

SiB_5H_7 ,^{2b} The formation of a 3:1 complex with $(\text{CH}_3)_3\text{N}$ at -78° compares with 2:1 adducts of $(\text{CH}_3)_3\text{N}$ with B_5H_9 ,¹³ $\text{CH}_3\text{B}_5\text{H}_8$,^{12,14} $2\text{-H}_3\text{SiB}_5\text{H}_8$,¹⁵ and $2\text{-H}_5\text{Si}_2\text{B}_5\text{H}_8$ ¹⁵ and 1:1 adducts of $(\text{CH}_3)_3\text{N}$ with 1- or 2- $\text{CH}_3\text{B}_5\text{H}_8$.¹⁶ A 3:1 adduct was obtained when $(\text{CH}_3)_3\text{N}$ was mixed with 2-(Cl-SiH₂)B₅H₈.¹⁵

Pentaboranyl-Group IV Compounds. Reaction between LiB_5H_8 and $\text{HCH}_3\text{SiCl}_2$ produced, in addition to 2,2'-(B₅H₈)₂SiHCH₃, the pentaborane(9) derivative 2-HCH₃ClSiB₅H₈. The 32.1-MHz ¹¹B nmr spectrum verifies that the silyl group occupies a terminal position on the base of the B₅H₉ pyramid. 2-HCH₃ClSiB₅H₈ is unstable at room temperature with respect to decomposition to 2-H₂CH₃SiB₅H₈. The re-

actions of LiB_5H_8 with $(\text{CH}_3)_2\text{SiCl}_2$ and with $(\text{CH}_3)_2\text{GeCl}_2$ gave the pentaboranyl-group IV compounds μ - and 2-(CH₃)₂-HSiB₅H₈ and μ - and 2-(CH₃)₂HGeB₅H₈, respectively. No compounds of the type $(\text{CH}_3)_2\text{CIM}^{\text{IV}}\text{B}_5\text{H}_8$ were isolated. Pure 2-(CH₃)₂HM^{IV}B₅H₈ was obtained by stirring the mixture of bridge and terminal isomers in diethyl ether. Identity of these compounds was confirmed by ¹H and ¹¹B nmr, infrared, and mass spectra.

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Registry No. 2,2'-(B₅H₈)₂SiHCH₃, 52570-92-0; 2-HCH₃ClSiB₅H₈, 52570-93-1; μ ,2'-(B₅H₈)₂Si(CH₃)₂, 52718-63-5; μ ,2'-(B₅H₈)₂-Ge(CH₃)₂, 52570-94-2; 2,2'-(B₅H₈)₂Ge(CH₃)₂, 52570-95-3; 2,2'-(B₅H₈)₂SiHCH₃-3N(CH₃)₃, 52570-96-4; 1,1'-Br₂-2,2'-(B₅H₈)₂-SiHCH₃, 52570-97-5; 2-(CH₃)₂HGeB₅H₈, 52570-98-6; HCH₃SiCl₂, 75-54-7; (CH₃)₂SiCl₂, 75-78-5; (CH₃)₂GeCl₂, 1529-48-2; LiB₅H₈, 34370-18-8; ¹¹B, 14798-13-1; 2-(CH₃)₂HSiB₅H₈, 52570-99-7.

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Basicity of Substituted Difluorophosphines

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The previously unreported compounds $\text{PF}_2\text{-}i\text{-Pr}$, $\text{PF}_2\text{-Et-BH}_3$, and $\text{PF}_2\text{-}t\text{-Bu-BH}_3$ have been prepared and characterized by ¹H, ¹⁹F, and ¹¹B nmr and ir spectroscopy and *PVT* molecular weights, as well as by stoichiometric data. A series of base displacement reactions established the base strengths toward borane as $\text{PF}_2\text{-}t\text{-Bu} \gtrsim \text{PF}_2\text{-Et} > \text{PF}_2\text{-C}\equiv\text{CMe} \gtrsim \text{PF}_2\text{-Me} > \text{PF}_2\text{-NMe}_2 > \text{PF}_2\text{-O-}i\text{-Pr} > \text{PF}_2\text{-OEt} > \text{PF}_2\text{-OMe} > \text{PF}_2\text{-OTf} \gtrsim \text{PF}_2\text{-SMe} > \text{PF}_3 > \text{PF}_2\text{-Cl} > \text{PF}_2\text{-Br}$. The basicity order is not mirrored by the series of values for the J_{PB} coupling constants or ν_{BH} stretching frequencies. The J_{PB} coupling constant peaks at $\text{PF}_2\text{-N(CH}_3)_2$ and then decreases as basicity increases and decreases. Although no overall correlations were evident, cases where the subject correlation is apparent are discussed. Association involving PF_2R (R = carbon group, H) compounds is proposed as a reason for the failure of general correlations.

Introduction

Comparison of the Lewis base strength of phosphines toward boron Lewis acids is somewhat difficult because of the many different methods that have been used to establish orders. Some of the various methods include gas-phase dissociation data, displacement methods, competition experiments, studies of the volatility of addition compounds, and calorimetric heats of reaction.¹⁻⁸ Recently a great interest has been aroused in the basicity of certain phosphines toward borane and in correlations of spectroscopic properties of borane adducts and basicity orders established by displacement equilibria methods.

The high base strength of PF_2OCH_3 and $\text{PF}_2\text{N(CH}_3)_2$ when

compared to PF_3 was initially explained in terms of basicity enhancement of the phosphorus by the formation of a dative π bond between the nitrogen or oxygen electron pairs and the vacant orbitals of the phosphorus.⁹ Since this effect would be absent in PF_2CH_3 , the recent observation that PF_2CH_3 is a stronger base than $\text{PF}_2\text{N(CH}_3)_2$ may require that basicity parameters be revised.^{2,10} Generally the relative displacement order toward BH_3 of PF_2X ligands where X is a member of the second row (C, N, O, F) follows an electronegativity order; however, examination of other PF_2X compounds shows that electronegativity-basicity correlations immediately fail PF_2NMe_2 and PF_2OMe from stronger adducts² with borane than PF_2SMe and the basicity order is $\text{PF}_3 > \text{PF}_2\text{Cl} > \text{PF}_2\text{Br}$ toward BH_3 .¹¹

Several workers have published rather elegant correlations of spectroscopic properties of borane adducts with displacement equilibria basicity orders. Attempts have been made

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(10) The position of PF_2Me as the strongest base in the series PF_2X (X = Me, OMe, NMe₂, SMe) has been attributed to the possible combination of both σ -electron donation and hyperconjugation effects.² From our work it is evident that a hyperconjugation effect is probably not involved since $\text{PF}_2\text{-}t\text{-Bu}$ is more basic than $\text{PF}_2\text{-Me}$ toward BH_3 . The high basicity must be attributed to a strong σ -donation of the methyl group or to some other effect.

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to correlate basicity with the magnitude of $J_{PB}^{1-4,12}$ and BH stretching frequencies,^{3,4,13-14} but Cohn² observed no simple relationship for J_{PB} and BH frequencies for a series of similar difluorophosphine-boranes.

An examination of the basicity of a series of alkyl difluorophosphines could help clarify the parameters responsible for phosphorus basicity and further define spectroscopic correlations. We wish to report on the examination of basicity of the PF_2X series and to indicate some of the possible problems associated with the failure of general correlations of spectroscopic properties and relative basicity orders by displacement equilibria.

Experimental Section

Material. Commercial B_2H_6 (Callery), $Hg(i-Pr)_2$ (Orgmet, Inc.), SbF_3 (Ozark-Mahoning), and $t-BuPCL_2$ (Orgmet, Inc.) were used without further purification. PF_2OEt , PF_2OMe , $PF_2OEt \cdot BH_3$, $PF_2OMe \cdot BH_3$,³ PF_2Me ,¹⁵ $PF_2Me \cdot BH_3$,³ PF_2N_3 ,¹⁶ PF_2NMe_2 , $PF_2NMe_2 \cdot BH_3$,⁹ PF_2Cl ,¹⁷ and $PF_2C_2H_5$ and $PF_2C_3H_7 \cdot BH_3$ ¹⁸ were prepared by literature methods. PF_2Et (~70%) and PF_2-t-Bu (~90%) were prepared in a manner similar to the preparation of PF_2Me utilizing pyridine as a solvent.¹⁵

General Techniques. Standard high-vacuum techniques were employed throughout.¹⁹ Molecular weights were determined by *PVT* measurements. ¹⁹F nmr spectra were obtained on a Varian T-60 operating at 56.4 MHz, while proton nmr spectra were traced with a Jeol MH-100 operating at 100 MHz. ¹¹B spectra were recorded at 32.1 MHz on a Varian Associates XL-100 nmr spectrometer. External TMS (except where noted) and external $CFCl_3$ and $B(C_2H_5)_3$ served as references for ¹H, ¹⁹F, and ¹¹B spectra, respectively. Infrared spectra were recorded at a sample pressure of 10 mm on a Perkin-Elmer 421 grating spectrophotometer using a 10-cm gas cell with KBr windows. All spectra were standardized vs. a polystyrene film.

Synthesis of $PF_2-t-Bu \cdot BH_3$ and $PF_2Et \cdot BH_3$. $PF_2Et \cdot BH_3$ and $PF_2-t-Bu \cdot BH_3$ were synthesized in a previously described manner.^{3,4} Both reactions gave 100% yields and (BH_3) to ligand ratios of 1:1. The adducts were characterized by *PVT* molecular weights and ir and ¹H, ¹⁹F, and ¹¹B nmr spectra.

The ¹H spectrum (neat, ambient temperature) of $PF_2Et \cdot BH_3$ consists of three sets of peaks.^{20,21} The BH protons (δ_{BH} , 0.24 ppm) are a quartet (q, $J_{BH} = 100.0$ Hz) of triplets (t, $J_{FBH} = 20.8$ Hz) of doublets (d, $J_{PBH} = 17.9$ Hz). The high-field protons (δ_{CH_3} , 0.84 ppm) exhibit a doublet (d, $J_{PCH} = 18.0$ Hz) of triplets (t, $J_{HCH} = 7.5$ Hz) structure, while the methylene protons (δ_{CH_2} , ~1.7 ppm) are a complex multiplet. The ¹⁹F spectrum confirms the proton spectrum. ¹⁹F (neat, ambient temperature): δ_F 85.8 ppm (d, $J_{PF} = 114.1$ Hz); each member of a doublet is a nonet (n, $J_{FBH} = 18.8$ Hz, $J_{HCF} = 9.4$ Hz). The presence of a PB bond is confirmed by the ¹¹B spectrum. ¹¹B (neat, ambient temperature): δ_B 131 ppm (q, $J_{BH} = 100.3$ Hz); each member of a quartet is a doublet (d, $J_{PB} = 58.9$ Hz). The ir spectrum of $PF_2Et \cdot BH_3$ showed expected peaks and is tabulated in Table I. $PF_2Et \cdot BH_3$ was also characterized by vapor-phase molecular weight at 24.3°, $P = 48.5$ mm (found, 110.2; calcd, 111.8).

The spectral data for $PF_2-t-Bu \cdot BH_3$ are very similar. The infrared

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(21) Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; n, nonet.

Table I. Infrared Spectra of $PF_2Me \cdot BH_3$, $PF_2Et \cdot BH_3$, and $PF_2-t-Bu \cdot BH_3$

| Freq, cm^{-1} , and intens | | | Tentative assignment |
|------------------------------|---------------------|---------------------|----------------------|
| $PF_2-t-Bu \cdot BH_3$ | $PF_2Et \cdot BH_3$ | $PF_2Me \cdot BH_3$ | |
| 2989 m | 3001 m | | CH str |
| 2927 w | 2966 mw | | |
| 2889 w | 2925 w | | BH str |
| 2444 s | 2455 s | 2459 s | |
| 2374 w | 2404 s | 2404 s | |
| 1487 m | 1465 w | | |
| 1411 w | 1410 w | 1417 m | |
| 1381 m | 1280 w | 1314 ms | |
| 1124 w | 1130 w | 1119 w | |
| 1068 w | | 1069 w | |
| 1025 w | 1030 m, br | | |
| 951 w | | 934 vvs | PF str |
| 899 vvs | 898 vs | 874 vs | |
| 829 s | 790 vvs | | |
| 744 s | | 739 w | |
| 659 m | 610 w, br | | |
| 515 w | | | |

spectrum supports the structure and is tabulated in Table I. The proton spectrum (neat, ambient temperature) exhibits two sets of absorptions. The BH protons (δ_{BH} 0.82 ppm) are a quartet (q, $J_{BH} = 101.4$ Hz) of triplets (t, $J_{FBH} = 22.2$ Hz) of doublets (d, $J_{PBH} = 15.6$ Hz), while the methyl protons are a doublet (δ_{CH_3} , 1.0 ppm, $J_{PCH} = 16.0$ Hz). The ¹⁹F spectrum (neat, ambient temperature) consists of a large doublet (δ_F 104 ppm (d, $J_{PF} = 117.5$ Hz) of quartets (q, $J_{FBH} = 22.6$ Hz).

As for $PF_2Et \cdot BH_3$, the ¹¹B spectrum confirmed the PB bond for $PF_2-t-Bu \cdot BH_3$. ¹¹B (neat, ambient temperature): δ_B 132 ppm (q, $J_{BH} = 102$ Hz); each member of a quartet is a doublet (d, $J_{PB} = 55.0$ Hz).

The spectral data for $PF_2Et \cdot BH_3$ and $PF_2-t-Bu \cdot BH_3$ are very similar to those of $PF_2Me \cdot BH_3$.² A complete ir spectrum for $PF_2-t-Bu \cdot BH_3$ is tabulated in Table I. The nmr data observed by Cohn² have been confirmed in this laboratory (see Table II).

Preparation of PF_2-i-Pr . A 19.3-mmole sample of PF_2Cl was condensed at -196° on a ~22-mmole sample of $Hg(i-Pr)_2$ in a 500-cm³ reaction vessel with a removable tube. The mixture was allowed to warm to room temperature and was shaken for ~96 hr. Reaction was indicated by the formation of yellow-green solids. The reaction mixture was then distilled through U traps held at -85 , -150 , and -196° . The -196° trap held 15.5 mmole of PF_3 and was discarded along with a trace of material at -85° . The -150° trap held 3.24 mmole of PF_2-i-Pr for a 16.8% yield based on consumed PF_2Cl . Solids remained in the vessel.

PF_2-i-Pr was identified by *PVT* molecular weight and ir and ¹H nmr spectra. The ¹H nmr spectrum (neat, ambient temperature) consisted of two absorptions in a 6:1 ratio. The high-field peak (δ_{CH_3} , 1.12 ppm) consisted of a doublet (d, $J_{PCH} = 14.0$ Hz) of doublets (d, $J_{HH} = 7.0$ Hz). High-resolution spectra indicated some fine structure ($J_{HF} < 1.0$ Hz) probably because of HF coupling. The low-field peak ($\delta_{CH} \sim 1.7$ ppm) was a very complex multiplet. The HH coupling constant was identified ($J_{HH} = 7.0$ Hz). The infrared spectrum yielded expected peaks which are listed with tentative assignments:²² 2979 m; 2889 mw (CH str); 1484 w; 1469 w; 1386 w; 1018 w, br; 973 w; 941 w; 897 w; 871 w; 823 vs (PF str); 782 w; 673 m (PC str); 639 w. PF_2-i-Pr was also characterized by *PVT* molecular weight at 21.6°, $P = 100.1$ mm (found, 112.5; calcd, 112.0). The spectral data for PF_2-i-Pr are very similar to those for other PF_2R compounds.²³

Homogeneous Base-Displacement Reactions. Mixtures of an uncoordinated phosphine and a borane adduct were prepared by condensing *in vacuo* measured amounts of each into a heavy-wall nmr tube. The tube was then sealed *in vacuo* and allowed to warm until the contents melted. The mixtures were held at a constant temperature (ice-H₂O slush or Dry Ice-acetone) for varying periods of time. Integration of the ¹⁹F and ¹H spectra²⁴ by cutting and weighing the resonance absorptions ascribed to the components of the equilibrium

(22) Vibrational frequencies are given in cm^{-1} followed by a tentative assignment in parentheses. Notation for intensities: v, very; s, strong; w, weak; m, medium.

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(24) Integration of the ¹H spectra was used only as a check on the ¹⁹F integrations.

Table II. Stoichiometric Data for Displacement Reactions

| Phosphine (mmol) | Adduct (mmol) | J_{PB} (adduct), Hz | Time, hr | K_{eq}^a | $T, ^\circ C$ | % displacement ^b |
|------------------------------------------------------|-----------------------------------------------------------------------|-----------------------|----------|---------------------|---------------|-----------------------------|
| PF ₂ Me (1.00) | PF ₂ Et·BH ₃ (1.00) | 58.9 ^m | 3432 | 1.39 ^g | 0 | 54 |
| PF ₂ Et (1.12) ^c | PF ₂ Me·BH ₃ (1.12) | 61.0 ^{m,n} | 3072 | 1.34 ^g | 0 | 54 |
| PF ₂ Et (1.34) ^c | PF ₂ OEt·BH ₃ (1.34) | 70.4 ^o | 2640 | $\infty^{g,h}$ | 0 | 100 |
| PF ₂ OEt (1.09) | PF ₂ Et·BH ₃ (1.09) | 58.9 ^m | 3360 | $\infty^{g,h}$ | 0 | 100 |
| PF ₂ Me (1.15) ^{d,k,l} | PF ₂ C ₃ H ₃ ·BH ₃ (1.15) | 62.0 ⁱ | 3192 | 1.06 ^g | -78 | 51 |
| PF ₂ Et (1.08) ^{d,l} | PF ₂ C ₃ H ₃ ·BH ₃ (1.08) | 62.0 ⁱ | 3192 | 2.85 ^g | -78 | 63 |
| PF ₂ Me (1.83) ^j | PF ₂ - <i>t</i> -Bu·BH ₃ (1.83) | 55.0 ^m | 984 | 1.36 ^g | 0 | 54 |
| PF ₂ - <i>t</i> -Bu (2.16) ^{c,j} | PF ₂ Me·BH ₃ (0.906) | 61.0 ^{m,n} | 168 | 1.25 ^{g,h} | 0 | 53 |
| P(OMe) ₃ (1.18) ^e | PF ₂ Me·BH ₃ (1.18) | 61.0 ^{m,n} | 2160 | | 0 | |
| PF ₂ N ₃ (1.97) | PF ₂ NMe ₂ ·BH ₃ (1.97) | 79.0 ^p | 24 | 2.52 ^f | ~25 | 61 |

^a Equilibrium constants are defined by the expression $K_{eq} = [\text{weaker base}][\text{adduct stronger base}]/[\text{adduct weaker base}][\text{stronger base}]$. See ref 1-4. ^b Per cent displacement is calculated using the formula $100\sqrt{K_{eq}}/\sqrt{K_{eq}+1}$. See ref 1-4. ^c Stronger base of the exchanging pair of ligands. ^d PF₂C≡CMe is a stronger base than PF₂Me; PF₂Et is a stronger base than PF₂C≡CMe. ^e No data were obtained because of F and OMe exchange. ^f Calculated from the PF₂NMe₂·BH₃:PF₂NMe₂ ratio. PF₂N₃·BH₃ and PF₂N₃ decomposed; PF₂NMe₂ is a stronger base than PF₂N₃ assuming that the decomposition rate of the azide and its adduct were not more rapid than the approach to equilibrium. ^g Integration on ¹⁹F nmr. ^h Integration on ¹H nmr. ⁱ E. L. Lines and L. F. Centofanti, *Inorg. Chem.*, **12**, 598 (1973), reported J_{PB} as 68.0 Hz; it should be 62.0 Hz. ^j Some decomposition is evident, probably PF₂Me, yielding PF₄Me and (PMe)_n.²³ This would indicate that the per cent displacement is a lower limit. ^k Extensive decomposition to yellow solids, probably because of the decomposition of PF₂C₃H₃·BH₃. This would indicate that the per cent displacement is a lower limit. ^l PF₂ and some yellow solids are visible in the nmr tube. Per cent displacement is probably an upper limit. ^m This work. ⁿ Reference 2. The J_{PB} value was confirmed for PF₂Me·BH₃ in this laboratory. However, the J_{BH} and ν_{BH} differed from the earlier reported values. ^o Reference 3. ^p Reference 9.

mixture indicated the relative compositions. The spectra were obtained at the appropriate temperature (0 or -78°) and the equilibrium was approached from both directions, where possible. The results of these reactions are given in Table II.

The reaction of PF₂NMe₂·BH₃ and PF₂N₃ was conducted at room temperature in a manner described previously¹⁸ (See Table II).

Discussion

Displacement Basicity. The data cited in Table II clearly indicate that the basicity order as measured by base-displacement reactions for the alkyldifluorophosphines is PF₂-*t*-C₄H₉ > PF₂C₂H₅ > PF₂CH₃. This order indicates the order of electron-releasing ability *t*-C₄H₉ > C₂H₅ > CH₃, which is in agreement with that found for the equivalent difluorophosphites.^{3,4} This mirrors the trend expected if the classical inductive effect plays the dominant role in determining the stability of this series of adducts.

An examination of other PF₂X compounds indicates a similar effect when moving across the periodic table. Thus the basicity order PF₂CH₃ > PF₂N(CH₃)₂ > PF₂OCH₃ > PF₃ follows the inductive effect. In order to determine whether this ordering can be completely explained by an inductive effect or if π -bonding arguments are still required, the displacement basicity of PF₂C≡CCH₃ was compared to that of alkyldifluorophosphines. The displacement order was found to be PF₂-*t*-C₄H₉ > PF₂C₂H₅ > PF₂C₃H₃ > PF₂-CH₃. Although the electronegativity of C₃H₃ is much greater^{25,26} than that of the corresponding alkane groups, the difference in the basicity of PF₂C₃H₃ and alkyldifluorophosphines is quite small. Therefore, π bonding in PF₂-C₃H₃ must be partially negating the increased inductive effect.

Combination of the displacement basicity of the alkyldifluorophosphines with other PF₂X ligands^{1-4,11,12,26} yields the base strength order toward borane PF₂-*t*-C₄H₉ > PF₂-C₂H₅ > PF₂C₃H₃ > PF₂CH₃ > PF₂N(CH₃)₂ > PF₂-*i*-OC₃H₇ > PF₂OC₂H₅ > PF₂OCH₃ > PF₂OCH₂CF₃ > PF₂SCH₃ > PF₃ > PF₂Cl > PF₂Br. Parameters responsible for this trend are not as obvious as those found within a related series such as the alkyldifluorophosphines or the alkyl difluorophosphites. Any explanation would have to include a variety of parameters (*i.e.*, electronegativity, π bonding, etc.)

(25) J. E. Huheey, "Inorganic Chemistry," Harper and Row, New York, N. Y., 1972, p 164.

(26) E. L. Lines and L. F. Centofanti, *Inorg. Chem.*, **13**, 1517 (1974).

Spectroscopic Correlations. Attempts have been recently made to correlate^{1-4,12,18,26} spectroscopic parameters J_{PB} , J_{BH} , and ν_{BH} with the displacement basicity. Several series of difluorophosphines are known in which the lone phosphorus substituents are related. As we see in Table III, within the family PF₂XR²⁻⁴ (XR = *O*-*i*-C₃H₇, OC₂H₅, OCH₃, OCH₂CF₃, SCH₃) a 1:1 correlation exists between J_{PB} , ν_{BH} , and the displacement basicity. In this work we have also found a correlation between J_{PB} , ν_{BH} , and the displacement basicity for the series PF₂R (R = C₄H₉, C₂H₅, CH₃). As mentioned earlier the relative order of base strength established for this series is PF₂-*t*-C₄H₉ > PF₂C₂H₅ > PF₂CH₃. The J_{PB} exhibits a linear relationship with the basicity; however, as the basicity increases, the PB coupling constant decreases. The amount of change is equivalent to that observed in the PF₂OR series (replacement of H for a CH₃ produces about a 2-Hz change) but is in the opposite direction.²⁷

The low J_{PB} and high basicity of PF₂R (R = Me, Et, *t*-Bu) have been major problems with a J_{PB} vs. basicity correlation. This work suggests that a J_{PB} vs. basicity correlation may still be possible. For example, if the displacement basicity order is correct, then instead of a steady increase in J_{PB} as basicity increases for difluorophosphines we see J_{PB} peak at PF₂NMe₂ (Table III). J_{PB} then decreases as basicity both increases and decreases indicating possible opposing parameters contributing to J_{PB} .

PF₂H could provide an excellent test for this proposal; it is undissociated and has a J_{PB} of 49 Hz. Therefore, if this J_{PB} correlation holds, PF₂H is a formidable base in comparison to the organodifluorophosphines and should be one of the strongest difluorophosphine bases known.

Verkade and White¹³ have recently correlated the relative stability of borane adducts, as determined by displacement equilibria, with BH stretching frequencies. Coyle and Stone¹⁴ originally suggested that BH ir stretching frequencies could be related to boron-ligand bond strength in boron adducts, but Cohn² found no simple relationships in a series of similar difluorophosphine-boranes. In the series of difluorophosphite-boranes PF₂OR·BH₃ (R = *i*-Pr, Et, Me, CH₂CF₃),^{3,4} a trend similar to that suggested by Coyle and Stone and demonstrated by Verkade and White is evident. In the alkyldifluorophosphine series we have also been able to correlate the aver-

(27) W. J. Lehmann, *J. Mol. Spectrosc.*, **7**, 26 (1961).

Table III. Basicity Data

| Compd ^a | J_{PB} , Hz | $\nu_{BH(av)}$, ^b cm ⁻¹ | Ref |
|------------------------------------------------------------|---------------|---------------------------------------------------|--------------|
| PF ₂ - <i>t</i> -C ₄ H ₉ | 55 | 2421 | This work |
| PF ₂ C ₂ H ₅ | 58.9 | 2438 | This work |
| PF ₂ C ₃ H ₃ | 62 | 2424 | 18 |
| PF ₂ CH ₃ | 61 | 2441 | 2, this work |
| PF ₂ N(CH ₃) ₂ | 79 | 2418 | 9 |
| PF ₂ - <i>i</i> -OC ₃ H ₇ | 72.5 | 2418 | 4 |
| PF ₂ OC ₂ H ₅ | 70.4 | 2426 | 3 |
| PF ₂ OCH ₃ | 68.2 | 2429 | 3 |
| PF ₂ OCH ₂ CF ₃ | 58.4 | 2431 | 3 |
| PF ₂ SCH ₃ | 41.4 | 2435 | 2 |
| PF ₃ | 39.0 | 2452 | 11 |
| PF ₂ Cl | 27 | 2445 | 11 |
| PF ₂ Br | 19 | 2440 | 11 |

^a In order of base displacement. ^b Reference 27.

age ν_{BH} with the displacement basicity PF₂-*t*-C₄H₉ (2421 cm⁻¹) > PF₂C₂H₅ (2438 cm⁻¹) > PF₂CH₃ (2441 cm⁻¹). However, attempts to correlate the whole PF₂X series examined in this study have been unsuccessful. No general trends could be found.^{28,29}

Many arguments have been developed to interpret the stability of phosphine-borane adducts and the resulting spectroscopic correlations, but, none of the arguments advanced is sufficient to rationalize unequivocally the experimental observations. Since no overall correlations between PB coupling constants or BH stretching frequencies and basicities are obvious, trends involving the spectroscopic properties and basicities of difluorophosphines, PF₂XR, where X remains constant and R is varied, are somewhat peculiar. This contrasts with the suggestion that quite different PB couplings undoubtedly reflect correct relative bond strengths but that a comparison of J_{PB} values of similar magnitude may not do so.¹²

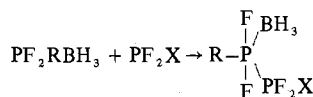
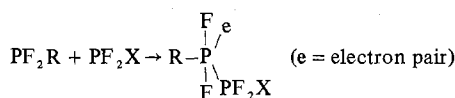
Throughout the examination of these correlations one assumption is of extreme importance.¹⁻⁴ Since the basicity series have been determined, not by enthalpy considerations but from equilibrium data, the contribution of entropy has been neglected or contributions to differences in entropy have been assumed to be correspondingly small. Since the structures of several difluorophosphines investigated were known to be similar and no gross distortions in the structures upon coordination were expected, this assumption would not seem to be unreasonable. However, upon considering the periodicity of acids and/or bases many unusual tendencies may be encountered which tend to discount independent correlations.³⁰ If PF₂R (R = alkyl, alkynyl, vinyl) and PF₂H are truly much stronger than anticipated by existing arguments, especially the J_{PB} correlation, then it is possible that much more subtle factors are involved. The basicity equilibria reactions have been assumed to be relatively simple, with only four species present; however, this is probably a gross simplification.

(28) Even plots of J_{BH} vs. ν_{BH} and J_{PB} vs. ν_{BH} have not proved to be linear and correlations of J_{PB} and J_{BH} or δ_{BH} seem to be of little value, if they exist. Although an independent correlation of J_{BH} vs. ν_{BH} could not be made, the data points involved do corroborate earlier findings.²⁹

(29) H. Watanabe and K. Nagasawa, *Inorg. Chem.*, **6**, 1068 (1967); J. R. Berschild and K. F. Purcell, *ibid.*, **9**, 624 (1970).

(30) R. Rich, "Periodic Correlations," W. A. Benjamin, New York, N. Y., 1965, p 85.

Association in phosphorus chemistry is well known and it is not unreasonable to assume that the displacement equilibria are complicated by the following types of processes³¹⁻³⁸



The ability to form a formally pentacoordinate species or an associated complex might be the determining factor in the equilibrium. At least three factors would then be involved: (1) basicity, (2) acidity, and (3) deformation energy.

Of all the difluorophosphines studied, PF₂X (X = R, H, OR, NR₂, F), only PF₂H^{38,39} and PF₂R (R = alkyl, alkynyl, vinyl)⁴⁰ exhibit a tendency to add MeOH and form the pentacoordinate compounds PF₂R(H)OMe. PF₂H⁴¹ and PF₂-Me⁴²⁻⁴⁵ have also been shown to add binary acids in a similar manner. The ability to form pentacoordinate and complexed species would then be expected to negate any basicity equilibrium data concerning these compounds (X = R) and dissimilar ones (X = OR, NR₂, F), but it probably would not entirely mask trends within similar difluorophosphine series. Unfortunately no gas-phase basicities to test this supposition have been obtained.

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Registry No. PF₂Me·BH₃, 35512-81-3; PF₂Et·BH₃, 52760-76-6; PF₂-*t*-Bu·BH₃, 52760-77-7; PF₂-*i*-Pr, 52760-78-8; PF₂OEt·BH₃, 40537-41-5; PF₂C₃H₃·BH₃, 37805-62-2; PF₂NMe₂·BH₃, 2857-73-2; PF₂Me, 753-59-3; PF₂Et, 430-78-4; PF₂OEt, 24933-27-5; PF₂-*t*-Bu, 29149-32-4; P(OMe)₃, 121-45-9; PF₂N₃, 37388-50-4; ¹¹B, 14798-13-1.

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