**polymer.**—A filtered reaction mixture containing poly(diethylaminochlorophosphazene) (22.9 g, 0.15 mol) and diethylamine in tetrahydrofuran (1000 ml) was added to a solution of piperidine (100 ml, 1.0 mol) in tetrahydrofuran (500 ml). The mixture was stirred at 25° for 3 days and then filtered to remove amine hydrochloride (10 g, 0.09 mol). Halogen tests at this stage revealed that chlorine replacement was incomplete. The filtrate was added to a solution of methylamine (75 ml, 0.75 mol) and triethylamine (55 g, 0.55 mol) in tetrahydrofuran (500 ml). The mixture was then boiled at reflux for 1 day and filtered to remove triethylamine (2.5 g, 0.018 mol).

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# The Lewis Basicity of Some Difluorophosphines toward Borane

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The previously unreported compounds $CH_3SPF_2$, $(CH_3S)_2PF$, $CH_3PF_2 \cdot BH_3$, $CH_3SPF_2 \cdot BH_3$, and $(CH_3S)_2PF \cdot BH_3$ have been prepared and characterized by $^{19}F$, $^{11}B$, $^{1}H$, and $^{31}P$ nmr and ir spectroscopy as well as by stoichiometric data. Mass spectral data were also used to help characterize $CH_3SPF_2$ and $(CH_3S)_2PF$. A series of base displacement reactions established the base strengths toward borane as $CH_3PF_2 > (CH_3)_2NPF_2 > CH_3OPF_2 > CH_3SPF_2 \geq (CH_3S)_2PF$ while $^1J_{BP}$ for the fluorophosphine–borane adducts decreases in the series $(CH_3)_2NPF_2 > CH_3OPF_2 > CH_3PF_2 > CH_3SPF_2 > (CH_3S)_2PF$. The basicity of $CH_3PF_2$ is not mirrored by the value of the $^1J_{BP}$ coupling constant.

Rudolph and Schultz reported[1] that there is an empirical relationship between the magnitude of $J_{BP}$ and the dative bond strength for the $BH_3$ adducts of a series of smoothly varying phosphine ligands such as $(Me_2N)_{3-n}PF_n \rightarrow BH_3$, $F_{3-n}H_nP \rightarrow BH_3$, and $F_2XP \rightarrow BH_3$ (X = F, Cl, Br).[1] However, the correlation did not appear to be general for the case when the phosphine belongs to different series.[1] Cowley and Damasco[2] also suggested that there is a correlation between the $J_{BP}$ coupling constant and the base strength of a series of 15 phosphines toward $BH_3$. Their data for two series of phosphines (containing three and four members, respectively) were obtained from the previous literature, and for the other phosphines they performed three selected displacement reactions. From these data they concluded that $J_{BP}$ of the borane adduct considered may be taken as a measure of the basicity of the phosphine examined toward $BH_3$.

We have been examining the base strength of phosphines of the type $PF_2X$ (X = Me, MeO, $Me_2N$, MeS) and $PFX_2$ (X = MeS) toward $BH_3$ to see if the dative $\pi$ bonding between the filled 2p orbitals of MeO, $Me_2N$, and MeS and the vacant P 3d or P 4p orbitals influences the basicity of the phosphine. In a previous article we suggested[3] that a dative bond of this type may be important in determining the PF bond distance and the FPF bond angle in a series of $PF_2X$ compounds. Our studies indicate that although the stability of phosphine–borane adducts correlates with $J_{BP}$ for a series of five phosphine–borane adducts, a 1:1 correlation between $J_{BP}$ and base strength is not possible. The base strengths of the phosphines we examined were determined by displacement reactions. In structurally similar compounds, the entropy change accompanying coordination to a specific acid should be approximately constant and contributions to differences in entropy correspondingly small. The structures of three of the four difluorophosphines we investigated were known to be similar, and we expect no gross distortions in the structures upon coordination.[3,4]

## Experimental Section

All work was carried out under inert atmosphere or by standard vacuum-line techniques. $^{31}P$ and $^{19}F$ nmr, ir, and mass spectral data were obtained by the use of previously described instrumentation.[5] $^{11}B$ nmr spectra were recorded with a Varian Model HA-100 nuclear magnetic resonance spectrometer operating at 32.1 MHz.

$MePF_2$,[6] $MeOPF_2$,[7a] $Me_2NPF_2$,[7b] and $B_2H_6$[8] were prepared as described in published methods and purified by either codistillation[9] or by trap-to-trap distillation.

**Preparation of $CH_3SPF_2$ and $(CH_3S)_2PF$.**—The hitherto unreported $MeSPF_2$ and $(MeS)_2PF$[10] were prepared by the interaction of $PF_2Cl$ and $CH_3SH$ in the presence of $Me_3N$. In a typical reaction 7.00-mmol samples of $PF_2Cl$,[7b] $Me_3N$[11] (dried over sodium), and MeSH (Amoco) were condensed sequentially at −196° into a previously dried 500-ml round-bottom flask equipped with a Teflon vacuum valve (Kontes). The reaction mixture was allowed to warm to 25° over a period of 5 min. An immediate reaction was indicated by formation of a white cloud. The volatile products were separated by first passing the mixture through traps held at −45 and −196° and then by codistillation of the material in the −196° trap. A 1.45-mmol sample of $PF_3$, a 0.04-mmol sample of $PF_2Cl$, and a 0.04-mmol sample of $Me_3N$ were recovered and were identified by their gas-phase ir spectra. In addition, a 1.92-mmol sample of $MeSPF_2$ and a

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TABLE I

STOICHIOMETRY OF BORANE ADDUCTS

| | Amt, mmol | | | Mol of phosphine: | | |
|---|---|---|---|---|---|---|
| Adduct | Phosphine | $B_2H_6$ | $B_2H_6$ recovered | mol of borane | Temp, °C | Time, min |
| $MeOPF_2 \cdot BH_3$ | 2.16 | 2.00 | 0.92 | 1.0 | −78 to 0 | 135 |
| $Me_2NPF_2 \cdot BH_3$ | 2.48 | 1.90 | 0.55 | 0.92 | −78 | 120 |
| $MePF_2 \cdot BH_3$ | 2.16 | 1.88 | 0.70 | 0.92 | −78 | 30 |
| $MeSPF_2 \cdot BH_3$ | 2.16 | 1.97 | 0.69 | 0.84 | −40 | 45 |
| $(MeS)_2PF \cdot BH_3$ | 1.74 | 1.82 | 0.92 | 0.97 | −78 | 30 |

TABLE II

NMR DATA FOR BORANE ADDUCTS

| | $^{11}$B nmr | | $^{1}$H nmr | | $^{19}$F nmr | |
|---|---|---|---|---|---|---|
| Complex | $^1J_{^{11}B-^{31}P}$, Hz | $^1J_{^{11}B-^{1}H}$, Hz | $J_{^{31}P-^{1}H(CH_3)}$, Hz | $J_{^{19}F-^{1}H(CH_3)}$, Hz | $^1J_{^{31}P-^{19}F}$, Hz | $^3J_{^{19}F-^{1}H(BH_3)}$, Hz |
| $MePF_2 \cdot BH_3$[a] | 61 | 61 | 6.7 | 12.6 | 1145 | 21.0 |
| $Me_2NPF_2 \cdot BH_3$[14] | 79 | | 10.6 | 3.2 | 1155 | 14.1 |
| $MeOPF_2 \cdot BH_3$ | 69.3 | 98.4 | 11.2 | | 1280 | 15.1 |
| $MeSPF_2 \cdot BH_3$ | 41.4 | 101.3 | 12.4 | 2.4 | 1235 | 18.7 |
| $(MeS)_2PF \cdot BH_3$ | ~30 | 92.1 | 13.8 | 1.8 | 1145 | 17.8 |

| | δ, ppm | | | |
|---|---|---|---|---|
| Complex | $^{11}$B[c] | $^{31}$P[d] | $^{1}$H[e] | $^{19}$F[b] |
| $MePF_2 \cdot BH_3$[a] | 42.2 | 99.9 | 1.7 | 102.0 |
| $Me_2NPF_2 \cdot BH_3$[14] | | | 2.3 | 73.2 |
| $MeOPF_2 \cdot BH_3$ | 46.8 | 15.1 | 3.6 | 65.6 |
| $MeSPF_2 \cdot BH_3$ | 39.9 | 86.3 | 2.4 | 68.1 |
| $(MeS)_2PF \cdot BH_3$ | 36.1 | 90.7 | 2.5 | 92.9 |

[a] $^4J_{HBPCH}$ = 1.2 Hz. [b] Relative to external $CCl_3F$. [c] Relative to external $BF_3OEt_2$. [d] Relative to external $(MeO)_3P$. [e] Relative to external $Me_4Si$.

0.50-mmol sample of $(MeS)_2PF$ were recovered after codistillation of the −196° fraction.

Unequivocal characterization of $MeSPF_2$ and $(MeS)_2PF$ was obtained from the $^1$H (60 MHz) and $^{19}$F (56.4 MHz) nmr spectra. The proton spectrum at −50° of $MeSPF_2$ shows a doublet ($^3J_{HP}$ = 7.3 Hz) centered at 2.0 ppm from TMS; each member of the doublet is split into a 1:2:1 triplet ($^4J_{HF}$ = 2.2 Hz). The fluorine spectrum consists of a doublet ($^1J_{PF}$ = 1248 Hz) centered at +72.2 ppm from $CCl_3F$; each member of the doublet is further split into a 1:3:3:1 quartet ($^4J_{HF}$ = 2.1 Hz). The proton spectrum at −50° of $(MeS)_2PF$ shows a doublet ($^3J_{HP}$ = 12.3 Hz) centered at 2.4 ppm from TMS; each member of the doublet is split into a doublet ($^4J_{HF}$ = 2.6 Hz). The fluorine spectrum consists of a doublet ($^1J_{PF}$ = 1114 Hz) centered at +116.4 ppm from $CCl_3F$; each member of the doublet is further split into a 1:6:15:20:15:6:1 septet ($^4J_{HF}$ = 2.4 Hz). Both the coupling constants and chemical shifts are consistent with the proposed formulation and are similar to values previously reported for fluorophosphines.[12] The mass spectra of $MeSPF_2$ and $(MeS)_2PF$ obtained at 70 eV are consistent with the proposed formulations. Distribution of the intensities of peaks due to more than one isotopic species agrees with the proposed assignments. The spectrum of $MeSPF_2$ consisted of the following peaks (listed as the *m/e* ratio, relative intensity, and tentative assignments): 118, 4.2, $CH_3{}^{34}SPF_2{}^+$; 116, 100, $CH_3{}^{32}SPF_2{}^+$; 115, 1.6, $CH_3{}^{32}SPF_2{}^+$; 101, 9.2, $^{32}SPF_2{}^+$; 97, 3.3, $CH_3{}^{32}SPF^+$; 88, 2.5, $PF_3{}^+$; 82, 1.6, $^{32}SPF^+$; 77, 2.5, ?; 69, 51.7, $PF_2{}^+$; 63, 3.3, $^{32}SP^+$; 50, 5.0, $PF^+$; 49, 1.6, $CH_3{}^{34}S^+$; 48, 4.2, $CH_3{}^{32}SH$; 47, 31.7, $CH_3{}^{32}S^+$; 46, 18.3, $CH_3P^+ + CH_2{}^{32}S^+$; 45, 32.5, $CH^{32}S^+$ + ?; 44, 3.3, $C^{32}S^+$; 32, 4.2, $O_2{}^+$; 28, 11.7, $N_2{}^+$; 18, 5.8, $H_2O^+$; 17, 1.6, $HO^+$; 15, 4.2, $CH_3{}^+$; 14, 11.7, $N^+$. The mass spectrum of $(MeS)_2PF$ shows peaks attributed to the following positive ions: 146, 3.2, $(CH_3)_2{}^{32}S^{34}SPF^+$; 144, 61.9, $(CH_3{}^{32}S)_2PF^+$; 116, 5.6, $CH_3{}^{32}SPF_2{}^+$; 114, 2.4, $^{32}S_2PF^-$; 99, 3.2, $CH_3{}^{34}SPF^+$; 98, 3.2, ?; 97, 59.5, $CH_3{}^{32}SPF^+$; 96, 1.6, $CH_2{}^{32}SPF^+$; 83, 1.6, ?; 82, 5.6, $^{32}SPF^+$; 79, 1.6, ?; 77, 14.3, ?; 69, 4.8, $PF_2{}^+$; 63, 11.1, $^{32}SP^+$; 61, 4, ?; 50, 4.8, $CH_3{}^{34}SH + PF^+$; 49, 5.6, ?; 48, 66.7, $CH_3{}^{32}SH^+$; 47, 100, $CH_3{}^{32}S^+$; 46, 16.7, $CH_2{}^{32}S^+$; 45, 61.9, $CH^{32}S^+$ + ?; 44, 10.3, $C^{32}S^+$; 32, 10.3, $O_2{}^+$; 28, 32.5, $N_2{}^+$; 18, 19.8, $H_2O^+$; 17, 4, $HO^+$; 15, 7.9, $CH_3{}^+$. The compound $MeSPF_2$ exhibits gas-phase ir absorptions at 2940 (w), 2850 (vw), 1438 (w), 1320 (w), 965 (w), 822 (vs), 695 (w), 543 (m), 512 (s), and 410 (w) cm$^{-1}$. We tentatively assign the broad absorption at 822 cm$^{-1}$ to overlapping PF symmetric and asymmetric stretches. The bands at 543 and 512 cm$^{-1}$ are assigned to the P–S stretching vibrations by comparison to the assignments of Chittenden and Thomas.[13] We observed that $MeSPF_2$ produced small amounts of $PF_3$ when allowed to warm to room temperature. Mol wt of $CH_3SPF_2$: calcd, 116; found, 112.

**Complex Formation and Characterization.**—All adducts were prepared in a 30-ml Kjeldahl flask equipped with a Teflon vacuum valve (Kontes), a standard taper joint, and a side arm to which an nmr tube was joined. The reaction mixture was stirred through the use of 1/2 in. × 1/8 in. Teflon-coated magnetic stirring bar. In all preparations, the phosphine and 1 molar excess of diborane were condensed into the Kjeldahl flask at −196°. The reaction mixture was allowed to warm to a temperature at which the reaction proceeded at a significant rate. The uptake of $B_2H_6$ by the phosphine was monitored by a mercury manometer attached to the manifold leading to the reaction flask. When the pressure above the reaction remained constant, the reaction flask was cooled to −196° and then allowed to warm to −112° ($CCl_3F$ slush) and the volatile $B_2H_6$ was removed. The valve on the reaction vessel was closed and the vessel was removed from the vacuum line. The adduct was then poured into the nmr tube attached to the side of the reaction flask and the tube was sealed *in vacuo* at −196°. Specific data for the reactions are contained in Table I.

The adducts were characterized by the stoichiometry of the reactions from which they were obtained and by their ir and nmr spectral patterns. The nmr data, presented and discussed in detail below, are consistent in every case with the proposed formulations and agree empirically with data obtained from similar compounds.[12]

Strong ir absorptions in the B–H stretching region for four of the adducts studied are as follows (adduct, cm$^{-1}$): $MePF_2 \cdot BH_3$, 2456, 2399; $MeOPF_2 \cdot BH_3$, 2449, 2438; $MeSPF_2 \cdot BH_3$, 2435; $Me_2NPF_2 \cdot BH_3$, 2436, 2430. The ir spectrum of $(MeS)_2PF \cdot BH_3$ could not be obtained because of rapid decomposition at 32°, the temperature at which spectra were obtained.

The $^1$H, $^{19}$F, $^{11}$B, and $^{31}$P nmr spectra of the hitherto unreported borane adducts $MePF_2 \cdot BH_3$, $MeSPF_2 \cdot BH_3$, and $(MeS)_2PF \cdot BH_3$ at −50° show first-order splitting patterns. The nmr data obtained for $Me_2NPF_2 \cdot BH_3$ and $MeOPF_2 \cdot BH_3$ are in agreement with previously published spectral data.[1,2,12,14] Miscellaneous coupling constants and chemical shifts obtained in these studies are contained in Table II.

$MePF_2 \cdot BH_3$ exhibits a $^1$H nmr spectrum consisting of a 1:1 doublet, $J_{PH(CH)_3}$, each member of which is split into a 1:2:1

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TABLE III

STOICHIOMETRIC DATA FOR DISPLACEMENT REACTIONS

| Phosphine | Amt of phosphine, mmol | Complex | Amt of complex, mmol | Time, hr | $K_{eq}(0°)^a$ | Per cent displacement$^b$ |
|---|---|---|---|---|---|---|
| $MePF_2$$^c$ | 1.08 | $MeOPF_2 \cdot BH_3$ | 1.08 | 46.5 | ∞ | 100 |
| $MeOPF_2$ | 1.08 | $MePF_2 \cdot BH_3$ | 1.08 | 45.0 | ∞ | 100 |
| $Me_2NPF_2$$^c$ | 1.14 | $MeOPF_2 \cdot BH_3$ | 1.14 | 67.5 | 79.7 | 90.0 |
| $MeOPF_2$ | 1.23 | $Me_2NPF_2 \cdot BH_3$ | 1.34 | 54.3 | 151 | 92.5 |
| $MeOPF_2$$^c$ | 1.08 | $MeSPF_2 \cdot BH_3$ | 1.08 | 64.0 | 1.60 | 55.8 |
| $MeSPF_2$ | 0.88 | $MeOPF_2 \cdot BH_3$ | 1.08 | 15.3 | 1.95 | 58.3 |
| $MeOPF_2$$^{c,d}$ | 0.93 | $(MeS)_2PF \cdot BH_3$ | 0.58 | 6.5 | 1.65 | 59.3 |
| $(MeS)_2PF$$^d$ | 1.77 | $MeOPF_2 \cdot BH_3$ | 1.02 | 6.5 | 1.35 | 53.7 |

[a] All equilibrium constants are defined by the expression: [weaker base][adduct of stronger base]/[adduct of weaker base][stronger base] = $K_{eq}$. [b] Per cent displacement is calculated using the formula $100\sqrt{K_{eq}}/(\sqrt{K_{eq}} + 1)$. [c] Indicates the stronger base of the exchanging pair of phosphines. [d] Extensive decomposition of $(MeS)_2PF \cdot BH_3$ at 0° into an unidentified yellow solid.

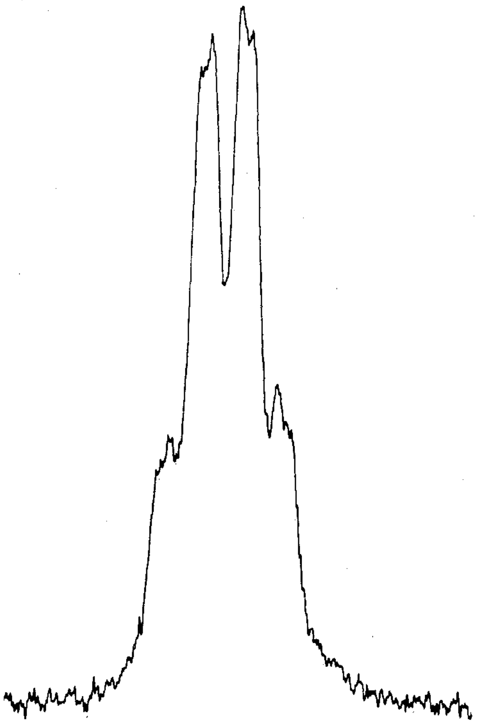

Figure 1.—The $^{11}B$ nmr spectrum (32.1 MHz) of $(CH_3S)_2PF \cdot BH_3$.

triplet, $J_{FH(CH_3)}$, the components of which are each split into a 1:3:3:1 quartet, $J_{HH}$, giving a total of 24 observed lines. In addition, a very broad 1:1:1:1 quartet, $J_{BH}$, appears in the $^1H$ spectrum. Each member of the quartet is split into a 1:3:3:1 quartet which arises from the overlap of two 1:2:1 triplets of equal intensity, $J_{PH(BH_3)}$ and $J_{FH(BH_3)}$. The $^{19}F$ nmr spectrum is composed of a 1:1 doublet, $J_{PF}$, each member of which is split into a 1:3:3:1 quartet, $J_{FH(BH_2)}$. Members of this quartet are further split into a 1:3:3:1 quartet, $J_{FH(CH_3)}$, giving 32 well-resolved lines. The $^{11}B$ spectrum shows a 1:1 doublet, $J_{BP}$, which is further split into a 1:3:3:1 quartet, $J_{BH}$. The $^{31}P$ nmr spectrum consists of a 1:3:1 triplet, $J_{PF}$, each member of which is split into a poorly resolved 1:1:1:1 quartet, $J_{BP}$.

The $MeSPF_2 \cdot BH_3$ $^1H$ nmr spectrum shows a 1:1 doublet, $J_{PH(CH_3)}$, which is further split into 1:2:1 triplets, $J_{FH(CH_3)}$. A broad 1:1:1:1 quartet, $J_{BH}$, is also observed in the $^1H$ spectrum. A 1:1 doublet, $J_{PF}$, is observed in the $^{19}F$ nmr spectrum; each member of the doublet is split into a 1:3:3:1 quartet, $J_{FH(BH_3)}$. The $^{11}B$ nmr spectrum consists of the expected 1:1 doublet, $J_{BP}$, which is further split into 1:3:3:1 quartets, $J_{BH}$. The $^{31}P$ nmr spectrum shows only a broad 1:3:1 triplet, $J_{PF}$.

$(MeS)_2PF \cdot BH_3$ exhibits a $^1H$ spectrum consisting of a 1:1 doublet, $J_{PH(CH_3)}$, each member of which is further split into a 1:1 doublet, $J_{FH(CH_3)}$. In addition, a very broad 1:1:1:1 quartet, $J_{HB}$, is observed. The $^{19}F$ nmr spectrum shows a 1:1 doublet, $J_{PF}$, each member of which is further split into a 1:3:3:1 quartet, $J_{FH(BH_3)}$. The $^{11}B$ nmr spectrum exhibits a poorly resolved 1:3:3:1 quartet, $J_{BH}$, shown in Figure 1. A broad 1:1 doublet is observed in the $^{31}P$ nmr, $J_{PF}$.

**Homogeneous Base Displacement Reactions.**—Mixtures of an uncoordinated phosphine and a borane adduct were prepared by condensing *in vacuo* a measured amount of the phosphine into the reaction vessel described previously which contained the adduct at −196°. The mixture was allowed to warm until it melted and was then poured into the nmr tube joined to the vessel. The nmr tube was cooled to −196°, sealed *in vacuo*, and removed. An initial $^{19}F$ nmr spectrum of the mixture was obtained at −50°. The mixture was then held at 0° for varying periods of time and $^{19}F$ nmr spectra were subsequently recorded at −50°. Integration of the $^{19}F$ resonance absorptions ascribed to the components of the equilibrium mixture indicated the composition. Successive spectra recorded at 1-hr intervals showed no change in the composition of the mixture, which suggests the rate of exchange at −50° is negligible. The equilibrium was approached from both directions to ensure that a true equilibrium constant was obtained. The results of the base displacement for the forward and reverse reactions are given in Table III.

## Discussion

The relative order of the base strengths established for the series of fluorophosphines we investigated is $MePF_2 > Me_2NPF_2 > MeOPF_2 > MeSPF_2 \geq (MeS)_2PF$, while $J_{BP}$ for the fluorophosphine–borane adducts decreases in the series $Me_2NPF_2 > MeOPF_2 > MePF_2 > MeSPF_2 > (MeS)_2PF$. It is clear that the high basicity of $MePF_2$ is not mirrored by a large value for $J_{BP}$ in the adduct. It is also worthy of note that $MeSPF_2$ and $(MeS)_2PF$ are of about the same base strength, yet their $J_{BP}$ values differ by more than 11 Hz. However, the lack of structural data for $(MeS)_2PF$ and the extensive decomposition of $(MeS)_2PF \cdot BH_3$ at 0° may reduce the value of the results obtained for this adduct.

Several arguments have been developed to interpret stability of phosphine–borane adducts. These have been reviewed.[1–3] None of the arguments advanced is sufficient unequivocally to rationalize the experimental observations. Although increasing the electronegativity of substituents attached to phosphorus might be expected to decrease the Lewis basicity of the phosphine, it was found, in contrast to what would be expected from this argument, that $Me_2NPF_2$ and $MeOPF_2$ formed stronger adducts with borane than either $MeSPF_2$ or $(MeS)_2PF$.

It has also been suggested that base strengths of phosphine may be rationalized by suggesting the formation of π molecular orbitals which arise from the delocalization of the lone pair(s) of electrons on the nitrogen or the oxygen into the empty d orbitals of phosphorus. This (p → d)π bond has the effect of increasing the electron density on the phosphorus thus increasing the strength of the phosphorus–boron bond. It appears that (p $\rightarrow$ d)$\pi$ bonding may also occur with second-row elements but to a much lesser extent. Structural studies seem to support the conclusion that the extent of (p $\rightarrow$ d)$\pi$ bonding is greater between first- and second-row elements than between two second-row elements. For example, although nitrogen has a planar environment in $H_2NPF_2$,[15] the $H_2PP$ moiety in $H_2PPF_2$ is not planar.[16] It has also been shown that while the heavy atoms in $(SiH_3)_3N$ are planar, those in $(SiH_3)_3P$ are not.[17] Results of other structural studies have been reviewed.[18] In a previous article we suggested that (p $\rightarrow$ d)$\pi$ bonding played a part in determining the PF bond distance and the FPF bond angle in difluorophosphines.[3] If this argument is used, the $Me_2NPF_2$ and $MeOPF_2$, which display the longest PF bond distance and the smallest FPF bond angle, would be expected to be the best Lewis bases toward $BH_3$ in the series we examined. The unexpected strength of $MePF_2$ may be a result of some unexpected structural deformation which occurs when the borane adduct is formed. We are currently examining the structures of $MePF_2$ and $MePF_2 \cdot BH_3$ to determine if this is the case.

Although the position of $MePF_2$ as the strongest base in the series investigated cannot be explained by (p $\rightarrow$ d)$\pi$ bonding since this type of bonding would be negligible for carbon, the electron-donating properties through $\sigma$ donation of the methyl group and its subsequent effect upon the electron density of the phosphorus may be responsible for the high base strength of $MePF_2$. Another possible explanation might involve hyperconjugation between the C–H $\sigma$-bonding electrons and the phosphorus 3d orbitals. A combination of both $\sigma$-electron donation and hyperconjugation may be responsible for the observed basicity of $MePF_2$.

Although Coyle and Stone[19] suggested that B–H ir stretching frequencies can often be correlated to the strength of the boron–ligand bond in boron complexes, in our study the B–H stretching frequencies in the complexes investigated exhibit no simple relationships to the observed base strengths.

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# Molecular Beam Mass Spectra and Pyrolyses of Fluorophosphine–Triborane(7) Complexes. Formation and Mass Spectrum of Triborane(7)[1,2]

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A molecular beam mass spectrometric characterization of $(CH_3)_2NF_2P \cdot {}^nB_3H_7$, $(CH_3)_2NF_2P \cdot {}^{10}B_3H_7$, and $F_3P \cdot {}^nB_3H_7$ and their respective pyrolysis products has been accomplished. The thermal decomposition of $(CH_3)_2NF_2P \cdot B_3H_7$ provided the first high-yield synthesis of the previously unobserved $B_3H_7$ reactive intermediate. The triborane(7) was characterized by mass spectrometric techniques, and its polyisotopic and $^{10}B$ enriched mass spectra are presented. The low parent ion intensity, $I(B_3H_7^+)$, suggests that the neutral progenitor $B_3H_7$ should be classified as an "unstable" borane. Decomposition of $(CH_3)_2NF_2P \cdot B_3H_7$ at room temperature also resulted in formation of $(CH_3)_2NF_2P \cdot B_4H_8$ which in turn acted as a high-yield source of $B_4H_8$. At elevated temperatures $B_5H_x$ and $B_6H_x$ species are formed. The appearance potentials of the principal ions are reported. The $F_3P \cdot B_3H_7$ complex decomposed at room temperature; however, the decomposition did not provide a good synthesis of $B_3H_7$. Attempts to prepare $B_3H_9$ were unsuccessful.

## Introduction

The systematic formation of higher boranes, $B_4H_{10}$, $B_5H_{11}$, . . . , during the pyrolysis of $B_2H_6$ has been long recognized[3] and actively investigated.[4-6] The initial steps of a commonly accepted mechanism[4-6] are

$$B_2H_6 \rightleftharpoons 2BH_3 \tag{1}$$

$$BH_3 + B_2H_6 \rightleftharpoons B_3H_9 \tag{2}$$

$$B_3H_9 \rightleftharpoons B_3H_7 + H_2 \tag{3}$$

$$B_3H_7 + B_2H_6 \rightleftharpoons B_4H_{10} + BH_3 \tag{4}$$

$$B_4H_{10} \longrightarrow B_4H_8 + H_2 \tag{5}$$

$$B_4H_8 + B_2H_6 \longrightarrow B_5H_{11} + BH_3 \tag{6}$$

Another step has been proposed

$$B_4H_{10} \longrightarrow B_3H_7 + BH_3 \tag{7}$$

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[2] Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971; see Abstracts, No. INOR 2.

[3] A. E. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, New York, 1933.

[4] The kinetic and mechanistic investigations of boron hydride pyrolysis reactions have been summarized in several review articles: (a) R. L. Hughes, I. C. Smith, and E. W. Lawless, "Production of the Boranes and Related Research," R. T. Holzmann, Ed., Academic Press, New York, N. Y., 1967; (b) R. W. Parry and M. K. Walter, "Preparative Inorganic Reactions," W. L. Jolly, Ed., Interscience Publishers, New York, N. Y., 1968; (c) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963; (d) R. M. Adams, "Boron, Metallo-Boron Compounds and Boranes," R. M. Adams, Ed., Interscience Publishers, New York, N. Y., 1964.

[5] R. Schaeffer, *J. Inorg. Nucl. Chem.*, **15**, 190 (1960).

[6] R. E. Enrione and R. Schaeffer, *ibid.*, **18**, 103 (1961).