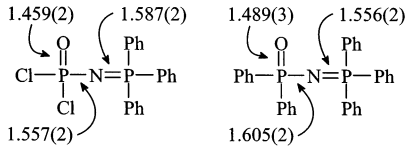


Figure 1. ORTEP representation of compound **4**. Thermal ellipsoids are drawn at the 50% probability level.

The X-ray diffraction study of **4** revealed the expected tetrahedral geometry at both 4-coordinate phosphorus centers and a central P—N—P bond angle of 137(1)°. The P—N bond distances are somewhat more interesting and, in the structures shown, are compared to data previously reported[5] for two similar compounds **20** and **21**. In the two dichlorophosphoryl derivatives **4** and **20**, the formal P(O)—N single bond is found to be shorter than the formal P═N double bond of the phosphoranimine group. This is in contrast to diphenylphosphoryl analogue **21** which exhibits more expected bond lengths of 1.603(5) and 1.553(5) Å for the formal single and double bonds, respectively.



4

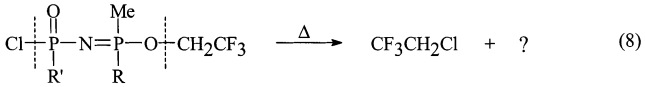


20

21

This apparent discrepancy in expected bond lengths is attributed[5] to electronic effects of the substituents on the phosphoryl center. The electronegative chlorine atoms withdraw electron density from phosphorus, thus enhancing any possibile π delocalization within the P—N—P unit. A similar shortening is also observed for the P═O double bond lengths in **4** and **20** compared to **21**. The fact that the P—N bond order to the phosphoryl center is somewhat greater than that in the phosphoranimine moiety in compounds such as **4** may help to account for the unexpected thermal degradation pathways (see later) that were observed for some of these *N*-phosphorylphosphoranimines.

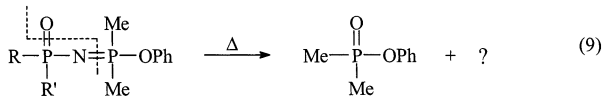
Thermolysis Reactions of *N*-phosphorylphosphoranimines. As noted earlier, the De Jaeger process[3] (eq 1) for preparing poly(dichlorophosphazene) involves the thermal condensation polymerization of *N*-(dichlorophosphoryl)-*P*-trichlorophosphoranimine **1**. We were interested in ascertaining whether these new alkyl/aryl substituted *N*-phosphorylphosphoranimines would exhibit similar thermolysis chemistry. Thus, the thermal decomposition reactions of selected *N*-phosphorylphosphoranimines were carried out in sealed, evacuated tubes that were heated to ca. 180−200 °C for several hours or days. In the case of the *P*-trifluoroethoxy compounds (eq 8), a volatile product generated, in high yield, during the heating period was identified as CF_3CH_2Cl by ^1H and ^{13}C NMR spectroscopy as well as GC/MS. Unfortunately, the solid residues that formed during thermolysis were only slightly soluble and showed numerous broad, undefined peaks in the ^{31}P NMR spectra.



(8)

3: R = Me, R' = Cl
4: R = Ph, R' = Cl
11: R = Ph, R' = Me
12: R = R' = Ph

The *P*-phenoxy compounds (eq 9) underwent a different, but equally surprising, fragmentation process upon thermolysis. In this case, the only characterizable product was the phosphine oxide $Me_2P(O)OPh$[9] which was identified by ^1H, ^{13}C, and ^{31}P NMR spectroscopy as well as GC/MS. Interestingly, the remaining fragment should have the composition of the phosphazene, $[NP(R)R']_n$. The dark solid products of these reactions, however, were insoluble in common solvents and were not further characterized. No cyclic or polymeric phosphazenes could be conclusively identified in the reaction mixture.



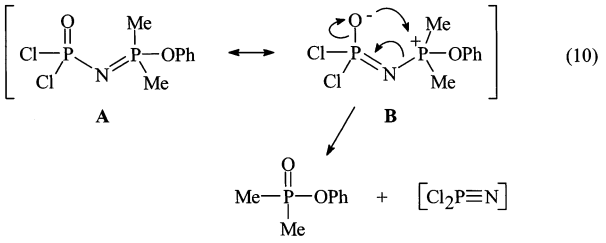
(9)

5: R = R' = Cl
9: R = R' = NMe_2
12: R = Cl, R' = Me

This particular thermolysis pattern is very interesting because it suggests that the thermal decomposition of $Cl_2P(O)N{=}PCl_3$ may not be as simple as indicated in eq 1. The results of the X-ray diffraction study of compound **4** may also be relevant here (eq 10). The observation of a short P—N bond to the phosphoryl center suggests a substantial contribution of resonance structure **B**. To whatever extent this may occur, it could facilitate bond formation between the phosphoryl oxygen and the phosphoranimine phosphorus

(9) Abraham, K. M.; Van Wazer, J. R. *J. Inorg. Nucl. Chem.* **1975**, *37*, 541.

and help to account for the otherwise unexpected formation of the phosphine oxide, $Me_2P(O)OPh$.



Further studies related to the possible polymerization of these and related *N*-phosphoryl-, *N*-boryl-, and *N*-silylphosphoranimine systems are in progress.

Experimental Section

Materials and General Procedures. The starting phosphoranimines, $Me_3SiN{=}P(Me)(R)OR'$ (R = Me, Ph; R′ = CH_2CF_3, Ph), were prepared according to published procedures.[10] Ether and CH_2Cl_2 were distilled under N_2 from CaH_2 immediately prior to use. The reagents $P(O)Cl_3$, $MeP(O)Cl_2$, $PhP(O)Cl_2$, $P(S)Cl_3$, and Me_3SiNMe_2 were obtained from commercial sources and used without further purification. Proton, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian XL-300 spectrometer using $CDCl_3$ 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. Elemental analyses were performed by E&R Microanalytical Laboratory, Inc., Corona, NY. GC/MS was done 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 **4** were collected at room temperature on a Rigaku AFC6S diffractometer with graphite-monochromated Cu Kα radiation, $\lambda = 1.54178$ Å. Crystallographic data are summarized in Table 1. The structure was solved using direct methods[11] and refined using the Texsan program package.[12] All non-hydrogen atoms were refined aniosotropically, while H atoms were constrained with a riding model. Selected bond distances and angles are listed in Tables 2 and 3, respectively. Further details regarding the crystal data and refinement, as well as full tables of bond lengths and angles for the structure of **4**, were deposited in CIF format at the Cambridge Crystallographic Data Centre and are available as Deposit Number 188270.

Preparation of *N*-(Dichlorophosphoryl)phosphoranimines, $Cl_2P(O)$-N=P(Me)(R)X. 3: R = Me, X = OCH_2CF_3. A three-neck, 100 mL flask was equipped with a magnetic stir bar, N_2 inlet, and a rubber septum. It was charged with Et_2O (50 mL) and $P(O)Cl_3$ (7.67 g, 50.0 mmol) and then cooled to 0 °C. The phosphoranimine, $Me_3SiN{=}P(Me)_2OCH_2CF_3$ (11.9 g, 48.1 mmol), was added dropwise via syringe to the stirred solution. After stirring for 0.5 h at 0 °C, the reaction mixture was allowed to warm to room temperature and was then stirred for an additional 1.5 h. The volatile components were removed under reduced pressure. Distillation gave product **3** as a colorless liquid that solidified to a white solid in the receiving flask. Yield: 78%. Bp: 122−125 °C (0.08 mmHg). Mp: 32−34 °C. ^1H NMR: δ 1.82 (d, PCH_3, $J_{PH} = 13.9$), 4.37 (dq, OCH_2, $J_{PH} = 9.7$, $J_{FH} = 8.1$). ^{13}C NMR: δ 15.4 (dd, PCH_3, $^1J_{PC} = 92.0$, $^3J_{PC} = 4.6$), 61.9 (dq, OCH_2, $J_{PC} = 6.6$, $J_{FC} = 37.8$), 122.2 (dq, CF_3, $J_{PC} = 8.8$, $J_{FC} = 276.1$). ^{31}P NMR: δ −6.7 (d, *P*=O, $J_{PP} = 18.3$), 53.9 (d, *P*=N, $J_{PP} = 18.3$). Anal. Calcd for $C_4H_8Cl_2F_3NO_2P_2$: C, 16.46; H, 2.76. Found: C, 16.12; H, 3.01.

4: R = Ph, X = OCH_2CF_3. The same procedure using $P(O)Cl_3$ and $Me_3SiN{=}P(Me)(Ph)OCH_2CF_3$ gave **4** as a colorless liquid that solidified to a white solid in the receiving flask. Yield: 91%. Bp: 135−140 °C (0.03 mmHg). Mp: 42−44 °C. ^1H NMR: δ 2.11 (d, PCH_3, $J_{PH} = 14.5$), 4.0−4.5 (m, OCH_2), 7.5−7.8 (m, P*Ph*). ^{13}C NMR: δ 15.1 (d, PCH_3, $J_{PC} = 93.2$), 61.8 (dq, OCH_2, $J_{PC} = 6.1$, $J_{FC} = 38.1$), 122.1 (dq, CF_3, $J_{PC} = 11.0$, $J_{FC} = 277.5$), 124.1 (dd, P*Ph*, $^1J_{PC} = 139.8$, $^3J_{PC} = 10.1$), 129.3 (d, *o-Ph*, $J_{PC} = 14.3$), 131.2 (d, *m-Ph*, $J_{PC} = 12.1$), 134.4 (d, *p-Ph*, $J_{PC} = 2.9$). ^{31}P NMR: δ −5.1 (d, *P*=O, $J_{PP} = 17.7$), 41.0 (d, *P*=N, $J_{PP} = 17.7$). Anal. Calcd for $C_9H_{10}Cl_2F_3NO_2P_2$: C, 30.53; H, 2.85. Found: C, 30.49; H, 2.98.

5: R = Me, X = OPh. The same procedure using $P(O)Cl_3$ and $Me_3SiN{=}PMe_2OPh$ gave **5** as a colorless liquid. Yield: 73%. Bp: 165−169 °C (0.03 mmHg). ^1H NMR: δ 1.77 (d, PCH_3, $J_{PH} = 14.3$), 7.0−7.3 (m, O*Ph*). ^{13}C NMR: δ 16.0 (dd, PCH_3, $^1J_{PC} = 93.3$, $^3J_{PC} = 5.0$), 150.1 (d, O*Ph*, $J_{PC} = 10.1$), 121.7 (d, *o-Ph*, $J_{PC} = 4.3$), 126.8 (d, *m-Ph*, $J_{PC} = 1.6$), 130.0 (s, *p-Ph*). ^{31}P NMR: δ −8.7 (d, *P*=O, $J_{PP} = 16.5$), 48.1 (d, *P*=N, $J_{PP} = 16.5$). Anal. Calcd for $C_8H_{11}Cl_2NO_2P_2$: C, 33.59; H, 3.88. Found: C, 32.82; H, 3.95.

Preparation of *N*-[(Dimethylamino)phosphoryl]phosphoranimines, $Cl(Me_2N)P(O)N{=}P(Me)(R)X$ (6) and $(Me_2N)_2P(O)N{=}P(Me)(R)X$ (7−9). 6: R = Me, X = OCH_2CF_3. A 1-neck, 100 mL flask was equipped with a magnetic stir bar, rubber septum, and a N_2 inlet needle. It was charged with CH_2Cl_2 (35 mL) and $P(O)Cl_3$ (6.75 g, 44.0 mmol) and then cooled to 0 °C. The phosphoranimine, $Me_3SiN{=}P(Me)_2OCH_2CF_3$ (10.7 g, 43.3 mmol), was added dropwise via a syringe to the stirred solution. After stirring for 0.5 h at 0 °C, the reaction mixture was allowed to warm to room temperature and was then stirred for an additional 0.5 h. The volatile components were removed under reduced pressure, leaving crude product **3**, $[Cl_2P(O)N{=}PMe_2OCH_2CF_3]$. Fresh CH_2Cl_2 (35 mL) was added, and the solution was cooled to 0 °C. The silylamine, Me_3SiNMe_2 (4.96 g, 42.3 mmol), was then added via syringe, and the mixture was stirred for 0.5 h while warming to room temperature. The volatile components were removed under reduced pressure. Distillation gave product **6** as a colorless liquid. Yield: 77%. Bp: 100−105 °C (0.05 mmHg). ^1H NMR: δ 1.75 (d, PCH_3, $J_{PH} = 14.3$), 1.76 (d, PCH_3, $J_{PH} = 14.3$), 2.56 (d, NMe_2, $J_{PH} = 15.5$), 4.39 (dq, OCH_2, $J_{PH} = 9.6$, $J_{FH} = 8.2$). ^{13}C NMR: δ 16.0 (d, PCH_3, $J_{PC} = 94.7$), 16.1 (d, PCH_3, $J_{PC} = 94.2$), 36.9 (s, NCH_3), 62.0 (dq, OCH_2, $J_{PC} = 6.4$, $J_{FC} = 37.3$), 122.6 (dq, CF_3, $J_{PC} = 8.7$, $J_{FC} = 277.7$). ^{31}P NMR: δ 15.3 (d, *P*=O, $J_{PP} = 24.7$), 54.8 (d, *P*=N, $J_{PP} = 24.7$). Anal. Calcd for $C_6H_{14}ClF_3N_2O_2P_2$: C, 23.98; H, 4.69. Found: C, 24.37; H, 4.64.

7: R = Me, X = OCH_2CF_3. The same procedure, using **3** and Me_3SiNMe_2 in a 1:2 mole ratio, gave **7** as a colorless liquid. Yield: 55%. Bp: 74−78 °C (0.03 mmHg). ^1H NMR: δ 1.59 (d, PCH_3, $J_{PH} = 14.2$), 2.49 (d, NCH_3, $J_{PH} = 10.2$), 4.36 (dq, OCH_2, $J_{PH} = 9.5$, $J_{FH} = 8.5$). ^{13}C NMR: δ 16.4 (d, PCH_3, $^1J_{PC} = 94.2$, $^3J_{PC} = 4.0$), 36.8 (d, NCH_3, $J_{PC} = 3.2$), 61.0 (dq, OCH_2, $J_{PC} = 5.8$, $J_{FC} = 37.2$), 122.9 (dq, CF_3, $J_{PC} = 8.3$, $J_{FC} = 277.6$). ^{31}P NMR: δ 16.8 (d, *P*=O, $J_{PP} = 20.8$), 48.7 (d, *P*=N, $J_{PP} = 20.8$). Anal. Calcd for $C_8H_{20}F_3N_3O_2P_2$: C, 31.08; H, 6.52. Found: C, 31.25; H, 6.33.

8: R = Ph, X = OCH_2CF_3. The same procedure, using **4** and Me_3SiNMe_2 in a 1:2 mole ratio, gave **8** as a colorless liquid.

(10) (a) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1980**, *19*, 1875. (b) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Synth.* **1989**, *25*, 69.
(11) Sheldrick, G. M. *SHELX86. Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, **1986**.
(12) *Texsan-Texray Structure Analysis Package*, Version 1.701; Molecular Structure Corporation: The Woodlands, TX, March, 1995.

Yield: 79%. Bp: 125−135 °C (0.05 mmHg). ^{1}H NMR: δ 1.89 (d, P*CH*$_3$, J_{PH} = 14.5), 2.60 (d, N*CH*$_3$, J_{PH} = 10.3), 2.61 (d, N*CH*$_3$, J_{PH} = 10.3), 4.0−4.6 (m, O*CH*$_2$), 7.4−7.9 (m, P*Ph*). ^{13}C NMR: δ 16.4 (d, P*CH*$_3$, J_{PC} = 92.5), 37.0 (d, N*CH*$_3$, J_{PC} = 7.5), 37.0 (d, N*CH*$_3$, J_{PC} = 7.6), 61.2 (dq, O*CH*$_2$, J_{PC} = 5.4, J_{FC} = 37.3), 122.9 (dq, *CF*$_3$, J_{PC} = 10.7, J_{FC} = 277.6), 129.7 (dd, P*Ph*, $^1J_{PC}$ = 141.0, $^3J_{PC}$ = 7.7), 128.7 (d, *o-Ph*, J_{PC} = 13.9), 131.1 (d, *m-Ph*, J_{PC} = 11.0), 132.8 (d, *p-Ph*, J_{PC} = 2.8). ^{31}P NMR: δ 16.5 (d, *P*═O, J_{PP} = 22.1), 36.3 (d, *P*═N, J_{PP} = 22.1). Anal. Calcd for $C_{13}H_{22}F_3N_3O_2P_2$: C, 42.06; H, 5.97. Found: C, 41.96; H, 6.08.

9: R = Me, X = OPh. The same procedure, using **5** and Me_3SiNMe_2 in a 1:2 mole ratio, gave **9** as a colorless liquid. Yield: 62%. Bp: 136−142 °C (0.03 mmHg). ^{1}H NMR: δ 1.73 (d, P*CH*$_3$, J_{PH} = 13.9), 2.46 (d, N*CH*$_3$, J_{PH} = 10.4), 7.1−7.3 (m, O*Ph*). ^{13}C NMR: δ 16.7 (dd, P*CH*$_3$, $^1J_{PC}$ = 93.4, $^3J_{PC}$ = 3.6), 36.9 (d, N*CH*$_3$, J_{PC} = 3.2), 150.4 (d, O*Ph*, J_{PC} = 9.5), 121.1 (d, *o-Ph*, J_{PC} = 4.4), 124.7 (s, *m-Ph*), 129.4 (s, *p-Ph*). ^{31}P NMR: δ 15.9 (d, *P*═O, J_{PP} = 25.1), 42.8 (d, *P*═N, J_{PP} = 25.1). Anal. Calcd for $C_8H_{11}Cl_2NO_2P_2$: C, 47.52; H, 7.64. Found: C, 47.55; H, 7.74.

Preparation of *N*-[Chloro(methyl)phosphoryl]phosphoranimines, Cl(Me)P(O)N═P(Me)(R)X (10−12), and *N*-[Chloro(phenyl)phosphoryl]phosphoranimines, Cl(Ph)P(O)N═P(Me)(R)X (13−14). 10: R = Me, X = OCH$_2$CF$_3$. A 1-neck, 100 mL flask, equipped with a magnetic stir bar, rubber septum, and a N_2 inlet needle, was charged with Et_2O (50 mL) and MeP(O)Cl_2 (6.38 g, 48.0 mmol). The solution was cooled to 0 °C, and the phosphoranimine, Me_3SiN═PMe_2OPh (9.10 g, 37.7 mmol), was added dropwise via syringe. The reaction mixture was allowed to stir at 0 °C for 0.5 h and then at room temperature for 0.5 h. The volatile components were removed under reduced pressure. Distillation gave compound **10** as a colorless liquid. Yield: 76%. Bp: 113−115 °C (0.05 mmHg). ^{1}H NMR: δ 1.79 (dd, *CH*$_3$P═O, $^2J_{PH}$ = 17.2, $^4J_{PH}$ = 2.2), 1.71 (d, P*CH*$_3$, J_{PH} = 14.3), 4.3−4.4 (m, O*CH*$_2$). ^{13}C NMR: δ 24.7 (dd, *CH*$_3$P═O, $^1J_{PC}$ = 131.3, $^3J_{PC}$ = 9.0), 16.1 (dd, P*CH*$_3$, $^1J_{PC}$ = 93.3, $^3J_{PC}$ = 4.7), 16.0 (dd, P*CH*$_3$, $^1J_{PC}$ = 90.1, $^3J_{PC}$ = 4.8), 61.6 (dq, O*CH*$_2$, J_{PC} = 6.2, J_{FC} = 37.7), 122.5 (dq, *CF*$_3$, J_{PC} = 8.6, J_{FC} = 277.5). ^{31}P NMR: δ 29.7 (d, *P*═O, J_{PP} = 8.7), 54.4 (d, *P*═N, J_{PP} = 8.7). Anal. Calcd for $C_5H_{11}ClF_3NO_2P_2$: C, 22.12; H, 4.08. Found: C, 22.27; H, 4.27.

11: R = Ph, X = OCH$_2$CF$_3$. The same procedure using MeP(O)Cl_2 and Me_3SiN═P(Me)(Ph)OCH_2CF_3 gave **11** as a colorless liquid. Yield: 41%. Bp: 150−160 °C (0.05 mmHg). ^{1}H NMR: δ 1.94 (d, *CH*$_3$P═O, J_{PH} = 17.1), 1.95 (d, *CH*$_3$P═O, J_{PH} = 17.1), 2.01 (d, P*CH*$_3$, J_{PH} = 14.7), 2.02 (d, P*CH*$_3$, J_{PH} = 14.7), 4.0−4.6 (m, O*CH*$_2$), 7.5−7.9 (m, P*Ph*). ^{13}C NMR: δ 23.3 (dd, *CH*$_3$P═O, $^1J_{PC}$ = 130.6, $^3J_{PC}$ = 5.2), 24.7 (dd, *CH*$_3$P═O, $^1J_{PC}$ = 130.5, $^3J_{PC}$ = 5.1), 15.6 (dd, P*CH*$_3$, $^1J_{PC}$ = 91.7, $^3J_{PC}$ = 1.7), 15.9 (dd, P*CH*$_3$, $^1J_{PC}$ = 91.5, $^3J_{PC}$ = 2.2), 61.4 (dq, O*CH*$_2$, J_{PC} = 5.8, J_{FC} = 37.5), 61.6 (dq, O*CH*$_2$, J_{PC} = 5.7, J_{FC} = 37.3), 122.3 (dq, *CF*$_3$, J_{PC} = 10.8, J_{FC} = 277.6), 122.3 (dq, *CF*$_3$, J_{PC} = 11.3, J_{FC} = 277.5), 126.7 (dd, P*Ph*, $^1J_{PC}$ = 137.8, $^3J_{PC}$ = 8.9), 126.8 (dd, P*Ph*, $^1J_{PC}$ = 139.7, $^3J_{PC}$ = 8.8), 131.0 (d, *o-Ph*, J_{PC} = 11.8), 131.0 (d, *o-Ph*, J_{PC} = 11.5), 129.0 (d, *m-Ph*, J_{PC} = 13.7), 133.6 (d, *p-Ph*, J_{PC} = 2.6). ^{31}P NMR: δ 29.5 (d, *P*═O, J_{PP} = 6.8), 29.3 (d, *P*═O, J_{PP} = 7.1), 42.2 (d, *P*═N, J_{PP} = 6.8), 41.5 (d, *P*═N, J_{PP} = 7.1). Anal. Calcd for $C_{10}H_{13}ClF_3NO_2P_2$: C, 36.00; H, 3.93. Found: C, 35.83; H, 3.36.

12: R = Me, X = OPh. The same procedure using MeP(O)Cl_2 and Me_3SiN═PMe_2OPh gave **12** as a colorless liquid. Yield: 71%. Bp: 165−175 °C (0.03 mmHg). ^{1}H NMR: δ 1.74 (dd, *CH*$_3$P═O, $^2J_{PH}$ = 17.0, $^4J_{PH}$ = 2.0), 1.81 (d, P*CH*$_3$, J_{PH} = 14.9), 7.1−7.3 (m, O*Ph*). ^{13}C NMR: δ 24.9 (dd, *CH*$_3$P═O, $^1J_{PC}$ = 130.4, $^3J_{PC}$ = 8.1), 16.1 (dd, P*CH*$_3$, $^1J_{PC}$ = 93.2, $^3J_{PC}$ = 5.2), 16.0 (dd, P*CH*$_3$, $^1J_{PC}$ = 92.3, $^3J_{PC}$ = 4.4), 149.6 (d, O*Ph*, J_{PC} = 9.8), 120.9 (d, *o-Ph*, J_{PC} = 4.3), 125.5 (s, *m-Ph*), 129.7 (s, *p-Ph*). ^{31}P NMR: δ 27.9 (s, *P*═O), 47.7 (s, *P*═N). A satisfactory elemental analysis of **12** was not obtained because of slight decomposition during distillation.

13: R = Me, X = OCH$_2$CF$_3$. The same procedure using PhP(O)Cl_2 and Me_3SiN═$PMe_2OCH_2CF_3$ gave **13** as a colorless liquid. Yield: 82%. Bp: 155−160 °C (0.03 mmHg). Mp: 47−50 °C. ^{1}H NMR: δ 1.84 (d, P*CH*$_3$, J_{PH} = 14.2), 1.84 (d, P*CH*$_3$, J_{PH} = 14.3), 4.4−4.5 (m, O*CH*$_2$), 7.3−8.0 (m, P*Ph*). ^{13}C NMR: δ 16.3 (d, P*CH*$_3$, J_{PC} = 93.4), 16.4 (d, P*CH*$_3$, J_{PC} = 93.1), 61.8 (dq, O*CH*$_2$, J_{PC} = 6.2, J_{FC} = 37.6), 122.5 (dq, *CF*$_3$, J_{PC} = 8.8, J_{FC} = 277.7), 136.5 (dd, P*Ph*, $^1J_{PC}$ = 177.4, $^3J_{PC}$ = 9.6), 128.1 (d, *o-Ph*, J_{PC} = 16.3), 130.2 (d, *m-Ph*, J_{PC} = 11.6), 131.8 (d, *p-Ph*, J_{PC} = 3.3). ^{31}P NMR: δ 19.3 (s, *P*═O), 56.0 (s, *P*═N). A satisfactory elemental analysis of **13** was not obtained because of slight decomposition during distillation.

14: R = Ph, X = OCH$_2$CF$_3$. The same procedure using PhP(O)Cl_2 and Me_3SiN═P(Me)(Ph)OCH_2CF_3 gave **14** as a pale yellow solid that decomposed on attempted distillation. ^{1}H NMR: δ 2.10 (d, P*CH*$_3$, J_{PH} = 14.6), 2.11 (d, P*CH*$_3$, J_{PH} = 14.4), 4.1−4.6 (m, O*CH*$_2$), 7.4−8.0 (m, *Ph*P═O and *Ph*P═N). ^{13}C NMR: δ 16.1 (dd, P*CH*$_3$, $^1J_{PC}$ = 92.2, $^3J_{PC}$ = 1.6), 16.4 (dd, P*CH*$_3$, $^1J_{PC}$ = 91.7, $^3J_{PC}$ = 1.6), 61.8 (dq, O*CH*$_2$, J_{PC} = 5.6, J_{FC} = 37.6), 62.0 (dq, O*CH*$_2$, J_{PC} = 5.7, J_{FC} = 37.6), 122.5 (dq, *CF*$_3$, J_{PC} = 11.3, J_{FC} = 276.2), 136.7 (dd, *Ph*P═O, $^1J_{PC}$ = 176.4, $^3J_{PC}$ = 9.4), 136.8 (dd, *Ph*P═O, $^1J_{PC}$ = 176.2, $^3J_{PC}$ = 9.2), 127.1 (dd, *Ph*P═N, $^1J_{PC}$ = 140.2, $^3J_{PC}$ = 9.3), 127.2 (dd, *Ph*P═N, $^1J_{PC}$ = 140.2, $^3J_{PC}$ = 8.8), 127.2 (dd, *o-Ph*P═O, $^2J_{PC}$ = 11.7, $^4J_{PC}$ = 3.9), 130.3 (d, *o-Ph*P═N, J_{PC} = 11.4), 128.2 (d, *m-Ph*P═O, J_{PC} = 16.5), 129.1 (d, *m-Ph*P═N, J_{PC} = 14.0), 131.8 (d, *p-Ph*, J_{PC} = 3.3), 133.8 (d, *p-Ph*, J_{PC} = 2.9). ^{31}P NMR: δ 19.0 (s, *P*═O), 19.2 (s, *P*═O), 43.4 (s, *P*═N), 43.9 (s, *P*═N).

Preparation of *N*-[(Dimethylamino)phosphoryl]phosphoranimines, R′(Me$_2$N)P(O)N═P(Me)(R)X (15−18). 15: R = R′ = Me, X = OCH$_2$CF$_3$. Using the same procedure as that described for the preparation of the *P*-dimethylamino derivatives **6**−**9**, the *P*-chloro derivative **10** was treated with Me_3SiNMe_2 in a 1:1 mole ratio. Distillation afforded **15** as a colorless liquid. Yield: 84%. Bp: 80−85 °C (0.05 mmHg). ^{1}H NMR: δ 1.16 (dd, *CH*$_3$P═O, $^2J_{PH}$ = 14.9, $^4J_{PH}$ = 1.9), 1.60 (d, P*CH*$_3$, J_{PH} = 14.3), 2.48 (d, N*CH*$_3$, J_{PH} = 10.6), 4.3−4.4 (m, O*CH*$_2$). ^{13}C NMR: δ 13.0 (dd, *CH*$_3$P═O, $^1J_{PC}$ = 119.8, $^3J_{PC}$ = 7.6), 16.5 (dd, P*CH*$_3$, $^1J_{PC}$ = 96.2, $^3J_{PC}$ = 3.6), 16.5 (dd, P*CH*$_3$, $^1J_{PC}$ = 90.5, $^3J_{PC}$ = 4.0), 36.7 (d, N*CH*$_3$, J_{PC} = 3.1), 61.1 (dq, O*CH*$_2$, J_{PC} = 5.5, J_{FC} = 37.2), 122.9 (dq, *CF*$_3$, J_{PC} = 8.7, J_{FC} = 277.5). ^{31}P NMR: δ 29.7 (d, *P*═O, J_{PP} = 8.7), 54.4 (d, *P*═N, J_{PP} = 8.7). Anal. Calcd for $C_7H_{17}F_3N_2O_2P_2$: C, 30.01; H, 6.12. Found: C, 30.11; H, 5.91.

16: R = Ph, R′ = Me, X = OCH$_2$CF$_3$. Likewise, *P*-chloro derivative **11** was treated with Me_3SiNMe_2 in a 1:1 mole ratio. Distillation afforded **16** as a colorless liquid. Yield: 64%. Bp: 125−130 °C (0.05 mmHg). ^{1}H NMR: δ 1.27 (dd, *CH*$_3$P═O, $^2J_{PH}$ = 15.0, $^4J_{PH}$ = 1.6), 1.29 (dd, *CH*$_3$P═O, $^2J_{PH}$ = 15.0, $^4J_{PH}$ = 1.6), 1.85 (d, *CH*$_{3P=N}$, J_{PH} = 14.5), 1.86 (d, *CH*$_{3P=N}$, J_{PH} = 14.5), 2.55 (d, N*CH*$_3$, J_{PH} = 10.5), 2.56 (d, N*CH*$_3$, J_{PH} = 10.5), 4.0−4.6 (m, O*CH*$_2$), 7.4−7.8 (m, P*Ph*). ^{13}C NMR: δ 13.4 (d, *CH*$_3$P═O, J_{PC} = 120.0), 13.5 (d, *CH*$_3$P═O, J_{PC} = 119.8), 16.4 (d, *CH*$_3$P═N, J_{PC} = 94.3), 16.5 (d, *CH*$_3$P═N, J_{PC} = 92.2), 36.7 (d, N*CH*$_3$, J_{PC} = 8.6), 36.7 (d, N*CH*$_3$, J_{PC} = 8.5), 61.1 (dq, O*CH*$_2$, J_{PC} = 5.3, J_{FC} = 37.4), 61.1 (dq, O*CH*$_2$, J_{PC} = 5.4, J_{FC} = 37.4), 122.8 (dq, *CF*$_3$, J_{PC} = 10.8, J_{FC} = 277.5), 126.7 (dd, P*Ph*, $^1J_{PC}$ = 137.8, $^3J_{PC}$ = 8.9), 129.3 (dd, P*Ph*, $^1J_{PC}$ = 139.0, $^3J_{PC}$ = 6.7), 129.4 (dd, P*Ph*, $^1J_{PC}$ = 139.0, $^3J_{PC}$ = 6.7), 128.6 (d, *o-Ph*, J_{PC} = 13.9), 128.7 (d, *o-Ph*, J_{PC} = 13.8), 131.0 (d, *m-Ph*, J_{PC} = 11.5), 131.0 (d, *m-Ph*, J_{PC} = 9.5), 132.7 (s, *p-Ph*), 132.8 (s, *p-Ph*). ^{31}P NMR: δ 25.9 (d, *P*═O, J_{PP} =

6.5), 26.0 (d, *P*═O, J_{PP} = 6.1), 36.2 (d, *P*═N, J_{PP} = 6.5), 36.5 (d, *P*═N, J_{PP} = 6.1). Anal. Calcd for $C_{12}H_{19}F_3N_2O_2P_2$: C, 42.11; H, 5.60. Found: C, 42.17; H, 6.07.

17: R = R′ = Me, X = OPh. Likewise, *P*-chloro derivative **12** was treated with Me_3SiNMe_2 in a 1:1 mole ratio. Distillation afforded **17** as a colorless liquid. Yield: 65%. Bp: 135−140 °C (0.04 mmHg). ^{1}H NMR: δ 1.12 (dd, *CH*$_3$P═O, $^2J_{PH}$ = 15.0, $^4J_{PH}$ = 1.7), 1.72 (d, *CH*$_3$P═N, J_{PH} = 13.6), 1.76 (d, *CH*$_3$P═N, J_{PH} = 13.5), 2.47 (d, N*CH*$_3$, J_{PH} = 10.6), 7.1−7.3 (m, O*Ph*). ^{13}C NMR: δ 13.5 (dd, *CH*$_3$P═O, $^1J_{PC}$ = 119.6, $^3J_{PC}$ = 5.9), 16.9 (dd, *CH*$_3$P═N, $^1J_{PC}$ = 91.2, $^3J_{PC}$ = 2.6), 17.0 (dd, *CH*$_3$P═N, $^1J_{PC}$ = 94.9, $^3J_{PC}$ = 3.6), 36.7 (d, N*CH*$_3$, J_{PC} = 3.0), 150.4 (d, O*Ph*, J_{PC} = 9.4), 121.1 (d, *o-Ph*, J_{PC} = 4.5), 124.8 (s, *m-Ph*), 130.0 (s, *p-Ph*). ^{31}P NMR: δ 15.9 (d, *P*═O, J_{PP} = 25.1), 42.8 (d, *P*═N, J_{PP} = 25.1). Anal. Calcd for $C_{11}H_{20}N_2O_2P_2$: C, 48.18; H, 7.35. Found: C, 48.46; H, 7.54.

18: R = Me, R′ = Ph, X = OCH$_2$CF$_3$. Likewise, *P*-chloro derivative **13** was treated with Me_3SiNMe_2 in a 1:1 mole ratio. Distillation afforded **18** as a colorless liquid that solidified to a white solid in the receiving flask. Yield: 88%. Bp: 135−140 °C (0.05 mmHg). Mp: 68−72 °C. ^{1}H NMR: δ 1.62 (d, P*CH*$_3$, J_{PH} = 14.0), 1.68 (d, P*CH*$_3$, J_{PH} = 14.3), 2.49 (d, N*CH*$_3$, J_{PH} = 10.5), 4.3−4.4 (m, O*CH*$_2$), 7.3−7.7 (m, P*Ph*). ^{13}C NMR: δ 16.9 (dd, P*CH*$_3$, $^1J_{PC}$ = 92.7, $^3J_{PC}$ = 3.4), 16.7 (dd, P*CH*$_3$, $^1J_{PC}$ = 94.8, $^3J_{PC}$ = 4.3), 36.8 (d, N*CH*$_3$, J_{PC} = 3.2), 61.2 (dq, O*CH*$_2$, J_{PC} = 5.8, J_{FC} = 37.2), 122.9 (dq, *CF*$_3$, J_{PC} = 8.8, J_{FC} = 277.7), 135.3 (dd, P*Ph*, $^1J_{PC}$ = 153.9, $^3J_{PC}$ = 6.0), 127.7 (d, *o-Ph*, J_{PC} = 13.0), 130.6 (d, *m-Ph*, J_{PC} = 9.0), 129.8 (d, *p-Ph*, J_{PC} = 2.9). ^{31}P NMR: δ 16.9 (d, *P*═O, J_{PP} = 12.2), 50.4 (d, *P*═N, J_{PP} = 12.2). Anal. Calcd for $C_{12}H_{19}F_3N_2O_2P_2$: C, 42.11; H, 5.60. Found: C, 42.15; H, 5.69.

Preparation of *N*-(Dichlorothiophosphoryl)phosphoranimine (19). A 3-neck, 100 mL flask, equipped with a magnetic stir bar, N_2 inlet, and rubber septum, was charged with Et_2O (50 mL) and $P(S)C1_3$ (10.2 g, 60.0 mmol). The solution was cooled to 0 °C, and the phosphoranimine, $Me_3SiN{=}PMe_2OCH_2CF_3$ (14.4 g, 58.2 mmol), was added dropwise via syringe. After stirring for 0.5 h at 0 °C, the reaction mixture was allowed to warm to room temperature and was then stirred for an additional 20 h. The volatile components were removed under reduced pressure. Distillation gave product **19** as a pale yellow liquid. Yield: 54%. Bp: 120−125 °C (0.05 mmHg). ^{1}H NMR: δ 1.89 (d, P*CH*$_3$, J_{PH} = 14.2), 4.44 (dq, O*CH*$_2$, J_{PH} = 9.7, J_{FH} = 8.1). ^{13}C NMR: δ 15.6 (dd, P*CH*$_3$, $^1J_{PC}$ = 91.8, $^3J_{PC}$ = 4.4), 62.3 (dq, O*CH*$_2$, J_{PC} = 6.9, J_{FC} = 38.0), 122.3 (dq, *CF*$_3$, J_{PC} = 9.0, J_{FC} = 277.7). ^{31}P NMR: δ 38.9 (d, *P*═S, J_{PP} = 12.2), 54.4 (d, *P*═N, J_{PP} = 12.2). Anal. Calcd for $C_4H_8Cl_2F_3NOP_2S$: C, 15.60; H, 2.62. Found: C, 15.70; H, 2.72.

Thermolysis of (*N*-Phosphoryl)-*P*-trifluoroethoxyphosphoranimines (3, 4, 11, and 14). In a typical experiment, a neat sample of compound **4** (3.4 g, 9.6 mmol) was sealed in an evacuated, thick-walled glass ampule and heated in an oven at 195 °C for 21 h. After first cooling to room temperature, the contents of the ampule were cooled to −196 °C, and the ampule was opened and quickly attached to a vacuum line. The ampule was allowed to warm to room temperature, and the volatile fraction was collected in a trap cooled to −196 °C. This product was identified as CF_3CH_2Cl (8.4 mmol, 87% yield) by ^{1}H and ^{13}C NMR spectroscopy as well as GC/MS. Similar results were obtained when compound **3**, **11**, or **14** was heated under the same conditions.

Thermolysis of (*N*-Phosphoryl)-*P*-phenoxyphosphoranimines (5, 9, and 12). Using the same procedure as described for the thermolysis of **4**, a neat sample of compound **12** (3.0 g, 10.7 mmol) was heated at 200 °C for 144 h. The contents of the ampule turned a dark brown color during the heating process, and some dark solid was formed. After cooling to room temperature, CH_2Cl_2 was added to extract the soluble products. The remaining solid was insoluble in all common solvents and was not further characterized. Solvent was removed from the CH_2Cl_2 extract leaving a thick brown liquid. This was identified as mainly $Me_2P(O)OPh$ by ^{1}H and ^{13}C NMR spectroscopy as well as GC/MS. Small amounts (ca. 5−10%) of other, unidentified products were also present. Similar results were obtained when compounds **5** and **9** were heated under the same conditions.

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