O_2 affinity by L^3 may be compatible with a square-pyramid structure in which the O donor in the macrocycle may reside at the axial position. The increases in cobalt(III) character by the interaction of O_2 would make the O atom ligation likely, especially the intramolecularly attached one as in L^3, which should exert some stabilizing effect on the trans O_2 bridge.

The μ-peroxo complexes have been well characterized for other pentaamine systems such as $(NH_3)_5$ and L^4.[24] Steric factors may account for less stable μ-peroxo complex with L^2 relative to L^4 (see Table III). Another possible explanation may be weaker electron-donating ability of L^2 (see Table I) which reduces Co → O_2 π-bonding effects.[25]

Oxygen-Uptake Kinetics. A difference in the O_2-uptake rates by linear and macrocyclic N_5 systems was initially observed at the potentiometric titrations where the equilibrating time after each addition of NaOH titrant was ~20 s for L_4, whereas for L^2 it required much longer time, ~35 min. The kinetic studies showed the slower rates of O_2 uptake by the macrocyclic system are ascribable to the extremely slow CoL^{2+} chelate formation.

The equilibrium study has shown that L^2 can form CoL^{2+} chelates and the subsequent O_2 adducts almost simultaneously around pH 5. The stopped-flow measurements of the appearance of the 320-nm peak found the second-order (first order in $[Co(OAc)^+]$ and first order in $[H_2L^{2+}]$) rate laws for the O_2-adduct formation in acetate buffers. This implies a slow formation of CoL^{2+} to be followed by a rapid oxygenation. The same conclusion was drawn for the macrocyclic tetraamine system including L^5.[3] Interestingly, the magnitude of the k_{2H} value is almost comparable to the rate constants k_H (=2.5 × 10^2 and 4.2 × 10^2 M^{-1} s^{-1}) for the 12- and 13-membered macrocyclic tetraamine complex formation between $Co(OAc)^+$ and monoprotonated N_4 observed at the oxygen uptake.[3] The availability of three free nitrogens in the macrocycles gives the similar rates for the interaction with Co(II). A similar situation is known for Cu^{2+}–macrocyclic N_5 and N_4 complex formations: k_{2H} (=2.4 × 10^6 M^{-1} s^{-1} for the reaction of $Cu(OAc)^+$ with diprotonated N_5)[15] is almost the same with k_H (=5.3 × 10^6 M^{-1} s^{-1} for the reaction of $Cu(OAc)^+$ with monoprotonated N_4).[26]

Separately, we have measured the rates of O_2 uptake by preformed CoL^{2+} chelates in acetate buffers. The reaction found was first order in [CoL] and first order in $[O_2]$. The same rate law has been reported for polyamines including L^5,[3] L^4,[12,25] or porphyrins.[8,9] The observed oxygenation rate may refer to slow formation of the 1:1 $CoL{\cdot}O_2$ species followed by immediate reaction with another CoL to give the final μ-peroxo products. Another interpretation is that the rapidly formed 1:1 species undergoes slow rearrangement for the fast 2:1 product formation, as invoked for O_2 uptake by cobalt porphyrins.[8,9]

In comparison of the rates in the same acetate buffer conditions, the reaction of CoL with O_2 occurs ca. 1.2 × 10^4 times faster than the prior formation of CoL. Namely, the CoL^{2+} chelate formation has determined the rate of the macrocycle O_2 uptake at the potentiometric titrations.

As seen in Table IV, the second-order rate constant k_2 for L^2 is 10^3 times as much as that for L^5. The fact may support the activation effect for O_2 coordination by the axial N donor atom. Comparison with L^4 indicates the cyclization of the linear pentaamine (although having a big unstabilizing effect on the O_2 uptake equilibrium; see Table III) has a minor retarding effect on the kinetics. In fact, a similar O_2-uptake rate of 10^5 M^{-1} s^{-1} was shown by other Co^{2+} polyamine chelates such as trien and $(en)_2$, which is supposed to be commonly limited by the rate of H_2O exchange.[24] It is yet to be investigated whether other substitution reactions on the macrocyclic L^2 complex show the paralleling rates.

In short, the present study has demonstrated that the compulsive axial ligation by the macrocyclic structures significantly promotes the rates and equilibrium of O_2 uptake of Co(II) surrounded by saturated tetraamines. The effects of such axial N ligation were not estimated from the previous studies using a linear tetraamine (trien)[5] and pentaamine (L^4),[11] due to the different oxygenation product formula. Predictably further studies using the macrocyclic system may find more efficient and biologically significant models.

Registry No. $L^3{\cdot}4Ts$, 73396-35-7; $L^3{\cdot}4HBr$, 73396-36-8; L^3, 73396-34-6; $[CoL']^{2+}$, 73396-74-4; $[CoL^2]^{2+}$, 73396-75-5; $[CoL^3]^{2+}$, 73396-76-6; O_2, 7782-44-7; $L^6{\cdot}4Ts$, 73396-37-9; bis(2-chloroethyl) ether, 111-44-4.

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Synthesis of New *N*-Silylphosphinimines: Phosphazene Precursors

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The reactions of some bis(trimethylsilyl)aminophosphines with bromine proceeded with elimination of Me_3SiBr to produce the new *P*-bromo-*N*-silylphosphinimines $RR'P(Br)=NSiMe_3$ (**1**, R = R′ = Me; **2**, R = Me, R′ = Ph; **3**, R = R′ = Ph; **4**, R = R′ = OCH_2CF_3). Other new *N*-silylphosphinimines, $R_2R'P=NSiMe_3$ (**5**, R = Me, R′ = NMe_2; **6**, R = OCH_2CF_3, R′ = NMe_2; **7**, R = Me, R′ = OCH_2CF_3), were prepared from **1** and **4** via their reactions with either Me_2NH or $LiOCH_2CF_3$. Compounds **1**–**4** eliminate Me_3SiBr on heating to form cyclic phosphazenes $(RR'PN)_n$ with nearly quantitative yields of $(Me_2PN)_n$ (n = 3, 4, 5) resulting from thermolysis of **1**.

Introduction

In a recent study we reported that the reaction of substituted fluorophosphoranes, $RR'PF_3$, with $LiN(SiMe_3)_2$ resulted in the formation of several new *P*-fluoro-*N*-silylphosphinimines $RR'P(F)=NSiMe_3$.[1] These compounds undergo thermal decomposition, eliminating Me_3SiF and forming cyclic phosphazenes, $(RR'P=N)_n$. On the basis of this fluorosilane

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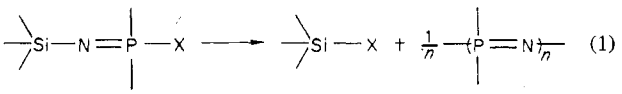
Table I. Preparative, Analytical, and NMR Spectroscopic Data for *N*-Silylphosphinimines

compd	signal	NMR spectra[a] δ(¹H)	J_{PH}	J_{FH}	δ(¹³C)	J_{PC}	J_{FC}	δ(³¹P)	preparative % yield	bp, °C (mm)	anal.[b] % C	% H
$Me_2P(Br)=NSiMe_3$ (1)	Me_3Si	0.15	~1.0		2.56	6.1		6.82[c]	85	47 (2.6)	26.01	6.38
	Me	2.12	13.0		28.83	79.3					(26.33)	(6.63)
$MeP(Br)(Ph)=NSiMe_3$ (2)	Me_3Si	0.38			2.74	5.5		−0.08[c]				
	Me	2.38	13.0		29.05	81.2						
	Ph	7.40										
		7.85										
$Ph_2P(Br)=NSiMe_3$ (3)	Me_3Si	0.45						−0.13[c]				
	Ph	7.50										
		7.95										
$(CF_3CH_2O)_2P(Br)=NSiMe_3$ (4)	Me_3Si	0.21	1.0		1.95	4.9		−34.90[d]	87	51 (3.8)	21.50	3.38
	CH_2	4.40	10.0	8.0	64.04	6.1	37.8				(21.22)	(3.31)
	CF_3				122.59	13.1	277.4					
$Me_2P(NMe_2)=NSiMe_3$ (5)	Me_3Si	0.02			3.25	3.7		21.23	72	62 (5.3)	43.59	10.93
	Me	2.30	13.0		15.82	84.8					(43.72)	(11.01)
	Me_2N	3.50	11.0		35.49	2.4						
$(CF_3CH_2O)_2P(NMe_2)=NSiMe_3$ (6)	Me_3Si	0.22			3.27	3.1		−0.35	75	53 (3.0)	30.14	5.42
	Me_2N	2.77	11.0		36.87	4.9					(30.00)	(5.32)
	CH_2	4.20	8.0	8.0	62.51	4.3	37.2					
	CF_3				125.53	11.0	277.1					
$Me_2P(OCH_2CF_3)=NSiMe_3$ (7)	Me_3Si	0.15			3.27	3.1		32.32	50	51 (9.5)	33.90	6.85
	Me	1.48	14.0		18.72	94.0					(34.00)	(6.93)
	CH_2	4.22	9.5	8.5	59.33	4.9	36.6					
	CF_3				123.75	7.9	18.5					

[a] Chemical shifts in ppm downfield from Me_4Si for ¹H and ¹³C spectra and from H_3PO_4 for ³¹P spectra; coupling constants in Hz. Solvents: ¹H, CH_2Cl_2; ¹³C, $CDCl_3$; ³¹P, $CDCl_3$ (unless otherwise noted). [b] Calculated values in parentheses. [c] Solvent: benzene. [d] Solvent: CH_2Cl_2.

elimination, it is possible to postulate a general phosphazene synthesis which involves the elimination of substituted silanes, R_3SiX, from suitably constructed *N*-silylphosphinimines (eq 1). As a potential route to linear polyphosphazenes, this



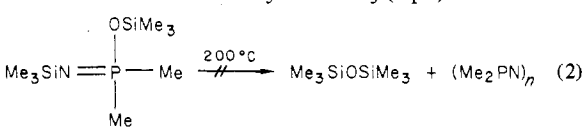
(1)

method offers the advantage of incorporating the desired phosphorus substituents directly in the starting materials, thereby eliminating the need for first preparing the dihalo polymers $(X_2PN)_n$.[2]

In order to test the generality of this scheme we have prepared a number of new *N*-(trimethylsilyl)phosphinimines with a variety of substituents at phosphorus, including several potential leaving groups (X = Br, NMe_2, OCH_2CF_3). We report here the synthesis, characterization, and the results of preliminary decomposition studies of these phosphinimines.

Results and Discussion

As a result of another study[3] we had at our disposal an *N*-silyl-*P*-siloxyphosphinimine which met the criteria for the general phosphazene synthesis. On being heated to 200 °C for 1 week, however, the compound failed to eliminate the expected substituted silane $Me_3SiOSiMe_3$ (eq 2). This result



(2)

was somewhat disappointing since the starting material is easily prepared in good yield and since there is precedence for disiloxane elimination from similar compounds.[4]

In theory, a number of other substituents (X), in particular the halogens, should be good leaving groups. In addition to the *P*-fluoro-substituted phosphinimines mentioned above,[1] several *P*-chloro-substituted compounds have also been reported[5] as products of the reaction of (silylamino)dialkylphosphines with CCl_4 (eq 3). There are, however, no known

(3)

examples of *P*-bromo-*P*,*P*-dialkyl-*N*-silylphosphinimines, and these presumably would not be readily accessible by either of the methods used to prepare the fluoro or chloro compounds.

In this study we have prepared such *P*-bromo compounds by extending the reaction of bromine with trialkyl- or triarylphosphines (eq 4)[6] to some [bis(trimethylsilyl)amino]-

$$R_3P + Br_2 \rightarrow [R_3PBr^+]Br^- \quad (4)$$
$$R = \text{alkyl, aryl}$$

phosphines[3,7] (eq 5). Not surprisingly, the phosphonium salts analogous to those in eq 4 were not isolated. Instead their logical decomposition products, Me_3SiBr and the new *P*-bromo-*N*-silylphosphinimines **1**–**4**, were obtained in high yields. Compounds **1** and **4** were purified by vacuum distillation and were fully characterized by elemental analysis and ¹H, ¹³C, and ³¹P NMR spectroscopy (see Table I). Due to their low

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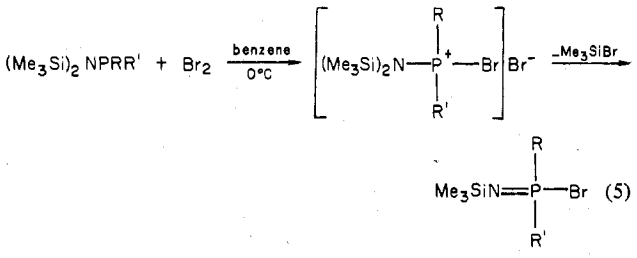


(5)

1, R = R′ = Me
2, R = Me, R′ = Ph
3, R = R′ = Ph
4, R = R′ = OCH_2CF_3

volatility compounds **2** and **3** could not be purified by vacuum distillation but were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and by their decomposition products. All of the bromo-substituted compounds are hydrolytically unstable liquids which fume profusely on exposure to the atmosphere.

It is interesting to note the relative thermal stability of compound **1**, which showed no signs of decomposition during distillation compared to the fluoro-substituted analogue $Me_2P(F)=NSiMe_3$ which could not be isolated even at ambient temperature.[1,8] On being heated at higher temperatures, however, compound **1** decomposes smoothly to give cyclic $(Me_2PN)_n$ oligomers and Me_3SiBr (eq 6). This decomposition

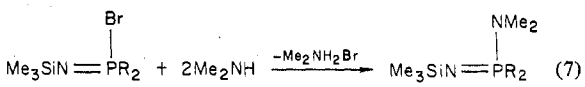
$$Me_3SiN{=}P(Br)Me_2 \xrightarrow{\Delta} (1/n)(Me_2P{=}N)_n + Me_3SiBr \quad (6)$$

was carried out under a variety of conditions with nearly quantitative yields of $(Me_2PN)_n$ being obtained from reactions in sealed tubes. Generally, trimer, tetramer, and pentamer were formed, but the 250 °C/26 h sealed-ampule reaction gave predominantly tetrameric dimethylphosphazene $(Me_2PN)_4$. Thus, the thermolysis of **1** is an efficient method for preparing the cyclic dimethylphosphazenes, $(Me_2PN)_3$ and $(Me_2P)_4$, which avoids the difficult preparation of Me_2PCl_3.[9] No polymeric $(Me_2PN)_n$ was observed among the decomposition products from any of the various reaction conditions (see Experimental Section). This is most unfortunate since **1** is easily prepared in high yields from $Me_2PN(SiMe_3)_2$ which can be conveniently synthesized in molar quantitites.[7] Polymeric phosphazenes with complete substitution of alkyl or aryl groups at phosphorus are not known, but it is anticipated that they may possess unusual thermal stability and perhaps unique physical properties.[10]

Under relatively mild conditions (150 °C/24 h) compound **3** also eliminated Me_3SiBr, forming cyclic diphenylphosphazenes. The trimer $(Ph_2PN)_3$ was isolated by recrystallization from CH_3CN and was identified by its melting point[11] and ^{31}P NMR spectrum.[12] Thermal decomposition of **2**, which is a potential route to nongeminal phenyl- and methyl-substituted phosphazenes, yielded a mixture of phosphazenes as indicated by a number of signals in the ^{31}P NMR spectra of the nonvolatile decomposition products. This is not unexpected because, in addition to various sizes of oligomers, cis and trans isomers of each oligomer are possible. In this cursory study, no attempt was made to separate and identify the individual isomers.

The thermal decomposition of the trifluoroethoxy compound **4** did not proceed as smoothly as the previous ones. Proton NMR analysis indicated that the volatile reaction products contained both Me_3SiBr and CF_3CH_2Br.[13] Presumably initial Me_3SiBr elimination and bis(trifluoroethoxy)phosphazene formation are followed by displacement of the trifluoroethyl moiety by the trimethylsilyl group[14] to form phosphazenes with at least partial Me_3SiO substitution at phosphorus. This is supported by the presence of a strong Me_3Si signal in the ^1H NMR spectrum of the nonvolatile decomposition products.

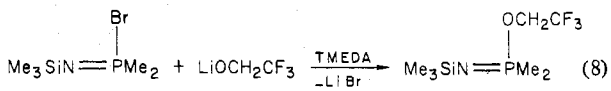
In addition to their potential as phosphazene precursors via Me_3SiBr elimination, the new bromo-substituted *N*-silylphosphinimines were of interest because reactions at the P–Br bond could result in the preparation of other new *N*-silylphosphinimines. Indeed, when compounds **1** and **4** were allowed to react with excess Me_2NH, high yields (ca. 75%) of the dimethylamino derivatives **5** and **6** were obtained (eq 7).



(7)

5, R = Me
6, R = OCH_2CF_3

Somewhat lower yields (ca. 50–60%) of the trifluoroethoxy compound **7** were obtained when **1** was allowed to react with $LiOCH_2CF_3$ (eq 8). This reaction did not occur unless



(8)

7

TMEDA was added to enhance the nucleophilicity of the lithium reagent. The presence of TMEDA, however, made purification of **7** difficult and necessitated several distillations to afford an analytically pure sample. Compounds **5**–**7** were fully characterized by NMR spectroscopy and elemental analysis (Table I).

Several attempts to prepare yet another new *N*-silylphosphinimine, $(CF_3CH_2O)_2P(Me){=}NSiMe_3$, which would complete the series $(CF_3CH_2O)_{3-n}P(Me_n){=}NSiMe_3$,[15] were unsuccessful. When **4** was allowed to react with either MeMgBr, MeLi, or $AlMe_3$, NMR analysis of the products indicated that starting material **4** was still present along with smaller amounts of what has tentatively been identified as the desired compound.

The new *N*-silylphosphinimines **5**–**7** are also suitably constructed phosphazene precursors and possess two new potential leaving groups, OCH_2CF_3 and NMe_2. Compound **5**, in which elimination of Me_3SiNMe_2 is the anticipated decomposition route, showed remarkable thermal stability on heating in a sealed ampule at 250 °C for 24 h. While **5** showed no signs of decomposition at this temperature, compound **6** underwent partial decomposition under the same conditions with both Me_3SiNMe_2 and $Me_3SiOCH_2CF_3$ being eliminated. The elimination of $Me_3SiOCH_2CF_3$ from *N*-silylphosphinimines is not unprecedented. Flindt and Rose[15] have reported that $(CF_3CH_2O)_3P{=}NSiMe_3$ eliminates this silane on heating at 200 °C to form low molecular weight polymeric $[(CF_3CH_2O)_2PN]_n$. It is, therefore, reasonable to assume that heating compound **7** would also result in elimination of $Me_3SiOCH_2CF_3$. On heating of the compound to 250 °C for 24 h in a sealed ampule, however, only Me_3SiF was found in the volatile reaction products and the residual black solids were not identified. Other decomposition studies of compound **7** are currently in progress, with preliminary results indicating the formation of polymeric $(Me_2PN)_n$.[16]

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In summary, a number of new *P*-bromo-*N*-silylphosphinimines with a variety of substitutents at phosphorus have been conveniently prepared by the direct bromination of (disilylamino)phosphines (eq 5). These phosphinimines are useful precursors to cyclic phosphazenes, especially $(Me_2PN)_n$ (n = 3, 4, 5) and to other new P-substituted *N*-silylphosphinimines which may ultimately lead to some much-sought-after polyphosphazenes, including $(Me_2PN)_n$.

Experimental Section

The (disilylamino)phosphines $Me_2PN(SiMe_3)_2$, $Me(Ph)PN(SiMe_3)_2$ and $Ph_2PN(SiMe_3)_2$ were prepared by published procedures.[7] Bromine, tetramethylethylenediamine (TMEDA), dimethylamine, trifluoroethanol, phosphorus trichloride, hexamethyldisilizane, and solutions of *n*-BuLi, MeLi, MeMgBr, and $AlMe_3$ were purchased from commercial sources. Benzene and Et_2O were freshly distilled from CaH_2 before use. Proton NMR spectra were recorded on a JEOL MH-100 spectrometer while $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL FX-60 spectrometer. Elemental analysis were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen. The following procedures are typical of those used to prepare the *P*-bromo-*N*-silylphosphinimines and their dimethylamino and trifluoroethoxy derivatives. Physical, analytical, and spectroscopic data are summarized in Table I.

Preparations of Bis(trifluoroethoxy)[bis(trimethylsilyl)amino]phosphine. Hexamethyldisilizane (68.3 mL, 328 mmol) and Et_2O (ca. 300 mL) were placed in a 2-L, three-necked flask equipped with a paddle stirrer, nitrogen inlet, and a rubber septum. After the solution was cooled to 0 °C, *n*-BuLi (205 mL, 1.6 M in hexane) was added slowly via syringe. The mixture was stirred at room temperature for 1 h and then cooled to −78 °C. Phosphorus trichloride (28.6 mL, 328 mmol) was added slowly via syringe, and the mixture was allowed to warm to room temperature. A solution of $LiOCH_2CF_3$ was prepared in a separate flask by slowly adding (ca. 1.5 h) *n*-BuLi (409 mL, 656 mmol) from an addition funnel to a stirred solution of CF_3CH_2OH (65.7 g, 656 mmol) in Et_2O (ca. 250 mL) at 0 °C. After being stirred at room temperature for 1 h, this mixture was transferred to an addition funnel which replaced the septum on the first flask. The $LiOCH_2CF_3$ solution was added (over ca. 15 min) to the $(Me_3Si)_2NPCl_2$ solution at 0 °C, and the resulting mixture was stirred overnight at room temperature. The mixture was filtered, solvent was removed under reduced pressure, and the residue was distilled, giving a colorless liquid (bp 60 °C (1.4 mm), 81% yield).

Anal. Calcd for $C_{10}H_{22}F_6NO_2PSi_2$: C, 30.85; H, 5.70. Found: C, 30.75; H, 5.67. ^1H NMR (CH_2Cl_2): δ 4.06 (q, J_{FH} = 7.5 Hz, CH_2), 0.44 (d, J_{PH} = 1.0 Hz, Me_3Si). ^{13}C NMR ($CDCl_3$): δ 124.16 (q of d, J_{PC} = 9.76 Hz, J_{FC} = 277.7 Hz, CF_3), 62.17 (q of d, J_{PC} = 22.58 Hz, J_{FC} = 36.01 Hz, CH_2), 3.92 (d, J_{PC} = 7.93 Hz, Me_3Si). ^{31}P NMR ($CDCl_3$): δ 173.32 (s).

Bromination of (Disilylamino)phosphines. In a typical reaction the (disilylamino)phosphine (30–50 mmol) and ca. 75 mL of benzene were placed in a two-necked round-bottom flask equipped with a magnetic stirrer, nitrogen inlet, and an addition funnel. The solution was cooled to 0 °C and an equimolar amount of Br_2 in benzene (ca. 75 mL) was added dropwise. After the solution was stirred for at least 1 h at room temperature, benzene and Me_3SiBr were removed under reduced pressure and, where applicable, the product was purified by distillation (see Table I).

Preparation of *P*-(Dimethylamino)-*P*,*P*-dimethyl-*N*-(trimethylsilyl)phosphinimine, 5. Ethyl ether (ca. 150 mL) was placed in a 500-mL, three-necked flask equipped with a magnetic stirrer, nitrogen purge, and a stopper. A −78 °C bath was placed around the flask and Me_2NH (ca. 10 mL) was added to the Et_2O. Then a solution of **1** (11.95 g, 52.4 mmol) in Et_2O (ca. 75 mL) was added slowly to the −78 °C solution. When addition was complete, the mixture was stirred at room temperature for 2 h and then filtered under nitrogen. The residue remaining after removal of the solvent from the filtrate was distilled (bp 61 °C (5.0 mm)) to give a colorless liquid identified as **5** (see Table I).

Preparation of *P*-(Trifluoroethoxy)-*P*,*P*-dimethyl-*N*-(trimethylsilyl)phosphinimine, 7. In a three-necked, 500-mL flask equipped with a magnetic stirrer, nitrogen inlet, and an addition funnel, $LiOCH_2CF_3$ was prepared by slow addition (over ca. 30 min) of *n*-BuLi (42.5 mL, 1.6 M in hexane) to an Et_2O (ca. 75 mL) solution of CF_3CH_2OH (5.28 mL, 68 mmol) at 0 °C. After the solution was stirred at room temperature for 30 min, compound **1** (15.47 g, 68 mmol) was added (over ca. 10 min), followed by addition of TMEDA (8.6 mL, 68 mmol). The mixture was stirred overnight at room temperature and then decanted. The residue remaining after removal of solvent from the decantate was distilled to give a colorless liquid identified as **7** (see Table I).

Attempted Preparations of *P*-Methyl-*P*,*P*-bis(trifluoroethoxy)-*N*-(trimethylsilyl)phosphinimine. Ethyl ether, benzene, or THF solutions of **4** treated with MeLi, $AlMe_3$, or MeMgBr, respectively, failed to produce detectable quantities of the desired compound even after refluxing for several hours. When Et_2O solutions of **4** were allowed to reflux with MeMgBr overnight, however, small amounts (ca. 50% yield) of a clear liquid were obtained after distillation (bp 48–51 °C (5.0 mm)). ^1H NMR (CH_2Cl_2): δ 0.22 (s, Me_3Si), 0.25 (s, Me_3Si), 1.60 (d, PMe), 4.30 (complex m, CH_2). ^{31}P NMR ($CDCl_3$): δ −12.6, 18.7.

Thermal Decomposition of the New *N*-Silylphosphinimines. The decomposition of **1** was studied under a variety of conditions. In all cases Me_3SiBr was identified as the volatile decomposition product by comparison of its ^1H NMR spectrum with that of an authentic sample. Very little decomposition occurred on heating for 3 h at 120 °C. After 5 days in refluxing benzene, a ^{31}P NMR spectrum of the white solid remaining after removal of benzene and Me_3SiBr indicated that nearly equal amounts of tetrameric (δ 27.1) and pentameric (δ 21.5)[17] $(Me_2PN)_n$ had formed. On heating of a neat sample at **1** in a sealed, heavy-walled glass ampule, the following results were obtained. White solid (250 °C/26 h): 90% yield of $(Me_2PN)_n$; ^{31}P NMR (D_2O) δ 32.9 (weak, trimer), 26.9 (strong, tetramer), 21.4 (weak, pentamer).[17] Black residue (350 °C/18 h): ^{31}P NMR (D_2O) δ 22.7 (strong), 26.9 (strong), 31.8 (weak), 35.3 (weak).

Compound **2** was heated to 130 °C/21 h. After removal of Me_3SiBr, sublimation (150 °C (0.1 mm)) of the residue yielded a small amount of white solid: ^{31}P NMR ($CDCl_3$) δ 23.1 (weak), 22.2 (strong), 21.5 (medium). At 250 °C/43 h in a sealed ampule the products were Me_3SiBr and a black tar: ^{31}P NMR ($CDCl_3$) δ 16.7 (weak, br m) and seven other signals δ 29.5, 28.6, 27.8, 26.9, 26.1, 25.2, 24.4.

Compound **3** was heated to 150 °C/2 h in a partially evacuated flask. The volatiles were removed (Me_3SiBr), and the solid was recrystallized from CH_3CN, giving a crystalline solid identified as $(Ph_2PN)_3$:[11,12] mp 224–227 °C; ^{31}P NMR ($CDCl_3$) δ 15.1.

The decompositions of **4**–**7** were done in sealed, heavy-walled glass ampules under the conditions indicated. Compound **4** (250 °C/41 h) ^1H NMR (CH_2Cl_2): volatiles δ 3.70 (q, J_{FH} = 9 Hz, CH_2), 0.35, 0.29, 0.18; residue (bp 95–96 °C (0.07 mm)) δ 4.22 (br m, CH_2), 0.39 (s, Me_3Si). Compound **5** (250 °C/24 h) was recovered unchanged. Compound **6** (250 °C/24 h): volatiles identified as $Me_3SiOCH_2CF_3$ and Me_3SiNMe_2 by comparison of the ^1H NMR spectrum to that of authentic samples; residue was not investigated. Compound **7** (250 °C/24 h): volatiles identified as Me_3SiF by comparison of the ^1H NMR spectrum to that of an authentic sample; residue, ^{31}P NMR (D_2O) δ 29.8, 34.0, 67.1.

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Registry No. **1**, 73296-38-5; **2**, 73296-39-6; **3**, 73296-40-9; **4**, 73296-41-0; **5**, 73296-42-1; **6**, 73296-43-2; **7**, 73296-44-3; hexamethyldisilizane, 999-97-3; phosphorus trichloride, 7719-12-2; $LiOCH_2CF_3$, 69163-14-0; bis(trifluoroethoxy)[bis(trimethylsilyl)amino]phosphine, 73296-45-4; Me_2NH, 124-40-3; $(Me_2PN)_3$, 6607-30-3; $(Me_2PN)_4$, 4299-49-4; $(Me_2PN)_5$, 52193-19-8; $(Me_3Si)_2NPMe_2$, 63744-11-6; $(Me_3Si)_2NPMePh$, 68437-87-6; $(Me_3Si)_2NPPh_2$, 13685-61-5.

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