

$\text{LiZn}_2(\text{CH}_3)_4\text{H}$  would also react with  $\text{AlH}_3$  to give an intermediate like XVI which would then undergo an intramolecular rearrangement to give VI and V. The critical step in this type of rearrangement would be a solvent-aided breakage of the Zn-H-Zn bond in XVI to give XVII through transition state XVIa. If, when the cation is K, the Zn-H-Zn bridge bond in XVI is too strong to be broken by a solvent attack on zinc, then XVI would be observed and not VI or V. With the lifetime of XVI increased, it could then undergo exchange with  $\text{AlH}_3$  to give  $\text{KZn}_2\text{H}_5$ . Our studies show that in solutions where the alkali metal:zinc ratio is 1:2, the percent  $\text{MZn}_2(\text{CH}_3)_4\text{H}$  present (see equation 8) is 60, 71, and 85 when the cation is Li, Na, and K, respectively. This certainly does indicate that the Zn-H-Zn bond in XVI would be stronger when the cation is K than when it is Li or Na.

In the mechanism shown in Scheme III, the first step involves the loss of solvent in five-coordinate alane to form four-coordinate alane, which then reacts with  $\text{LiZn}_2(\text{CH}_3)_4\text{H}$  to give intermediate XVIII via transition state XVIIIa. Intermediate XVI is then formed via transition state XVIIIb. The Zn-H-Zn bridge bond in X is then cleaved by reaction with solvent via transition state XVIa to form intermediate XVII. Intermediate XVII then undergoes loss of solvent from zinc and aluminum via transition states XIIa and VIa, respectively, to form the final products VI and V. Again, the equilibrium lies largely in favor of VI and V since they are the species observed spectroscopically.

A discussion of why a solid with a Li:Zn ratio of 1:2 forms when  $\text{LiZn}(\text{CH}_3)_2\text{AlH}_4$  is allowed to stand at room temperature will be more appropriately included in a later paper<sup>18</sup> dealing with the mechanisms of the reactions of  $\text{NaZn}(\text{C}_6\text{H}_5)_2\text{H}$  and  $\text{NaZn}_2(\text{CH}_3)_4\text{H}$  with  $\text{AlH}_3$  in THF. The mechanisms of the reactions of  $\text{KZn}(\text{CH}_3)_2\text{H}$  and  $\text{KZn}_2(\text{C}_6\text{H}_5)_4\text{H}$  with  $\text{AlH}_3$  to produce  $\text{KZn}_2\text{H}_5$  will also be discussed at that time.

The discovery of  $\text{LiZn}(\text{CH}_3)_2\text{AlH}_4$  and  $\text{LiZn}_2(\text{CH}_3)_4\text{AlH}_4$  provides some insight into the nature of alkyl-hydrogen exchange reactions between zinc and aluminum. For example, the reaction of  $\text{LiAlH}_4$  with  $(\text{CH}_3)_2\text{Zn}$  in diethyl ether is a

standard method for the preparation of zinc hydride.<sup>19</sup> One would expect this reaction to involve an intermediate such as  $\text{LiZn}(\text{CH}_3)_2\text{AlH}_4$ . A study of the reaction of  $(\text{CH}_3)_2\text{Zn}$  and  $\text{LiAlH}_4$  in THF does provide evidence concerning this point.<sup>16</sup>

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**Registry No.**  $\text{LiZn}(\text{CH}_3)_2\text{AlH}_4$ , 59092-43-2;  $\text{LiZn}_2(\text{CH}_3)_4\text{AlH}_4$ , 62166-60-3;  $\text{LiZn}(\text{CH}_3)_2\text{H}$ , 26520-83-2;  $\text{LiZn}_2(\text{CH}_3)_4\text{H}$ , 62126-56-1;  $(\text{CH}_3)_2\text{Zn}$ , 544-97-8;  $\text{AlH}_3$ , 7784-21-6.

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## The Reaction of Amines, Ammonia, and Pyridine with Tetra- and Trifluorophosphorane. The Formation of $\text{HPF}_5^-$ and $\text{H}_2\text{PF}_4^-$ Anions

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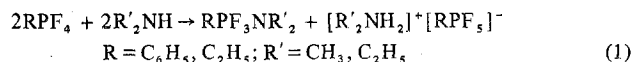
The liquid-phase reactions of  $\text{HPF}_4$  and  $\text{H}_2\text{PF}_3$  with  $(\text{CH}_3)_3\text{N}$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{NH}_3$ , and pyridine have been investigated. Treatment of  $\text{HPF}_4$  with these bases results in the production of the pentafluorophosphate anion,  $\text{PF}_6^-$ , as its ammonium, substituted ammonium, or pyridinium salt. The liquid-phase reaction of  $\text{H}_2\text{PF}_3$  with  $(\text{CH}_3)_3\text{N}$  or  $(\text{CH}_3)_2\text{NH}$  results in the production of the tetrafluorophosphate anion,  $\text{H}_2\text{PF}_4^-$ , as its substituted ammonium salt. However, treatment of  $\text{H}_2\text{PF}_3$  with  $\text{CH}_3\text{NH}_2$ ,  $\text{NH}_3$ , or pyridine produces unidentified insoluble orange precipitates which do not contain detectable quantities of the  $\text{H}_2\text{PF}_4^-$  anion. NMR data are reported for the  $\text{HPF}_5^-$  and  $\text{H}_2\text{PF}_4^-$  anions and mechanisms are suggested for their formation reactions.

### Introduction

It is widely recognized<sup>2</sup> that  $\text{PF}_5$  exhibits a Lewis acid behavior comparable to that of  $\text{BF}_3$ . Thus, treatment of  $\text{PF}_5$  with a variety of Lewis bases such as the fluoride anion, dimethyl sulfoxide, and amines yields adducts of the composition  $\text{base} \rightarrow \text{PF}_5$ . Octahedral coordination around the phosphorus atom has been confirmed by x-ray crystallography in the cases of the  $\text{PF}_6^-$  anion<sup>3</sup> and the pyridine adduct of  $\text{PF}_5$ .<sup>4</sup> Much less attention, however, has been paid to the acceptor

capabilities of substituted phosphorus(V) fluorides. In part this stems from the fact that the acceptor strength<sup>5</sup> is known to decrease in the sequence  $\text{PF}_5 > \text{ArylPF}_4 > \text{AlkylPF}_4 \gg \text{R}_2\text{PF}_3$ . Nevertheless, tetrafluorophosphoranes can function as acceptors toward sufficiently strong donors<sup>5,6</sup> and trifluorophosphoranes can be induced into intramolecular N→P coordinate bonding in certain cyclic systems.<sup>7</sup> However, in many cases, treatment of a tetrafluorophosphorane with a Lewis base leads to products other than simple adducts. For

example, the reaction of alkyl or aryltetrafluorophosphoranes with dialkylamines leads to the appropriate dialkylamino-substituted trifluorophosphorane and novel anions of the type  $\text{RPF}_5^-$ .<sup>6</sup>



In view of the foregoing it seemed appropriate to attempt the reactions of the parent tetra- and trifluorophosphoranes,  $\text{HPF}_4$ <sup>8,9</sup> and  $\text{H}_2\text{PF}_3$ ,<sup>9</sup> with a selection of simple Lewis bases. If adduct formation did not take place this type of reaction would lead to the interesting anions  $\text{HPF}_5^-$ <sup>10</sup> and  $\text{H}_2\text{PF}_4^-$ .<sup>11</sup> On the other hand, if stable adducts of the general formula  $\text{base} \rightarrow \text{PF}_n\text{H}_{5-n}$ ,  $n = 3, 4$ , were isolable, experiments could be devised for the quantitative assay of the relative acceptor capabilities of  $\text{PF}_5$ ,  $\text{PF}_4\text{H}$ , and  $\text{PF}_3\text{H}_2$  (and possibly  $\text{PF}_2\text{H}_3$  also).<sup>12</sup> While ligand electronegativity considerations would suggest the Lewis acidity sequence  $\text{PF}_5 > \text{PF}_4\text{H} > \text{PF}_3\text{H}_2 > \text{PF}_2\text{H}_3$ , the possibility of unusual acceptor behavior is raised by the interesting observation<sup>13</sup> that the fluorophosphine,  $\text{PF}_2\text{H}$ , exhibits an unusually high Lewis basicity compared to its symmetrical counterparts  $\text{PF}_3$  and  $\text{PH}_3$ . Finally, whichever way these reactions proceeded, several of the potential products possessed stereochemical interest.

### Experimental Section

**Physical Measurements.** Infrared spectra were measured on either a Perkin-Elmer Model 337 or a Beckman IR 9 spectrophotometer. Vapor samples were run between 10 and 40 Torr of pressure in a 10-cm path length Pyrex glass cell equipped with KBr optics. Solid samples were run as Nujol mulls between KBr plates. Mass spectra were obtained with a Consolidated Electro Dynamics Corporation Model CE C 21-491 spectrometer using an ionizing voltage of 70 eV. The <sup>1</sup>H and <sup>19</sup>F NMR spectra were obtained with either a Varian Associates HA-100 or a Varian Associates A 56/60 spectrometer.

**Materials.** The methylamines,  $\text{NH}_3$ , and dimethyl sulfoxide- $d_6$  were procured commercially and used without subsequent purification. Pyridine and  $\text{CH}_2\text{Cl}_2$  were dried by refluxing over, then distilling from,  $\text{CaH}_2$  prior to use, and  $\text{CD}_3\text{CN}$  was dried by storage over  $\text{CaH}_2$ . Tetrafluorophosphorane,<sup>8d</sup>  $\text{H}_2\text{PF}_3$ ,<sup>14</sup> and  $(\text{CH}_3)_2\text{NPF}_4$ <sup>15</sup> were prepared and purified according to published procedures. Trimethylstannane was prepared by the action of  $\text{LiAlH}_4$  on  $(\text{CH}_3)_3\text{SnCl}$ .<sup>14</sup>

**General Techniques.** All manipulations of volatile materials were carried out using a conventional Pyrex glass vacuum line operating between  $10^{-4}$  and  $10^{-5}$  Torr. Apiezon L grease was used on most of the ground glass joints. Nonvolatile solids were handled in a helium filled drybox. All reactions were carried out in a 200-mL capacity Pyrex bulb reactor equipped with a 14/20 ground glass joint and several side arms to which NMR tubes could be attached. In some cases a glass wool filter was placed in the side arm to permit the removal of suspended solids. The reactor was attached to the vacuum line via a stopcocked adapter, thus allowing removal of the assembly from the vacuum system for further manipulations.

**Reaction of  $(\text{CH}_3)_3\text{N}$  with  $\text{HPF}_4$ .** Equimolar quantities (2.96 mmol) of  $(\text{CH}_3)_3\text{N}$  and  $\text{HPF}_4$  were condensed into the reaction bulb at  $-196^\circ\text{C}$ . Reaction took place suddenly upon warming the reactor from  $-196$  to  $-78^\circ\text{C}$  as evidenced by the formation of white clouds of solid. After 1–2 h at  $-78^\circ\text{C}$  the reaction mixture was warmed to ambient temperature and approximately 2.8 mmol of vapor was transferred into the vacuum line. Mass spectroscopic analysis of the vapor indicated that it comprised 1.46 mmol of  $(\text{CH}_3)_3\text{N}$  and 1.35 mmol of  $\text{PF}_3$ . This assay was made on the basis of comparing the intensities of the parent peaks of  $(\text{CH}_3)_3\text{N}$  ( $m/e$  59) and  $\text{PF}_3$  ( $m/e$  88) in the unknown sample with those in mixtures of known composition. The presence of  $(\text{CH}_3)_3\text{N}$  and  $\text{PF}_3$  in the vapor was also established by IR spectroscopy.

Following the removal of the volatiles,  $\text{CD}_3\text{CN}$  was distilled onto the white residue in the reactor. After removing the reactor from the vacuum line the mixture was shaken gently and the  $\text{CD}_3\text{CN}$  solution and white solid were transferred into the NMR tube. In order to maximize the solute concentration it was necessary to distill the solvent back on the the residual solid in the reactor and to repeat the washing procedure several times. Following this, small amounts of

the internal standards  $\text{CCl}_3\text{F}$  and  $(\text{CH}_3)_4\text{Si}$  were distilled into the NMR tube which was then sealed off in vacuo at an appropriate constriction after cooling to  $-196^\circ\text{C}$ . The solute was shown to be  $[(\text{CH}_3)_3\text{NH}]^+[\text{HPF}_5]^-$  by NMR spectroscopy.<sup>16</sup> The <sup>1</sup>H spectrum comprised singlets at  $\delta$  2.86 and 7.54 for the  $\text{CH}_3$  and  $\text{NH}$  groups, respectively, and a doublet of quintets at  $\delta$  5.66 for the  $\text{PH}$  group, with  $J_{\text{PH}} = 948$  Hz,  $J_{\text{F,PH}} = 127$  Hz, and  $J_{\text{F,PH}} \approx 0$  Hz. The <sup>19</sup>F spectra of all the  $\text{HPF}_5^-$  salts reported here were superimposable and consisted of a doublet of doublets of doublets at 56.0 ppm for the  $\text{F}_a$  groups ( $J_{\text{PF}_a} = 818$  Hz,  $J_{\text{F}_b\text{PF}_a} = 42$  Hz, and  $J_{\text{HPF}_a} = 126$  Hz), and a doublet of quintets at 65.9 ppm for the  $\text{F}_b$  group ( $J_{\text{PF}_b} = 730$  Hz,  $J_{\text{F}_a\text{PF}_b} = 42$  Hz, and  $J_{\text{HPF}_b} \approx 0$  Hz). The reactor, containing residual  $[(\text{CH}_3)_3\text{NH}]^+[\text{HPF}_5]^-$ , was then transferred to the drybox in order to prepare a Nujol mull sample. Peaks attributable to the  $\text{HPF}_5^-$  anion were detected at 2390 w,<sup>17</sup> 1310 w, 1240 m, 1152 w, 1119 w, 987 m, 770 s, br, 655 m, 607 m, 560 m, 545 w, 515 m, and 482  $\text{cm}^{-1}$ .

**Reaction of  $(\text{CH}_3)_2\text{NH}$  with  $\text{HPF}_4$ .** The procedure which was employed was similar to that described above using 2.02 mmol each of  $(\text{CH}_3)_2\text{NH}$  and  $\text{HPF}_4$ . However, in this case no white solid formation was observed. The reaction mixture was a viscous, clear liquid at  $-78^\circ\text{C}$  which gradually solidified at room temperature as the volatiles were removed. The presence of the  $\text{HPF}_5^-$  anion in the solid material was established by NMR<sup>16</sup> and IR spectral data. The <sup>1</sup>H NMR spectrum ( $\text{CD}_3\text{CN}$  solution) consisted of singlets at  $\delta$  2.60 and 6.92 for the  $\text{CH}_3$  and  $\text{NH}_2$  groups, respectively, and a doublet of quintets at  $\delta$  5.65 for the  $\text{PH}$  group, with  $J_{\text{PH}} = 951$  Hz,  $J_{\text{F,PH}} = 127$  Hz, and  $J_{\text{F,PH}} \approx 0$  Hz. IR peaks corresponding to  $\text{HPF}_4^-$  were detected at 2420 w,<sup>17</sup> 2380 w, 1582 w, 1515 sh, 1310 w, br, 1255 sh, 1240 m, 1155 w, br, 1095 w, br, 1015 sh, 945 sh, 770 vs, br, 608 s, 559 m, 515 m, and 485  $\text{cm}^{-1}$ . Numerous attempts to secure <sup>1</sup>H and <sup>19</sup>F NMR spectral data for the initially formed liquid phase at either low or ambient temperature were unsuccessful due to its facile decomposition. However, mass spectrometric assay of the vapor above the liquid revealed a peak of relative intensity 1.6 at  $m/e$  133 which is assignable to  $(\text{CH}_3)_2\text{NPF}_3\text{H}^+$ . Other major peaks, together with tentative assignments and relative intensities, were: 132 ( $\text{C}_2\text{H}_6\text{NPF}_3^+$ , 5.7); 113 ( $\text{C}_2\text{H}_6\text{NPF}_2^+$ , 49.2); 112 ( $\text{C}_2\text{H}_5\text{NPF}_2^+$ , 51.6); 94 ( $\text{C}_2\text{H}_5\text{NPF}^+$ , 14.8); 89 ( $\text{HPF}_3^+$ , 8.0); 88 ( $\text{PF}_3^+$ , 15.7); 69 ( $\text{PF}_2^+$ , 38.2); 51 ( $\text{HPF}^+$ , 22.9); 50 ( $\text{PF}^+$ , 51.6); 45 ( $\text{C}_2\text{H}_5\text{NH}^+$ , 14.8); 44 ( $\text{C}_2\text{H}_6\text{N}^+$ , 37.7); 43 ( $\text{C}_2\text{H}_5\text{N}^+$ , 16.4); 42 ( $\text{C}_2\text{H}_4\text{N}^+$ , 100). IR spectroscopic examination of the volatiles (0.42 mmol) revealed the presence of  $(\text{CH}_3)_2\text{NPF}_2$  and traces of  $\text{PF}_3$ . This conclusion was based on the detection of P–F stretching vibrations at 778 and 812  $\text{cm}^{-1}$  for  $(\text{CH}_3)_2\text{NPF}_2$  (lit.<sup>18</sup> 772 and 812  $\text{cm}^{-1}$ ) and 865 and 888  $\text{cm}^{-1}$  for  $\text{PF}_3$  (lit.<sup>19</sup> 860 and 892  $\text{cm}^{-1}$ ).

In another experiment 4.94 mmol of  $(\text{CH}_3)_2\text{NH}$  and 9.89 mmol of  $\text{HPF}_4$  were allowed to remain at  $-78^\circ\text{C}$  for 2 h and at  $-15$  to  $-20^\circ\text{C}$  for 10 min. Some of the volatiles were removed by pumping through a  $-196^\circ\text{C}$  trap while maintaining the reaction flask at  $-15$  to  $-20^\circ\text{C}$ . In order to complete the reaction (i.e., to transform the viscous liquid in the reaction vessel to a white solid) the reaction mixture was allowed to warm to ambient temperature, pumping being continued for 1.5 h. Upon transferring the volatiles in the  $-196^\circ\text{C}$  trap further reaction took place as evidenced by the deposition of traces of white solid. Mass spectrometric assay of the volatiles revealed peaks corresponding to the parent ions  $\text{HPF}_4^+$ ,  $(\text{CH}_3)_2\text{NPF}_2^+$ , and  $\text{PF}_3^+$ . <sup>19</sup>F NMR spectroscopic examination of the volatiles ( $\text{CHCl}_2\text{F}$  solution) at  $-20^\circ\text{C}$  and  $-70^\circ\text{C}$  confirmed the presence of  $\text{HPF}_4$ ,<sup>8d</sup>  $(\text{CH}_3)_2\text{NPF}_2$ ,<sup>17a</sup> and  $\text{PF}_3$ . The relative intensity of the  $\text{PF}_3$  resonance was not sensitive to temperature.

**Reaction of  $\text{CH}_3\text{NH}_2$  with  $\text{HPF}_4$ .** Using the procedure described above equimolar quantities (2.0 mmol) of  $\text{CH}_3\text{NH}_2$  and  $\text{HPF}_4$  reacted at  $-78^\circ\text{C}$  to afford a viscous liquid which solidified upon warming to ambient temperature as the volatiles were removed. The white solid was identified as  $[\text{CH}_3\text{NH}_3]^+[\text{HPF}_5]^-$  on the basis of NMR<sup>16</sup> and IR data. The <sup>1</sup>H NMR spectrum ( $\text{CD}_3\text{CN}$  solution) consisted of singlets at  $\delta$  2.54 and 6.52 for the  $\text{CH}_3$  and  $\text{NH}_3$  groups, respectively, and a doublet of quintets at  $\delta$  5.66 for the  $\text{PH}$  group, with  $J_{\text{PH}} = 953$  Hz,  $J_{\text{F,PH}} = 127$  Hz, and  $J_{\text{F,PH}} \approx 0$  Hz. IR peaks were detected at 2370 w,<sup>17</sup> 2040 w, 1620 m, br, 1233 m, br, 1210 w, 1090 w, 965 m, 940 m, 920 w, 770 s, br, 605 m, 558 m, 510 m, 473 m, and 450  $\text{cm}^{-1}$ . IR spectroscopic examination of the volatiles (0.61 mmol) revealed the presence of  $\text{CH}_3\text{N}(\text{H})\text{PF}_2$ <sup>20</sup> and trace quantities of  $\text{PF}_3$  and  $\text{P}(\text{O})\text{F}_3$ .

**Vapor Phase Reaction of  $\text{CH}_3\text{NH}_2$  with  $\text{HPF}_4$ .** This reaction was conducted in a two-bulb reactor similar to that described by Treichel,

Goodrich, and Pierce.<sup>9b</sup> The volumes of the bulbs were approximately 200 and 1000 mL. An NMR tube was attached to the larger bulb via a side arm containing a constriction. Methylamine (3.0 mmol) was condensed into the smaller bulb and 3.0 mmol of  $\text{HPF}_4$  was condensed into the larger bulb. The whole apparatus was allowed to assume ambient temperature and the interconnecting stopcock was opened. Immediate formation of a white solid was observed. Deuterated acetonitrile was distilled into the larger bulb and the resulting solution was poured into the NMR tube which was then sealed off in vacuo at  $-196^\circ\text{C}$ . Examination of the solid and vapor products by NMR and IR spectroscopy indicated that the reaction had proceeded in the same manner as the liquid phase reaction.

**Reaction of  $\text{NH}_3$  with  $\text{HPF}_4$ .** Using the procedure described above for the  $(\text{CH}_3)_3\text{N}/\text{PF}_5\text{H}$  reaction an equimolar (2.22 mmol) mixture of  $\text{NH}_3$  and  $\text{HPF}_4$  reacted suddenly upon warming from  $-196$  to  $-78^\circ\text{C}$  as evidenced by the formation of a cloud of white solid. The white solid was identified as  $[\text{NH}_4]^+[\text{HPF}_5]^-$  on the basis of NMR<sup>16</sup> and IR data. The  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{CN}$  solution) consisted of a singlet at  $\delta$  5.96 for the ammonium cation and a doublet of quintets at  $\delta$  5.64 for the  $\text{HPF}_5^-$  anion, with  $J_{\text{PH}} = 951$  Hz,  $J_{\text{F,PH}} = 127$  Hz, and  $J_{\text{F,PH}} \approx 0$  Hz. The following characteristic IR frequencies were detected for  $\text{HPF}_5^-$ : 2520 vw, br,<sup>17</sup> 2420 sh, 2400 m, 2060 w, br, 1820 w, br, 1710 w, 1300 w, 1238 m, 1140 vw, 1090 vw, 780 s, br, 608 m, 560 m, 518 m, and 480  $\text{cm}^{-1}$ .

**Reaction of Pyridine with  $\text{HPF}_4$ .** Approximately 3.0 mL of pyridine and 2.8 mmol of  $\text{HPF}_4$  were condensed into the 200-mL reaction bulb and the reaction mixture was warmed to  $-42^\circ\text{C}$  and maintained at this temperature for 30 min. The bulb was shaken, cooled to  $-196^\circ\text{C}$ , and warmed to  $-42^\circ\text{C}$  several times, thereby facilitating complete mixing of the reagents. IR spectroscopic examination of the volatiles (1.4 mmol) revealed the presence of  $\text{PF}_3$ . Following the removal of the volatiles excess pyridine was eliminated by pumping overnight. The identity of the residual white solid was established as  $[\text{C}_5\text{H}_5\text{NH}]^+[\text{HPF}_5]^-$  by means of NMR<sup>16</sup> and IR data. The  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{CN}$  solution) comprised complex multiplets at  $\delta \sim 8.56$  and  $\sim 8.72$  corresponding to the pyridine ring protons, a singlet at  $\delta$  13.78 for the NH group, and a doublet of quintets for the  $\text{HPF}_5^-$  anion, with  $J_{\text{PH}} = 951$  Hz,  $J_{\text{F,PH}} = 127$  Hz, and  $J_{\text{F,PH}} \approx 0$  Hz. Characteristic IR frequencies were detected at 2730 vw,<sup>17</sup> 2495 w, 2375 m, 1890 vw, br, 1302 w, 1250 m, 1208 w, 1107 w, 1029 w, 1000 w, 750–800 s, br, 670 s, 600 m, 553 m, 510 m, and 478  $\text{cm}^{-1}$ .

**Reaction of  $(\text{CH}_3)_2\text{NPF}_4$  with  $(\text{CH}_3)_3\text{SnH}$ .** Two procedures were employed. The first method involved sealing equimolar quantities of  $(\text{CH}_3)_2\text{NPF}_4$  and  $(\text{CH}_3)_3\text{SnH}$  in an NMR tube at  $-196^\circ\text{C}$ . In the second method 5.0 mmol each of  $(\text{CH}_3)_2\text{NPF}_4$  and  $(\text{CH}_3)_3\text{SnH}$  were allowed to react in the vapor phase at ambient temperature using the two-bulb apparatus which was described above. Trimethylstannane was placed in the smaller bulb. After rapidly cooling the reaction mixture to  $-196^\circ\text{C}$  and rewarming to ambient temperature the products were condensed into an NMR tube which was sealed off at  $-196^\circ\text{C}$ .

Samples prepared by both methods were allowed to warm slowly in the probe of the NMR spectrometer. However, it was not possible to obtain satisfactory NMR spectra because of the rapid decomposition of the liquid phase. Similar observations have been made by Goodrich and Treichel.<sup>21</sup>

**Reaction of  $(\text{CH}_3)_3\text{N}$  with  $\text{H}_2\text{PF}_3$ .** Using the apparatus described above for the  $\text{HPF}_4$  reactions 3.83 mmol of  $\text{H}_2\text{PF}_3$ , 3.70 mmol of  $(\text{CH}_3)_3\text{N}$ , and  $\sim 4$  mL of  $\text{CH}_3\text{CN}$  were condensed together at  $-196^\circ\text{C}$  and allowed to warm slowly to  $-100^\circ\text{C}$ . After 2 h at  $-100^\circ\text{C}$  a slight yellow color was apparent. A rapid color change to bright orange occurred upon warming the reaction mixture to between  $-70$  and  $-80^\circ\text{C}$ . After 30 min at  $-80^\circ\text{C}$  the reaction mixture was allowed to warm to ambient temperature. At this point the reaction mixture was dark brown; however, traces of a white solid were clearly visible. The reaction mixture was then filtered through a glass wool plug into an NMR tube which was sealed in vacuo at  $-196^\circ\text{C}$ . Initially the solution in the NMR tube was relatively clear; however, in the process of measuring the  $^{19}\text{F}$  NMR spectra sample decomposition was evident from the precipitation of yellow-orange solids. However, NMR data clearly establish the identity of the product as  $[(\text{CH}_3)_3\text{NH}]^+[\text{H}_2\text{PF}_4]^-$ . The  $^1\text{H}$  spectrum consisted of singlets at  $\delta$  2.75 and 8.2 for the  $\text{CH}_3$  and NH groups and a doublet of quintets at  $\delta$  5.8 for the  $\text{H}_2\text{PF}_4^-$  anion with  $J_{\text{PH}} = 936$  Hz and  $J_{\text{FPH}} = 123$  Hz. The  $^{19}\text{F}$  spectrum comprised a doublet of triplets at 53.3 ppm with  $J_{\text{PF}} = 806$  Hz and  $J_{\text{HPF}} = 123$  Hz.

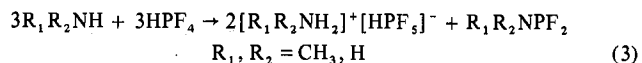
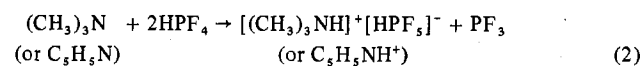
In another experiment equimolar quantities (2.13 mmol) of  $\text{H}_2\text{PF}_3$  and  $(\text{CH}_3)_3\text{N}$  were allowed to react at  $-78^\circ\text{C}$  for 30 min before warming to ambient temperature. The volatile product for this reaction ( $\sim 0.5$  mmol) was identified as  $\text{HPF}_2$  on the basis of IR spectroscopy.<sup>22</sup>

**Reaction of  $(\text{CH}_3)_2\text{NH}$  with  $\text{H}_2\text{PF}_3$ .** Equimolar quantities (4.8 mmol) of  $\text{H}_2\text{PF}_3$  and  $(\text{CH}_3)_2\text{NH}$  were condensed together at  $-196^\circ\text{C}$  and allowed to warm slowly to  $-78^\circ\text{C}$ . After  $\sim 2$  h at  $-78^\circ\text{C}$  the reaction mixture was warmed to ambient temperature. The volatile product (0.31 mmol) was shown to be  $\text{HPF}_2$  on the basis of IR spectroscopy.<sup>22</sup> As in the case of the reaction of  $(\text{CH}_3)_3\text{N}$  with  $\text{H}_2\text{PF}_3$  large quantities of yellow-orange colored solids were precipitated. However,  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectra of the freshly formed solid in  $\text{CD}_3\text{CN}$  solution indicated the presence of  $[(\text{CH}_3)_2\text{NH}_2]^+[\text{H}_2\text{PF}_4]^-$ . The  $^1\text{H}$  spectrum featured singlets at  $\delta$  2.66 and 7.21 corresponding to the  $\text{CH}_3$  and  $\text{NH}_2$  groups, respectively, and a doublet of quintets at  $\delta$  5.63 ( $J_{\text{PH}} = 943$  Hz and  $J_{\text{FPH}} = 120$  Hz) for the  $\text{H}_2\text{PF}_4^-$  anion. The  $^{19}\text{F}$  spectrum exhibited a doublet of triplets at 50.9 ppm, with  $J_{\text{PF}} = 800$  Hz and  $J_{\text{HPF}} = 124$  Hz.

**Reactions of  $\text{CH}_3\text{NH}_2$ ,  $\text{NH}_3$ , and Pyridine with  $\text{H}_2\text{PF}_3$ .** Several attempts were made to treat equimolar quantities of  $\text{H}_2\text{PF}_3$  and these amines in the manner described above. In each case large quantities of  $\text{HPF}_2$ <sup>22</sup> and unreacted  $\text{H}_2\text{PF}_3$  were detected in the vapor products by means of IR spectroscopy. It was not possible to detect an  $^{19}\text{F}$  NMR spectrum of the  $\text{H}_2\text{PF}_4^-$  anion due to rapid decomposition of solutions of the solid reaction products.

## Results and Discussion

The liquid-phase reaction of  $\text{HPF}_4$  with  $(\text{CH}_3)_3\text{N}$ ,  $(\text{C}_5\text{H}_5)_2\text{NH}$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{NH}_3$ , or pyridine leads to the production of the  $\text{HPF}_5^-$  anion as its ammonium, substituted ammonium, or pyridinium salt.



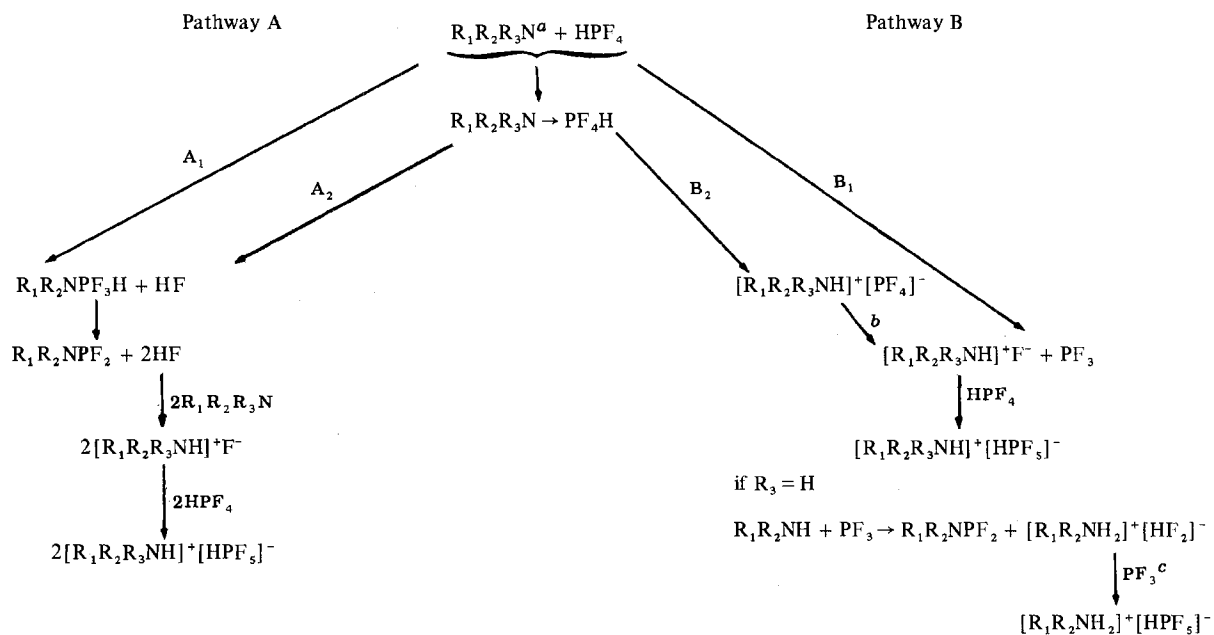
Note that the volatile products and reaction stoichiometries are different in eq 2 and 3. For the  $(\text{CH}_3)_3\text{N}$  and pyridine reactions the volatile product is  $\text{PF}_3$ , while for the  $(\text{CH}_3)_2\text{NH}$ ,  $\text{CH}_3\text{NH}_2$ , and  $\text{NH}_3$  reactions the volatile product is an aminodifluorophosphine,  $\text{R}_1\text{R}_2\text{NPF}_2$ . The overall base/ $\text{HPF}_4$  stoichiometries are 1:2 and 1:1 in eq 2 and 3, respectively. The vapor-phase reaction of  $\text{CH}_3\text{NH}_2$  with  $\text{HPF}_4$  yielded the same results as the liquid-phase reaction. In no reaction was it possible to detect an adduct of the type base $\rightarrow\text{HPF}_4$ .

The liquid-phase reactions of  $\text{H}_2\text{PF}_3$  with nitrogen bases were not as clean as the  $\text{HPF}_4$  reactions because of the thermal instability of the trifluorophosphorane in Pyrex glass. However, the reaction of  $\text{H}_2\text{PF}_3$  with  $(\text{CH}_3)_3\text{N}$  or  $(\text{CH}_3)_2\text{NH}$  produced the  $\text{H}_2\text{PF}_4^-$  anion as its substituted ammonium salt, along with an unidentified orange-yellow precipitate. In both cases the volatile reaction product was  $\text{HPF}_2$ . No  $\text{H}_2\text{PF}_4^-$  anion could be detected in the reaction of  $\text{H}_2\text{PF}_3$  with  $\text{CH}_3\text{NH}_2$ ,  $\text{NH}_3$ , or pyridine.

The  $\text{HPF}_5^-$  and  $\text{H}_2\text{PF}_4^-$  anions have been prepared previously<sup>10,11</sup> and the NMR spectral data presented here (see Experimental Section) are in satisfactory agreement with the available literature values. Slight differences in chemical shifts and coupling constants can be attributed to  $\text{N}^+\text{---H}\cdots\text{F}^-$  interionic hydrogen bonding interactions. In accord with the very recent work of Christe, Schack, and Curtis,<sup>11</sup> we find that only the trans isomer of  $\text{H}_2\text{PF}_4^-$  is formed since the  $^{19}\text{F}$  NMR spectrum exhibits a doublet of triplets and the  $^1\text{H}$  NMR spectrum consists of a doublet of quintets.

No attempt has been made to assign the IR spectra of the  $\text{HPF}_5^-$  and  $\text{H}_2\text{PF}_4^-$  salts (see Experimental Section) in a rigorous manner since (a) a normal coordinate analysis has already been carried out on the  $\text{H}_2\text{PF}_4^-$  anion,<sup>11</sup> and (b) the present IR spectra are complicated by  $\text{N}^+\text{---H}\cdots\text{F}^-$  hydrogen bonding interactions. Nevertheless, the anticipated spectral frequencies are apparent in all cases, e.g., P-H stretching

Scheme I

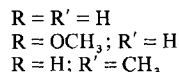
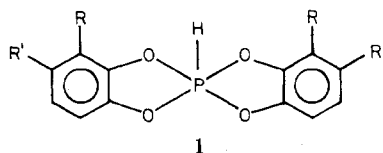


<sup>a</sup> R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> = H, CH<sub>3</sub>. Pyridine would be analogous to (CH<sub>3</sub>)<sub>3</sub>N. <sup>b</sup> The PF<sub>4</sub><sup>-</sup> anion is evidently unstable since fluoride ion donors such as (n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NF fail to react with PF<sub>3</sub> up to several atmospheres of pressure: A. H. Cowley and J. L. Mills, unpublished observations. <sup>c</sup> See ref 10 for the reaction of HF<sub>2</sub><sup>-</sup> with PF<sub>3</sub>.

(2300–2400 cm<sup>-1</sup>), P–F stretching (770–780 cm<sup>-1</sup>), and P–F deformation (600–650 cm<sup>-1</sup>).

The results of the present study can be understood by reference to Scheme I which comprises two stoichiometrically distinct pathways, A and B, for the reaction of HPF<sub>4</sub> with nitrogen bases. In turn, each pathway is divided into sub-pathways, A<sub>1</sub>, A<sub>2</sub> and B<sub>1</sub>, B<sub>2</sub>. Pathway A involves the substitution of a fluorine ligand of HPF<sub>4</sub> by an amino group, either directly (pathway A<sub>1</sub>) or via an unstable base→HPF<sub>4</sub> adduct (pathway A<sub>2</sub>). Pathway B involves a base-promoted dehydrofluorination of HPF<sub>4</sub> which can proceed directly (pathway B<sub>1</sub>) or through a labile base→HPF<sub>4</sub> complex (pathway B<sub>2</sub>).

It is obvious that the reaction of HPF<sub>4</sub> with (CH<sub>3</sub>)<sub>3</sub>N or pyridine must proceed according to pathway B because amine substitution (pathway A) is precluded for tertiary amines. Furthermore, the observed 1:2 amine/HPF<sub>4</sub> stoichiometry is consistent with that which is predicted for pathway B. Our inability to detect base→HPF<sub>4</sub> adducts by NMR does not constitute sufficient evidence to discriminate between pathways B<sub>1</sub> and B<sub>2</sub> since such species could be quite labile and thus elude spectroscopic detection. In this connection, however, it is interesting to note that bicyclic phosphoranes, **1**, form stable 1:1 adducts with pyridine.<sup>23</sup>



It has not been possible to distinguish between pathways A and B in the cases of the reactions of HPF<sub>4</sub> with (CH<sub>3</sub>)<sub>2</sub>NH, CH<sub>3</sub>NH<sub>2</sub>, and NH<sub>3</sub>. Experimentally, the distinguishability of these pathways is contingent upon the stoichiometry of the reaction and/or observation of the phosphorane R<sub>1</sub>R<sub>2</sub>NPF<sub>3</sub>H.

In the case of the reaction of (CH<sub>3</sub>)<sub>2</sub>NH with HPF<sub>4</sub> it was, in fact, possible to detect a mass spectral peak corresponding to (CH<sub>3</sub>)<sub>2</sub>NPF<sub>3</sub>H<sup>+</sup> in the initially formed liquid phase,<sup>21</sup> thereby suggesting that pathway A is operative. However, per se this datum is not definitive since when HPF<sub>4</sub> and (CH<sub>3</sub>)<sub>2</sub>NH were allowed to interact in a 2:1 molar ratio, significant quantities of PF<sub>3</sub> (which could only be formed by pathway B) were detected in the volatile products along with (CH<sub>3</sub>)<sub>2</sub>NPF<sub>2</sub>. Obviously, some or all of the (CH<sub>3</sub>)<sub>2</sub>NPF<sub>2</sub> could have arisen from the reaction of PF<sub>3</sub> with unused (CH<sub>3</sub>)<sub>2</sub>NH,<sup>24</sup> a feature that would render the stoichiometric differentiability invalid. Thus, not only is it impossible to choose between pathways A and B for the nontertiary amines, but it is conceivable that both reaction pathways are operative concurrently.

Finally, a series of reactions analogous to these in Scheme I could be written for the reactions of H<sub>2</sub>PF<sub>3</sub> with bases. However, in these cases reaction pathways could not be delineated because of extensive decomposition.

**Acknowledgment.** The authors are grateful to the National Science Foundation (Grant CHE 76-10331) and the Robert A. Welch Foundation for generous financial support. Michel Sanchez expresses gratitude to the North Atlantic Treaty Organization for a fellowship.

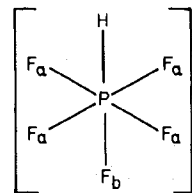
**Registry No.** [(CH<sub>3</sub>)<sub>3</sub>NH]<sup>+</sup>[HPF<sub>5</sub>]<sup>-</sup>, 61950-28-5; (CH<sub>3</sub>)<sub>2</sub>NPF<sub>2</sub>, 814-97-1; [CH<sub>3</sub>NH<sub>3</sub>]<sup>+</sup>[HPF<sub>5</sub>]<sup>-</sup>, 61950-29-6; [NH<sub>4</sub>]<sup>+</sup>[HPF<sub>5</sub>]<sup>-</sup>, 61950-30-9; [C<sub>5</sub>H<sub>5</sub>NH]<sup>+</sup>[HPF<sub>5</sub>]<sup>-</sup>, 61951-30-2; [(CH<sub>3</sub>)<sub>3</sub>NH]<sup>+</sup>[H<sub>2</sub>PF<sub>4</sub>]<sup>-</sup>, 61950-32-1; [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]<sup>+</sup>[H<sub>2</sub>PF<sub>4</sub>]<sup>-</sup>, 61951-22-2; (CH<sub>3</sub>)<sub>3</sub>N, 75-50-3; HPF<sub>4</sub>, 13659-66-0; (CH<sub>3</sub>)<sub>2</sub>NH, 124-40-3; CH<sub>3</sub>NH<sub>2</sub>, 74-89-5; NH<sub>3</sub>, 7664-41-7; pyridine, 110-86-1; H<sub>2</sub>PF<sub>3</sub>, 13659-65-9.

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$F_b$  subscripts of  $\text{HPF}_5^-$  are defined according to



- The  $\text{H}_2\text{PF}_4^-$  anion has a trans conformation of H ligands. See text.
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  - (24) Trifluorophosphine reacts readily with  $(\text{CH}_3)_2\text{NH}$  to afford  $(\text{CH}_3)_2\text{NPF}_2$ . 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,  $\text{Me}_3\text{SiN}(\text{R})\text{H}$  (R = Me, Si, t-Bu, Me), reacted readily with the appropriate halophosphine to afford good yields of the trimethylsilylamminophosphines,  $\text{Me}_3\text{SiN}(\text{R})\text{PX}_2$  (X = CF<sub>3</sub>, F). Halogen exchange reactions were observed between  $\text{BCl}_3$  and two of the aminodifluorophosphines, resulting in the formation of the corresponding dichlorophosphines,  $\text{Me}_3\text{SiN}(\text{R})\text{PCl}_2$  (R = Me, Si, t-Bu). Two new silylamminophosphines,  $\text{H}_3\text{SiN}(\text{R})\text{P}(\text{CF}_3)_2$  (R = Me, H), were obtained from the dehydrobromination reaction of  $(\text{CF}_3)_2\text{PN}(\text{R})\text{H}$  with  $\text{H}_3\text{SiBr}$ . Unsuccessful attempts to prepare disilylamminophosphines via the Si-N cleavage reaction of  $(\text{H}_3\text{Si})_3\text{N}$  with  $\text{PF}_2\text{Br}$  or  $(\text{CF}_3)_2\text{PCl}$  are also described. Rotational barriers, determined by  $^1\text{H}$  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.<sup>2</sup> 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<sup>3</sup> and stereochemical processes<sup>4</sup> 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  $\text{NR}_2$ , OR, and SR.<sup>5</sup> It is therefore reasonable to expect silylamminophosphines to function as reagents for transferring the  $>\text{N}-\text{P}<$  moiety to other substrates. (iii) Silylamminophosphines can be considered to be related formally to the well-known silylamminoboranes<sup>6</sup> and it seemed of interest to explore the extent of this analogy.

The present paper is concerned with both the preparative chemistry of silylamminophosphines 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.<sup>7</sup> Except as otherwise described the reaction vessels consisted of Pyrex tubes or bulbs equipped with glass-Teflon stopcocks.

**Physical Measurements.** The  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were recorded on Perkin-Elmer R-12, Varian HA-100, or Varian A 56/60 spectrometers. The  $^1\text{H}$  and  $^{19}\text{F}$  chemical shifts were measured relative to external tetramethylsilane and fluorotrichloromethane, respectively. The  $^{31}\text{P}$  NMR spectra were recorded on a Bruker HFX-90 spectrometer and were referenced to external 85%  $\text{H}_3\text{PO}_4$ . 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,<sup>8</sup> bromodifluorophosphine,<sup>9</sup> bromosilane,<sup>10</sup> trisilylamine,<sup>11</sup> the dialkylaminobis(trifluoromethyl)phosphines<sup>12</sup>