Contribution from the Departments of Chemistry, Duke University, Durham,
North Carolina 27706, and The University of Texas at Austin, Austin, Texas 78712

Reactions of Lithium Bis(trimethylsilyl)amide with some Fluorophosphoranes

PATTY WISIAN-NEILSON,[1a] ROBERT H. NEILSON,*[1a] and ALAN H. COWLEY*[1b]

Received July 26, 1976 AIC60529E

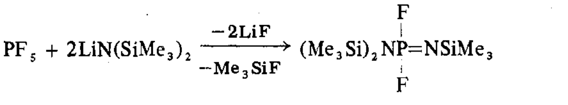
The reactions of various fluorophosphoranes with $LiN(SiMe_3)_2$ were found to proceed with elimination of both LiF and Me_3SiF to produce *N*-trimethylsilylphosphinimines rather than bis(trimethylsilyl)aminophosphoranes. Thus, the reaction with PF_5 afforded $(Me_3Si)_2NPF_2NSiMe_3$ (**1**) while the substituted fluorophosphoranes RPF_4 (R = Ph, NMe_2, Me) and Ph_2PF_3 gave rise to simpler *N*-trimethylsilylphosphinimines, $FPR(R')NSiMe_3$ (**2**, R = F, R′ = Ph; **3**, R = F, R′ = NMe_2; **4**, R = F, R′ = Me; **5**, R = R′ = Ph). Under similar conditions, $LiN(SiMe_3)_2$ did not react with $(Me_2N)_2PF_3$. In the case of Me_2PF_3 only decomposition products of the expected phosphinimine $Me_2PFNSiMe_3$ (**6**) were detected. Preliminary studies have shown that these *P*-fluoro-*N*-trimethylsilylphosphinimines undergo thermal decomposition, eliminating Me_3SiF and forming cyclic phosphazenes $(RR'PN)_n$.

Introduction

In recent years compounds containing the silicon–nitrogen–phosphorus linkage have been of interest for at least two reasons. First, there is the question of how N-silylation affects such stereochemical processes as N–P bond rotation.[2,3] Second, upon treatment with reactive halides, Si–N–P compounds are potentially useful reagents for transferring the N–P moiety to other substrates.[4–6] The known types of Si–N–P compounds include numerous examples of both two-[7,8] and three-coordinate[3,9] trivalent phosphorus as well as three-[10] and four-coordinate[9,11] pentavalent compounds. There does not, however, appear to be any report of an acyclic five-coordinate pentavalent phosphorus compound (i.e., a phosphorane) which contains an Si–N substituent. Thus, the present study, which involves the reactions of lithium bis(trimethylsilyl)amide with PF_5 or substituted fluorophosphoranes, was undertaken as a possible synthetic route to bis(trimethylsilyl)aminophosphoranes. This synthetic approach was adopted because the reaction of phosphorus(III) halides with $LiN(SiMe_3)_2$ has proved to be a valuable source of several Si–N–P compounds.[3,7–9]

Results and Discussion

When PF_5 was allowed to react with lithium bis(trimethylsilyl)amide, neither the desired phosphorane, $(Me_3Si)_2NPF_4$, nor the previously unreported phosphinimine, $F_3P{=}NSiMe_3$, analogous to the product of the reaction of PCl_5 and $LiN(SiMe_3)_2$,[12] was obtained. Instead, the reaction (eq 1) proceeded in a 1:2 stoichiometry to afford high yields of



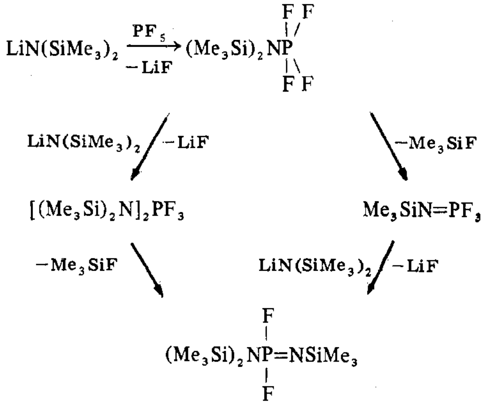
$$PF_5 + 2LiN(SiMe_3)_2 \xrightarrow[-Me_3SiF]{-2LiF} (Me_3Si)_2N\overset{F}{\underset{F}{P}}{=}NSiMe_3 \qquad (1)$$

1

P,P-difluoro-*P*-bis(trimethylsilyl)amino-*N*-trimethylsilylphosphinimine (**1**). This unexpected product could have been produced via at least two pathways (Scheme I). No attempts were made, however, to elucidate the actual course of the reaction.

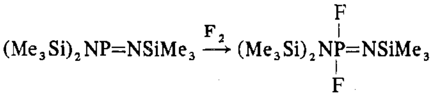
Compound **1** is a colorless, thermally stable (to at least 200 °C) liquid which was fully characterized by ^1H and ^{19}F NMR spectroscopy (Table I), elemental analysis, mass spectrometry, and infrared spectroscopy. Interestingly, the ^1H NMR spectrum consisted of a doublet and a triplet in the intensity ratio 1:2. The doublet can be reasonably assigned to the "imino" Me_3Si groups with splitting (~1 Hz) resulting from coupling to phosphorus. The triplet can then be attributed to the two equivalent "amino" Me_3Si groups with splitting (~1 Hz) resulting from coupling to the two fluorine nuclei. It is somewhat surprising that no coupling to phosphorus was observed for the "amino" Me_3Si groups, although similar preferential couplings have been observed in other Si–N–P systems.[2,13]

Scheme I



1

Independent of our work, compound **1** has been synthesized by another method[14] (eq 2) which involves the direct fluorination of a novel two-coordinate phosphorus compound, $(Me_3Si)_2NPNSiMe_3$.[7]

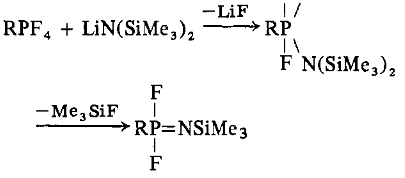


$$(Me_3Si)_2NP{=}NSiMe_3 \xrightarrow{F_2} (Me_3Si)_2N\overset{F}{\underset{F}{P}}{=}NSiMe_3 \qquad (2)$$

1

All physical and spectroscopic data reported[14] for the product of this reaction are identical with those found in the present study. This method is less advantageous, however, because it necessitates the use of special fluorine-handling equipment and because it requires the prior two-step preparation of $(Me_3Si)_2NPNSiMe_3$.[7]

In contrast to the behavior of PF_5,[13] the tetrafluorophosphoranes RPF_4 (R = Ph, Me, NMe_2) reacted with $LiN(SiMe_3)_2$ to produce a different type of Si–N–P compound. These reactions, which exhibited a 1 : 1 stoichiometry, presumably proceed via initial formation of a phosphorane (eq 3) followed by elimination of Me_3SiF to produce the *P,P*-



$$RPF_4 + LiN(SiMe_3)_2 \xrightarrow{-LiF} \overset{F\ F}{\underset{F\ N(SiMe_3)_2}{RP}} \xrightarrow{-Me_3SiF} R\overset{F}{\underset{F}{P}}{=}NSiMe_3 \qquad (3)$$

2, R = Ph
3, R = NMe_2
4, R = Me

Table I. ^{1}H and ^{19}F NMR Data for *P*-Fluoro-*N*-trimethylsilylphosphinimines

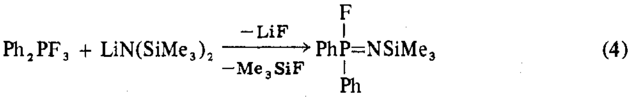
	^{1}H NMR spectra^a		^{19}F NMR spectra^b	
Compd	$\delta(^1\mathrm{H})^c$	Coupling const, Hz	$\delta(^{19}\mathrm{F})^d$	Coupling const, Hz
$(\mathrm{Me_3Si})_2\mathrm{NPF_2NSiMe_3}$ (1)	0.30 $[(\mathrm{Me_3Si})_2\mathrm{N}]$ 0.00 $(\mathrm{Me_3SiN{=}})$	$J_{\mathrm{FPNSiCH}} = 1$ $J_{\mathrm{PNSiCH}} = 1$	51.0	$J_{\mathrm{PF}} = 1021$
$\mathrm{PhPF_2NSiMe_3}$ (2)	0.20 $(\mathrm{Me_3Si})$ 7.68 (Ph)	$J_{\mathrm{PNSiCH}} = 0.6$	57.8	$J_{\mathrm{PF}} = 1078$
$\mathrm{Me_2NPF_2NSiMe_3}$ (3)	0.04 $(\mathrm{Me_3Si})$ 2.70 $(\mathrm{Me_2N})$	$J_{\mathrm{PNSiCH}} = 0.6$ $J_{\mathrm{PNCH}} = 11.3$ $J_{\mathrm{FPNCH}} = 1.6$	73.8	$J_{\mathrm{PF}} = 979$ $J_{\mathrm{HCNPF}} = 1.6$
$\mathrm{MePF_2NSiMe_3}$ (4)	0.02 $(\mathrm{Me_3Si})$ 1.68 (Me)	J_{PNSiCH} 0.8 $J_{\mathrm{PCH}} = 19.5$ $J_{\mathrm{FPCH}} = 5.0$	53.5	$J_{\mathrm{PF}} = 1076$ $J_{\mathrm{HCPF}} = 5.0$
$\mathrm{Ph_2PFNSiMe_3}$ (5)	0.16 $(\mathrm{Me_3Si})$ 7.72 (Ph)	$J_{\mathrm{PNSiCH}} = 0.6$	69.5	$J_{\mathrm{PF}} = 1002$

^{a} Measured relative to external $\mathrm{Me_4Si}$. ^{b} Measured relative to external $\mathrm{CCl_3F}$. ^{c} Solvents: $\mathrm{CCl_2FH}$ for **1**; $\mathrm{CH_2Cl_2}$ for others. ^{d} Solvents: $\mathrm{CCl_2FH}$ for **1–3**; $\mathrm{CH_2Cl_2}$ for **4** and **5**.

difluoro-*N*-trimethylsilylphosphinimines (**2–4**).

These new *N*-trimethylsilylphosphinimines were readily identified by their ^{1}H and ^{19}F NMR spectra (Table I) and were more fully characterized by infrared and mass spectroscopy. Only for the *P*-phenyl compound **2**, however, was a good elemental analysis obtained. Although no impurities were detectable in either the ^{1}H or ^{19}F NMR spectra (Table I) of **3**, repeated fractional distillations failed to produce a sample which exhibited a sharp boiling point and gave a satisfactory elemental analysis. Moreover, analytical data were not obtained for compound **4** because of its thermal instability (see below).

The reactions of $\mathrm{LiN(SiMe_3)_2}$ with some trifluorophosphoranes, $\mathrm{R_2PF_3}$ (R = Ph, $\mathrm{NMe_2}$, Me), were also investigated in this study although the results were not entirely satisfactory. Only $\mathrm{Ph_2PF_3}$ reacted in a straightforward manner (eq 4) to afford good yields of the *N*-silylphosphinimine **5** which was easily purified and fully characterized.



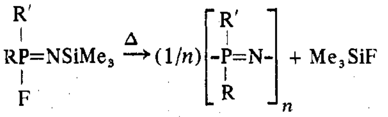
$$\mathrm{Ph_2PF_3 + LiN(SiMe_3)_2 \xrightarrow[-Me_3SiF]{-LiF} Ph\overset{\overset{\textstyle F}{|}}{\underset{\underset{\textstyle Ph}{|}}{P}}{=}NSiMe_3} \qquad (4)$$

5

Another trifluorophosphorane, $(\mathrm{Me_2N})_2\mathrm{PF_3}$, failed to react with $\mathrm{LiN(SiMe_3)_2}$ under conditions similar to those employed for the other reactions. While this may be due to the steric bulk of the two $\mathrm{Me_2N}$ groups, it is possible that the reaction could be made to occur under more vigorous conditions. The third trifluorophosphorane, $\mathrm{Me_2PF_3}$, reacted readily with $\mathrm{LiN(SiMe_3)_2}$; however, only the thermal decomposition products of the expected phosphinimine, $\mathrm{Me_2PFNSiMe_3}$, **6**, could be detected in the reaction mixture (see below).

Compounds **2** and **5**, together with the previously reported $\mathrm{Ph_3P{=}NSiMe_3}$,[15,16] complete a series of *N*-silylphosphinimines with fluorine and phenyl groups as phosphorus substituents. It should be pointed out, however, that *P*-fluoro-*N*-trimethylsilylphosphinimines such as **2** and **5** are not accessible by the other general synthetic routes[11] to *N*-silylphosphinimines.

As part of a study of the chemistry of these new *P*-fluoro-*N*-trimethylsilylphosphinimines, preliminary investigation of their thermal stability has revealed a potentially useful method of preparing a number of cyclic phosphazenes.[17] When compounds **2**, **3**, and **5** were heated at or above 200 °C for several hours, they decomposed (eq 5) via elimination of $\mathrm{Me_3SiF}$ affording previously reported[17] compounds of the general formula $(\mathrm{RR'PN})_n$. The *P*-methylphosphinimine **4** was much less stable and slowly eliminated $\mathrm{Me_3SiF}$ at room temperature (eq 5). The *P*,*P*-dimethyl compound **6** apparently decomposed (eq 5) even more rapidly, thus precluding its isolation from the reaction of $\mathrm{Me_2PF_3}$ and $\mathrm{LiN(SiMe_3)_2}$.



$$\mathrm{R\overset{\overset{\textstyle R'}{|}}{\underset{\underset{\textstyle F}{|}}{P}}{=}NSiMe_3 \xrightarrow{\Delta} (1/\mathit{n})\left[-\overset{\overset{\textstyle R'}{|}}{\underset{\underset{\textstyle R}{|}}{P}}{=}N-\right]_{\mathit{n}} + Me_3SiF} \qquad (5)$$

2, R = F, R′ = Ph
3, R = F, R′ = $\mathrm{NMe_2}$
4, R = F, R′ = Me
5, R = R′ = Ph
6, R = R′ = Me

These phosphazenes are very viscous liquids or waxlike solids, the mass spectra of which contain intense peaks corresponding to the cyclic trimers (n = 3) and tetramers (n = 4) and smaller peaks assignable to the higher oligomers (n = 5, 6). More complete characterization of these products and further investigation of the decomposition reactions which produce them are clearly indicated, particularly since phosphazenes containing two different substituents, $(\mathrm{RR'PN})_n$, are not easily prepared by other methods.[17]

Thus, the reactions of $\mathrm{LiN(SiMe_3)_2}$ with $\mathrm{PF_5}$ and various substituted fluorophosphoranes failed to produce the first Si–N-substituted phosphorane. Indeed, it appears that such compounds are unstable with respect to $\mathrm{Me_3SiF}$ elimination and formation of phosphinimines. These observations are not surprising in view of the facile cleavage of the Si–N bond in silylamines by fluorophosphoranes.[19] More significant, perhaps, is the observation that the resulting *P*-fluoro-*N*-trimethylsilylphosphinimines may be useful precursors to some previously inaccessible phosphazenes.

Experimental Section

Physical Measurements. Proton NMR spectra were obtained using either a JEOL MH-100 or a Perkin-Elmer R-12 spectrometer. Varian A56-60 and Perkin-Elmer R-12 spectrometers were used to obtain the ^{19}F NMR spectra. Routine mass spectra were measured on a CEC 21-491 spectrometer operating at a voltage of 70 eV. High-resolution mass spectra were obtained on a MS-902 spectrometer at the Research Triangle Institute Center for Mass Spectrometry, Research Triangle Park, N.C. Infrared spectra were obtained using a Perkin-Elmer 137, 237, or 337 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Materials. Phosphorus pentafluoride, *n*-butyllithium (*n*-hexane solution), and bis(trimethylsilyl)amine were obtained commercially and used without further purification. Published procedures were used to prepare $\mathrm{PhPF_4}$,[18] $\mathrm{Ph_2PF_3}$,[18] $\mathrm{Me_2NPF_4}$,[19] $(\mathrm{Me_2N})_2\mathrm{PF_3}$,[19] $\mathrm{MePF_4}$,[20] and $\mathrm{Me_2PF_3}$.[18]

General Procedures. Reactions involving volatile starting materials [$\mathrm{PF_5}$, $\mathrm{MePF_4}$, $\mathrm{Me_2PF_3}$, $\mathrm{Me_2NPF_4}$, and $(\mathrm{Me_2N})_2\mathrm{PF_3}$] were performed using a standard Pyrex-glass vacuum line. In these cases, the reaction flask was attached to the vacuum line via a portable U-trap which was equipped with two Teflon stopcocks to permit isolation of the trap contents upon its removal from the vacuum system. Reactions involving less volatile reagents ($PhPF_4$ and Ph_2PF_3) were performed under an atmosphere of dry nitrogen. The solid by-product (presumably LiF) formed in these reactions was not identified. Routinely, the volatile by-product, Me_3SiF, was identified by comparing its infrared spectrum with that of an authentic sample. Solvents were distilled from calcium hydride just prior to use.

***P*,*P*-Difluoro-*P*-bis(trimethylsilyl)amino-*N*-trimethylsilylphosphinimine (1).** An ethyl ether suspension of $LiN(SiMe_3)_2$ was prepared by placing *n*-butyllithium (35.4 mL of 1.45 M, 50 mmol) in a dry, nitrogen-filled flask equipped with a magnetic stirrer. The *n*-hexane was removed from the *n*-BuLi under vacuum before $(Me_3Si)_2NH$ (10.4 mL, 50 mmol) and ethyl ether (20 mL) were condensed into the flask at −196 °C. The mixture was allowed to warm to −78 °C and stirred for 1 h. Phosphorus pentafluoride (60 mmol) was allowed to condense into the stirred suspension of $LiN(SiMe_3)_2$ at −78 °C. After the mixture was allowed to warm slowly to ambient temperature, the bulk of the solvent and other volatiles were removed under vacuum. IR spectroscopy indicated the presence of Me_3SiF in this volatile fraction. The remaining components were transferred by pumping into the U-trap which was cooled to −30 °C. The trap was then isolated from the vacuum system and further manipulations of the contents were performed under an atmosphere of dry nitrogen. Distillation afforded compound **1** as a colorless liquid (5.64 g, 71% yield, bp 55 °C (1.0 Torr)). Both ^1H and ^{19}F NMR spectra were recorded (Table I). The IR spectrum (neat) consisted of absorptions at 2940 (s),[21] 2880 (m), 1390 (s), 1250 (s), 925 (s), 850 (b,vs), 770 (m), 750 (m), 680 (m) cm^{-1}. The major peaks in the mass spectrum were *m*/*e* (relative intensity) 316 (M^+, 15), 301 (100), 229 (25), 160 (28), 73 (90). Anal. Calcd for $C_9H_{27}F_2N_2PSi_3$: C, 34.18; H, 8.54. Found: C, 34.66; H, 8.75.

***P*,*P*-Difluoro-*P*-phenyl-*N*-trimethylsilylphosphinimine (2).** A 500-mL two-neck flask was equipped with a magnetic stirrer, a reflux condenser, and a septum cap, then purged with nitrogen, and charged with $(Me_3Si)_2NH$ (25 mL, 120 mmol) and hexane (125 mL). *n*-Butyllithium (50 mL of 1.5 M, 125 mmol) was added slowly from a syringe to the stirred solution of $(Me_3Si)_2NH$. An exothermic reaction occurred and evolution of a gas (presumably *n*-butane) was observed. After stirring of the mixture at ambient temperature for 45 min, the septum cap was replaced by an addition funnel containing $PhPF_4$ (16.2 mL, 119 mmol). This was added dropwise to the stirred suspension of $LiN(SiMe_3)_2$ at −78 °C. The mixture was allowed to warm and was stirred overnight at ambient temperature. The solid was removed by filtration under nitrogen and the solvent was removed under reduced pressure leaving a viscous, yellow liquid. Distillation afforded compound **2** as a colorless liquid (17.7 g, 64% yield, bp 75 °C (6.0 Torr)). Both ^1H and ^{19}F NMR spectra were recorded (Table I). The IR spectrum (neat) consisted of absorptions at 3065 (vw),[21] 2955 (s), 2900 (vw), 1608 (w), 1450 (vs, b), 1254 (s), 1140 (s), 900 (s), 830 (s), 750 (s), 680 (m) cm^{-1}. The major peaks in the mass spectrum, which did not include the molecular ion, were *m*/*e* (relative intensity), 219 (16), 218 (100), 188 (7), 126 (8), 122 (9), 77 (27), 51 (9). Anal. Calcd for $C_9H_{14}F_2NPSi$: C, 46.35; H, 6.00; N, 6.00. Found: C, 46.86; H, 6.10; N, 5.91.

***P*,*P*-Difluoro-*P*-dimethylamino-*N*-trimethylsilylphosphinimine (3).** The procedure was the same as that described above for the synthesis of compound **1**. Thus, Me_2NPF_4 (44 mmol) reacted with $LiN(SiMe_3)_2$ (44 mmol) to afford compound **3** as a colorless liquid (7.91 g, 90% yield, bp 55–67 °C (62 Torr)). Although no impurities were detected in either the ^1H or ^{19}F NMR spectra (Table I), repeated fractional distillation failed to produce a sample which gave a satisfactory elemental analysis or a sharp boiling point. IR spectrum (vapor phase): 2950 (s),[21] 1460 (s), 1425 (s), 1320 (w), 1270 (m), 1245 (m), 1180 (w), 1060 (w), 1010 (m), 910 (s), 860 (sh, s), 845 (vs), 752 (m), 690 (w), 650 (m), 475 (m) cm^{-1}. Mass spectrum: *m*/*e* (relative intensity) 200 (0.3), 185 (40), 170 (8), 141 (29), 126 (9), 122 (5), 92 (6), 81 (9), 78 (8), 77 (100), 73 (5). The high-resolution mass spectrum contained a molecular ion minus methyl peak at *m*/*e* 185.0477 (calcd 185.0475). Anal. Calcd for $C_5H_{15}F_2NPSi$: C, 30.0; H, 7.50; N, 14.0. Found: C, 32.83, 33.31, 33.36; H, 8.05, 8.17, 8.50; N, 12.88, 12.25, 14.16.

***P*,*P*-Difluoro-*P*-methyl-*N*-trimethylsilylphosphinimine (4).** The procedure was the same as that described above for the synthesis of compound **1**. Thus, $MePF_4$ (32 mmol) reacted with $LiN(SiMe_3)_2$ (32 mmol) to afford compound **4** as a colorless liquid (2.73 g, 50% yield, bp 26–29 °C (56 Torr)). IR spectrum (vapor phase): 2960 (s),[21] 2900 (s), 1445 (s), 1251 (s), 1176 (s), 940 (vs), 850 (vs, b), 760 (m, b) cm^{-1}. Mass spectrum: *m*/*e* (relative intensity) 171 (M^+, 0.1), 156 (64), 126 (15), 92 (4), 77 (100). Satisfactory elemental analyses were not obtained due to the thermal instability of **4**. A freshly prepared NMR sample of **4** exhibited a typical ^1H NMR spectrum (Table I) with only a slight impurity (doublet at δ 0.2, J_{FSiCH} = 7 Hz) which was identified as Me_3SiF.[22] After 2 weeks only the Me_3SiF doublet was observed in the Me_3Si region of the spectrum.

***P*,*P*-Diphenyl-*P*-fluoro-*N*-trimethylsilylphosphinimine (5).** The procedure was the same as that described above for the synthesis of compound **2**. Thus, Ph_2PF_3 (50 mmol) reacted with $LiN(SiMe_3)_2$ (50 mmol) to afford compound **5** as a colorless liquid (10.4 g, 72% yield, bp 98 °C (0.1 Torr)). IR spectrum (neat): 3140 (w),[21] 3030 (m), 1601 (w), 1475 (w), 1427 (s), 1330 (vs, b), 1230 (s), 1117 (s), 1030 (w), 992 (w), 857 (s), 820 (m), 799 (m), 745 (m), 720 (m), 687 (m) cm^{-1}. Mass spectrum: *m*/*e* (relative intensity) 291 (M^+, 0.5), 277 (20), 276 (100), 264 (2), 201 (3), 199 (2), 198 (3), 184 (6), 139 (15), 122 (5), 92 (3), 77 (17). Anal. Calcd for $C_{15}H_{19}FNPSi$: C, 62.0; H, 6.52; N, 4.82. Found: C, 61.60; H, 6.59; N, 4.71.

Reaction of $(Me_2N)_2PF_3$ with $LiN(SiMe_3)_2$. When $(Me_2N)_2PF_3$ (12 mmol) and $LiN(SiMe_3)_2$ (12 mmol) were combined in the same manner as that described above for the synthesis of compound **1**, only unreacted $(Me_2N)_2PF_3$ (1.32 g, 63% recovery) was obtained.

Reaction of Me_2PF_3 with $LiN(SiMe_3)_2$. When Me_2PF_3 and $LiN(SiMe_3)_2$ were allowed to react in the usual manner (see preparation of compound **1**), the Me_2PF_3 was consumed but no appreciable quantities of the expected product $Me_2PFNSiMe_3$ were isolated. In a separate experiment, the reaction mixture was filtered under dry nitrogen after being stirred overnight. Upon standing of the mixture at ambient temperature for several days, the formation of a white precipitate in the filtrate was observed. The mass spectrum of this solid contained peaks corresponding to the cyclic phosphazenes $(Me_2PN)_5$ (*m*/*e* 375), $(Me_2PN)_4$ (*m*/*e* 300), and $(Me_2PN)_3$ (*m*/*e* 225).

Thermal Decomposition Reactions of *P*-Fluoro-*N*-trimethylsilylphosphinimines. A typical experiment is described. Approximately 2 mL of *P*,*P*-difluoro-*P*-phenyl-*N*-trimethylsilylphosphinimine (**2**) was heated in a sealed ampule at 200 °C for 16 h and at 240 °C for 2 h. Two distinct layers formed upon cooling of the mixture to ambient temperature. The volatile component was removed and identified as Me_3SiF by its IR spectrum. The mass spectrum of the viscous liquid contained peaks corresponding to the tetramer $(PhPFN)_4$ (*m*/*e* 564) and the trimer $(PhPFN)_3$ (*m*/*e* 423). Compounds **3**–**5** decomposed similarly, eliminating Me_3SiF and forming nonvolatile residues, the mass spectra of which contained peaks corresponding to the cyclic phosphazenes $(RR'PN)_n$ (R = F, R′ = NMe_2; R = F, R′ = Me; R = R′ = Ph). In all cases peaks assignable to the cyclic trimers (n = 3) and tetramers (n = 4) predominated.

Acknowledgment. The authors are grateful to the National Science Foundation (Grant CHE 76-10331) and the Robert A. Welch Foundation for generous financial support.

Registry No. **1**, 58972-02-4; **2**, 61701-83-5; **3**, 61701-84-6; **4**, 33310-82-6; **5**, 61701-85-7; $(Me_3Si)_2NH$, 999-97-3; PF_5, 7647-19-0; $PhPF_4$, 666-23-9; Me_2NPF_4, 2353-98-2; $MePF_4$, 420-64-4; Ph_2PF_3, 1138-99-4; $LiN(SiMe_3)_2$, 4039-32-1.

References and Notes

(1) (a) Duke University. (b) The University of Texas at Austin.

(2) R. H. Neilson, R. C.-Y. Lee, and A. H. Cowley, *J. Am. Chem. Soc.*, **97**, 5302 (1975).

(3) R. H. Neilson, R. C.-Y. Lee, and A. H. Cowley, *Inorg. Chem.*, preceding paper in this issue.

(4) J. S. Harman, M. E. McCartney, and D. W. A. Sharp, *J. Chem. Soc. A*, 1547 (1971).

(5) R. Appel and I. Ruppert, *Chem. Ber.*, **108**, 589 (1975).

(6) W. Wolfsberger, *J. Organomet. Chem.*, **88**, 133 (1975).

(7) E. Niecke and W. Flick, *Angew. Chem., Int. Ed. Engl.*, **12**, 585 (1973).

(8) O. J. Scherer and N. Kuhn, *Angew. Chem., Int. Ed. Engl.*, **13**, 811 (1974).

(9) R. Keat, *J. Chem. Soc. A*, 1795 (1970).

(10) E. Niecke and W. Flick, *Angew. Chem., Int. Ed. Engl.*, **13**, 134 (1974).

(11) H. Schmidbaur, *Adv. Organomet. Chem.*, **9**, 259 (1970).

(12) E. Niecke and W. Bitter, *Inorg. Nucl. Chem. Lett.*, **9**, 127 (1973).

(13) P. J. Wisian, Ph.D. Dissertation, The University of Texas at Austin, 1976. It was found that CF_3PF_4 reacted with $LiN(SiMe_3)_2$ to produce $(Me_3Si)_2NPF(CF_3)NSiMe_3$. The ^1H NMR spectrum consisted of two doublets in the intensity ratio 1:2 which is very similar to that of compound **1**.

(14) E. Niecke and W. Bitter, *Chem. Ber.*, **109**, 415 (1976).

(15) L. Birkofer, A. Ritter, and P. Richter, *Chem. Ber.*, **96**, 2750 (1963).
(16) H. Schmidbaur and G. Jonas, *Chem. Ber.*, **100**, 1120 (1967).
(17) For an extensive survey of phosphazene chemistry see H. R. Allcock, "Phosphorus-Nitrogen Compounds", Academic Press, New York, N.Y., 1972.
(18) R. Schmutzler, *Inorg. Synth.*, **9**, 63 (1967).
(19) R. Schmutzler, *J. Chem. Soc., Dalton Trans.*, 2687 (1973).
(20) P. M. Treichel, J. Benedict, and R. G. Haines, *Inorg. Synth.*, **13**, 37 (1972).
(21) Key: s, strong; m, medium; w, weak; sh, shoulder; b, broad; v, very.
(22) R. Fields, *Annu. Rep. NMR Spectrosc.*, **5A**, 204 (1972).

Contribution from the Department of Chemistry,
The University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Phosphoranes. 4. Methylbis(trifluoromethyl)phosphoranes, $CH_3(CF_3)_2PXY$, with Monofunctional [F, Cl, OCH_3, $N(CH_3)_2$] Substituents

KWAT I. THE and RONALD G. CAVELL*

Received November 3, 1976

AIC607884

Direct oxidation of $CH_3(CF_3)_2P$ with Cl_2 yields the new phosphorane $CH_3(CF_3)_2PCl_2$ from which $CH_3(CF_3)_2PF_2$, $CH_3(CF_3)_2P(F)OCH_3$, $CH_3(CF_3)_2P(OCH_3)_2$, and $CH_3(CF_3)_2P(F)N(CH_3)_2$ can be obtained by appropriate metathetical substitution reactions. Alternate synthesis of $CH_3(CF_3)_2PF_2$ can be achieved by methylation of $(CF_3)_2PF_3$ with $(CH_3)_4Sn$. Variable-temperature ^{19}F NMR spectroscopy of $CH_3(CF_3)_2PX_2$ (X = F, Cl) is consistent with axial location of the halogens on the trigonal-bipyramidal framework in both cases. The substituted monofluorides $CH_3(CF_3)_2P(F)Y$ (Y = OCH_3, $N(CH_3)_2$) show two nonequivalent (axial and equatorial) CF_3 environments in the low-temperature ^{19}F NMR spectrum. At very low temperatures the axial CF_3 signals in $CH_3(CF_3)_2P(OCH_3)_2$ split into a clear AB_2 pattern due to stopped rotation of OCH_3 and/or CF_3 groups. Heating $CH_3(CF_3)_2P(F)N(CH_3)_2$ yields principally $CH_3(CF_3)PF_2N(CH_3)_2$ presumably by means of CF_2 elimination. Other thermolysis products (e.g., CF_3H) are also found which suggest the participation of other processes. Decomposition of the postulated intermediate $CH_3(CF_3)_2P(Cl)OCH_3$ during synthesis of $CH_3(CF_3)_2P(OCH_3)_2$ from $CH_3(CF_3)_2PCl_2$ is thought to be responsible for the formation of $CH_3(CF_3)_2PO$ in the reaction.

Introduction

Recent studies of the chemistry and stereochemistry of phosphoranes containing CF_3 groups[1,2] indicated that the position of the CF_3 substituents in the five-coordinate framework can be deduced from the NMR spectral parameters.[3] We describe herein a series of trialkylphosphoranes containing two CF_3 groups, one methyl group, and a variety of monofunctional substituents [F, Cl, OCH_3, $N(CH_3)_2$] which provide additional evidence in support of this proposal. In addition low-temperature NMR spectroscopic studies reveal further details of the intramolecular rearrangement processes which occur in these molecules.

Results and Discussion

A. Synthetic Considerations. Chlorine smoothly oxidized methylbis(trifluoromethyl)phosphine to the dichlorophosphorane $CH_3(CF_3)_2PCl_2$ in good yield in a manner analogous to the behavior of $(CF_3)_3P$[4]

$$\mathrm{CH_3(CF_3)_2P + Cl_2 \rightarrow CH_3(CF_3)_2PCl_2} \tag{1}$$

The fluorophosphorane was obtained by fluorination of the chlorophosphorane with antimony trifluoride

$$\mathrm{CH_3(CF_3)_2PCl_2 \xrightarrow{SbF_3} CH_3(CF_3)_2PF_2} \tag{2}$$

or by methylation of $(CF_3)_2PF_3$ with $(CH_3)_4Sn$[5]

$$\mathrm{(CF_3)_2PF_2 + (CH_3)_4Sn \rightarrow CH_3(CF_3)_2PF_2 + (CH_3)_3SnF} \tag{3}$$

Although good yields were obtained in both cases, the latter route is potentially less useful because some of the reactant is lost to salt formation[6]

$$\mathrm{(CF_3)_2PF_3 + (CH_3)_3SnF \rightarrow [(CH_3)_3Sn][(CF_3)_2PF_4]} \tag{4}$$

but only a small quantity of the complex salt was found in the solid residues. $(CH_3)_4Sn$ is difficult to separate from $CH_3(CF_3)_2PF_2$;[5] however, the use of excess $(CF_3)_2PF_3$ followed by careful fractionation leads to relatively pure product.

Simple substitution of both of the halogenophosphoranes was effected by means of the silane reagents[7] $(CH_3)_3SiY$; for example, reaction of $CH_3(CF_3)_2PCl_2$ with excess methoxytrimethylsilane gave methylbis(trifluoromethyl)dimethoxyphosphorane, $CH_3(CF_3)_2P(OCH_3)_2$, in variable yield along with $CH_3(CF_3)_2PO$[8]

$$\mathrm{CH_3(CF_3)_2PCl_2 + 2(CH_3)_3SiOCH_3 \rightarrow (1-\mathit{x})CH_3(CF_3)_2P(OCH_3)_2 + \mathit{x}CH_3(CF_3)_2PO + (2-\mathit{x})(CH_3)_3SiCl + \mathit{x}CH_3Cl} \tag{5}$$

Interestingly, the best yield of the dimethoxyphosphorane was obtained if the reaction was carried out in the presence of a catalytic amount of iodine. In the absence of iodine $CH_3(CF_3)_2PO$ constituted about 50% of the phosphorus-containing products. The formation of equal proportions of $CH_3(CF_3)_2PO$ and CH_3Cl in reaction 5 suggested that the partially substituted chlorophosphorane $CH_3(CF_3)_2P(OCH_3)Cl$ was unstable and decomposed to the phosphine oxide and methyl chloride

$$\mathrm{CH_3(CF_3)_2P(OCH_3)Cl \rightarrow CH_3(CF_3)_2PO + CH_3Cl} \tag{6}$$

The dimethoxyphosphorane $CH_3(CF_3)_2P(OCH_3)_2$ is stable under normal conditions and is easily handled under vacuum. The phosphine oxide was alternatively prepared by reaction of the phosphine $CH_3(CF_3)_2P$ with NO_2,[9] an easier method than those used initially to prepare this compound.[8]

The partially substituted fluorophosphoranes $CH_3(CF_3)_2P(F)Y$ [Y = OCH_3, $N(CH_3)_2$] were synthesized from $CH_3(CF_3)_2PF_2$ and equimolar quantities of the appropriate trimethylsilane derivative $(CH_3)_3SiY$

$$\mathrm{CH_3(CF_3)_2PF_2 + (CH_3)_3SiY \rightarrow CH_3(CF_3)_2P(Y)F + (CH_3)_3SiF} \tag{7}$$
$$\mathrm{Y = OCH_3,\ N(CH_3)_2}$$

The mono(dimethylamino) derivative was also obtained by direct gaseous aminolysis of the fluorophosphorane with dimethylamine

$$\mathrm{2CH_3(CF_3)_2PF_2 + 3(CH_3)_2NH \rightarrow 2CH_3(CF_3)_2P[N(CH_3)_2]F + (CH_3)_2NH_2HF_2} \tag{8}$$

A large excess of dimethylamine under more strenuous conditions did not effect further substitution of the remaining fluorine substituent. Further heating led to the thermal decomposition of the monofluorophosphorane by CF_2 elimination and other processes.