Fluorophosphine Ligands. IV. The Apparent Base Strengths of Difluorophosphine, Trifluorophosphine, and Phosphine toward the Lewis Acid Borane

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Abstract: Difluorophosphine borane has been prepared and completely characterized. It boils at 6.2° and is stable against decomposition into HPF_2 and B_2H_6 when stored at 25° under pressures near 1 atm. Under comparable conditions, F_3PBH_3 and H_3PBH_3 would be highly dissociated into B_2H_6 and the appropriate phosphorus ligand. The base strength toward borane increases in the order $PH_3 < PF_3 < PHF_2$. The ^1H, ^{11}B, and ^{19}F nmr spectra of F_2HPBH_3 show clearly that the structure is that of a normal borane adduct. The unusual stability of the compound H_3BPHF_2 has been rationalized in terms involving internal FHF interactions in the parent base, HPF_2.

Phosphine borane, $[H_3PBH_3]_n$, was first characterized by Gamble and Gilmont in 1940.[1] A kinetic study of its formation was completed by Brumberger and Marcus[2] in 1956. In 1961 McGandy and Eriks[3] established unequivocally the monomeric formula for the solid. A very recent spectroscopic study[4] has also shown that H_3BPH_3 is the species existing in the molten state. The compound is dissociated completely to B_2H_6 and PH_3 in the gas phase.

The compound F_3PBH_3, first prepared in this laboratory by Bissot,[5] has C_{3v} symmetry as established by infrared,[6] Raman,[6] and microwave spectroscopy.[7] The compound exists in the gas phase at 25° but is extensively dissociated.

In the study reported herein it has been found that the recently reported[8] compound F_2PH forms a borane adduct as expected when PHF_2 and B_2H_6 are mixed at 25°.

$$2PHF_2(g) + B_2H_6(g) \xrightarrow{25^\circ} 2HF_2PBH_3(g)$$

The major unexpected feature of the system is the unusual stability of HF_2PBH_3. This compound, presumably intermediate between F_3PBH_3 and H_3PBH_3, is so stable that it is not dissociated to a detectable degree at 25° and 1 atm pressure. This behavior stands in stark contrast to that observed for H_3PBH_3 and F_3PBH_3, both of which are highly dissociated under comparable conditions.

Experimental Section

Procedures and Materials. The compounds investigated were manipulated by conventional high-vacuum techniques.[9] In general, volatile materials were checked for purity by vapor pressure, vapor density, and/or infrared spectroscopy. Purification was effected by fractional condensation. Diborane was kindly supplied by Callery Chemical Co.; phosphine was prepared by the pyrolysis of phosphorous acid[10] at 200–250°; trifluorophosphine was obtained from the Ozark Mahoning Co.; difluorophosphine was prepared as outlined in the literature;[8] phosphine borane was formed at −105° from the combination of liquid diborane and phosphine;[1] trifluorophosphine borane of high purity was kindly donated by R. J. Wyma and had been prepared by literature methods.[5]

Preparation and Characterization of F_2HPBH_3. Diborane (1.94 mmoles) and difluorophosphine (1.92 mmoles) were condensed into a 150-cc vessel attached to a manometer and allowed to warm to 25°. After 4 hr, when the pressure in the vessel had become constant at about three-fourths of its calculated initial value, the products were separated by fractional condensation (−135, −196°). Retained in the −135° trap was $PHF_2 \cdot BH_3$ (1.57 mmoles, 82% yield). A mixture of B_2H_6 and PF_3 (1.35 mmoles) was stopped at −196°. The amount of PF_3 was estimated to be about 0.20 mmole from the infrared spectrum of the mixture. A small amount of yellow solid and a trace of noncondensable gas were also formed during the reaction. Pure difluorophosphine borane has been maintained for 22 hr at 25° and a pressure of *ca.* 600 mm with no evidence for dissociation or decomposition. The stable new borane adduct may also be prepared by displacement of PH_3 or PF_3 from their respective borane adducts (see later).

Although classical methods were not used to obtain an elemental analysis, the formula $PHF_2 \cdot BH_3$ is supported unequivocally by physical methods such as ^{19}F, ^{11}B, and ^1H nmr spectroscopy and by mass spectroscopy.

The density of the vapor corresponds well with that expected for the monomer $PF_2H \cdot BH_3$ (obsd, 83.9; calcd, 83.8 g/mole). The mass spectrum (Table I) displays no peaks at *m/e* values higher than 84 and thus is consistent with the vapor density molecular weight; however, some features should be noted in the fragmentation pattern. Most of the peaks listed in Table I are anticipated from the assigned formula HF_2PBH_3. Only a few need special comment. The low-intensity peaks at *m/e* 71 and 52 can be assigned to the $PF_2H_2^+$ and PFH_2^+ ions, respectively. Recombination peaks of this type, arising in the present case from recombination of a proton and the appropriate fragment, are rather common in high-pressure mass spectroscopy[11] and have been reported in conventional mass spectroscopy.[12] Other possible recombination peaks might be assigned as $m/e = 49$, $^{11}BF_2^+$; 48, $^{10}BF_2^+$. The peak at *m/e* 30 is assigned to $^{10}BHF^+$ rather than $^{11}BF^+$ since no peak for *m/e* 29 ($^{10}BF^+$) is observed.

The vapor pressure data for $PHF_2 \cdot BH_3$ (−78.5°, 5.2 mm; −63.9°, 14.3 mm; −45.6°, 53.4 mm; −37.5°, 88.8 mm; −31.9°, 122.7 mm; −23.6°, 191.8 mm) are summarized by the equation

$$\log p\,(\text{mm}) = -\frac{1407}{T} + 7.917$$

The boiling point, extrapolated from the above equation, is 6.2° with a Trouton constant of 23.04 cal/deg mole.

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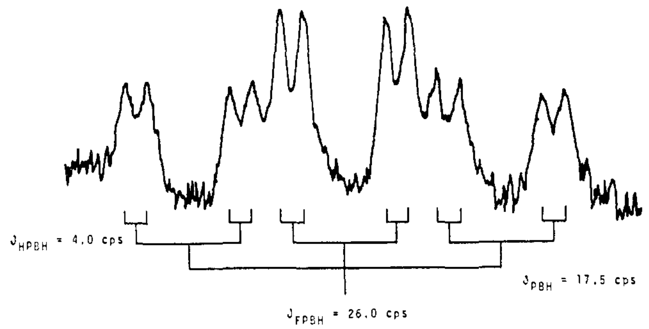

Figure 1. ^{1}H nmr spectrum of $PHF_2 \cdot BH_3$(l): one member of borane quartet.

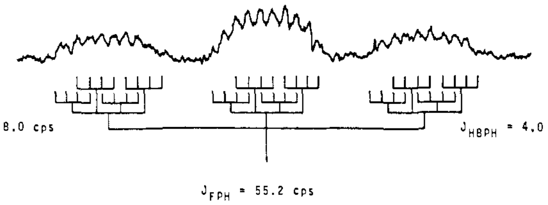

Figure 2. ^{1}H nmr spectrum of $PHF_2 \cdot BH_3$(l): one member of phosphine doublet.

The infrared spectrum (4000–200 cm^{-1}) of $PHF_2 \cdot BH_3$(g) shows absorption at the following frequencies (cm^{-1}): 2475.5 m, 2473.0 m, 2464.2 vs, 2462.2 vs, 2440 m, 2423.7 vs, 2422.3 vs, 2406 m, 1120 w, 1035 m, 1031 w, 1026.9 m, 1023.2 vs, 1021.8 m, 1013 m, 978.5 w, 921.1 vs, 912.8 vvs, 904.5 vs, 903.0 vs, 820 vw, 732.3 w, 729.7 w, 728.2 w, 723.2 s, 720.8 s, 577 w, 567 w, 389.2 m, 379.8 m, 374.7 m, 230 w, 225 w.[13]

Table I. Mass Spectrum of Difluorophosphine Borane[a]

m/e	Rel peak height	Possible assignment[b]	m/e	Rel peak height	Possible assignment[b]
84	19.7	$H_3BPHF_2^+$	49	7.8	BF_2^+
83	69.8	$H_3BPF_2^+$, $H_2BPHF_2^+$	48	1.9	$^{10}BF_2^+$
82	100.0	$H_2BPF_2^+$, $HBPHF_2^+$	44	1.0	$HPBH^+$
81	22.9	$H_2{}^{10}BPF_2^+$, $HBPF_2^+$	43	3.2	HPB^+
80	1.8	$H^{10}BPF_2^+$	42	1.9	BP^+
71	3.7	$PF_2H_2^+$	41	0.3	$^{10}BP^+$
70	13.7	PHF_2^+	35	3.2	PH_4^+
69	46.1	PF_2^+	33	28.6	PH_2^+
63	1.6	H_2BPF^+, $HBPHF^+$	32	17.9	PH^+
62	3.0	$HBPF^+$, $BPFH^+$	31	63.2	BHF^+, P^+
61	9.4	BPF	30	14.2	$^{10}BHF^+$
60	2.1	^{10}BPF	19	0.6	F^+
52	1.0	PH_2F^+	13	31.5	BH_2^+
51	36.7	PHF^+	12	23.4	BH^+
50	25.9	PF^+			

[a] Obtained on a Consolidated Electrodynamics Model 21-103B mass spectrometer operating at 70 ev. [b] Additional assignments are possible for many peaks. Only where the peak is thought to be due primarily to a ^{10}B fragment is the ^{10}B isotope noted.

The ^{1}H, ^{11}B, and ^{19}F nmr spectra show unquestionably that difluorophosphine borane may be formulated as F_2HPBH_3. The basic proton spectrum consists of a 1:1:1:1 quartet ($J_{^{11}B-H}$ = 103 cps) and a doublet (J_{P-H} = 467 cps) of 1:2:1 triplets centered 0.78 and 7.68 ppm downfield from TMS, respectively. As expected the area of the quartet (BH_3) was three times that of the doublet (PH). Each member of the borane quartet is split into a 1:2:1 triplet (J_{FPBH} = 26.0 cps) and each member of the triplet is split further into a doublet of doublets (J_{PBH} = 17.5, J_{HPBH} = 4.0 cps); see Figure 1.

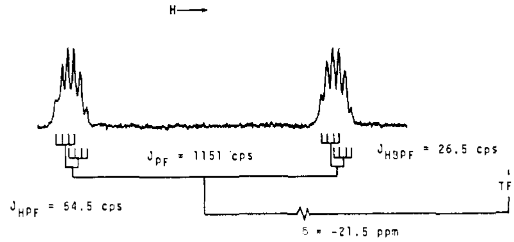

Figure 3. 94.1-Mc ^{19}F nmr spectrum of $PHF_2 \cdot BH_3$(l) at 37°.

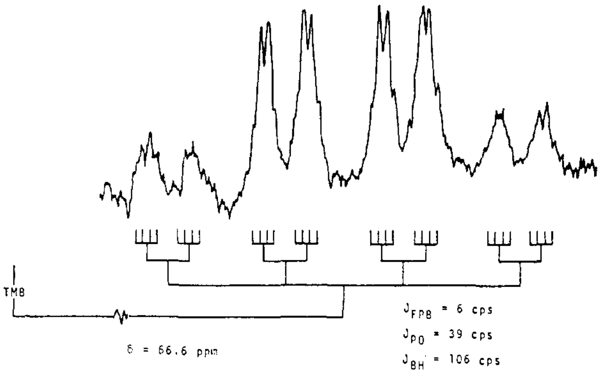

Figure 4. 32.1-Mc ^{11}B nmr spectrum of $PF_3 \cdot BH_3$(l) at 37°.

Each member of the basic P–H doublet is split into a 1:2:1 triplet by the two equivalent fluorine nuclei (J_{FPH} = 55.2 cps). Each component of the 1:2:1 triplet consists of a 1:3:4:4:4:4:4:4:3:1 ten-line multiplet which can be attributed to a 1:1:1:1 quartet (J_{BPH} = 8.0 cps), each member of which is split into a 1:3:3:1 quartet (J_{HBPH} = 4.0 cps) by borane hydrogens. Overlap of peaks gives the spectrum shown in Figure 2.

In the ^{11}B nmr spectrum of $PHF_2 \cdot BH_3$, a 1:3:3:1 quartet (J_{HB} = 102 cps) typical of BH_3 is displayed 60.4 ppm upfield from (TMB).[14a] Each member of the quartet is split into a doublet by the ^{31}P (J_{PB} = 48.6 cps).

The basic ^{19}F nmr spectrum consists of a doublet resulting from P–F coupling, which is centered 21.5 ppm downfield from TFA[14b] (Figure 3) (J_{PF} = 1151 cps). Each member of the doublet consists of a 1:3:4:4:3:1 sextet, which can be attributed to the overlap of a doublet (J_{HPF} = 54.5 cps) of 1:3:3:1 quartets (J_{HBPF} = 26.5 cps).

The coupling constants derived from the proton, boron, and fluorine nmr spectra agree within experimental error.

Nmr Spectra of F_3PBH_3 and H_3PBH_3. The nmr spectra of F_2HPBH_3 and of F_3PBH_3 and H_3PBH_3 indicate an isostructural relationship for these three compounds. The nmr spectra of F_2HPBH_3, determined in the present study, show clearly an ethane type of configuration in which free rotation about the P–B bond occurs at a faster rate than the nmr time constant, thus averaging out the magnetic environments of the fluorine and hydrogen nuclei.

The boron nmr spectrum of liquid $PF_3 \cdot BH_3$ at 37° (Figure 4) consists of the expected 1:3:3:1 quartet of doublets centered 66.6 ppm upfield from TMB (J_{BH} = 106, J_{PB} = 39 cps). Fine structure indicative of B–F coupling is seen in the 1:3:3:1 quartets (J_{BPF} = 6 cps).

The proton nmr spectrum of $PF_3 \cdot BH_3$ at 40° (Figure 5) consists of the expected 1:1:1:1 quartet (J_{BH} = 108 cps) of quintets centered on the signal for TMS. The fine structure of each member of the quartet (1:4:6:4:1 pattern) is attributed to the superposition of two 1:3:3:1 quartets from fluorine coupling (J_{FPBH} = 18 cps) and ^{31}P splitting (J_{PBH} = 18 cps).

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[13] v = very, s = strong, m = medium, and w = weak intensity bands. A complete vibrational study is now underway.

[14] (a) TMB = trimethyl borate; (b) TFA = trifluoroacetic acid.

Coupling of the borane hydrogens of $PF_3 \cdot BH_3$ with the ^{10}B ($I_{^{10}B} = 3$) present in the sample is evidenced by the three small peaks ($J_{^{10}B-H} = 36$ cps) displayed between the members of the 1:1:1:1 quartet (Figure 5); the four other lines of the expected 1:1:1:1:1:1:1 seven-line multiplet are masked by the middle two members of the ^{11}B–H quartet. The assignment of the three small peaks to a septet associated with the ^{10}B–H signal is substantiated by the agreement between the measured ratio $J_{^{11}BH}$: $J_{^{10}BH}$ = 108:36 and the expected ratio $\gamma_{^{11}B} = \gamma_{^{10}B}$ = 1.792:0.6002. Furthermore the area under the septet is approximately one-fourth of the area under the quartet, a fact consistent with the approximate 1:4 natural abundance ratio of ^{10}B:^{11}B in boron.

In the ^{19}F nmr spectrum of $PF_3 \cdot BH_3$, a basic doublet attributed to P–F spin-spin coupling (J_{PF} = 1406 cps) is observed centered 19.9 ppm downfield from TFA. If the values of J_{FPBH} = 18 cps from the ^1H spectrum and J_{FPB} = 6 cps from the ^{11}B spectrum are used to determine the expected fine structure pattern for each member of the doublet, a 13-line multiplet with intensity ratios of 1:1:1:4:3:3:6:3:3:4:1:1:1 and spacings of 6 cps is predicted. Although the expected 13-line multiplet could not be completely resolved, a pattern which shows the prominent features of the expected multiplet was observed.

The ^1H and ^{11}B nmr spectra of molten $H_3P \cdot BH_3$ have been reported previously.[4] A comparison of the chemical shifts and coupling constants derived from the ^1H, ^{19}F, and ^{11}B nmr spectra of $PF_3 \cdot BH_3$, $PHF_2 \cdot BH_3$, and $PH_3 \cdot BH_3$ is given in Table II. All of these spectra are easily interpretable with first-order spin-spin coupling rules.

Table II. Coupling Constants (cps) and Chemical Shifts (ppm) from ^1H, ^{19}F, and ^{11}B Nmr Spectra[a]

	$PF_3 \cdot BH_3$	$PHF_2 \cdot BH_3$	$PH_3 \cdot BH_3$
J_{BH}	107	103	104
J_{PF}	1406	1151	. . .
J_{PH}	. . .	467	372
J_{PB}	39	49	27
J_{HBPH}	. . .	4	8
J_{FPBH}	18	26	. . .
J_{FPH}	. . .	55	. . .
J_{PBH}	18	17	16
J_{BPF}	6	. . .	. . .
	^1H Nmr (TMS standard)		
δ(BH)	0	−0.78	−0.53
δ(PH)	. . .	−7.68	−4.31
	^{19}F Nmr (TFA standard)		
δ(PF)	−19.9	−21.5	. . .
	^{11}B Nmr (TMB standard)		
δ(B)	66.6	60.4	60.8

[a] Spectra were determined on Varian instruments operating at the appropriate radiofrequency: ^{11}B (32.1 Mc), ^{19}F (94.1 Mc), ^1H (60 and 100 Mc). The following abbreviations are used to denote chemical shift standards: TMS = tetramethylsilane, TFA = trifluoroacetic acid, TMB = trimethyl borate. Chemical shifts were obtained by tube interchange.

The Reaction of PHF_2 with $F_3P \cdot BH_3$. Difluorophosphine effected the displacement of PF_3 from $PF_3 \cdot BH_3$ at −78 to −45°. The equation is $F_2HP(g) + F_3PBH_3(g) \xrightarrow{-45°} F_2HPBH_3(g) + F_3P(g)$. In a typical experiment, 0.59 mmole of PHF_2 was condensed into a 40-cc tube with 0.83 mmole of PF_3BH_3. The tube was maintained at −78° for 25.5 hr, after which time 0.34 mmole of PF_3 was isolated (57% yield). Everything was condensed back into the tube, and the reaction was allowed to proceed for 24.5 additional hr at −45° before the products were finally separated by fractional condensation (−126, −160, −196°). Trifluorophosphine (0.58 mmole) passed through the −160° trap, while $PF_3 \cdot BH_3$ (0.22 mmole) was retained at −160°. Difluorophosphine borane (0.57 mmole, 97% yield) was retained at −126°. The best separation was effected when distillation through the −126° U-tube was rapid. Upon prolonged standing at −126°, $PHF_2 \cdot BH_3$ slowly passed to colder regions.

The Reaction of PHF_2 with H_3PBH_3. The reaction occurs as follows

$$H_3PBH_3(s) + HPF_2(g) \xrightarrow[12\text{ hr}]{0°} HF_2PBH_3(g) + PH_3(g)$$

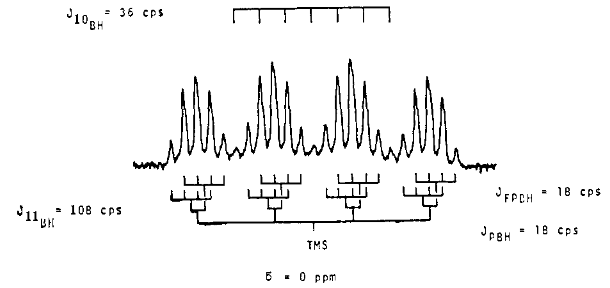

Figure 5. 60-Mc ^1H nmr spectrum of $PF_3 \cdot BH_3(l)$ at −40°.

Phosphine borane (1.93 mmoles) and difluorophosphine (0.91 mmole) were condensed into a 43-cc reaction tube. The tube was maintained at −23° for 5.5 hr, after which time the products were recovered. It was found that displacement had not proceeded to an appreciable extent. Everything was condensed back into the tube and maintained at 0° for 12 additional hr. The tube was then cooled to −78° and the volatiles were removed through U-tubes held at −126, −160, and −196°. A very small amount of H_2 (0.02 mmole) passed through the −196° trap which held a 0.96-mmole mixture of PH_3 and PF_3 plus a trace of B_2H_6. This mixture weighed 34.4 mg, which indicates that it contained *ca.* 0.04 mmole of PF_3 and *ca.* 0.91 mmole of PH_3. All of the PHF_2 had been consumed as indicated by the fact that nothing was retained at −160°. The −126° trap held 0.84 mmole of $PHF_2 \cdot BH_3$. The solids left in the reaction tube were composed of a small amount of a nonvolatile yellow species and 0.97 mmole of $PH_3 \cdot BH_3$. The latter decomposed on warming to room temperature to give a mixture (1.46 mmoles) of B_2H_6 and PH_3.

When the displacement of PH_3 from $PH_3 \cdot BH_3$ by PHF_2 was attempted at higher pressures, it was complicated by an increased amount of disproportionation as indicated by the formation of appreciable amounts of PF_3 and nonvolatile yellow solids.[15]

The PH_3–F_3PBH_3 System. The following equilibrium has been demonstrated.

$$F_3PBH_3(g) + PH_3(g) \rightleftharpoons PF_3(g) + H_3PBH_3(s)$$

Trifluorophosphine borane (1.00 mmole) was condensed into a 43-cc reaction tube equipped with a stopcock. H_3P (1.82 mmoles) was also added to the tube which was then warmed to −78° for 4 hr; however, the reaction proceeded only slowly at this temperature. After an additional 10 hr at −35°, separation of the products showed that 0.56 mmole of PF_3 had been displaced. All the products and reactants were returned to the tube which was then maintained at 0° for 16 additional hr. Finally, the products were separated (−112, −160, −196°). A mixture (1.91 mmoles) of PF_3 and PH_3 (trace of B_2H_6) which weighed 109.4 mg passed the −160° trap. Retained at −160° was 0.13 mmole of $PF_3 \cdot BH_3$. The −112° trap contained $PH_3 \cdot BH_3$. A mass balance of products and reactants indicates that 87% of the PF_3 was displaced under these conditions (0°).

A similar experiment was conducted, but trifluorophosphine was added to the system in order to test its effect on the extent of displacement. Equal amounts (0.99 mmole) of $PF_3 \cdot BH_3$, PH_3, and PF_3 were held at −35° for 10 hr; separation of the products and reactants indicated that 27% of the PF_3 was displaced. Everything was returned to the reaction tube and maintained at 0° for an additional 20 hr. Separation yielded 2.17 mmoles of a mixture (153.9 mg) of PF_3 and PH_3 (traces of B_2H_6), plus 0.51 mmole of $PF_3 \cdot BH_3$. Thus 48% of the PF_3 was displaced at 0°.

Base Displacement Reactions in the Borane Adducts of H_3P, F_3P, and HPF_2

From the data cited above the equilibrium constant at 0° for the process

$$F_3PBH_3(g) + PH_3(g) \rightleftharpoons PF_3(g) + H_3PBH_3(s)$$

can be calculated as 2.0 ± 0.3 × 10^{-5} (partial pressures

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(15) Under these conditions the displaced PH_3 appeared to react with free PHF_2 to give an unstable species which was not characterized completely but which did display spectral characteristics similar to those attributed to $PHF_2 \cdot HI$: R. W. Rudolph, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1966.

in atmospheres). This value of K cannot, however, be used as a measure of the relative base strengths of F_3P and H_3P. Base-strength values and related B–P bond-strength values imply interactions of the acid and base in the *gaseous* state to give gaseous products, *i.e.*

$$F_3PBH_3(g) + PH_3(g) \rightleftharpoons PF_3(g) + H_3PBH_3(g)$$

On the other hand, the measured process cited above involves formation of a solid product as represented by an extra equation

$$\begin{array}{ll} \text{(acid–base)} & F_3PBH_3(g) + PH_3(g) \longrightarrow PF_3(g) + H_3PBH_3(g) \\ \text{lattice formation} & \underline{\qquad\qquad H_3PBH_3(g) \longrightarrow H_3BPH_3(s)\qquad\qquad} \\ & F_3PBH_3(g) + PH_3(g) \longrightarrow PF_3(g) + H_3BPH_3(s) \end{array}$$

If $H_3BPH_3(g)$ has a large lattice energy, the over-all displacement process could be shifted strongly to the right even though H_3P were a relatively weak base toward BH_3 and the $H_3P–BH_3$ bond were very weak in the vapor phase.

An apportionment of the energy for the over-all process between these two equations can be made only on qualitative grounds. It is significant that $H_3BPH_3(g)$ is so completely dissociated that it has not yet been detected in the vapor phase by vapor density or infrared measurements. Furthermore, while H_3BPH_3 is known to sublime slowly under high vacuum[16] its vapor pressure is lower than that of mercury at the trap temperature (about −75°) (*i.e.*, the white ring of H_3BPH_3 will condense in the trap before the black ring of mercury). These observations taken together imply weak interaction between H_3P and BH_3 in the gaseous state (low base strength for H_3P) and a high lattice energy for the solid H_3BPH_3. One would estimate that the equilibrium constant for the process $PH_3BH_3(g) \rightarrow 0.5B_2H_6(g) + PH_3(g)$ is *much* larger than 1, and the very existence of the compound $H_3BPH_3(s)$ is dependent upon the large lattice energy of the solid, not upon a strong B–P bond. It is suggested that one possible source of this lattice energy is interaction of the acidic phosphine hydrogens and the hydridic borane hydrogens in an unusual type of hydrogen bond

$$P\text{–}\overset{\delta+}{H}\cdots\cdots\overset{\gamma-}{H}\text{–}B$$

A sizable amount of data on the vapor pressures and physical properties of the amine boranes and phosphine boranes can be interpreted on the basis of such a postulate.[17]

For the dissociation of $F_3PBH_3(g)$

$$F_3PBH_3(g) \longrightarrow F_3P(g) + 0.5B_2H_6(g)$$

the equilibrium constant (pressure given in atmospheres) is approximately 1.[1,18] ΔH for the above process is given[18] as 11.9 kcal/mole. Note that all products and reactants are gases. The above thermodynamic data, the existence of F_3PBH_3 in the gaseous state, and the instability of H_3BPH_3 in the gaseous state indicate clearly that the P–B bond in F_3PBH_3 is stronger than the P–B bond in H_3PBH_3.

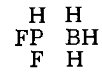
In marked contrast to the behavior of H_3P and B_2H_6, F_2HP and B_2H_6, when mixed in 2:1 mole ratio, combine quantitatively. No $B_2H_6(g)$ or $HPF_2(g)$ can be detected in equilibrium with HF_2PBH_3 at 25°. Clearly the equilibrium constant for the dissociation (pressures in atmospheres)

$$F_2HPBH_3(g) \longrightarrow F_2HP(g) + 0.5B_2H_6(g)$$

is much less than 1 at 25°. This fact plus reactions in which F_2HP displaces F_3P and H_3P from borane complexes indicate conclusively that HF_2P is a stronger base toward borane than either F_3P or H_3P. The order of base strength toward borane is thus $H_3P < F_3P << F_2HP$.

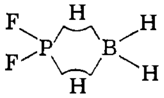
Discussion

Since the proton, boron, and fluorine nmr spectra of F_2HPBH_3 are "textbook examples" of first-order nmr spectra for structure i, the unusual stability of the compound cannot be attributed to gross structural anomalies. Structures such as ii–iv are clearly eliminated.



$$\begin{array}{cc} H & H \\ FP & BH \\ F & H \end{array}$$

i



ii

$$[F_2P]^+[BH_4]^-$$

iii

$$[F_2PH_2]^+[BH_2]^-$$

iv

Any useful model must explain a P–B bond in HF_2PBH_3 which is significantly stronger than that in H_3PBH_3 or F_3PBH_3. Unfortunately, none of the models currently in vogue is sufficiently quantitative to justify convincing predictive utility.

In one model used by several investigators[19–24] to analyze various phosphine and sulfide boranes, it is assumed that the BH_3 group releases electron density to the base in a manner analogous to methyl hyperconjugation. Electrons released in hyperconjugation are presumed to be available for formation of a $p\pi$–$d\pi$ bond between boron and phosphorus. Fluorine bonded to phosphorus presumably removes charge from the phosphorus and makes it a better π acceptor.[25] Certainly this model offers no suggestion of a stronger π bond in F_2HPBH_3 than in F_3PBH_3. Clearly, quite the reverse would be expected; phosphorus in F_3PBH_3 should be the better electron acceptor because it has more fluorine atoms attached.[25,26]

An alternative model is desired. A fairly large body of data indicate that the coordinating ability of phosphines, sulfides, and similar polarizable ligands is strongly dependent upon the field strength of the reference acid, the acid of higher field strength forming a stronger coordinate link with the more polarizable ligand,[27,28] *i.e.*, phosphine or sulfide.

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[16] H. I. Schlesinger and A. B. Burg, *Chem. Rev.*, **31**, 11 (1942).

[17] R. W. Parry and J. R. Weaver, to be published.

[18] A. B. Burg and Y. C. Fu, *J. Am. Chem. Soc.*, **88**, 1145 (1966), also confirmed in this study.

[19] W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1956).

[20] A. B. Burg, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **15**, 159 (1954).

[21] S. Ahrland, J. Chatt, and N. R. Davis, *Quart. Rev.* (London), 12, 265 (1958).

[22] F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958).

[23] T. D. Coyle, H. D. Kaesz, and F. G. A. Stone, *J. Am. Chem. Soc.*, **81**, 2989 (1959).

[24] T. D. Coyle and F. G. A. Stone, *Progr. Boron Chem.*, **1**, 137 (1964).

[25] H. H. Jaffé, *J. Inorg. Nucl. Chem.*, **4**, 372 (1957).

[26] Since the σ bond in H_3PBH_3 is so weak that H_3PBH_3 is not found in the vapor phase, and since F_3P is assumed in π-bond arguments to have essentially no σ-bonding ability, rationalization of the strong bond by a synergistic σ–π interaction is not particularly reasonable.

[27] D. E. Young, G. E. McAchran, and S. G. Shore, *J. Am. Chem. Soc.*, **88**, 4390 (1966).

[28] R. W. Parry and R. N. Keller, "Chemistry of the Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, p 121.

In H_3P the free electron-pair dipole vector is small; the electron pair is largely s in character and is *tightened* by the protons attached to phosphorus.[29] Under these circumstances the interaction energy in the σ bond formed by PH_3 must come from distortion of the H_3P electron pair by the positive field of the Lewis acid; thus the *over-all bonding energy of phosphine is strongly dependent upon the field strength of the* positive center.[28,30] Hydrogens attached to phosphorus tighten the cloud and reduce the polarizability of the lone pair; thus PH_3 is a poor coordinating agent even in strong fields. Replacement of hydrogens by alkyl groups loosens the lone-pair cloud; as a result, R_3P is a better coordinating agent than H_3P for cations of high field strength.[29] Fluorines attached to the phosphorus would be expected to increase the *effective positive charge* on the phosphorus nucleus, thus pulling the free electron pair inward and making it available for reasonably strong σ bonding only at *unusually short* bond distances.[30]

The field strength of the positive Lewis acid is strongly dependent upon its distance of approach to the electron cloud of the ligand. Since PF_3 can form σ bonds only at very short distances, it will bind only to those Lewis acids which can approach the PF_3 molecule closely with a reasonable expenditure of deformation energy. Energy required for conversion of the normally planar Lewis acid BX_3 to a tetrahedral structure with longer B–X distance is strongly dependent upon the nature of X. When X is hydrogen, the reorganization energy is small, and close approach is easily achieved. When X is fluorine, reasonable estimates give a deformation energy about three times as large as that for BH_3,[31] and close approach to PF_3 is more severely limited by steric factors.[32] Thus BH_3 coordinates to PF_3, while BF_3 does not. With BH_3 the reorganization energy required to permit very close approach between boron and phosphorus is less than the bonding energy. With BF_3 the reverse is true because of the large reorganization energy required at short B–P bond distances. In short, *any property of acid or base which promotes a close approach of the positive acid center to the electron cloud of the ligand will generate stronger interaction.* The arguments suggest that in F_3PBH_3 the B–P bond can be both short and comparatively weak.

The unusual base strength of HPF_2 can be rationalized in terms of the above model, if reasonable assumptions about the internal geometry of HPF_2 are allowed. It is suggested that an internal "hydrogen bond" between the protonic hydrogen of HPF_2 and the two fluorines would tend to pull fluorines and hydrogens together to give a "tighter pyramid" than that found in PF_3. Because of the tighter pyramid in HPF_2, closer approach between P and B can be achieved with a given expenditure of deformation energy. The bond is thus stronger than that found in F_3PBH_3. Further, such hydrogen-bonding interaction can be pictured as reducing the effective positive charge of the hydrogen. This permits a distortion of the *P–H bonding* electrons toward phosphorus and a loosening of the phosphorus *lone pair* electrons to give a stronger B–P bond.

An extrapolation of this model to the still unknown monofluorophosphine, H_2PF, would predict that it would be a weaker base than HPF_2 but a stronger base than H_3P. It should be comparable to PF_3 in base strength.

The foregoing arguments make definite predictions about the geometry of HPF_2 and HPF_2BH_3 which are subject to experimental test. It is clearly required that the F–P–F angles of HPF_2 be smaller than those in PF_3 and that the B–P bond distance in HPF_2BH_3 be noticeably shorter than that in F_3PBH_3. Although no definitive structural data are yet available, several facts can be cited which support the above model. The P–H stretching frequency (2240.5[8]) is noticeably lower than that found in PH_3[33] (2327 and 2421 cm^{-1}). Further, a preliminary vibrational analysis of PHF_2 suggests that an appreciable interaction between P–H and P–F motions may exist. Further, the spin–spin coupling constants for PHF_2 ($J_{PH} = 182.4$, $J_{PF} = 1134$ cps) are closer to those for PH_3 ($J_{PH} = 183$ cps) and F_2PNR_2 ($J_{PF} = 1194$ cps), where the HPH angle is 93.3°[34] and the FPF angle is 92.5°[35] than they are to PF_3 ($J_{PF} = 1400$ cps) where the FPF bond angle is known to be 98.2 ± 0.6°.[36] The precise structural parameters, when available for HPF_2, will be of considerable interest.

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(29) J. R. Weaver and R. W. Parry, *Inorg. Chem.*, **5**, 718 (1966).

(30) These arguments may be illustrated by the following highly simplified polarization model. Assume that the strength of the σ bond can be formulated as a sum of two terms; the first represents the interaction of the cation with the projecting free pair (approximated by free pair dipole vector) and the second represents the additional perturbation of the bonding pair by the positive field (approximated by induced dipole vector). Then the interaction energy can be approximated as interaction energy $= F[\rho + (F\alpha/2)]$ where $F =$ the field strength of Lewis acid, $\rho =$ permanent dipole vector due to the lone pair, and $\alpha =$ polarizability or deformability of the lone pair. Note that if ρ is small, the binding energy is dependent on the square of the cation field strength, not the first power. Further, if ρ is small, α is extremely significant. ρ is assumed to be small in phosphines. α is assumed to vary in the order $PH_3 \leqslant F_3P \ll PR_3$. The model is not too different from that used by R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965).

(31) (a) E. R. Alton, Jr., and R. W. Parry, to be published; (b) E. R. Alton, Jr., Ph.D. Dissertation, University of Michigan (1960); (c) F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, **30**, 993 (1959).

(32) The large reorganization energy of BF_3 relative to BH_3 can be used to account for the dimeric nature of B_2H_6 and the monomeric nature of BF_3. The deformation energy of BF_3 is larger than energy generated by bridge bonds. Because the reorganization energy of BH_3 is small, the reverse situation applies.

(33) E. Lee and C. K. Wu, *Trans. Faraday Soc.*, **35**, 1366 (1939).

(34) M. H. Sirvetz and R. E. Weston, Jr., *J. Chem. Phys.*, **21**, 892 (1953).

(35) E. D. Morris, Jr., and C. E. Nordman, University of Michigan, to be published.

(36) O. L. Hersh, Ph.D. Dissertation, University of Michigan, 1963 (Laboratory of Professor L. O. Brockway).