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The Reaction of Mono- and Dimethylamines with Phosphorus Trifluoride Borane

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Received September 22, 1964

The reaction between F_3PBH_3 and CH_3NH_2 gives $[CH_3NH]F_2PBH_3$, $[CH_3NH]_2FPBH_3$, or $[CH_3NH]_3PBH_3$ depending upon the experimental conditions used. In no case was $CH_3NH_2BH_3$ ever detected as a product of the methylamine reaction. On the other hand the reaction between F_3PBH_3 and $(CH_3)_2NH$ gave good yields of $(CH_3)_2NHBH_3$ under conditions comparable to those used for methylamine, and gave $[(CH_3)_2N]F_2PBH_3$ or $[(CH_3)_2N]_2FPBH_3$ under more severe conditions. Displacement reactions provide a basis for listing the above bases in order of increasing base strength using BH_3 as a reference acid. The order is: $F_3P < (CH_3NH)F_2P$, $[(CH_3)_2N]F_2P < N(CH_3)_3$, $NH(CH_3)_2 < (CH_3NH)_2FP$, $[(CH_3)_2N]_2FP$. The results are discussed.

In an earlier study[1] it was shown that a stoichiometric quantity of trimethylamine will replace F_3P from F_3PBH_3 at 25° to give $(CH_3)_3NBH_3$ and free PF_3. In a subsequent study[2] it was shown that excess ammonia will *not* replace F_3P in F_3PBH_3 but will react with the fluorides of the base, even at −35°, to give $(H_2N)_3PBH_3$. This paper reports the results of a study of the reactions of methyl- and dimethylamines with F_3PBH_3. The reaction using CH_3NH_2 is analogous in general form to the reaction of H_3N and F_3PBH_3 except that the extent of aminolysis with methylamine is always less than that with ammonia at the same temperature. The stepwise process can be represented by the equations

$$F_3PBH_3 + 2CH_3NH_2 \xrightarrow[(C_5H_5)_2O]{-111^\circ} (CH_3NH)F_2PBH_3 + [CH_3NH_3]F\text{[3]} \qquad (1)$$

$$(CH_3NH)F_2PBH_3 + 2CH_3NH_2 \xrightarrow[(C_2H_5)_2O]{25^\circ} (CH_3NH)_2FPBH_3 + [CH_3NH_3]F\text{[3]} \qquad (2)$$

$$(CH_3NH)_2FPBH_3 + 2CH_3NH_2 \xrightarrow[\substack{\text{liq.}\\ CH_3NH_2}]{25^\circ} (CH_3NH)_3PBH_3 + [CH_3NH_3]F\text{[3]} \qquad (3)$$

The reaction of $(CH_3)_2NH$ with F_3PBH_3 is particularly interesting since *both* aminolysis (eq. 4 and 5) and base displacement (eq. 6) are indicated by product analysis. A resemblance of $(CH_3)_2NH$ to either $(CH_3)_3N$ or $(CH_3)NH_2$ may be observed depending upon the conditions used. The observations can be summarized by the equations

$$F_3PBH_3 + 1.5(CH_3)_2NH \xrightarrow[\substack{\text{no}\\ \text{solvent}}]{-78^\circ} [(CH_3)_2N]F_2PBH_3 + 0.5[(CH_3)_2NH_2]HF_2\text{[3]} \qquad (4)$$

$$[(CH_3)_2N]PBH_3 + 1.5(CH_3)_2NH \xrightarrow[\substack{\text{no}\\ \text{solvent}}]{25^\circ} [(CH_3)_2N]_2FPBH_3 + 0.5[(CH_3)_2NH_2]HF_2\text{[3]} \qquad (5)$$

Base displacement

$$F_3BPH_3 + (CH_3)_2NH \xrightarrow[\substack{(C_2H_5)_2O\\ \text{(excess)}}]{-196 \text{ to } 25^\circ} (CH_3)_2HNBH_3 + \text{other products} \qquad (6)$$

Experimental

(I) **General.**—Standard vacuum line techniques were used throughout. Commercial (Matheson) CH_3NH_2 and $(CH_3)_2NH$ were purified by low-temperature fractionation at 400 mm. pressure and dried over Na before use. Phosphorus trifluoride borane was prepared by literature procedures.[1] Commercial reagent grade diethyl ether was vacuum distilled from $LiAlH_4$ into the reaction vessel.

(II) **The Reactions of Methylamine with Phosphorus Trifluoride Borane.** (a) **The Synthesis and Properties of $(CH_3NH)F_2PBH_3$.** (1) **The Reaction of F_3PBH_3 and CH_3NH_2 in Ether Solution at Low Temperature.**—A 1.70-mmole sample of F_3PBH_3 was dissolved in about 10 ml. of diethyl ether at −111°. Methylamine vapor was admitted slowly above the clear solution until an amount of gas equal to 4.54 mmoles had been absorbed. The system was stirred for 30 min. at −111°, then warmed slowly to −78° where a white precipitate formed slowly. After standing for 16 hr. at −78°, the reaction mixture was allowed to warm very slowly to room temperature while the volatile components were taken off through traps at −78 and −196°. A mixture consisting of $(C_2H_5)_2O$ and $(CH_3NH)F_2PBH_3$ collected in the −78° trap. Separation was achieved by holding the mixture at −35° and passing the volatile components through traps at −65 and −196°. A 1.12-mmole sample of $(CH_3NH)F_2PBH_3$ was retained in the −65° trap, giving a recovered yield of 66% based on the F_3PBH_3 used. *Anal.* Calcd. for $(CH_3NH)F_2PBH$: hydridic hydrogen (assuming the equation: $(CH_3NH)F_2PBH_3 + 3H^+ \rightarrow 3H_2 +$ residues), 26.6 mmoles/g.; N, 12.41%. Found: hydridic hydrogen by acid hydrolysis, 26.3 mmoles/g.; N, 12.20%; f.p. −65 ± 3°; b.p. 129° (extrapolated). The infrared spectrum is similar in general form to that for the carefully characterized compound $(CH_3)_2NF_2PBH_3$. The spectrum is shown in Figure 1. Principal infrared absorptions in $cm.^{-1}$ for $(CH_3NH)F_2PBH_2$ are: 3369 ± 10, N–H stretch; 3010; 2947 ± 10, C–H stretch; 2426, 2374 ± 10, B–H stretch; 1480; 1464; 1438; 1408; 1336; 1125; 1073; 1065; 1018; 915; 868; 848; 645; 464.

The clear stable liquid $(CH_3NH)F_2PBH_3$ has an obnoxious odor resembling phosphine; it undergoes no detectable decomposition on exposure to air at 25° for several hours, but decomposes to give a yellow nonvolatile residue when heated in a sealed tube above 50°. The vapor pressure of the liquid over the range 0–60° can be expressed by the equation

$$\log P_{\mathrm{mm}} = \frac{-2237.4}{T} + 8.4472$$

Observed vapor pressures (mm.) at several temperatures are

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[1] R. W. Parry and T. C. Bissot, *J. Am. Chem. Soc.*, **78**, 1524 (1956).

[2] G. Kodama and R. W. Parry, *J. Inorg. Nucl. Chem.*, **17**, 125 (1961).

[3] An unequivocal characterization of the alkyl ammonium fluoride was not carried out. The composition was inferred from stoichiometry. In all cases the expected crystalline solid could be filtered off.

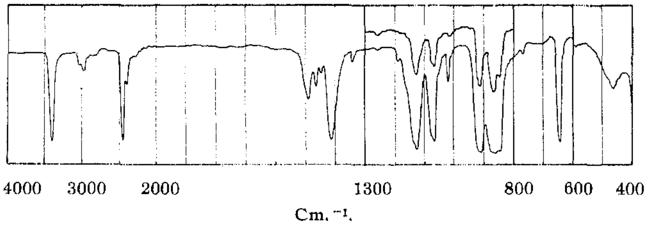

Figure 1.—The infrared spectrum of $(CH_3NH)F_2PBH_3$.

recorded below. The corresponding values calculated from the above equation are given in parentheses: 0.0°, 2.1 (1.8); 25.°0, 8.7 (8.8); 36.2°, 16.5 (16.4); 46.8°, 28.8 (28.4); 50.4°, 34.4 (34.2); 58.9°, 50.5 (51.3). [ΔH_{vap} = 10,230 ± 100 cal./mole; ΔS_{vap} at 1 atm. and 402°K. = 25.4 cal./(mole deg.).]

(2) **The Reaction of $(CH_3NH)F_2PBH_3$ and $N(CH_3)_3$.**—A sample of $CH_3NHF_2PBH_3$ (1.94 mmoles) was mixed at room temperature with a slight excess of $(CH_3)_3N$ (2.19 mmoles). After 2 hr. a 1.33-mmole sample of $(CH_3)_3NBH_3$ was isolated (69% yield), but the mixture could not be further resolved into pure components. Trimethylamine displaces $(CH_3NH)F_2P$ from $(CH_3NH)F_2PBH_3$.

(b) **The Synthesis and Properties of $(CH_3NH)_2FPBH_3$. (1) The Reaction of F_3PBH_3 and CH_3NH_2 in Ether Solution at Moderate Temperatures.**—A 1.90-mmole sample of F_3PBH_3 was dissolved in 10 ml. of diethyl ether at −111°. An excess of CH_3NH_2 (23.7 mmoles) was condensed on top of the solution by cooling the tube with liquid nitrogen; the system was sealed off. The mixture was stirred for 20 min. at −111°, for 10–12 hr. at −78°, and for 2 days at 25°. When the tube was opened to the vacuum system, a trace of noncondensable gas was removed; the volatile components were distilled out; fresh ether was condensed into the tube; then $[CH_3NH_3]F$ was removed by vacuum line filtration. When the solvent ether was distilled from the filtrate, $(CH_3NH)_2FPBH_3$ was recovered as a clear nonvolatile liquid which could not be easily moved in the vacuum line. The yield was almost quantitative based on the F_3PBH_3 used.

Anal. Calcd. for $(CH_3NH)_2FPBH_3$: H_2 by acid hydrolysis, 24.18 mmoles/g; N, 22.37%. Found: H_2 by acid hydrolysis, 24.11 mmoles/g.; N, 22.61%. Despite a vapor pressure which was too low to permit easy manipulation in the vacuum line, the liquid had a disagreeable odor in the air. It underwent no observable change on exposure to air for 2 days at room temperature and was soluble in ethers and CCl_4. Principal infrared absorptions in cm.⁻¹ for $(CH_3NH)_2FBPH_3$ are: 3346 ± 10, N–H stretch; 2947; 2913, C–H stretch; 2387, 2286, B–H stretch; 1475; 1465; 1453; 1407; 1147; 1117; 1100, 1062, B–H deformation; 882; 859; 794; 747; 634.

(2) **The Attempted Reaction of $(CH_3NH)_2FPBH_3$ with $N(CH_3)_3$.**—When nonvolatile liquid $(CH_3NH)_2FPBH_3$ was mixed with an excess of $(CH_3)_3N$ at room temperature for 3 hr., no reaction could be detected and the $(CH_3)_3N$ was recovered unchanged.

(c) **The Synthesis and Properties of $(CH_3NH)_3PBH_3$. The Reaction of F_3PBH_3 with CH_3NH_2 without a Solvent.**—A 2.33-mmole sample of F_3PBH_3 was frozen (−196°) into a reaction tube with about 2 ml. of liquid CH_3NH_2. After the tube was sealed off, the temperature was raised to −111° for 15 min., then warmed gradually to 25° and held for 1 week. The tube was then opened to the vacuum line; volatiles were removed at 25°, and the residue was leached with diethyl ether. Evaporation of ether from the leachate at 0° left large crystals contaminated with a significant amount of a nonvolatile liquid. When the temperature of the system was raised to 25°, the crystals dissolved to give a single viscous liquid phase. The low-temperature crystalline phase was separated by a special vacuum centrifugal filtration procedure. The apparatus shown in Figure 2 was attached to the vacuum filtration assembly and the mixture was filtered into A using a small amount of diethyl ether. The solvent ether was distilled out; the contents of A were frozen with liquid nitrogen, and the evacuated tube was sealed off at S. The unit was warmed to room temperature, then immersed in ice–water with the B side up. When a significant number of crystals had formed in A, the unit was rapidly placed in a suitable centrifuge with the B side down. On spinning, the crystals remained on the frit; the ground joint was pulled apart, the section containing the crystals was attached to the vacuum line filtration apparatus, and the product in A was washed out with diethyl ether. Removal of the ether left crystals which appeared reasonably dry after a final washing with a small amount of ether. The infrared spectrum of the original liquid clinging to the crystals indicated that it was mainly a mixture of $(CH_3NH)_2FPBH_3$ and $(CH_3NH)_3PBH_3$. The solid crystals were $(CH_3NH)_3PBH_3$. *Anal.* Calcd. for $(CH_3NH)_3PBH_3$: H_2 on acid hydrolysis, 22.23 mmoles/g.; N, 31.14%. Found: H_2 on acid hydrolysis 22.21 mmoles/g.; N, 30.64%; m.p. 30.5–31.0°.

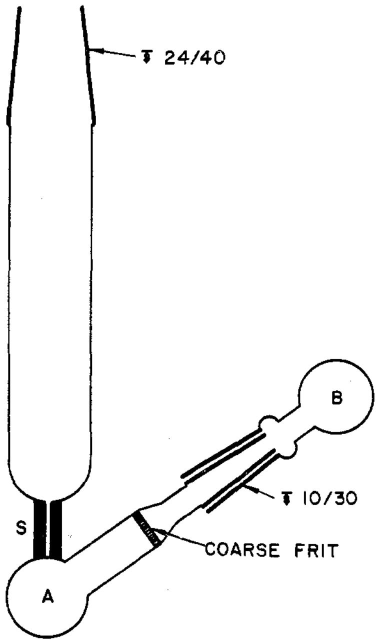

Figure 2.—Special vacuum centrifugal filtration apparatus.

The compound $(CH_3NH)_3PBH_3$ is soluble in ethers, benzene, toluene, CCl_4, $CHCl_3$, and acetone. It dissolves in water without loss of H_2. In 6 *N* HCl H_2 loss is not observed until the solution is heated to above 60°.

A reaction analogous to that described above between anhydrous CH_3NH_2 and F_3PBH_3 was conducted at temperatures below −78°. The only product which could be isolated was a small yield of $(CH_3NH)F_2PBH_3$. The compounds $(CH_3NH)_2FPBH_3$ and $(CH_3NH)_3PBH_3$, if present, could not be separated from the reaction mixture.

(III) **The Reactions of Dimethylamine with Phosphorus Trifluoride Borane.** (a) **The Synthesis and Properties of $[(CH_3)_2N]F_2PBH_3$.** (1) **The Reaction of F_3PBH_3 with $(CH_3)_2NH$ under Mild Conditions (No Solvent).**—A 1.97-mmole sample of $(CH_3)_2NH$ was frozen with liquid nitrogen into a thin layer inside the reaction tube. A 1.01-mmole sample of F_3PBH_3 was condensed above it, then the temperature was raised to −100°. Loss of F_3PBH_3 by reaction was negligible at −100° (pressure constant), but as the temperature was raised slowly above −100°, F_3PBH_3 was consumed. The reaction was checked several times by cooling the system to −100°. Repeated cycles of warming and cooling resulted in reaction of all of the F_3PBH_3 at temperatures below −78° (pressure of F_3PBH_3 dropped to zero). The system was warmed slowly to room temperature and volatile components were distilled out through a trap held at −78° into a trap at −196°. A 0.41-mmole sample of $(CH_3)_2NH$ passed through the −78° trap and condensed in the −196° trap. An approximately 0.75-mmole sample of $(CH_3)_2NPF_2BH_3$ was retained in the −78° trap. The $(CH_3)_2NF_2PBH_3$ was purified by distillation from −45° into a trap at −78°. After three such distillations a 0.72-mmole sample of

$(CH_3)_2NF_2PBH_3$ remained, giving a 72% yield based on the F_3PBH_3 used; m.p. −56.7°; b.p. (extrapolated) 119.4°. *Anal.* Calcd. for $(CH_3)_2NPF_2BH_3$: hydridic hydrogen by acid hydrolysis, 23.64 mmoles/g. (2.38%); N = 11.04%; mol. wt., 127. Found: hydridic hydrogen by acid hydrolysis, 23.59 mmoles/g. (2.38%); N, 11.05%; mol. wt. by gaseous effusion at a pressure below 0.5 mm., 131.[4] The vapor pressure of $(CH_3)_2NPF_2BH_3$ over the temperature range 16–63° is given by the equation

$$\log P_{\text{mm}} = \frac{-2064.4}{T} + 8.1393$$

Observed vapor pressures (mm.) at several temperatures are recorded below. The corresponding values calculated from the above equation are given in parentheses: 16.5°, 10.1 (10.3); 19.9°, 12.2 (12.4); 25.5°, 16.7 (16.9); 28.7°, 20.0 (20.0); 31.6°, 23.4 (23.2); 41.4°, 38.1 (37.7); 49.8°, 56.4 (55.9); 52.0°, 62.3 (61.9); 58.9°, 83.1 (83.7); 63.0°, 97.4 (99.5). [ΔH_{vap} = 9430 ± 100 cal./mole; ΔS_{vap} at 1 atm. and 392°K. = 24.0 ± 0.5 cal./(mole deg.).]

(2) **The Reaction of $[(CH_3)_2N]F_2PBH_3$ with Trimethylamine.**—A sample of $(CH_3)_2NPF_2BH_3$ [run a, 0.715 mmole; run b, 8.45 mmoles] was frozen (−196°) with $(CH_3)_3N$ [run a, 0.72 mmole; run b, 12 mmoles]. When the system was warmed to room temperature, $(CH_3)_3N$ displaced $[(CH_3)_2N]F_2P$ from $[(CH_3)_2N]F_2PBH_3$. After 1 hr. at 25° initial fractionation yielded $(CH_3)_3NBH_3$ in the −35° trap (run a, 0.59 mmole, m.p. 93°; lit. 94°); a trace of unreacted $(CH_3)_2NPF_2BH_3$ in the trap at −78° (run a, 0.05 mmole); and a mixture of $(CH_3)_3N$ (run a, 0.14 mmole) and F_2PNR_2 (run a, 0.54 mmole; run b, 7.15 mmoles) in the trap at −196°. The latter mixture was separated by passing the vapors through a trap at −95°; the $(CH_3)_3N$ passed, but the $(CH_3)_2NPF_2$ was retained. The compound $(CH_3)_2NPF_2$ was first prepared by the above procedure and characterized in 1959. Its preparation by two other routes has been reported recently,[5,6] and a more detailed description of the compound is reported elsewhere.[6]

(b) **The Displacement of F_3P from F_3PBH_3 by $(CH_3)_2NH$. The Use of Ether as a Solvent.**—The reaction of 1.78 mmoles of F_3PBH_3 and 16.0 mmoles of $(CH_3)_2NH$, dissolved in 10 ml. of $(C_2H_5)_2O$, was carried out by warming the system from −196° to room temperature with intermediate stops at −111 and −78°. After 3 days at 25° the system gave 0.02 mmole of noncondensable gas and a solid which was filtered off using the vacuum filtration assembly. Removal of solvent from the filtrate by vacuum distillation left a 1.60-mmole sample of CH_3NHBH_3 (90% yield; product identified by X-ray powder diffraction and melting point).

(c) **The Synthesis and Properties of $[(CH_3)_2N]_2FPBH_3$.** (1) **The Reaction of $[(CH_3)_2N]F_2PBH_3$ with $(CH_3)_2NH$ without a Solvent.**—A sample of $[(CH_3)_2N]F_2PBH_3$ (0.72 mmole) was mixed with a 0.80-mmole sample of $(CH_3)_2NH$ and held for 0.5 hr. at 25°. The resulting mixture was distilled through a −78° trap into a −196° trap. The fraction retained at −196° was passed through a −100° trap. A 0.28-mmole sample of $(CH_3)_2NH$ passed *through* the −100° trap, and a 0.35-mmole sample of $[(CH_3)_2N]F_2P$ was retained *in* the −100° trap.

The mixture retained at −78° was first fractionated by raising its temperature to −45° and distilling out $[(CH_3)_2N]F_2PBH_3$; then at a sample temperature of −23° $[(CH_3)_2N]_2FPBH_3$ was distilled out, leaving solid $(CH_3)_2HNBH_3$.

The infrared spectrum of $[(CH_3)_2N]_2FPBH_3$ was identical with that of the product made by the direct interaction of $[(CH_3)_2N]_2FP$ and B_2H_6; the latter reaction is described elsewhere along with a thorough characterization of the product $[(CH_3)_2N]_2FPBH_3$.[7]

(2) **The Attempted Reactions of $[(CH_3)_2N]_2FPBH_3$ with $(CH_3)_3N$ and $(CH_3)_2NH$.**—When $[(CH_3)_2N]_2FPBH_3$ was mixed with a large excess of either $(CH_3)_3N$ or $(CH_3)_2NH$ at 25° for 40 min., no reaction was detectable.

(3) **The Synthesis of $[(CH_3)_2N]_2FPBH_3$ from $[(CH_3)_2N]F_2PBH_3$.**—When 0.433 mmole of $[(CH_3)_2N]_2PF$, prepared as described elsewhere,[7] was mixed with 0.505 mmole of $(CH_3)_2NF_2PBH_3$ and allowed to stand for 2 hr. at room temperature, a 0.242-mmole sample of $(CH_3)_2NPF_2$ and a 0.237-mmole sample of $[(CH_3)_2N]_2FPBH_3$ were fractionated from the reaction mixture. The reaction indicated is a displacement of $(CH_3)_2NPF_2$ by $[(CH_3)_2N]_2PF$.

$$(CH_3)_2NF_2PBH_3 + [(CH_3)_2N]_2PF \rightarrow (CH_3)_2NPF_2 + [(CH_3)_2N]_2FPBH_3$$

Discussion

A Comparison of the Reactions of F_3PBH_3 with NH_3, CH_3NH_2, and $(CH_3)_2NH$ in Ether Solution. Decreasing Acidity of the *Amine Proton*.—The reactions of ammonia and the methylamines with F_3PBH_3 in ether solution may be summarized by the equations

$$H_3N\text{ (excess)} + F_3PBH_3 \xrightarrow[(C_2H_5)_2O]{-111\text{ to }-78^\circ} (H_2N)_2FPBH_3\text{[8]} \xrightarrow[(C_2H_5)_2O]{-78\text{ to }25^\circ} (H_2N)_3PBH_3 \qquad (7)$$

$$CH_3NH_2\text{ (excess)} + F_3PBH_3 \xrightarrow[(C_2H_5)_2O]{-111\text{ to }-78^\circ} (CH_3NH)F_2PBH_3 \xrightarrow[(C_2H_5)_2O]{-78\text{ to }25^\circ} (CH_3NH)_2FPNH_3 \qquad (8)$$

$$(CH_3)_2NH\text{ (excess)} + F_3PBH_3 \xrightarrow[(C_2H_5)_2O]{-111\text{ to }+25^\circ} CH_3NHBH_3 + PF_3 \hookrightarrow \text{reacts with excess amine} \qquad (9)$$

Ammonia, with the most strongly acidic protons in the series of amines, replaces two fluorides with amide groups at −78°; at −35° a mixture of $(H_2N)_2FPBH_3$ and $(H_2N)_3PBH_3$ was obtained, while at 25° the completely solvolyzed product $(H_2N)_3PBH_3$ was obtained in 82% yield. Earlier evidence[2] indicated clearly that the phosphorus–boron bond was not broken during the course of this reaction.

Under comparable conditions CH_3NH_2 with less acidic protons replaces only one fluoride rather than two at −78° to give $(CH_3NH)F_2PBH_3$ at −78° and replaces two fluorides at 25° to give $(CH_3NH)_2FPBH_3$. The completely solvated, fluorine-free product $(CH_3NH)_3PBH_3$, which would be expected by an extrapolation of the ammonia result, was not obtained in ether.

In the case of $(CH_3)_2NH$ the low acidity of the proton and the increased basicity of the nitrogen gave rise to a reaction of *completely different form* under comparable conditions. Instead of the solvolysis reactions observed with ammonia and monomethylamine, a base displacement reaction was obtained (eq. 9). The latter reaction is analogous to that between $(CH_3)_3N$ and F_3PBH_3.

The vigorous direct interaction of F_3PBH_3 and the neat bases further illustrates the trend observed in pass-

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(4) The authors wish to thank Sr. Mary Albert Fleming for making the molecular weight measurement.

(5) R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964).

(6) Sr. M. A. Fleming, G. Kodama, and R. W. Parry, to be published; G. Terhaar, Sr. M. A. Fleming, and R. W. Parry, *J. Am. Chem. Soc.*, **84**, 1767 (1962).

(7) Sr. M. A. Fleming and R. W. Parry, to be published.

(8) Although the compound $(H_2N)_2FPBH_3$ was never isolated in the earlier study, the stoichiometry of the reaction at −78° clearly indicated this formula.[2]

ing from ammonia to trimethylamine and illustrates clearly the role of ether in the reaction. The observation can be summarized by the equations

$$F_3PBH_3 + NH_3\text{ (excess liq.)} \xrightarrow[\text{liq. }NH_3]{-78^\circ} (H_2N)_3PBH_3\text{ (92\% yield)} \quad (10)$$

$$F_3PBH_3 + NH_2CH_3\text{ (excess liq.)} \xrightarrow[\text{liq. }NH_2CH_3]{-78^\circ} \left.\begin{matrix}(CH_3NH)F_2PBH_3\\ (CH_3)NH)_2FPBH_3\end{matrix}\right\}\text{ mixtures of mono- and diamido products}$$
$$\begin{matrix}\text{mixture of}\\ \text{bis- and tris-}\\ \text{monomethyl amido products}\end{matrix}\left\{\begin{matrix}(CH_3NH)_2FPBH_3\\ (CH_3NH)_3PBH_3\end{matrix}\right. \xleftarrow[\text{excess }CH_3NH_2]{25^\circ} \quad (11)$$

$$F_3PBH_3 + NH(CH_3)_2 \xrightarrow[\text{liq. }NH(CH_3)_2]{-78^\circ} [(CH_3)_2N]F_2PBH_3\text{ (72\% yield)} \xrightarrow[\text{excess }(CH_3)_2NH]{25^\circ} [(CH_3)_2N]_2FPBH_3 + (CH_3)_2NHBH_3 \quad (12)$$

It will be noted that *liquid* ammonia replaced all fluorides smoothly *at −78°* to give a 92% yield of $(H_2N)_3PBH_3$; *liquid* methylamine replaced one or two fluorides to give a badly mixed product at −78°; while liquid dimethylamine replaced only a single fluoride at −78° to give a 72% recovered yield of $[(CH_3)_2N]F_2PBH_3$. The same trend continued at 25° where methylamine gave a sizable yield of $(CH_3NH)_3PBH_3$ while *only* $[(CH_3)_2N]_2FPBH_3$ and $(CH_3)_2NHBH_3$ could be obtained under comparable conditions from dimethylamine. Under the conditions of this study $[(CH_3)_2N]_2FPBH_3$ and excess $(CH_3)_2NH$ did *not* react further at 25°. The data for the attack of neat $NH(CH_3)_2$ on $[(CH_3)_2N]F_2PBH_3$ at 25° indicate clearly that even the fluoride on $[(CH_3)_2N]F_2PFH_3$ is attacked very slowly by the very weakly basic proton of dimethylamine. Under these conditions the competing base displacement process involving replacement of $[(CH_3)_2N]F_2P$ by $HN(CH_3)_2$ becomes dominant even in the absence of solvent. Two competing reactions can be formulated

$$[(CH_3)_2N]F_2PBH_3 + HN(CH_3)_2 \rightarrow (CH_3)_2NHBH_3 + (CH_3)_2NPF_2 \quad (13)$$

$$[(CH_3)_2N]F_2PBH_3 + 2HN(CH_3)_2 \rightarrow [(CH_3)_2N]_2FPBH_3 + [(CH_3)_2NH_2{}^+]F^- \quad (14)$$

Yield data indicate that reaction 13 is about twice as fast as reaction 14 under the conditions of this study.

It is of interest to ask why dimethylamine replaces F_3P from F_3PBH_3 in ether solution, but brings about solvolysis and formation of $(CH_3)_2NF_2PBH_3$, etc., in reactions involving the pure reagents. It seems reasonable to postulate by analogy to the ammonia reaction that direct attack of dimethylamine on F_3PBH_3 will bring about slow solvolysis. On the other hand, it is almost certain that F_3PBH_3 dissociates in ether solution to give some $(C_2H_5)_2OBH_3$. Reaction of this etherate with dimethylamine through a base displacement process would give the observed $(CH_3)_2HNBH_3$. If one accepts the foregoing premises, a solvent would be expected to change the nature of the reaction when: (a) the solvolysis of F_3PBH_3 is slow, (b) the F_3PBH_3 undergoes dissociation in the solvent, and (c) the attacking reagent is a stronger base than the solvent toward BH_3.

From the foregoing displacement reactions the relative strengths of the various bases used can be given.

$$\underset{\text{weakest base}}{F_3P} < \left\{\begin{matrix}F_2PNHCH_3\\ F_2PN(CH_3)_2\end{matrix}\right\} < \left\{\begin{matrix}N(CH_3)_3\\ NH(CH_3)_2\end{matrix}\right\} < \underset{\text{strongest base}}{\left\{\begin{matrix}FP(NHCH_3)_2\\ FP[N(CH_3)_2]_2\end{matrix}\right\}}$$

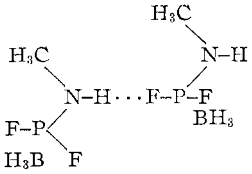
Presumably $P(NHCH_3)_3$ and $P[N(CH_3)_2]_3$ are stronger bases than any of the above[7], but this is not established unequivocally by the data cited. The fact that $P[N(CH_3)_2]_3$ is a stronger base than $N(CH_3)_3$ has been shown, however.[9] In short, a rapid increase in base strength is noted as fluorides on the phosphorus are replaced by alkyl amido groups. Such an increase would be consistent with the assumption that the σ-bond is increasing in strength as fluorides are lost and that any π-bonding to P which *might* have arisen from delocalization of hydrogen electrons contributes little to the over-all bond strength. In general, fluorides attached to phosphorus should increase the ability of phosphorus to π-bond since removal of negative charge would lower the d-electron levels, making them more available for bond formation. Such an argument suggests that the bonding in $H_3BP[N(CH_3)_2]_3$ is largely σ in character. Reetz and Katlafsky[9] suggested considerable π-bonding from boron to phosphorus on the basis of the resistance to hydrolysis of hydridic hydrogens in $[(CH_3)_2N]_3PBH_3$. It was assumed in their argument that such π-bonding would remove charge from hydrogens attached to boron, thus rendering the hydrogens less subject to attack by protons. If strong π-bonding were common in these systems and were the dominant factor in determining resistance to hydrolysis, the hydrogens of F_3PBH_3 should be strongly resistant to solvolysis—a prediction which is in direct opposition to experimental fact. The resistance to hydrolysis of hydrogens attached to boron is more easily rationalized in terms of a probable dissociative mechanism rather than in terms of electron density around the hydrogen.[10] The electron density around hydrogens would be a variable of secondary importance since a fairly good correlation can be drawn between resistance of the borane adduct to hydrolysis and increasing strength of the base coordinated to BH_3.[10] If electron density on hydrogen were the dominant factor, the relationship should be reversed.

The estimated values for the entropies of vaporization at the normal boiling point for $[(CH_3)NH]F_2PBH_3$ and $[(CH_3)_2N]F_2PBH_3$ are somewhat higher than values for normal nonassociated liquids. Either liquid phase association or vapor phase dissociation is implied. The measured vapor phase molecular weight value of 131 for $[(CH_3)_2N]F_2PBH_3$ [theor. 127] would

(9) T. Reetz and B. Katlafsky, *J. Am. Chem. Soc.*, **82**, 5036 (1960).

(10) R. W. Parry and L. J. Edwards, *ibid.*, **81**, 3560 (1959); T. C. Bissot, D. H. Campbell, and R. W. Parry, *ibid.*, **80**, 1549 (1958).

argue against significant vapor phase dissociation. In $[CH_3NH]F_2PBH_3$ intermolecular hydrogen bonding of the form



would seem to be a reasonable cause of some liquid phase association and would indeed account for the fact that the entropy of vaporization of the compound $H_3CHNF_2PBH_3$ is about 1.4 cal./(mole deg.) above that for the compound $(H_3C)_2NF_2PBH_3$, in which hydrogen bonding is not expected.

Acknowledgment.—This work was supported in part by the National Science Foundation under the terms of Grant NSF-G10372 and in part under Contract AF33(616)-5874 with the U. S. Air Force, the sponsoring agency being the Aeronautical Research Laboratory of Wright Air Development Center Air Research and Development Command. Such support is gratefully acknowledged.

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Tridentate Chelate Compounds. VI.[1] Copper(II) Complexes Derived from Pyridine-2-aldehyde-2′-pyridylhydrazone

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Received August 17, 1964

Some copper(II) coordination complexes of the tridentate chelating agent pyridine-2-aldehyde-2′-pyridylhydrazone have been prepared in which the configuration of donor atoms around the copper atom is square-planar or trigonal-bipyramidal. Reactions involving substitution of ligands coordinated at the fourth site in the square-planar complexes are reported. Some conversions of square-planar to trigonal-bipyramidal copper(II) complexes are also described. The trigonal-bipyramidal structure has been assigned to these complexes after consideration of their electrical conductivity data, infrared spectra, and elemental analyses.

Introduction

Previous work[3,4] has shown that coordination compounds can be prepared from pyridine-2-aldehyde-2′-pyridylhydrazone (1,3-di(2-pyridyl)1,2-diaza-2-propene; PAPHY; I) or heterocyclic hydrazones of similar type and copper(II) salts in which the coordinated copper atoms apparently exist in octahedral or square-planar arrangements. In this paper we report the chemistry of some of the square-planar complexes containing one PAPHY residue per copper atom. The stability of this type of PAPHY–copper(II) complex[5] has enabled us to study the substitution reactions of ligands bonded to the fourth coordination position. We also report the preparation of some complexes in which the copper atom is apparently surrounded by and bonded to five donor atoms in a trigonal-bipyramidal arrangement.

Experimental

Conductivities.—Electrical conductivities were measured with a Philips Philoscope and platinum-coated electrodes of the dip type. Unless otherwise indicated, the values quoted are given in ohm.$^{-1}$ cm.^{2} for about 10^{-3} *M* solutions in purified nitrobenzene at 25°.

Magnetic moments were measured on a Gouy balance at room temperature.

Preparation of the Copper(II) Complexes.[6] **Chloro(PAPHY)-copper(II) Perchlorate (IIIa).**—An ethanolic solution of I (0.6 g.) and an aqueous solution of copper(II) chloride–2-water (0.5 g. in 5 ml.) were mixed and heated on a water bath. Aqueous sodium perchlorate solution was added, and, after cooling, green prisms of IIIa separated. The product was recrystallized from aqueous ethanol.

Chloro(PAPY)copper(II) (IVa).—IIIa or IIa was treated in aqueous ethanol with aqueous sodium bicarbonate solution until effervescence stopped. The solution was diluted with water and the product collected and recrystallized from benzene–petroleum ether in brown microcrystals.

Dibromo(PAPHY)copper(II) (IIb).—I (0.5 g.) and copper(II) bromide (0.55 g.) were heated together in ethanolic solution for 5 min. The mixture was cooled and the product collected.

Ammine(PAPY)copper(II) Perchlorate (Va).—Tetraamminecopper(II) sulfate–1-water (0.6 g.) in water and an ethanolic solution of I (0.5 g.) were mixed and heated for 5 min. After cooling and adding aqueous sodium perchlorate solution, the dark brown product was collected and crystallized from acetone–petroleum ether, yield 0.5 g. Vb was prepared similarly from tetraamminecopper(II) sulfate–1-water (0.6 g.) and 1-(3-methyl-2-pyrazinyl)3-(2-pyridyl)1,2-diaza-2-propene[4] (0.5 g.).

Thiocyanato(PAPHY)copper(II) Perchlorate–1-water (IIIb).—Va was treated with one molecular proportion of perchloric acid

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(1) For the previous paper in this series see B. Chiswell, J. F. Geldard, F. Lions, and A. T. Phillip, *Inorg. Chem.*, **3**, 1272 (1964).

(2) Petroleum Research Fund Fellow of the University of Sydney.

(3) F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **80**, 3858 (1958).

(4) J. F. Geldard and F. Lions, *ibid.*, **84**, 2262 (1962); *Inorg. Chem.*, **2**, 270 (1963).

(5) R. W. Green, P. Hallman, and F. Lions, *ibid.*, **3**, 376 (1964).

(6) The full names of these complexes and their physical properties and elemental analyses are given in Table I. PAPY is deprotonated PAPHY.