distance of 1.752 Å compare well with the B–B distance of 1.72 Å in 1,6-$B_4C_2H_6$. The boron–carbon distances are also quite close, being 1.605 Å for B(4)–C(3) in 2,3-$B_4C_2H_6$ and 1.620 Å in 1,6-$B_4C_2H_6$. If one considers the 2,3-$B_4C_2H_6$ and 1,6-$B_4C_2H_6$ to be "near" octahedra, the B----B nonbonded distances between opposite vertices are 2.436 and 2.41 Å, respectively. However, in contrast to the microwave data, which estimated the B–H apex distance to be 1.183 Å, the present electron diffraction data show 1.244 Å for 1,6-$B_4C_2H_6$. As noted above, the latter value compares favorably with preliminary data on the *closo*-2,4-$B_5C_2H_7$[18] and with the electron diffraction data on bis(trifluorophosphine)diborane(4), in which the B–H was reported to be 1.252 Å.[20]

The compound 1,5-$B_3C_2H_5$ differs markedly from either the 1,6- or 2,3-$B_4C_2H_6$. In contrast to the six-membered polyhedra, the B–C is shorter (1.556 Å *vs.* 1.62 Å for the 1,6-$B_4C_2H_6$) and the B–B distance longer (1.85 Å compared to 1.72 Å for the 1,6-$B_4C_2H_6$). The B–H distance is 1.183 Å, in closer agreement with B–H terminal bond lengths as determined in other molecules.[21] The B–B distance of 1.85 Å is long in comparison with comparable separations found in the octahedral carboranes. As noted by Beaudet[19] this suggests the 1,5-$B_3C_2H_5$ may be viewed as a classically bonded structure, in which the trigonal bipyramid is bonded through the C–B–C bonds, but involves no strong B–B overlap.

In this particular case the closer approach of the boron to carbon distance (1.556 Å in 1,5-$B_3C_2H_5$ and 1.62 Å in 1,6-$B_4C_2H_6$) may result in a substantially weakened B–B bond. The more electronegative carbon atoms can drain electron density away from the boron atoms resulting in a decrease in the boron–carbon distance, thus allowing a weakening and substantial lengthening of the boron–boron bond. This effect has been noted previously by Bohn in the electron diffraction structures of the ortho, meta, and para carboranes. The B(2)–B(3) bond in *m*-$B_{10}Br_2H_8C_2H_2$, in which the B(2,3) borons are bonded to two carbon atoms each, has a particularly long distance of 1.89 Å as determined by X-ray diffraction.[22]

Registry No. 1,5-$B_3C_2H_5$, 20693-66-7; 1,6-$B_4C_2H_6$, 20693-67-8.

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Preparation and Lewis Basicity toward Borane of Difluorophosphites

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Ethyl and trifluoroethyl difluorophosphites (PF_2OTfet), as well as the previously reported methyl difluorophosphite, have been prepared directly from the reaction of PF_3, pyridine, and the appropriate alcohol. PF_2OEt and PF_2OTfet combine with B_2H_6 to form adducts which exhibit temperature-dependent ^1H nmr spectra. A series of base displacement reactions established the base strength toward borane as $PF_2OEt > PF_2OMe > PF_2OTfet$. This basicity order is mirrored by the series of values of the J_{PB} coupling constants.

The main synthetic route to difluorophosphites[1,2] has involved a metathetical reaction using a fluorinating agent, mainly SbF_3, and the corresponding chloro compound. The chloro derivative is prepared from the reaction of PCl_3, an alcohol, and a tertiary amine. Difluorophosphites are also produced in the reaction of either PF_5 or PF_3 and $P(OMe)_3$[3] and from the reaction of PF_3, epoxides, and a tertiary amine.[4] The utility of the latter reactions is limited by many side products and low yields. No good single-step syntheses have been reported for the preparation of difluorophosphites.

Recently there has been considerable interest in the basicity toward borane of certain phosphines. Cowley and Damasco[5] have reported an empirical relationship between the J_{PB} coupling constant and the base strength of a series of phosphines; however, in a study by Rudolph and Schultz[6] a correlation between the magnitude of J_{PB} and the dative bond strength for the adducts did not appear to be general except for the case where the phosphine belongs to a series of smoothly varying phosphine ligands [*i.e.*, $PF_2X \cdot BH_3$ (X = F, Cl, Br) or $PF_{3-n}H_n \cdot BH_3$]. Foester and Cohn[7] have reported that a 1:1 correlation between base strength and J_{PB} is not possible in a series of the type PF_2X (X = Me, MeO, Me_2N, MeS). The base strengths of these structurally similar phosphines[8,9] were determined by displacement reactions with the assumptions that the entropy change upon coordination should be fairly constant and any contributions to entropy differences small.

The order of base strengths and of J_{PB} values for a series

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of difluorophosphites would be interesting. We report herein the one-step preparation of ethyl, trifluoroethyl, and methyl difluorophosphites by the reaction of PF_3, pyridine, and the appropriate alcohol and the investigation of the basicity toward borane of these phosphites.

Experimental Section

Material. Commercial PF_3 (Ozark-Mahoning), C_5H_5N (Mallinckrodt), CH_3OH, CF_3CH_2OH, and CH_3CH_2OH (Eastman), and B_2H_6 (Callery) were used without further purification. $PF_2OCH_3 \cdot BH_3$[5] was prepared by literature methods.

General Techniques. Standard high-vacuum techniques were used throughout.[10] Mass spectra were obtained on a Varian M66 (70 eV). Infrared spectra were recorded at a sample pressure of 10 mm on Perkin-Elmer 137 NaCl and 421 grating spectrophotometers using a 10-cm gas cell with KBr windows. ^{19}F nmr spectra were recorded on a Jeol JNM-C-60 HL operating at 56.4 MHz while proton nmr spectra were determined with a Jeol MN-100 operating at 100 MHz. ^{11}B and ^{31}P spectra were recorded with a Varian Associates XL-100 nmr spectrometer operating at 32.1 and 40.5 MHz. Internal tetramethylsilane and external $CFCl_3$, $B(C_2H_5)_3$, and 85% H_3PO_4 served as references for ^1H, ^{19}F, ^{11}B, and ^{31}P spectra, respectively.

Synthesis of PF_2OMe, PF_2OEt, and PF_2OTfet. A 140-mmol sample of PF_3 was condensed at −196° in a 3000-cm^3 reaction bulb. A 140-mmol amount of CH_3OH and 12.6 g (~150 mmol) of pyridine were then frozen on top of the PF_3 and the mixture was allowed to warm to ambient temperature. Immediate reaction was indicated by the formation of white clouds and solids. After 2.5 hr at room temperature, the mixture was frozen at −196° and allowed to warm slowly while distilling through traps held at −66, −140, and −196°. White solids remained behind in the reaction vessel. An 84.0-mmol sample of PF_2OCH_3, identified by ^1H and ^{31}P nmr,[1,2,11,12] was isolated in the −140° trap and an unidentified oil at −66° was discarded along with 5.2 mmol of PF_3 at −196°. The PF_3 was identified by ir. The yield based on consumed PF_3 was 62%. The gas-phase infrared spectrum of PF_2OMe showed expected peaks[13] which are listed with tentative assignments: 3020 (vw), 2970 (w), 2920 (vvw), 2855 (vw) (CH str); 1065 (sh, s), 1055 (s), 1045 (s) (POC str); 830 (sh, m), 825 (s), 805 (sh, s), 787 (br, s) (PF str).

In a similar manner an 18.7-mmol amount of PF_3, a 13.1-mmol sample of CH_3CH_2OH (anhydrous), and a 13.1-mmol sample of pyridine (1.027 g) were frozen at −196° in a 500-cm^3 reaction bulb with a removable tube. The reaction proceeded as in the preparation of PF_2OCH_3. After distillation white solids remained in the vessel while an unidentified oil at −66° was discarded. A 10.4-mmol sample of PF_2OEt was isolated in the −140° trap and 0.04 mmol of PF_3 was contained at −196°. PF_3 was identified by ir. The yield based on consumed PF_3 was 56%. The gas-phase infrared spectrum[13] exhibited the following peaks: 3001 (ms), 2948 (m), 2924 (mw, sh) (CH str); 1397 (mw), 1177 (w, sh), 1137 (mw), 1097 (m, sh), 1047 (vs), 967 (s), 820 (vs), 792 (vs), 557 (w).

The mass spectrum of PF_2OEt is relatively simple and can be fitted very nicely to the compound. Following are the mass numbers (species) and relative abundances of the ions in the mass spectrum of $PF_2OC_2H_5$: 115 ($PF_2OC_2H_6^+$), 14.2; 114 ($PF_2OC_2H_5^+$), 100.0; 99 ($PF_2OCH_2^+$), 72.5; 95 ($PFOC_2H_5^+$), 3.2; 87 ($PF_2OH_2^+$), 4.2; 86 (PF_2HO^+), 55.5; 85 (PF_2O^+), 3.2; 84 ($C_2F_3H_3^+$), 2.1; 71 (POC_2^+), 4.5; 69 (PF_2^+), 67.2; 67 ($PFHO^+$), 24.1; 50 (PF^+), 4.8; 47 (PO^+), 2.6; 43 ($OC_2H_3^+$), 9.0; 40 (C_2O^+), 4.2; 32 (PH^+, O_2^+), 25.2; 31 (P^+), 1.6; 29 ($C_2H_5^+$, CHO^+), 43.1; 28 ($C_2H_4^+$, CO^+, N_2^+), 67.2; 27 ($C_2H_3^+$), 30.4; 26 ($C_2H_2^+$), 8.4; 18 (H_2O^+), 14.7; 17 (OH^+), 3.2; 15 (CH_3^+), 1.6; 14 (CH_2^+, N^+), 3.2.

The nmr spectra are consistent with the ethyl difluorophosphite structure. The ^1H spectrum ($CHCl_3$, −40°) consists of a low-field pentet ($\delta(CH_2)$ 4.09 ppm (p, $J_{HCH} = 7.0$ Hz $= J_{PCH} = 7.0$ Hz)) and a high-field triplet ($\delta(CH_3)$ 1.28 ppm (t, $J_{HCH} = 7.0$ Hz)).[14] [s = singlet, d = doublet, t = triplet, q = quartet, and p = pentet.] The ^{19}F and ^{31}P spectra confirm the proton spectrum. The ^{19}F spectrum ($CHCl_3$, −40°) is a doublet (δ_F 50.1 ppm (d, $J_{PF} = 1288$ Hz)). The ^{31}P spectrum (ambient temperature) consisted of a triplet (δ_P −114 ppm (t, $J_{PF} = 1291$ Hz)); each peak of a triplet is a triplet (t, $J_{PH} = 7.3$ Hz).

The synthesis of PF_2OTfet proceeded in much the same manner. A 20.7-mmol sample of PF_3 was frozen at −196° in a 500-cm^3 bulb with a removable tube. A 13.1-mmol sample (1.027 g) of pyridine and a 12.2-mmol sample of CF_3CH_2OH were condensed on top of the PF_3 and the mixture was allowed to warm slowly to ambient temperature. The formation of white solids indicated immediate reaction. After 4 hr the reaction was frozen to −196° and then allowed to warm slowly through traps held at −65, −140, and −196°. The −140° trap yielded 5.42-mmol of PF_2OTfet. A white-brown solid remained in the bulb and was discarded along with an unidentified oil at −65°. A 4.36-mmol amount of PF_3 was found at −196°. The yield based on consumed PF_3 was 33.4%. Longer reaction times were accompanied by reduced yields and the formation of more brown solids. PF_2OTfet was also formed in the reaction of PF_3, TfetOH, and $N(CH_3)_3$ but it could not be separated from any unreacted amine. The gas-phase ir[13] showed the following peaks: 2987 (mw), (CH str); 1417 (m), 1365 (w), 1277 (vs), 1187 (vs), 1088 (vs), 971 (s), 854 (vs), 817 (vs, br), 666 (w), 562 (w).

PF_2OTfet exhibits a ^1H nmr ($CHCl_3$, −40°) spectrum consisting of a quartet of doublets ($\delta(CH_2)$ 4.32 ppm (q, $J_{FCH} = 7.9$ Hz)); each member of a quartet is a doublet (d, $J_{PCH} = 6.6$ Hz). ^{19}F nmr ($CHCl_3$, −40°): $\delta(PF)$ 50.2 ppm, (d, $J_{PF} = 1331$ Hz)); each member of a doublet is a triplet (t, $J_{HF} = 8.0$ Hz); each member of a triplet is a very poorly resolved quartet (q, $J_{CF_3F} \approx 1.4$ Hz); $\delta(CF_3)$ 76.6 ppm, very poorly resolved quartet (q, $J_{CF_3F} \approx 1.4$ Hz). No P–CF_3 coupling is evident in the ^{19}F spectrum because of the broadness of the CF_3 peak; however, a small J_{PCF_3} coupling constant is evident in the ^{31}P spectrum. ^{31}P nmr (ambient temperature): $\delta(P)$ −110 ppm, (t, $J_{PF} = 1327$ Hz; each member of a triplet is a triplet (t, $J_{PH} = 6.7$ Hz); each member of a triplet of triplets is a very poorly defined quartet (q, $J_{PCF_3} < 1$ Hz).

Following are the mass numbers (species) and relative abundances of the mass spectrum of PF_2OTfet: 168 ($PF_2OC_2H_2F_3^+$), 27.6; 149 ($PFOC_2H_2F_3^+$), 2.8; 99 ($PF_2OCH_2^+$, $OC_2H_2F_3^+$), 99.5; 85 (PF_2O^+), 4.2; 83 ($C_2H_2F_3^+$), 13.8; 71 (POC_2^+), 11.7; 69 (PF_2^+), 100.0; 64 ($C_2H_2F_2^+$), 52.5; 61 ($POCH_2^+$), 50.0; 51 (PFH^+, CF_2H^+), 10.7; 50 (PF^+, CF_2^+), 9.0; 47 (PO^+), 2.8; 40 (C_2O^+), 6.2; 33 (CH_2F^+), 31.1; 32 (PH^+, O_2^+), 39.4; 31 (P^+), 2.8; 29 (CHO^+), 11.7; 28 (CO^+, N_2^+), 72.5; 18 (H_2O^+), 17.8; 17 (OH^+), 4.2; 14 (CH_2^+, N^+), 4.2.

Syntheses of $PF_2OEt \cdot BH_3$ and $PF_2OTfet \cdot BH_3$. A 14.95-mmol sample of B_2H_6 was condensed at −196° in a 500-cm^3 reaction bulb. A 4.16-mmol amount of PF_2OTfet was frozen on top of the B_2H_6 and the mixture was allowed to warm slowly to room temperature. After 65 hr at ambient temperature the mixture was distilled through traps held at −72 and −196°. A 12.70-mmol quantity of B_2H_6 was recovered from the −196° trap while 4.07-mmol of $PF_2OTfet \cdot BH_3$ was isolated at −72°. A small amount of a nonvolatile oil remained behind in the flask. The yield was 98.2% and BH_3 combined with PF_2OTfet in a 1.08:1 ratio. B_2H_6 was identified by ir.

Long reaction times are required as the reaction is slow and the ligand is difficult to separate from its adduct. Reaction time can be shortened and yields increased by the use of high-pressure reactions. An 8.73-mmol amount of B_2H_6 was condensed at −196° into a 20-cm^3 Kjeldahl flask equipped with a 10/30 standard taper joint. A 4.72-mmol amount of PF_2OTfet was frozen on top of the B_2H_6, the flask was sealed *in vacuo*,[10] and the mixture was allowed to warm to ambient temperature. After 34 hr the mixture was frozen and the tube was opened *in vacuo*. Following distillation through traps held at −75 and −196°, 6.37 mmol of B_2H_6 was recovered from the −196° trap and 4.72 mmol of $PF_2OTfet \cdot BH_3$ was isolated at −75°. The yield was 100% and BH_3 combined with PF_2OTfet in a 1:1 ratio. The gas-phase ir spectrum[13] exhibits the following peaks: 2991 (m) (CH str); 2616 (vw); 2456 (vs), 2382 (w, sh) (BH str), 1462 (mw), 1422 (s), 1305 (vvs), 1195 (vvs), 1120 (vvs), 1082 (vs), 1058 (s, sh), 972 (vs), 938 (vvs), 912 (vs), 876 (vs), 737 (w), 667 (w); 617 (s) (PB str), 547 (vw).

The adduct was found to be undissociated by ir and vapor-phase molecular weight from 10.0 to 127.0 mm. The vapor-phase molec-

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(14) Conventions from IUPAC International Bulletin No. 4, "Appendices on Tentative Nomenclature, Symbols, Units and Standards," 1970. Signals downfield from tetramethylsilane are reported as positive.

ular weight at 24.3° and $P = 127.0$ mm was found to be 180.6 (calcd 181.8).

Following are the mass numbers (species) and the relative abundances of the mass spectrum of $PF_2OTfet\cdot BH_3$ (^{11}B peaks only): 182 ($PF_2OC_2H_2F_3{}^{11}BH_3^+$), 2.7; 169 ($PF_2OC_2H_3F_3^+$), 28.4; 150 ($PFOC_2H_3F_3^+$), 13.3; 99 ($OC_2H_2F_3^+$), 100; 83 ($C_2H_2F_3^+$, $PF_2{}^{11}BH_3^+$), 9.8; 71 ($POCH^{11}B^+$), 8.9; 69 (PF_2^+), 99.0; 64 ($C_2H_2F_2^+$, $PF^{11}BH_3^+$), 57.5; 61 ($PF^{11}B^+$), 38.1; 51 (PFH^+, CF_2H^+), 8.0; 50 (PF^+, CF_2^+), 8.0; 47 (PO^+), 1.8; 44 (PBH_2^+, CO_2^+), 1.3; 43 ($P^{11}BH^+$), 1.3; 40 (C_2O^+), 3.5; 33 (CH_2F^+), 23.9; 32 (PH^+), 34.5; 31 (P^+), 5.5; 29 (CHO^+), 8.0; 28 (CO^+), 73.5; 18 (H_2O^+), 8.0; 17 (OH^+), 6.2; 14 ($^{11}BH_3^+$), 3.5.

$PF_2OEt\cdot BH_3$ was synthesized using the low-pressure technique applied to the preparation of $PF_2OTfet\cdot BH_3$. After 3 hr distillation gave quantitative yields of $PF_2OEt\cdot BH_3$. The yield was 100% and BH_3 combined with PF_2OEt in a 1:1 ratio.

$PF_2OEt\cdot BH_3$ was found to be undissociated by ir and vapor-phase molecular weight from 10.0 to 52.2 mm. The vapor-phase molecular weight at 25.0° and $P = 52.2$ mm was found to be 126.7 (calcd 127.8). The gas-phase ir spectrum includes the following peaks: 3007 (ms), 2956 (w) (CH str); 2617 (vw, br); 2448 (vs), 2382 (w) (BH str); 1407 (w), 1307 (vs), 1179 (m, sh), 1097 (s), 1054 (vs), 981 (ms), 922 (vs), 902 (vs), 820 (ms), 633 (m), 602 (m) (PB str).

Following are the mass numbers (species) and relative abundances of the mass spectrum of $PF_2OEt\cdot BH_3$ (^{11}B peaks only): 128 ($PF_2OC_2H_5{}^{11}BH_3^+$), 21.0; 127 ($PF_2OC_2H_5{}^{11}BH_2^+$), 6.0; 126 ($PF_2OC_2H_5{}^{11}BH^+$), 27.0; 125 ($PF_2OC_2H_5{}^{11}B^+$), 25.5; 124 ($PF_2OC_2H_4{}^{11}B^+$), 3.9; 115 ($PF_2OC_2H_6^+$), 13.5; 114 ($PF_2OC_2H_5^+$), 93.0; 99 ($PF_2OCH_2^+$), 67.5; 98 (PF_2OCH^+), 9.0; 97 (PF_2OC^+), 22.2; 96 ($PF_2O^{11}B^+$), 4.5; 95 ($PFOC_2H_5^+$), 3.0; 87 ($POC_2H_5{}^{11}B^+$), 5.4; 86 ($POC_2H_4{}^{11}B^+$), 39.0; 71 ($POCH^{11}B^+$), 9.3; 69 (PF_2^+), 100.0; 67 ($FPOH^+$), 36.0; 50 (PF^+), 4.5; 47 (PO^+), 9.0; 43 ($OC_2H_3^+$), 9.0; 40 (C_2O^+), 3.0; 32 (PH^+), 12.0; 31 (P^+), 3.0; 29 ($C_2H_5^+$), 60.0; 28 ($C_2H_4^+$), 66.0; 27 ($C_2H_3^+$), 33.0; 26 ($C_2H_2^+$), 6.0; 18 (H_2O^+), 3.9; 15 (CH_3^+), 3.0; 13 (CH^+, $^{11}BH_2^+$), 3.0.

Both adducts were characterized by proton, fluorine, and boron nmr spectra. The proton spectrum of $PF_2OEt\cdot BH_3$ consists of three sets of peaks. A broad upfield 1:1:1:1 quartet was assigned to the BH protons ($CHCl_3$, +10°, $\delta(BH_3)$ 0.5 ppm (q, $J_{BH} = 103.2$ Hz, +20°, neat)); each member of the quartet was further split into a broad quartet (q, $J_{PBH} = 20.0$ Hz, $J_{FPBH} = 16.6$ Hz, +20°, neat), a lower field triplet ($CHCl_3$, +10°, $\delta(CH_3)$ 1.39 ppm, (t, $J_{HCH} = 7.0$ Hz, +20°, neat)), and a low-field doublet of quartets ($CHCl_3$, +10°, $\delta(CH_2)$ 4.38 ppm (d, $J_{PCH} = 8.2$ Hz, +20°, neat)); each member of the doublet was a quartet (q, $J_{HCH} = 7.0$ Hz, +20°, neat). The ^{11}B spectrum (neat, ambient temperature) confirmed the proton spectrum and the presence of a PB bond: $\delta(B)$ 133 ppm (q, $J_{BH} = 102.6$); each member of the quartet is a doublet (d, $J_{PB} = 70.4$ Hz). ^{19}F nmr (neat, +20°): $\delta(F)$ 62.4 ppm (d, $J_{PF} = 1289$ Hz); each member of a doublet is a quartet (q, $J_{HBPF} = 16.9$ Hz).

The ^1H, ^{19}F, and ^{11}B spectra of $PF_2OTfet\cdot BH_3$ were similar. The proton spectrum consisted of a broad high-field 1:1:1:1 quartet assigned to the BH protons ($CHCl_3$, +10°, $\delta(BH)$ 0.6 ppm, (q, $J_{BH} = 103.2$ Hz, neat, +22°)); each member of the quartet was a very broad quartet (q, $J_{PBH} = 19.2$ Hz, $J_{FBH} = 16.0$ Hz, neat, +22°) and a low-field doublet of quartets ($CHCl_3$, 0°, $\delta(CH_2)$ 4.57 ppm (d, $J_{PCH} = 10.0$ Hz, 0°, neat)); each member of a doublet is a quartet (q, $J_{HCF_3} = 7.8$ Hz, 0°, neat). ^{19}F nmr (+20°, neat): $\delta(PF) = 61.7$ ppm (d, $J_{PF} = 1244$ Hz); each member of a doublet is a very broad quartet (q, $J_{HBPF} = 16.2$ Hz; +20°, neat, $\delta(CF_3)$ 76.8 ppm (t, $J_{HCF_3} = 7.9$ Hz)). The ^{11}B spectrum provides evidence for a PB bond. ^{11}B nmr (ambient temperature, neat): $\delta(B)$ 134 ppm (q, $J_{BH} = 102.6$ Hz)); each member of a quartet is a doublet (d, $J_{PB} = 58.4$ Hz).

The nmr spectra of $PF_2OEt\cdot BH_3$ and $PF_2OTfet\cdot BH_3$ exhibit a temperature dependence. The most vivid temperature effects are seen when observing the BH protons. At ~20° and above the spectra consist of broad 1:1:1:1 quartets of quartets (J_{BH}, J_{FPBH}, and J_{PBH}). As the temperature is lowered, collapse of J_{FPBH} occurs between −20 and −30° for both adducts, while the broad quartets of doublets (J_{BH} and J_{PBH}) collapse as the temperature is lowered from −40 to −50°. As the temperature is lowered further, the 1:1:1:1 quartets begin to collapse. At −95° the outer members are hardly discernible. Further cooling caused complete decoupling and at −125° broad singlets were observed. Line widths for the CH protons in both cases decreased on cooling. These effects have been explained as the result of the variable rates of ^{10}B and ^{11}B quadrupolar spin-lattice relaxation.[15-18]

Base Displacement Reactions. Mixtures of an uncoordinated phosphine and a borane adduct were prepared by condensing *in vacuo* a measured amount of each into an nmr tube at −196°.[10] The tube was sealed *in vacuo* and removed and the mixture was allowed to warm until it melted. The mixture was held at 0° in an ice-H_2O slush for varying periods of time.[7] Integration of the ^1H spectra by cutting and weighing the resonance absorptions ascribed to the components of the equilibrium mixture indicated the relative compositions. The spectra were obtained at 0° and the equilibrium was approached from both directions. The results of these reactions are given in Table I.

The mixtures were also held at ambient temperature for approximately 600 hr. Temperature variances (integration of ^1H, see Table I) make these figures less accurate (>1%), although the trend of basicity is in the same direction. ^{31}P nmr spectra on these samples also indicated the same relative order of basicity but decomposition and severe overlapping hindered the study (not included in Table I).

Results and Discussion

1. Preparation and Characterization of Ligands and Adducts.

From the reaction

$$PF_3 + ROH + C_5H_5N \rightarrow PF_2OR + [C_5H_5NH^+F^-] + [\text{oils}]$$

where $R = CH_3$, CH_2CH_3, and CH_2CF_3, methyl, ethyl, and trifluoroethyl difluorophosphites have been obtained in yields of 25–65%. The previously unreported ethyl[19] and trifluoroethyl ligands are clear volatile liquids at room temperature and both form glasses upon freezing. No decomposition at room temperature *in vacuo* is noted by ir and nmr for a period of 400 hr.

PF_2OEt and PF_2OTfet were characterized by vapor density molecular weights (for PF_2OEt, 23.7° and $P = 105.9$ mm, found 115.3 and calcd 114.0; for PF_2OTfet, 26.8° and $P = 124.0$ mm, found 169.1 and calcd 168.0) and by ir, ^{19}F, ^1H, and ^{31}P nmr, and mass spectra. Complete mass, ir, and nmr spectral data are in the Experimental Section.

The borane adducts of these phosphites are obtained from the direct reaction of B_2H_6 and the ligands. The gas-phase infrared spectra of $PF_2OEt\cdot BH_3$ and $PF_2OTfet\cdot BH_3$ are listed in the Experimental Section where they may be compared with those of the free ligands. The 1:1 adducts were characterized by the stoichiometry of the reactions from which they were obtained and by ^{11}B, ^{19}F, and ^1H nmr and mass spectral data. Complete mass and nmr spectral data and vapor-phase molecular weight data are in the Experimental Section. No dissociation is evident from vapor-phase molecular weight and ir data and no decomposition is revealed by ir and nmr after 400 hr at room temperature *in vacuo*.

2. Basicity Studies.

In an effort to ascertain what effects the R group might have upon Lewis basicity we investigated the basicity of a series of difluorophosphites by displacement equilibria. The relative order of base strengths established for the series of phosphites ($R = CH_3$, Et, Tfet) is $PF_2OEt > PF_2OMe > PF_2OTfet$, while J_{PB} for the difluorophosphite-borane adducts decreases in the same order. This is in agreement with the J_{PB} *vs.* basicity correlation proposed by

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Table I.

Phosphine (mmol)	J_{PB}, Hz (adduct)	Adduct (mmol)	Time (at 0°), hr	K_{eq}[a] 0°	K_{eq}[a] Ambient temp[f]	% displacement[b] 0°	% displacement[b] Ambient temp[f]
PF_2OCH_3 (0.845)	68.2[d]	$PF_2OC_2H_5 \cdot BH_3$ (0.845)	859	2.36	2.88	61	63
$PF_2OC_2H_5$[c] (1.02)	70.4	$PF_2OCH_3 \cdot BH_3$ (1.02)	834	2.19	3.01	60	63
$PF_2OCH_2CF_3$ (1.04)	58.4	$PF_2OC_2H_5 \cdot BH_3$ (1.04)	888	4.45[e]	4.60	68[e]	68
$PF_2OC_2H_5$[c] (1.09)	70.4	$PF_2OCH_2CF_3 \cdot BH_3$ (1.09)	786	3.48[e]	3.86	65[e]	66

[a] Equilibrium constants are defined by the expression: K_{eq} = [weaker base][adduct of stronger base]/[adduct of weaker base][stronger base]. See ref 7. [b] Per cent displacement is calculated using the formula: $100(K_{eq})^{1/2}/(K_{eq})^{1/2} + 1)$. See ref 7. [c] Stronger base of the exchanging pair of ligands. [d] Reference 5. [e] K_{eq} = [adduct of stronger base]/[stronger base]. [f] Samples were held at ambient temperature for ~600 hr. See Experimental Section.

Cowley and Damasco[5] and Rudolph and Schultz.[6] See Table I.

It is important to note here that it is inadvisable to make *a priori* assessments of Lewis basicities on the basis of equilibrium data because of entropy effects; however, in a series of structurally similar compounds the entropy changes accompanying coordination to a reference acid should be approximately constant.[7-9,20] The structures of several difluorophosphines[8,9] are known to be similar and we expect no gross distortions in the structures of the difluorophosphites or in their structures upon coordination.

Although many theories[5-7] have been proposed to interpret the base strengths of phosphines toward borane, none are sufficient alone to explain the experimental observations. The basicity order of the phosphites follows the simple order expected considering the apparent electron-withdrawing abilities of the OR groups as determined in solution, OEt < OMe < Tfet.[21,22] This explanation for the series of basicities is not without merit but the fact that PF_2OMe and PF_2NMe_2 form stronger adducts with borane than with PF_2SCH_3[7] indicates that a more plausible explanation must be sought.

In certain phosphines dative π bonding between the filled 2p orbitals of R_2N or RO groups and vacant P(3d) or P(4p) orbitals has been postulated to explain the unusual basicity of these compounds toward borane.[23] $(p \rightarrow d)\pi$ bonding has the effect of increasing electron density on phosphorus thus influencing the phosphorus-boron bond strength. The importance of this interaction has been fairly well established by a series of stereochemical, structural, and basicity observations which have been reviewed recently.[5,7]

(p-d)π bonding in the difluorophosphites can be represented as

$$F_2\bar{P}=\overset{+}{O}-R$$

If (p-d)π bonding is the mechanism for causing the unusual basicity of NR_2- and OR-substituted phosphines, then any R group which was inductively electron releasing would stabilize the resonance structure and increase the basicity toward borane. Contrastingly, any highly electron-withdrawing group would destabilize the structure and decrease base strength. The base strengths of the substituted difluorophosphites predict that the electron-withdrawing ability is Et < Me < Tfet. This is a classically accepted order.[21,22,24-28] The influence of steric effects on the equilibria[28] must be insignificant in relation to electron drift from the oxygen system since the basicity order is not that expected for steric requirements, $PF_2OMe > PF_2OEt \sim PF_2OTfet$.

Coyle and Stone[29] have suggested that B-H ir stretching frequencies can often be correlated to boron-ligand bond strength in boron adducts. However, Cohn and Foester[7] have found no obvious relationships between the B-H stretching frequencies and observed strengths. Although the differences in frequencies (cm^{-1}) are small in the series PF_2OR [R = Et (2448, 2382), Me (2452, 2383), Tfet (2456, 2382)],[30] a trend similar to that suggested by Coyle and Stone is evident.

Registry No. PF_3, 7783-55-3; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; CF_3CH_2OH, 75-89-8; PF_2OCH_3, 381-65-7; $PF_2OC_2H_5$, 24933-27-5; $PF_2OCH_2CF_3$, 40537-39-1; B_2H_6, 19287-45-7; $PF_2OCH_3 \cdot BH_3$, 35512-89-1; $PF_2OC_2H_5 \cdot BH_3$, 40537-41-5; $PF_2OCH_2CF_3 \cdot BH_3$, 40537-42-6.

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