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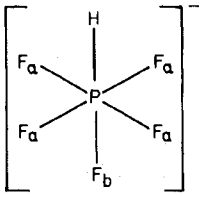

The $H_2PF_4^-$ anion has a trans conformation of H ligands. See text.
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(24) Trifluorophosphine reacts readily with $(CH_3)_2NH$ to afford $(CH_3)_2NPF_2$. See, for example ref 18a.

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Synthesis and Stereochemistry of Some *N*-Trimethylsilyl- and *N*-Silyl-Substituted Aminophosphines

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The preparative chemistry and the N–P torsional barriers of several compounds containing the Si–N–P linkage have been investigated. The *N*-lithium derivatives of the silylamines, $Me_3SiN(R)H$ (R = Me_3Si, *t*-Bu, Me), reacted readily with the appropriate halophosphine to afford good yields of the trimethylsilylaminophosphines, $Me_3SiN(R)PX_2$ (X = CF_3, F). Halogen exchange reactions were observed between BCl_3 and two of the aminodifluorophosphines, resulting in the formation of the corresponding dichlorophosphines, $Me_3SiN(R)PCl_2$ (R = Me_3Si, *t*-Bu). Two new silylaminophosphines, $H_3SiN(R)P(CF_3)_2$ (R = Me, H), were obtained from the dehydrobromination reaction of $(CF_3)_2PN(R)H$ with H_3SiBr. Unsuccessful attempts to prepare disilylaminophosphines via the Si–N cleavage reaction of $(H_3Si)_3N$ with PF_2Br or $(CF_3)_2PCl$ are also described. Rotational barriers, determined by ^1H DNMR studies, about the N–P bond in several of these compounds are discussed in terms of possible steric effects of the *N*-trimethylsilyl and *N*-silyl substituents.

Introduction

The literature contains surprisingly few references to the synthesis of silicon-substituted aminophosphines.[2] A study of simple compounds featuring the Si–N–P linkage has been initiated in our laboratory for essentially three reasons: (i) The ground state geometries[3] and stereochemical processes[4] in aminophosphines have attracted significant attention recently. As the next stage in the development of the chemistry of these compounds it seemed important to probe the stereochemical consequences of heteroatom substitution at nitrogen. (ii) The cleavage of element–silicon bonds by reactive halides now represents an important means for effecting substitution by groups such as NR_2, OR, and SR.[5] It is therefore reasonable to expect silylaminophosphines to function as reagents for transferring the >N–P< moiety to other substrates. (iii) Silylaminophosphines can be considered to be related formally to the well-known silylaminoboranes[6] and it seemed of interest to explore the extent of this analogy.

The present paper is concerned with both the preparative chemistry of silylaminophosphines and their N–P torsional barriers. A related study dealing with compounds containing the silicon–nitrogen–phosphorus(V) linkage will be the subject of a separate publication.

Experimental Section

General. Standard high vacuum and inert atmosphere techniques were employed for all manipulations.[7] Except as otherwise described the reaction vessels consisted of Pyrex tubes or bulbs equipped with glass–Teflon stopcocks.

Physical Measurements. The ^1H and ^{19}F NMR spectra were recorded on Perkin-Elmer R-12, Varian HA-100, or Varian A 56/60 spectrometers. The ^1H and ^{19}F chemical shifts were measured relative to external tetramethylsilane and fluorotrichloromethane, respectively. The ^{31}P NMR spectra were recorded on a Bruker HFX-90 spectrometer and were referenced to external 85% H_3PO_4. The mass spectra (70 eV) were determined on a CEC 21-491 spectrometer, and the infrared spectra were measured on a Perkin-Elmer 337 grating spectrophotometer.

Materials. Phosphorus trifluoride, chlorotrimethylsilane, ammonia, methylamine, trimethylamine, *tert*-butylamine, bis(trimethylsilyl)-amine, boron trichloride, and *n*-butyllithium were obtained from commercial sources and used without purification. Chlorobis(trifluoromethyl)phosphine,[8] bromodifluorophosphine,[9] bromosilane,[10] trisilylamine,[11] the dialkylaminobis(trifluoromethyl)phosphines[12]

$[R_2NP(CF_3)_2$ (R = Et, *i*-Pr)], and *tert*-butyl(trimethylsilyl)amine[13] were prepared according to published procedures. The known compounds $Me_3SiN(Me)H$[13] and $(CF_3)_2PN(H)R$ (R = Me, H)[14] were obtained using substantially modified procedures which are described below.

Caution! The interaction of silyl-substituted amines with phosphorus compounds is potentially hazardous as illustrated by one experiment involving trisilylamine and chlorobis(trifluoromethyl)phosphine (vide infra). The use of appropriate safety shields is advised.

Preparation of Methyl(trimethylsilyl)amine. Chlorotrimethylsilane (75 mmol) and methylamine (200 mmol) were condensed together at −196 °C in a 60-mL heavy-walled Pyrex tube. The vessel was placed in a −78 °C bath for 1 h and then allowed to warm to room temperature. After 3 h the mixture was distilled through U-traps held at −40, −78, and −196 °C. The −78 °C fraction was redistilled using the same trap temperatures to afford pure $Me_3SiN(Me)H$ in the −78 °C trap in ~50% yield. The ^1H NMR spectrum (10% CCl_4 solution) was identical to that of a sample prepared by the literature method[13] and consisted of a Me_3Si singlet at δ 0.10 and an N–Me doublet (J_{HNCH} = 5.5 Hz) at δ 2.48 in the intensity ratio 2.9:1.0 (calcd 3:1). The N–H proton was not detected. The compound disproportionates slowly at room temperature to $MeNH_2$ and $(Me_3Si)_2NMe$ so consequently it was redistilled prior to use in subsequent reactions.

Preparation of Aminobis(trifluoromethyl)phosphines. Ammonia (20 mmol) and $(CF_3)_2PCl$ (10 mmol) were condensed together at −196 °C in a 1-L vessel. The mixture was allowed to warm to room temperature and after standing overnight the products were distilled through U-traps held at −45, −78, and −196 °C. The −78 °C trap retained $(CF_3)_2PNH_2$ (9.5 mmol, 95% yield) which was identified by its infrared spectrum.[14] An identical procedure was used to prepare $(CF_3)_2PN(Me)H$ (identified by its infrared spectrum[14]) from methylamine and $(CF_3)_2PCl$. Again the yield was almost quantitative. Apparently the vapor-phase reactions described by Harris[14] for the preparation of these compounds are not essential.

Preparation of Bis(trimethylsilyl)aminobis(trifluoromethyl)phosphine (1). A 1-L reaction bulb was evacuated, flame dried, filled with dry N_2, and charged with *n*-BuLi (33 mmol, 16.5 mL of 2.0 M *n*-hexane solution). The solution was degassed by freeze–thawing and $(Me_3Si)_2NH$ (33 mmol) was condensed in at −196 °C. The vessel was placed in a −78 °C bath for 1 h, during which time a reaction occurred to give a white solid (presumably the *N*-lithium derivative) which dissolved completely when the mixture was warmed to room temperature. Chlorobis(trifluoromethyl)phosphine (33 mmol) was condensed into the bulb at −196 °C and the mixture was allowed to warm slowly to room temperature with occasional shaking. After 15 min the contents of the bulb were distilled through U-traps held at −30 and −196°C. Because of the low volatility of the product the reaction vessel was warmed gently after the bulk of the solvent had been removed. Compound **1** condensed slowly in the −30 °C trap as a colorless liquid (9.77 g, 91% yield). The product was pure as determined by its ^1H and ^{19}F NMR but could be distilled (bp 56–57 °C (4 Torr)) without decomposition. The ^1H NMR spectrum (20% cyclohexane solution) consisted of a broad singlet at δ 0.18. The ^{19}F NMR spectrum consisted of a doublet (J_{PCF} = 93.1 Hz) at +59.2 ppm. The mass spectrum contained a molecular ion at *m/e* 329 (calcd 329). Anal. Calcd for $C_8H_{18}F_6NPSi_2$: C, 29.17; H, 5.51. Found: C, 29.10; H 5.75.

Preparation of *tert*-Butyl(trimethylsilyl)aminobis(trifluoromethyl)phosphine (2). The apparatus and procedure were the same as that described above for the synthesis of compound **1**. Thus, $(CF_3)_2PCl$ (4.0 mmol) reacted with $Me_3SiN(t\text{-}Bu)Li$ (~4 mmol) to afford **2** as a colorless liquid (0.47 g, 37% yield). The ^1H NMR spectrum (20% $CHFCl_2$ solution) consisted of a doublet (J_{PNCCH} = 1.2 Hz) at δ 1.51 (*t*-Bu), a singlet at δ 1.44 (*t*-Bu), a doublet (J_{PNSiCH} = 3.2 Hz) at δ 0.46 (Me_3Si), and a septet ($J_{FCPNSiCH}$ = 0.7 Hz) at δ 0.39 (Me_3Si). The ^{19}F NMR spectrum consisted of two doublets (+54.9 ppm, J_{PCF} = 100.0 Hz, and +55.4 ppm, J_{PCF} = 101.0 Hz). The ^{31}P NMR spectrum consisted of two septets centered at −49.7 and −34.7 ppm. The mass spectrum contained a molecular ion at *m/e* 313 (calcd 313). Anal. Calcd for $C_9H_{18}F_6NPSi$: C, 34.50; H, 5.79. Found: C, 34.50; H, 5.81.

Preparation of Methyl(trimethylsilyl)aminobis(trifluoromethyl)-phosphine (3). In a 175-mL reaction tube $Me_3SiN(Me)H$ (12 mmol) was condensed at −196 °C onto degassed *n*-BuLi (12.9 mmol, 5.4 mL of 2.4 M *n*-hexane solution). The mixture was warmed to −30 °C and allowed to stand for 1 h. A white solid (presumably the *N*-lithium derivative) was formed. After cooling the vessel to −196 °C, $(CF_3)_2PCl$ (12.5 mmol) was added and the mixture was warmed to −30 °C. A vigorous reaction ensued and the mixture turned brown. After warming to room temperature and shaking occasionally for 30 min the mixture was distilled through U-traps held at 0, −30, −78, and −196 °C. The −30 and −78 °C fractions were combined and redistilled through a −45 °C trap which retained compound **3** as a colorless liquid (2.40 g, 73% yield). The ^1H NMR spectrum (20% chloroform solution) consisted of a Me_3Si doublet (J_{PNSiCH} = 1.5 Hz) at δ 0.05 and an N–Me doublet (J_{PNCH} = 5.6 Hz) of septets (J_{FCPNCH} = 1.0 Hz) at δ 2.65 in the intensity ratio 3.0:1.0 (calcd 3:1). The ^{19}F NMR spectrum consisted of a doublet (J_{PCF} = 83.8 Hz) of quartets (J_{FCPNCH} = 1.0 Hz) at +65.2 ppm. The mass spectrum contained a molecular ion at *m/e* 271 (calcd 271). Anal. Calcd for $C_6H_{12}F_6NPSi$: C, 26.57; H, 4.46; N, 5.16. Found: C, 26.43; H, 4.46; N, 4.95.

Preparation of Bis(trimethylsilyl)aminodifluorophosphine (4). The apparatus and procedure were similar to that described above for the synthesis of compound **1**. Thus, PF_3 (50 mmol) was condensed at −196 °C onto a solution of $(Me_3Si)_2NLi$ (40 mmol) in hexane (20 mL) and the mixture was allowed to assume ambient temperature with occasional shaking. A viscous yellow suspension was formed. After 1 h the mixture was distilled through U-traps held at 0, −30, and −196 °C. The −30 °C trap retained compound **4** as a colorless liquid (5.85 g, 64% yield). The product was pure as determined by its ^1H and ^{19}F NMR but could be distilled (bp 66–67 °C (4 Torr)) without decomposition. The ^1H NMR spectrum (10% CCl_4 solution) consisted of a doublet (J_{PNSiCH} = 1.8 Hz) of triplets ($J_{FPNSiCH}$ = 0.5 Hz) centered at δ 0.31. The ^{19}F NMR spectrum consisted of a doublet (J_{PF} = 1239 Hz) at +50.0 ppm. The mass spectrum contained a molecular ion at *m/e* 229 (calcd 229). Anal. Calcd for $C_6H_{18}F_2NPSi_2$: C, 31.40; H, 7.93. Found: C, 31.71; H, 7.88.

Preparation of *tert*-Butyl(trimethylsilyl)aminodifluorophosphine (5). The apparatus and procedure were similar to that described above for the syntheses of compounds **1** and **4**. Thus, PF_3 (5 mmol) reacted with $LiN(t\text{-}Bu)SiMe_3$, (5 mmol) to afford **5** as a colorless liquid (68% yield) which was retained in a −30 °C trap. The ^1H NMR spectrum (20% $CHFCl_2$ solution) consisted of a Me_3Si doublet (J_{PNSiCH} = 2.5 Hz) of triplets ($J_{FPNSiCH}$ = 1.0 Hz) at δ 0.15 and a *t*-Bu doublet (J_{PNCCH} ~ 1.0 Hz) of triplets (J_{FPNCCH} ~ 1.0 Hz) at δ 1.26. The ^{19}F NMR spectrum consisted of a doublet (J_{PF} = 1212 Hz) at +58.3 ppm. The mass spectrum contained a molecular ion at *m/e* 213 (calcd 213). Anal. Calcd for $C_7H_{18}F_2NPSi$: C, 39.42; H, 8.51 Found: C, 39.66; H, 8.49.

Preparation of Methyl(trimethylsilyl)aminodifluorophosphine (6). When PF_3 was allowed to react with $LiN(Me)SiMe_3$ in a 1-L bulb in a manner similar to that described above for the preparation of compound **1**, a low yield (14%) of **6** was obtained along with considerable quantities of Me_3SiF (identified by comparison of the infrared spectrum with that of an authentic sample). The synthesis was improved by adopting the following procedure. A 60-mL heavy-walled tube was evacuated, flame dried, filled with N_2, and charged with *n*-BuLi (10 mmol, 8.9 mL of 1.1 M *n*-hexane solution). The *n*-hexane was removed under vacuum and diethyl ether (10 mL) was condensed into the vessel at −196 °C along with $Me_3SiN(Me)H$ (10 mmol). The mixture was warmed to room temperature with occasional shaking over a 30-min period to give an almost colorless solution (the *N*-lithium derivative is soluble in diethyl ether). Phosphorus trifluoride (12 mmol) was then condensed in at −196 °C and the vessel was placed in a −78 °C bath. A vigorous reaction occurred as the contents melted and mixed. After 1 h at −78 °C the mixture (a viscous yellow suspension) was allowed to warm to room temperature. The bulk of the solvent and other volatiles (*n*-butane, excess phosphorus trifluoride, etc.) were then distilled out of the reaction tube which was maintained at −30 °C. The remaining material was distilled through U-traps held at −30, −63, and −196 °C. The −63 °C trap retained compound **6** as a solid which melted to a colorless liquid (0.91 g, 53% yield) upon warming. The ^1H NMR spectrum (50% $CHFCl_2$ solution) consisted of a Me_3Si doublet (J_{PNSiCH} = 2.1 Hz) of triplets ($J_{FPNSiCH}$ ~ 0.3 Hz) at δ 0.16 and an N–Me doublet (J_{PNCH} = 5.8 Hz) of triplets (J_{FPNCH} = 1.8 Hz) at δ 2.51. The ^{19}F NMR spectrum consisted of a doublet (J_{PF} = 1214 Hz) of quartets (J_{FPNCH} ~ 1.7 Hz which was poorly resolved due to additional coupling to the Me_3Si protons) at +69.4 ppm. The mass spectrum contained a molecular ion at *m/e* 171 (calcd 171). The NMR and mass spectroscopic data are in good agreement with those published previously.[15]

Preparation of Bis(trimethylsilyl)aminodichlorophosphine (7). Boron trichloride (1.9 mmol) and $(Me_3Si)_2NPF_2$ (2.8 mmol) were condensed together at −196 °C in a 60-mL reaction tube. The vessel was placed in a −30 °C bath and after standing 1 h at this temperature the volatile material (1.9 mmol) was removed and identified as BF_3 by comparison of the IR spectrum with that of an authentic sample. A white crystalline solid remained in the reaction vessel at −30 °C. The product melted to a colorless liquid on warming. The ^1H NMR spectrum (20% cyclohexane solution) consisted of one doublet (J_{PNSiCH} = 2.5 Hz, lit.[16] 2.5 Hz) which is characteristic of $(Me_3Si)_2NPCl_2$. The product slowly evolved chlorotrimethylsilane (identified by comparison of the IR spectrum with that of an authentic sample) and deposited a yellow solid on standing at room temperature, which is consistent with the previously reported[16] instability of compound **7**.

Preparation of *tert*-Butyl(trimethylsilyl)aminodichlorophosphine (8). The apparatus and procedure were the same as that described above for the preparation of compound **7**. Thus, BCl_3 (2.26 mmol) reacted with $Me_3SiN(t\text{-}Bu)PF_2$ (3.38 mmol) to afford BF_3 (2.2 mmol) and a colorless liquid which was subsequently identified as compound **8**. The ^1H NMR spectrum (14% $CHFCl_2$ solution) consisted of a Me_3Si doublet (J_{PNSiCH} = 2.9 Hz) at δ 0.35 and a *t*-Bu doublet (J_{PNCCH} = 2.0 Hz) at δ 1.41. The high-resolution mass spectrum contained a molecular ion at *m*/e 245.0333 (calcd 245.0323).

Preparation of Methyl(silyl)aminobis(trifluoromethyl)phosphine (9). Trimethylamine (2.0 mmol), bromosilane (2.0 mmol), and $(CF_3)_2PN(Me)H$ (1.8 mmol) were condensed together in a 100-mL vessel and then allowed to warm to room temperature. After standing overnight the mixture was distilled through U-traps held at −45, −78, and −196 °C. The −78 °C trap retained $H_3SiN(Me)P(CF_3)_2$ as a colorless liquid (1.75 mmol, 97% yield). The IR spectrum contained two intense bands (ν_{Si-H}) at ~2200 cm^{-1}. The ^1H NMR spectrum (20% $CHFCl_2$ solution) consisted of a H_3Si doublet (J_{PNSiH} = 14.4 Hz) at δ 4.26 and an N–CH_3 doublet (J_{PNCH} = 6.0 Hz) at δ 2.66 which also showed poorly resolved fine structure (J_{FCPNCH} ~ 0.3 Hz). The ^{19}F NMR spectrum consisted of a doublet (J_{PCF} = 86.1 Hz) at +59.0 ppm. The mass spectrum contained a molecular ion at *m*/e 229 (calcd 229).

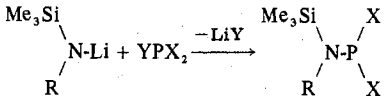
Preparation of Silylaminobis(trifluoromethyl)phosphine (10). When bromosilane (4.2 mmol), trimethylamine (4.0 mmol), and $H_2NP(CF_3)_2$ (2.0 mmol) were combined at −196 °C and allowed to warm to room temperature, the only volatile products were a noncondensable gas (hydrogen?) and silane (~3 mmol). A yellow nonvolatile solid was not investigated. Compound **10**, however, could be prepared by the following procedure. Bromosilane (3.0 mmol) and $H_2NP(CF_3)_2$ (3.0 mmol) were sealed together at −196 °C in a small (~5 mL) glass ampule and allowed to warm to room temperature. After standing overnight (a preliminary experiment showed the reaction to be incomplete after 1 h at 25 °C) the mixture was distilled through U-traps held at −45, −78, and −196 °C. The −78 °C trap retained $H_3SiN(H)P(CF_3)_2$ as a crystalline solid which on warming melted to a colorless liquid (1.7 mmol, 89% yield). The IR spectrum contained N–H and Si–H stretching bands at 3380 and 2190 cm^{-1}, respectively. The ^1H NMR spectrum (20% $CHFCl_2$ solution) consisted of a H_3Si doublet (J_{PNSiH} = 12.0 Hz) of doublets (J_{HNSiH} = 3.0 Hz) at δ 4.30 and a broad N–H resonance centered at δ 2.1 in the approximate intensity ratio 3:1. The ^{19}F NMR spectrum consisted of a doublet (J_{PCF} = 80.5 Hz) at +66.5 ppm. The mass spectrum contained a molecular ion at *m*/e 215 (calcd 215).

Attempted Reaction of Trisilylamine with Chlorobis(trifluoromethyl)phosphine. Trisilylamine (1.0 mmol) and $(CF_3)_2PCl$ (1.0 mmol) were condensed together at −196 °C in a 20-mL tube and warmed to −78 °C. After 1 h the vessel was removed from the −78 °C bath and a colorless liquid was observed. Within a few seconds, however, a violent explosion occurred which shattered the reaction vessel. The cause of the detonation has not been determined. In another attempt 1.0 mmol each of trisilylamine and $(CF_3)_2PCl$ were condensed together at −196 °C in a 100-mL bulb and allowed to warm directly to room temperature. After 48 h an IR spectrum of the mixture indicated that no reaction had occurred. The same mixture was then heated in a heavy-walled sealed tube at 100 °C for 1 h. The products of the reaction could not be separated by trap-to-trap distillation; however, all fractions gave IR spectra containing only peaks characteristic of the starting materials. Chlorosilane (which would have been easily separated) was not observed.

Attempted Reaction of Trisilylamine with Bromodifluorophosphine. Trisilylamine (1.0 mmol) and bromodifluorophosphine (1.0 mmol) were condensed together at −196 °C in a 100-mL bulb and allowed to warm to room temperature. After 24 h traces of a yellow solid were observed. Once again, however, only starting materials were detected in the mixture. No evidence for the formation of an aminophosphine or bromosilane was obtained.

Results and Discussion

Synthesis. The reactions (eq 1) of chlorobis(trifluoromethyl)phosphine and phosphorus trifluoride with various lithium trimethylsilylamides have been used to prepare the *N*-trimethylsilyl-substituted aminophosphines **1–6**.



(1)

1, R = Me_3Si; X = CF_3; Y = Cl
2, R = *t*-Bu; X = CF_3; Y = Cl
3, R = Me; X = CF_3; Y = Cl
4, R = Me_3Si; X = Y = F
5, R = *t*-Bu; X = Y = F
6, R = Me; X = Y = F

The silylaminophosphines **1–6** are colorless liquids which are thermally stable to at least 100 °C. All of the compounds were easily handled in an inert atomsphere and, with the exception of **1** and **2**, had sufficient volatility to allow manipulation in a conventional high-vacuum system. Their characterization was accomplished primarily by ^1H and ^{19}F NMR spectroscopy which revealed several long-range coupling constants. With the exception of **1** (see below) all compounds exhibit four-bond P–N–Si–C–H coupling constants and the difluorophosphines (**4–6**) even show five-bond F–P–N–Si–C–H couplings in the Me_3Si proton region. Additional confirmation of the proposed structures was provided by the observation of the expected infrared active vibrations, mass spectral parent peaks, and fragmentation patterns. Satisfactory C and H analyses were obtained for compounds **1–5**.

The reaction of metalated silylamines with phosphorus halides has, in fact, been used previously for the synthesis of silylaminophosphines. Thus, the bis(trimethylsilyl)amino[17] and alkyl(trimethylsilyl)amino[2] derivatives of chlorodiphenylphosphine have been prepared as indicated in eq 2.

$$Me_3SiN(R)Li + ClPPh_2 \xrightarrow{-LiCl} Me_3SiN(R)PPh_2 \quad (2)$$
$$R = Me, Et, i\text{-}Pr, Me_3Si$$

While the syntheses of the bis(trifluoromethyl)phosphines **1–3** are reported here for the first time, the difluorophosphines **4** and **5** have been mentioned previously,[18] although no details of the preparations are available. Compound **6** has been prepared previously via the silicon–nitrogen bond cleavage procedure (eq 3)[19] and by fluorination of $Me_3SiN(Me)PCl_2$.[15]

$$(Me_3Si)_2NMe + PF_2Cl \xrightarrow{90\ °C} Me_3SiCl + \underset{6}{Me_3SiN(Me)PF_2} \quad (3)$$

The present synthesis of **6** is, however, more direct and results in higher yields. The NMR and mass spectral data for **6** are in good agreement with the literature values.

Niecke and Flick[20] have reported that compound **4** reacts further with lithium bis(trimethylsilyl)amide, eliminating both lithium fluoride and fluorotrimethylsilane, to form the stable, monomeric aminophosphine (eq 4). Scherer and Kuhn[21]

$$(Me_3Si)_2NPF_2 + LiN(SiMe_3)_2 \xrightarrow[-Me_3SiF]{-LiF} (Me_3Si)_2NP{=}NSiMe_3 \quad (4)$$

obtained the same product from the reaction of phosphorus trihalides with an excess of the *N*-lithium derivative (eq 5). However, if a 1:1 stoichiometry was employed (eq 6)[16] it was possible to isolate the thermally unstable dichlorophosphine **7**.

$$2(Me_3Si)_2NLi + PX_3 \xrightarrow[-Me_3SiX]{-2LiX} (Me_3Si)_2NP{=}NSiMe_3 \quad (5)$$
$$X = Cl, Br$$

$$(Me_3Si)_2NLi + PCl_3 \xrightarrow{-LiCl} (Me_3Si)_2NPCl_2 \quad (6)$$
$$7$$

In the present study compound **7** and the analogous dichlorophosphine **8** were prepared in nearly quantitative yield by a different method. When boron trichloride was allowed to react with the amidofluorophosphines **4** and **5**, an interesting halogen exchange reaction (eq 7) was observed. This result

$$3Me_3SiN(R)PF_2 + 2BCl_3 \xrightarrow{-30\ °C} 3Me_3SiN(R)PCl_2 + 2BF_3 \quad (7)$$
$$7, R = Me_3Si$$
$$8, R = t\text{-Bu}$$

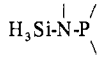
was quite surprising in view of the ease with which BCl_3 causes cleavage of the Si–N bond in many silylamines.[22] More significantly, however, the chlorination of the phosphorus–fluorine bond with BCl_3 might be a useful procedure for the synthesis of some otherwise inaccessible P–Cl compounds. In one important instance this has already been demonstrated.[23] It was found that phosphorus pentafluoride reacts with BCl_3 in the gas phase according to eq 8, thus providing a convenient

$$3PF_5 + BCl_3 \rightarrow 3PF_4Cl + BF_3 \quad (8)$$

synthesis of the useful phosphorane intermediate, PF_4Cl, previously reported preparations[24] of which were fraught with difficulties.

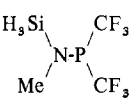
The dichlorophosphines **7** and **8** were thermally unstable, undergoing Me_3SiCl elimination and condensation to unidentified yellow solids upon standing at room temperature thus making elemental analysis impractical. Their characterization was accomplished by ^1H NMR spectroscopy, the stoichiometries of the reactions, and, in the case of **8**, by high-resolution mass spectroscopy. Compounds **7** and **8** were sufficiently stable, however, to permit investigation of their ^1H NMR spectra at low temperatures as discussed below.

In addition to the *N*-trimethylsilyl-substituted aminophosphines described above, interest in this laboratory has been directed toward the synthesis of some analogous compounds containing the



linkage. Two potential routes to silylaminophosphines have been investigated. The first involved the dehydrohalogenation reaction of a halosilane with an aminophosphine containing an N–H functional group. The second was based on possible Si–N cleavage reactions of trisilylamine with halophosphines. It should perhaps be pointed out that a metalation reaction similar to that used for preparing the *N*-trimethylsilyl-substitued aminophosphines (eq 1) is precluded by the instability of the necessary silylamine precursors of the type H_3SiNRH.[25] When equimolar amounts of bromosilane and methylaminobis(trifluoromethyl)phosphine were combined at −196 °C and allowed to warm to room temperature in the presence of trimethylamine, the new silylaminophosphine, **9**, was obtained in essentially quantitative yield (eq 9).

$$H_3SiBr + (CF_3)_2PN(Me)H \xrightarrow[-Me_3NHBr]{Me_3N} \quad (9)$$



$$9$$

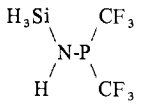
Analogous attempts to prepare *N*-silyl derivatives of $H_2NP(CF_3)_2$ using an identical procedure, however, were unsuccessful. The products of such reactions were always a noncondensable gas (probably hydrogen), large amounts of SiH_4, and nonvolatile yellow solids. These observations are consistent with those of Wells and Schaeffer,[26] who demonstrated that trisilylamine undergoes a base (e.g. Me_3N) catalyzed decomposition in the condensed phase to afford silane and low volatile Si–N polymers. The possibility that the decomposition products result from the thermal instability of the silylaminophosphine itself is obviated by the observation that H_3SiBr and $H_2NP(CF_3)_2$ react (eq 10) *in the absence of* Me_3N to form silylaminobis(trifluoromethyl)phosphine (**10**) in high yield.

Table I. N–P Rotational Barriers for Some Silylaminophosphines and Related Compounds, $RR'NPX_2$

R	R′	X	$\Delta G^{\ddagger}_{NP}$, kcal/mol
Me_3Si	*t*-Bu	CF_3	20.8
Me_3Si	Me_3Si	CF_3	15.3
i-Pr	*i*-Pr	CF_3	14.8
Et	Et	CF_3	10.0
Me	Me	CF_3	8.9[a]
Me	H	CF_3	~8.5[b]
H_3Si	Me	CF_3	<7
H_3Si	H	CF_3	<7
t-Bu	*t*-Bu	Cl	17.0[c]
Me_3Si	*t*-Bu	Cl	12.8
Me_3Si	Me_3Si	Cl	10.0

[a] Taken from ref 4e. [b] Taken from ref 4d. [c] Taken from ref 32.

$$2H_3SiBr + 3H_2NP(CF_3)_2 \xrightarrow[-NH_4Br]{-(CF_3)_2PBr} 2 \quad (10)$$



$$10$$

A similar reaction between H_3SiBr and H_2NPF_2 has been reported by Ebsworth, Rankin, and co-workers[27] and the product, $H_3SiN(H)PF_2$, appears to be the only other example of an aminophosphine containing the H_3Si–N moiety. Compounds **9** and **10** are colorless, volatile, spontaneously flammable liquids which were characterized by IR, ^1H and ^{19}F NMR, and mass spectroscopy. Their thermal stability has not been studied although samples kept at room temperature for several months in sealed ampules showed no evidence of decomposition.

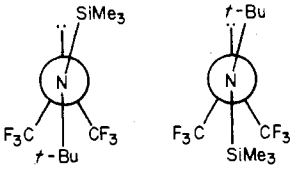
Finally, the reactions of trisilylamine with halophosphines were attempted (eq 11) in an effort to prepare the novel disilylaminophosphines. In general when the reactants were

$$(H_3Si)_3N + R_2PX \rightarrow (H_3Si)_2NPR_2 + H_3SiX \quad (11)$$
$$R = CF_3, X = Cl$$
$$R = F, X = Br$$

allowed to warm from −196 °C to room temperature (and heated to 100 °C for R = CF_3) no reaction was observed. However, in one case an unexplained explosion occurred in an experiment involving trisilylamine and $(CF_3)_2PCl$ (see Experimental Section). The failure of these reactions, especially with F_2PBr, is surprising since the related silyl-substituted compounds $(H_3Si)_2O$ and $(H_3Si)_2S$ react readily with F_2PBr to form the phosphines H_3SiEPF_2 (E = O, S).[28]

Stereochemistry. The N–P torsional barriers,[29] $\Delta G^{\ddagger}_{NP}$, for several of the silylaminophosphines and some related compounds are summarized in Table I. At the outset it is appropriate to point out that recent molecular orbital calculations[30] on the parent aminophosphine, H_2NPH_2, indicate that the nitrogen geometry changes from trigonal planar to approximately tetrahedral when the nitrogen–phosphorus inter-lone-pair angle is increased from 90 to 180°. The "N–P torsional barrier" therefore refers to a hybrid process which involves N–P bond rotation and pyramidal inversion at nitrogen.

In a preliminary communication[31] it was reported that $(Me_3Si)_2NP(CF_3)_2$ (**1**) and $Me_3SiN(t\text{-}Bu)P(CF_3)_2$ (**2**) exhibited unusually high $\Delta G^{\ddagger}_{NP}$ values of 15.3 and 20.8 kcal/mol, respectively. Of particular interest were the ^1H and ^{19}F NMR data for **2** which indicated the presence of two rotational isomers, **2A** and **2B**. In the present work this interpretation



2A **2B**

is confirmed by the observation of two septets in the ambient temperature ^{31}P NMR spectrum of **2** (see Experimental Section). The high $\Delta G^{\ddagger}_{NP}$ values for **1** and **2** can be attributed to the steric bulk of the nitrogen substitutents. In the rotational transition state, increasing the steric bulk of the nitrogen substituents renders it more difficult for them to adopt the requisite nonplanar geometry at this center. A similar sterically related trend is seen (Table I) in the $\Delta G^{\ddagger}_{NP}$ values for the series of compounds $R_2NP(CF_3)_2$ (R = Me, Et, *i*-Pr, Me_3Si) and $RR'NPCl_2$ (R = Me_3Si, *t*-Bu; R′ = Me_3Si, *t*-Bu).

The proton NMR spectra of the less sterically hindered silylaminophosphines **9** and **10** were essentially unchanged at temperatures down to −120 °C, permitting only an estimate of ~7 kcal/mol for the upper limit to the N–P torsional barriers. The fact that these values are significantly lower than those reported earlier for the closely related aminophosphines $(CF_3)_2PN(Me)R$ (R = Me, H) (Table I) can be attributed to the difference in the C–N and Si–N bond distances. The longer Si–N bond distance renders steric effects in the rotational transition state less important. A similar comment can be made regarding the $\Delta G^{\ddagger}_{NP}$ values of the *tert*-butylamino and trimethylsilylamino compounds (Table I).

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Registry No. **1**, 57259-78-6; **2**, 57259-79-7; **3**, 61916-02-7; **4**, 50732-22-4; **5**, 61916-03-8; **6**, 33310-82-6; **7**, 54036-90-7; **8**, 61916-04-9; **9**, 61966-90-3; **10**, 61966-91-4; chlorotrimethylsilane, 75-77-4; methylamine, 74-89-5; $Me_3SiN(Me)H$, 16513-17-0; $(CF_3)_2PCl$, 650-52-2; $(CF_3)_2PNH_2$, 431-95-8; $(CF_3)_2PN(Me)H$, 431-98-1; $(Me_3Si)_2NH$, 999-97-3; $(Me_3Si)_2NLi$, 4039-32-1; $Me_3SiN(t\text{-}Bu)Li$, 18270-42-3; $Me_3SiN(Me)Li$, 10568-44-2; PF_3, 7783-55-3; bromosilane, 13465-73-1.

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