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The Synthesis, Characterization, and Stability of Halodifluorophosphine–Borane(3) and –Tetraborane(8) Complexes

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The $F_2XP \cdot BH_3$ (X = F, Cl, Br, I) complexes have been prepared by symmetrical cleavage of B_2H_6 with F_2XP ligands and by base displacement of CO from $OCBH_3$. The new complexes were characterized by their vapor pressures, mass spectra, infrared spectra, and ^1H, ^{11}B, ^{19}F, and ^{31}P nmr spectra. In addition, the room-temperature gas-phase dissociation equilibrium constant was estimated for each complex. An increasing value for K_{eq} suggests decreasing $F_2XP \cdot BH_3$ complex stability in the order: X = F > Cl > Br > I. The $F_2XP \cdot B_4H_8$ (X = F, Cl, Br, I) complexes have been prepared by symmetrical cleavage of B_5H_{11} with F_2XP. Each complex was characterized by mass spectrometry, infrared spectroscopy, and ^{11}B and ^{19}F nmr spectroscopy. Temperature dependence of the ^{19}F nmr spectra suggests that structural isomers are present in solutions of $F_2XP \cdot B_4H_8$ complexes. Reaction stoichiometry and product distributions support the postulate that B_4H_8 is a stronger acid than BH_3 toward F_2XP ligands.

The fact that F_3P showed rather unexpected coordination with metal atoms as well as with borane fragments has generated argument and speculation over the nature of the bond between phosphorus and "acceptor" atoms such as metals or boron.[1-8] Simple inductive arguments indicate low availability for the σ lone electron pair on the phosphorus of PF_3. The $F_3P \cdot BH_3$ complex formation demanded the introduction of more sophisticated models.[3] A recent observation has shown that $F_2HP \cdot BH_3$ is significantly more stable than $F_3P \cdot BH_3$.[9] This fact requires some perturbation of the existing models for fluorophosphine complexes and raises interesting questions relative to the stability of general complexes of the type $F_2XP \cdot BH_3$. This paper describes the study of the previously unknown borane(3) and tetraborane(8) complexes of the closely related series of fluorophosphine ligands, F_2XP, where X = Cl, Br, or I. Equilibrium constant measurements have been used to show that when borane acids are used as a reference, the apparent base strength of F_2XP *decreases* as X goes from F to I. The data also indicate that B_4H_8 is a stronger acid than BH_3 in accordance with earlier generalizations.[10]

The borane(3) adducts were prepared by using the well-known symmetrical cleavage of diborane by the phosphorus base

$$2F_2XP + B_2H_6 \longrightarrow 2F_2XP \cdot BH_3$$

and by displacement of CO from $OCBH_3$

$$OC \cdot BH_3 + F_2XP \longrightarrow F_2XP \cdot BH_3 + CO$$

The tetraborane(8) adducts were prepared by the "symmetrical cleavage" of B_5H_{11} with a phosphorus base

$$B_5H_{11} + 2F_2XP \longrightarrow F_2XP \cdot B_4H_8 + F_2XP \cdot BH_3$$

Attempts to synthesize $F_2XP \cdot B_4H_8$ by cleavage of the $(CH_3)_2N$ group from $(CH_3)_2NF_2P \cdot B_4H_8$ with HX were not classed as successful. The process is complex

$$(CH_3)_2NF_2P \cdot B_4H_8 + HX \longrightarrow \begin{cases} \text{complex product mixture} \\ \text{containing less that 20\%} \\ \text{of } XF_2P \cdot B_4H_8 \end{cases}$$

Experimental Section

General Information.—Standard high-vacuum techniques were used for the manipulation of the volatile compounds. Mass spectra were recorded on a Consolidated Electrodynamics Model 21-103B spectrometer operating at 60 eV. Infrared spectra were recorded on a Beckman IR-20 spectrometer using a cell fitted with CsI windows. The nmr spectra were recorded on a Varian HA/HR-100 instrument operating at 100.0 MHz (^1H), 32.1 MHz (^{11}B), 94.1 MHz (^{19}F), and 40.4 MHz (^{31}P). External standards, $(CH_3)_3B$ and orthophosphoric acid, were used for the ^{11}B and ^{31}P spectra and internal standards, $(CH_3)_4Si$ and $CFCl_3$, were used for the ^1H and ^{19}F spectra. All spectra were recorded at −80° unless noted otherwise in the text.

Materials.—Diborane(6) was prepared by the reaction of $LiAlH_4$ with boron trifluoride etherate[11] and purified by repeated fractionation through a −160° bath. Borane–carbonyl was prepared by the method of Carter[12] and pentaborane(11) was prepared by the "hot-cold tube" pyrolysis of B_2H_6.[13,14] Trifluorophosphine was purchased from Ozark-Mahoning Co. and was distilled through a −160° bath. The F_2ClP, F_2BrP, and F_2IP ligands were prepared by the method of Morse, *et al.*[15]

The Synthesis of $F_2XP \cdot BH_3$. (a) From B_2H_6 and F_2XP.—A 1.6-mmol sample of B_2H_6 and a 5.0-mmol sample of F_2XP (X = F, Cl, Br, I) were condensed into a 5-ml reaction tube and sealed off under vacuum. After standing at 0° for 3–5 days, the tube was opened and the volatile products were vacuum distilled through cold baths: F_3P, −160 and −196°; F_2ClP and F_2BrP, −126, −160, and −196°; F_2IP, −96, −112, and −196°. In each case the $F_2XP \cdot BH_3$ complex stopped at the warmest trap, the unreacted ligand stopped in the middle trap, and free B_2H_6 and PF_3 stopped at −196°. The $F_2IP \cdot BH_3$ complex slowly passed the −96° bath. The yields from these reactions, based on the B_2H_6 consumed, were approximately 80% $F_3P \cdot BH_3$, 50% $F_2ClP \cdot BH_3$, 35% $F_2BrP \cdot BH_3$, and 25% $F_2IP \cdot BH_3$.

(b) From $OC \cdot BH_3$ and F_2XP.—A 3.0-mmol sample of $OC \cdot BH_3$ was combined with a 2.5-mmol sample of F_2XP (X = F, Cl, Br, I) in a 300-ml flask. The flask was closed off by a

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stopcock and then held at −78°. The progress of the reaction was monitored by periodically freezing the flask at −196° and removing the evolved carbon monoxide into a Toepler pump system of known volume. After 2–3 days, 95% or more of the CO was recovered and the remaining volatile products were then vacuum distilled as described above. Yields, based on the F_2XP consumed, were *ca.* 95% $F_3P\cdot BH_3$, 95% $F_2ClP\cdot BH_3$, 85% $F_2BrP\cdot BH_3$, and 85% $F_2IP\cdot BH_3$. Very pure $F_2XP\cdot BH_3$ samples (*ca.* 99%) could be obtained by the reaction between a sample prepared in the above fashion and excess $OC\cdot BH_3$ at −78°.

(c) **Properties of $F_2XP\cdot BH_3$ Complexes.**—Properties of $F_3P\cdot BH_3$ prepared in this study agreed well with known properties for this complex.[3]

(1) **$F_2ClP\cdot BH_3$.**—Vapor pressure data can be summarized by the equation $\log P_{mm} = -1212.1/T + 7.380$. Experimental and calculated vapor pressure values are compared as follows [T°K, observed P_{mm} (calculated P_{mm})]: 153.4, 0.4 (0.5); 169.9, 1.7 (1.8); 178.7, 3.7 (4.0); 185.0, 6.7 (6.8); 208.3, 40.3 (36.5); 219.0, 73.2 (71.3); 233.9, 166.2 (160.0). Trouton constant 20.8 cal deg^{-1} mol^{-1}; bp −6.3° (extrapolated); mp −132.9 ± 0.5°. Molecular weight by vapor density: observed, 116.0; calculated, 118.3. Mass spectrum at 60 eV [m/e (assignment) relative intensity]: 118 $(F_2{}^{35}ClP^{11}BH_3{}^+)$ 9.7; 117 $(F_2ClP^{11}BH_2{}^+$ and $F_2ClP^{10}BH_3{}^+)$ 22.1; 116 $(F_2ClP^{11}BH^+$ and $F_2ClP^{10}BH_2{}^+)$ 18.5; 115 $(F_2ClP^{11}B^+$ and $F_2ClP^{10}BH^+)$ 3.0; 104 (F_2ClP^+) 32.8; 85 $(FClP^+)$ 29.5; 69 (F_2P^+) 100.0; 66 (ClP^+) 3.9; 50 (FP^+) 13.1; 35 (Cl^+) 10.7; 31 (P^+) 21.8. Contributions from ^{37}Cl have been subtracted out. Infrared spectrum (gas) (cm^{-1}): 2445 (ν(B–H)), 1055 ($\delta(BH_3)$), 925 (ν_{as}(P–F)), 914 (ν_s(P–F)), 700 ($\rho(BH_3)$), 630 (ν(P–B)), 545 (ν(P–Cl)), 390 ($\delta(PF_2)$) [ν = stretch, δ = deformation, ρ = rock]. Nmr spectra ($CFCl_3$): ^1H: δ −0.54 ppm (TMS standard), J(HB) = 108 Hz, J(HBP) = 17 Hz, J(HBPF) = 17 Hz; ^{11}B: δ 124.2 ppm ($B(CH_3)_3$ standard), J(BH) = 105 Hz, J(BP) = 27 Hz; ^{19}F: δ −34.4 ppm (TFA standard), J(FP) = 1367 Hz, J(FPBH) = 20 Hz; ^{31}P: δ −175.1 ppm (OPA standard), J(PF) = 1374 Hz.

(2) **$F_2BrP\cdot BH_3$.**—Vapor pressure data can be summarized by the equation $\log P_{mm} = -1183.4/T + 6.863$. Experimental and calculated vapor pressure values are compared as follows [T°K, observed P_{mm} (calculated P_{mm})]: 189.7, 3.7 (4.2); 198.6, 7.8 (7.9); 213.8, 10.7 (11.1); 225.0, 40.3 (39.5); 232.5, 58.8 (59.4); 239.3, 82.4 (82.4); 244.5, 109.5 (106.0). Trouton constant 18.3 cal deg^{-1} mol^{-1}; bp 23.7° (extrapolated); mp −125.0 ± 1.0°. Molecular weight by vapor density: observed, 160.3; calculated, 162.7. Mass spectrum at 60 eV [m/e (assignment) relative intensity]: 162 $(F_2{}^{79}BrP^{11}BH_3{}^+)$ 4.4; 161 $(F_2BrP^{11}BH_2{}^+$ and $F_2BrP^{10}BH_3{}^+)$ 5.0; 160 $(F_2BrP^{11}BH$ and $F_2BrP^{10}BH_2{}^-)$ 6.4; 159 $(F_2BrP^{11}B^+$ and $F_2BrP^{10}BH^-)$ 1.3; 148 (F_2BrP^+) 39.7; 129 $(FBrP^+)$ 17.3; 110 (BrP^+) 7.0; 79 (Br^+) 10.2; 69 (F_2P^+) 100.0; 50 (FP^+) 22.1; 31 (P^+) 16.6. Contributions from ^{81}Br have been subtracted out. Infrared spectrum (cm^{-1}) (gas): 2440 (ν(B–H)), 1040 ($\delta(BH_3)$), 914 (ν_{as}(P–F)), 908 (ν_s(P–F)), 680 ($\rho(BH_3)$), 605 (ν(P–B)), 450 (ν(P–Br)), 380 ($\delta(PF_2)$). Nmr spectra ($CFCl_3$): ^1H: δ −0.97 ppm (TMS standard), J(HB) = 117 Hz; ^{11}B: δ 120.7 ppm ($B(CH_3)_3$ standard), J(BH) = 105 Hz, J(BP) = 19 Hz; ^{19}F: δ −36.6 ppm (TFA standard), J(FP) = 1357 Hz, J(FPBH) = 20 Hz; ^{31}P: δ −158.5 ppm (OPA standard), J(PF) = 1369 Hz.

(3) **$F_2IP\cdot BH_3$.**—Vapor pressure data were not obtained for F_2IPBH_3 because of rapid dissociation of the complex at the temperatures required, about −45 to +23°. The following data were obtained. Molecular weight by vapor density: observed, 204.5; calculated, 209.9. Mass spectrum at 60 eV [m/e (assignment) relative intensity]: 210 $(F_2{}^{127}IP^{11}BH_3{}^+)$ 0.2; 209 $(F_2IP^{11}BH_2{}^+$ and $F_2IP^{10}BH_3{}^+)$ 0.1; 196 (F_2IP^+) 100.0; 177 (FIP^+) 10.6; 158 (IP^+) 3.2; 127 (I^+) 28.4; 69 (F_2P^+) 60.5; 50 (FP^+) 48.2; 31 (P^+) 8.6. Infrared spectrum (cm^{-1}) (gas): 2435 (ν(B–H)), 1038 ($\delta(BH_3)$), 905 (ν_{as}(P–F)), 898 (ν_s(P–F)), 675 ($\rho(BH_3)$), 590 (ν(P–B)), 365 (ν(P–I)), 400 ($\delta(PF_2)$). Nmr spectra ($CFCl_3$): ^1H: δ −1.22 ppm (TMS standard), J(HB) = 117 Hz; ^{11}B: δ 115.7 ppm ($B(CH_3)_3$ standard), J(BH) = 109 Hz, J(BP) < 15 Hz; ^{19}F: δ −37.3 ppm (TFA standard), J(FP) = 1334 Hz, J(FPBH) = 20 Hz; ^{31}P: δ −150.3 ppm (OPA standard), J(PF) = 1351 Hz.

The nmr splitting patterns are described in the text.

Each complex was found to be stable in the vacuum system for weeks at temperatures of −78° or below, but rapid and almost complete dissociation occurred at room temperature. It is significant that no evidence for hydrogenation of the P–X bond by the attached BH_3 was observed.

The Synthesis of $F_2XP\cdot B_4H_8$. (a) **From B_5H_{11} and F_2XP.**—A 2.6-mmol sample of B_5H_{11} was combined with a 5.6-mmol sample of F_2XP (X = F, Cl, Br, I) in a 300-ml flask and held at −78° for 3–5 days. The resulting products were distilled through −78, −126, −160, and −196° traps. In each case, the $F_2XP\cdot B_4H_8$ complex formed was retained at −78°. (The $F_3P\cdot B_4H_8$ slowly passes −78° but stops at −96°.) The −126° trap stopped $F_2ClP\cdot BH_3$, $F_2BrP\cdot BH_3$, $F_2IP\cdot BH_3$, F_2IP, and B_5H_{11}. The −160° trap stopped F_2ClP, F_2BrP, or $F_3P\cdot BH_3$. The yields of $F_2XP\cdot B_4H_8$ and $F_2XP\cdot BH_3$ complexes ranged between 50 and 80%. When 1:1 reactant ratios were used, much smaller amounts of the $F_2XP\cdot BH_3$ complexes were obtained while the yields of $F_2XP\cdot B_4H_8$ remained high. One system was carefully measured. Equal amounts (1.5 mmol) of B_5H_{11} and F_2ClP were condensed into an nmr tube and sealed off. The tube was held at 0° for 3 days. The ^{19}F nmr spectrum was recorded and the peak areas for $F_2ClP\cdot BH_3$ and $F_2ClP\cdot B_4H_8$ were measured. The resulting $F_2ClP\cdot B_4H_8$:$F_2ClP\cdot BH_3$ ratio was 4.3.

(b) **Attempted Synthesis from $(CH_3)_2NF_2P\cdot B_4H_8$ and HX.**—The expected equation is

$$(CH_3)_2NF_2P\cdot B_4H_8 + 2HX \longrightarrow F_2XP\cdot B_4H_8 + [(CH_3)_2NH_2]X$$

Unfortunately the process is much more complex. A 3.0-mmol sample of $(CH_3)_2NF_2P\cdot B_4H_8$[16,17] was combined with a 6.2-mmol sample of HCl or HBr in a 300-ml reaction flask and the flask was then held at 0° for 30 min. A gummy solid formed during this time. The volatile products were passed through −45, −78, and −196° traps. The −45° trap stopped an unidentified oil, the −78° trap stopped a small amount (*ca.* 0.5 mmol) of $F_2XP\cdot B_4H_8$, and the −196° trap stopped HX and F_2XP.

(c) **Properties of $F_2XP\cdot B_4H_8$ Complexes.**—Properties of $F_3P\cdot B_4H_8$ prepared in this study agree well with known properties for the complex.[18] Each of the complexes is a colorless liquid at room temperature. Low vapor pressures below 30° and instability above this temperature made direct determinations of vapor pressures impractical in our system. The X = I complex is visually the least stable of the four complexes at 30°. Each decomposes slowly at 0° and each appears stable for greater than 1 month at −78°. The mass spectral data at 60 eV are listed as follows [m/e (assignment) relative intensity]: 156 $(F_2{}^{35}ClP^{11}B_4H_8{}^+)$ 5; 156–148 $(F_2ClP^nB_4H_x{}^+$ envelope) 41 for most intense peak at m/e 154; 148 (F_2ClP^+) 52; 85 $(FClP^+)$ 15; 69 (F_2P^-) 100; 52–44 $(B_4H_x{}^+)$ 54 at m/e 48; 40–33 $(B_3H_x{}^+)$ 23 at m/e 37; 201 $(F_2{}^{79}BrP^{11}B_4H_8{}^+)$ 3; 201–193 $(F_2XP^{11}B_4H_x{}^+)$ 37 at m/e 198; 149 (F_2BrP^+) 67; 130 $(FBrP^+)$ 10; 69 (F_2P^+) 100; 52–44 $(B_4H_x{}^+)$ 48 at m/e 48; 40–33 $(B_3H_x{}^+)$ 18 at m/e 37; 248 $(F_2{}^{127}IP^{11}B_4H_8{}^+)$ 2; 248–240 $(F_2IP^{11}B_4H_x{}^+)$ 27 at m/e 245; 196 (F_2IP^+) 75; 177 (FIP^+) 21; 158 (IP^+) 10; 69 (F_2P^+) 100; 52–44 $(B_4H_x{}^+)$ 44 at m/e 48; 40–33 $(B_3H_x{}^+)$ 14 at m/e 14. Contributions from ^{37}Cl and ^{81}Br have been subtracted out. No isotopic stripping of the "normal" borane envelopes has been performed. Infrared spectra (cm^{-1}) (gas): $F_2ClP\cdot B_4H_8$: 2580 (ν_{as}(B–H)), 2540 (ν_s(B–H)), 2470 (?), 1940–1870 (B–H–B), 1620 (?), 1600 (B_2H_6 impurity), 1580 (?), 1490–1400 (B–H–B), 1160 ($\rho(BH_2)$), 1060 ($\rho(BH_2)$), 900 (ν_{as}(P–F)), 850 (ν_s(P–F)), 700 (?), 670 ($\delta(BH_2)$), 585 (ν(P–B)), 535 (ν(P–Cl)); $F_2BrP\cdot B_4H_8$: 2580 (ν_{as}(B–H)), 2540 (ν_s(B–H)), 2460 (?), 1940–1870 (B–H–B), 1620 (?), 1600 (B_2H_6 impurity), 1580 (?), 1490–1400 (B–H–B), 1160 ($\rho(BH_2)$), 1060 ($\rho(BH_2)$), 910 (ν_{as}(P–F)), 850 (ν_s(P–F)), 690 (?), 670 ($\delta(BH_2)$), 570 (ν(P–B)), 460 (ν(P–Br)); $F_2IP\cdot B_4H_8$: 2580 (ν_{as}(B–H)), 2540 (ν_s(B–H)), 2430 (?), 1940–1870 (B–H–B), 1620 (?), 1600 (B_2H_6 impurity), 1580 (?), 1490–1400 (B–H–B), 1150 ($\rho(BH_2)$), 1060 ($\rho(NH_2)$), 900 (ν_{as}(P–F)), 850 (ν_s(P–F)), 670 ($\delta(BH_2)$), 590 (ν(P–B)), 400 (ν(P–I)) [ν = stretch, δ = deformation, ρ = rock]. Nmr spectra ($CFCl_3$): $F_3P\cdot B_4H_8$, ^{11}B: $\delta(B_3)$ 84.3, $\delta(B_2, B_4)$ 88.9, $\delta(B_1)$ 143.7 ppm ($B(CH_3)_3$ standard), $J(B_3H)$ = 122, $J(B_2H, B_4H)$ = 123, $J(B_1H)$ = 149, $J(B_1P)$ = 149 Hz; ^{19}F: δ_A −38.1, δ_B −36.0 ppm (TFA standard), J_A(FP) = 1290, J_B(FP) = 1354 Hz. $F_2ClP\cdot B_4H_8$, ^{11}B: $\delta(B_3)$ 82.0, $\delta(B_2, B_4)$ 90.2, $\delta(B_1)$ 137.9 ppm ($B(CH_3)_3$ standard), $J(B_3H)$ = 125, $J(B_2H, B_4H)$ = 136, $J(B_1H)$ = 150, $J(B_1P)$ = 150 Hz; ^{19}F: δ_A −36.2, δ_B −35.0 ppm (TFA standard), J_A(FP) = 1262, J_B(FP) = 1328 Hz. $F_2BrP\cdot B_4H_8$, ^{11}B: $\delta(B_3)$

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81.7, $\delta(B_2, B_4)$ 89.5, $\delta(B_1)$ 137.9 ppm ($B(CH_3)_3$ standard), $J(B_3H) = 136$, $J(B_2H, B_4H) = 136$, $J(B_1H) = 150$, $J(B_1P) = 150$ Hz; ^{19}F: δ_A −40.9, δ_B −39.9 ppm (TFA standard), $J_A(FP) = 1282$, $J_B(FP) = 1322$ Hz. $F_2IP \cdot B_4H_8$, ^{11}B: $\delta(B_3)$ 84.0, $\delta(B_2, B_4)$ 94.9, $\delta(B_1)$ 137.1 ppm ($B(CH_3)_3$ standard), $J(B_3H) = 132$, $J(B_2H, B_4H) = 132$, $J(B_1H) = 141$, $J(B_1P) = 141$ Hz; ^{19}F: δ_A −47.0, δ_B −42.9 ppm (TFA standard), $J_A(FP) = 1269$, $J_B(FP) = 1295$ Hz. The nmr spectral details are discussed in the text.

Relative Stability Measurements. Dissociation Constants.—Equilibrium constants for the general formation reaction

$$2F_2XP + B_2H_6 \rightleftharpoons 2F_2XP \cdot BH_3$$

were obtained by condensing known amounts of PF_2X and B_2H_6 (ratios about 2:1 and about 4:1) into a 500-ml reaction flask of accurately known volume. The flasks and contents were then thermostated at 297.3°K. The initial pressure in the flasks was about 200 mm. After 3–4 months, each flask was opened through a break-seal and the contents were rapidly vacuum distilled. The B_2H_6 and $F_2XP \cdot BH_3$ were each converted to $(CH_3)_3N \cdot BH_3$ and the resulting separate samples were weighed. No pyrolysis of B_2H_6 was observed. Equilibrium constants, converted to the dissociation process $2F_2XP \cdot NH_3 \rightleftharpoons 2F_2XP + B_2H_6$, obtained from duplicate runs at 297.3°K are as follows: X = F, 0.68 and 0.67; X = Cl, 2.69 and 2.66; X = Br, 7.92 and 7.95. The PF_2I decomposed during equilibration at 297.3°K and at lower temperatures equilibrium was not obtained over a 4-month period; hence no data were obtained for the formation of $F_2IP \cdot BH_3$.

Burg and Fu[19] reported a dissociation constant of 0.99 at 297.76°K for $F_3P \cdot BH_3$ and a ΔH_d of 11.87 kcal/mol. Their values were obtained under pressures in excess of 4 atm and this fact plus other differences in conditions probably accounts for the difference in K_{eq} in the region of 297°K. In our hands the higher pressure technique gave some irreversible decomposition of the diborane and free ligand. Low-pressure tensimetry, using mercury manometers, was also unsuccessful for ligands other than PF_3 because of the reaction between the ligands and the mercury. On the other hand, the direct dissociation of $F_3P \cdot BH_3$ was studied in a known-volume tensimeter similar to the type described by Shriver.[20] A weighed quantity of pure $F_3P \cdot BH_3$ was condensed into the tensimeter. After the system had been held at 303.0°K for 9 days, the pressure was measured. Multiple runs gave a dissociation constant of 0.72 which checks well with the comparable value of 0.68 obtained at 297.3°K from the formation process. The average dissociation constant of 0.70 ± 0.03 at 300°K and low pressure is thus cross-checked by both the formation and the dissociation processes.

Attempts to study the variation of K_{eq} with temperature for the formation process were blocked by slow reaction below room temperature and by disproportionation of the ligands at higher temperatures.

Competitive Base-Displacement Reactions.—Two base-displacement reactions were used to estimate relative base strengths. These are

$$H_3P \cdot BH_3 + F_2XP \underset{\text{toluene}}{\overset{-35°}{\rightleftharpoons}} H_3P + F_2XP \cdot BH_3 \qquad (1)$$

$$F_2BrP \cdot BH_3 + F_2XP \underset{CFCl_3}{\overset{-45°}{\rightleftharpoons}} F_2XP \cdot BH_3 + F_2BrP \qquad (2)$$

The reactions were run in sealed nmr tubes with the reactants on the left of the equations in an exact 1:1 ratio (1.3 mmol of each in 0.5 ml of toluene for reaction 1; 1.5 mmol of each in 0.4 ml of $CFCl_3$ for reaction 2). The tubes were thermostated at the temperatures indicated for 1 month. Analyses of the resulting mixtures were carried out by ^{19}F nmr. Since detailed solubility data for PH_3 and F_2XP in toluene were not available, it was *not* convenient to obtain equilibrium constants for process 1. Instead, results were conveniently summarized in terms of the $F_2XP \cdot BH_3 : F_2XP$ equilibrium ratio in solution. A high ratio indicates greater relative base strength for F_2XP. Values of the ratio obtained are as follows: F, 1.0; Cl, 0.66; Br, 0.15; I, decomposed.

For reaction 2, displacement of F_2BrP, the $F_2XP \cdot BH_3 : F_2BrP \cdot BH_3$ ratios obtained are as follows: F, 2.1; Cl, 1.4; Br, 1.0; I, 0.3. Clearly with these F_2XP ligands the base strength toward BH_3 decreases in the series $X = F > Cl > Br \gg I$.

Discussion

Stability Trends.—Data just cited plus available literature information[9] show clearly that the order of decreasing stability of the borane complexes is $F_2HP \cdot BH_3 \gg F_3P \cdot BH_3 > F_2ClP \cdot BH_3 > F_2BrP \cdot BH_3 > F_2IP \cdot BH_3$. The data also indicate roughly comparable base strength values for F_3P and H_3P in solution. Other data favor F_3P as a stronger base than H_3P in the absence of a solvent.[9] The overall trend is directly opposite to that expected if the inductive effect of the substituent X were to play a dominant role in determining the stability of the complex.

Several other interesting trends in the physical data are apparent in the series. A plot of J_{BP} against the value of the $F_2XP \cdot BH_3 : F_2BrP \cdot BH_3$ ratio from the displacement reaction 2 is linear (Figure 1), indicating that in this closely related series of bases, J_{BP} is a measure of complex stability. This qualitative relationship has been noted earlier by Rudolph,[21] Cowley and Damasco,[22] and Rudolph and Schultz.[23] The last authors point out that the relationship is applicable only when closely related systems involving a given boron reference acid are studied.

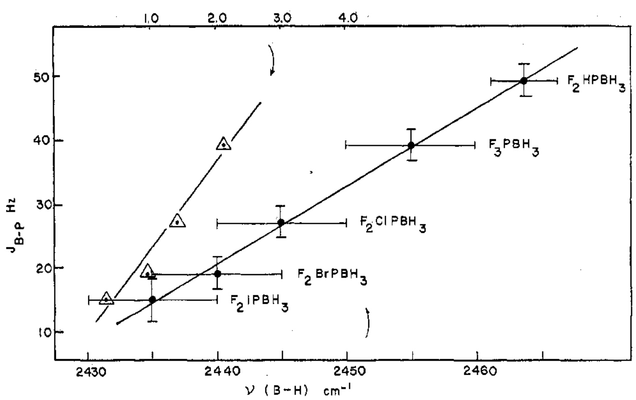

Figure 1.—Plots of J_{B-P} *vs.* ν_{B-H} and J_{B-P} *vs.* $F_2XP \cdot BH_3 : F_2BrP \cdot BH_3$ from the base-displacement reactions.

A second correlation is also apparent in the data. If J_{PB} is plotted against ν(B–H)(gas phase), a linear relationship is observed (Figure 1). If one makes the reasonable assumption that the light hydrogen atom is vibrating against a massive molecule, then ν(B–H) is an approximate measure of the B–H force constant.[24] The data imply a slight decrease in this force constant coincident with decreasing B–P bond strength. In our judgement this latter fact is difficult to harmonize with the hyperconjugative bond model[4,5] for fluorophosphine–boranes. According to such a model, electron density from the B–H bond would be effective in formation of a B–P π bond involving d acceptor orbitals of the phosphorus atom. Thus, one would anticipate

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[19] A. B. Burg and Y. C. Fu, *J. Amer. Chem. Soc.*, **88**, 1147 (1966).

[20] D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., p 64.

[21] R. W. Rudolph, Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1966.

[22] A. H. Cowley and M. C. Damasco, *J. Amer. Chem. Soc.*, **93**, 6815 (1971).

[23] R. W. Rudolph and C. W. Schultz, *ibid.*, **93**, 6821 (1971).

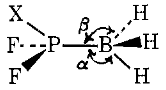
[24] This assumption is valid in the case of the vibration of a light atom against a much heavier one; however, it is anticipated, for instance, that ν(B–P) and the force constant for this interaction cannot be directly correlated because of vibrational coupling and mass effects.

that as π bonding between boron and phosphorus atoms increases, the electron density in the B–H bond should decrease. Such a decrease in electron density should then give rise to a decrease in the B–H stretching force constant. The data show the opposite trend: an increase in the strength of the B–P bond is correlated with an *increase* in the B–H force constant.

The value of ν(B–H) for H_3PBH_3 is available only from the solid-phase measurements.[21] This value, 2392 cm^{-1}, is significantly lower than the value suggested using the above relationship and the known J_{BP} value of 27 Hz. The marked reduction in the B–H stretching frequency is consistent with a solid-phase interaction involving the H–P protons and the B–H protons. Such a model was suggested earlier from this laboratory[9] in order to account for the low volatility of $H_3P \cdot BH_3$.

The correlation between J_{BP} and ν(B–H) also fails for $(CH_3)_2NF_2P \cdot BH_3$. The value of $J_{BP} = 79$ Hz is unusually high in relationship to the value of ν(B–H) = 2440 cm^{-1}. The unusually high value of J_{BP} would be consistent with increased electron density on phosphorus resulting from N–P double bonding.

Stability trends in the series of borane adducts with the bases F_2HP, F_3P, F_2ClP, F_2BrP, and F_2IP can be rationalized in terms of an earlier polarization model.[6,9] If it is accepted that the coordination of phosphorus ligands is strongly field dependent and if it is further accepted that the field generated by a given acid such as the boron of BH_3 is determined by the distance between the boron and phosphorus nuclei, then the stability trend in the series $F_3P \cdot BH_3$, $F_2ClP \cdot BH_3$, $F_2BrP \cdot BH_3$, and $F_2IP \cdot BH_3$ follows. Direct repulsion between the hydridic hydrogens of BH_3 and the halogen X of PF_2X would restrict approach between P and B. It would be anticipated that in the series $F_2ClP \cdot BH_3$, $F_2BrP \cdot BH_3$, and $F_2IP \cdot BH_3$ the boron–phosphorus bond distance would increase as the size of the halogen increased. It might also be anticipated that a "bent molecule" geometry may result as observed with $F_2HP \cdot BH_3$;[25] however, with X = halogen a distortion in the opposite direction would be expected, *i.e.*, $\alpha < \beta$.



Thus as the size of the halogen increases, the B–P distance would increase and/or the molecule would distort and the stability of the complex would decrease. For $F_2HP \cdot BH_3$ quite the opposite is true. Pasinski and Kuczkowski[25] have found that $F_2HP \cdot BH_3$ is distorted such that the BH_3 group is tipped toward the hydrogen of F_2HP. This geometric anomaly is consistent with electrostatic attraction between the protonic hydrogen of F_2HP and the hydridic hydrogens of BH_3.[25] The electrostatic attraction may be, in part, responsible for the unusual stability of $F_2HP \cdot BH_3$.

Product yields obtained in the reaction of B_5H_{11} with F_2XP suggest that the base strength of F_2XP toward B_4H_8 also decreases in the order X = F > Cl > Br > I. Under comparable conditions, $F_2XP:B_5H_{11}$ = 2:1 reactant ratio, the yields were 80% F, 70% Cl, 65% Br, and 50% I. The products obtained when $F_2XP:B_5H_{11}$ = 1:1 offer evidence that B_4H_8 is a stronger acid than BH_3 toward F_2XP. In fact the value of the ratio $F_2ClP \cdot B_4H_8:F_2ClP \cdot BH_3$ of 4.3 clearly indicated that under comparable conditions B_4H_8 competes more effectively for a limited supply of base than does BH_3. Similar experiments for B_4H_{10} and F_2ClP gave a ratio $F_2ClP \cdot B_3H_7:F_2ClP \cdot BH_3$ of 1.3; however this system is not as reliable because of competing reactions.[25] The data indicate increasing acid strength in the series $BH_3 < B_3H_7 < B_4H_8$ in accordance with earlier predictions regarding electron delocalization in borane frameworks.[10]

Structure of Adducts. Structural Implications of the Nmr Data. $F_2XP \cdot BH_3$ Complexes.—The nmr data for $F_3P \cdot BH_3$ have been reported[9] and are in agreement with known structural information.[26–29] The ^1H spectrum of $F_2ClP \cdot BH_3$ contains the expected 1:1:1:1 quartet (J_{HB} = 108 Hz) each member of which consists of an overlapping doublet (J_{HBP} = 17 Hz) of triplets (J_{HBPF} = 17 Hz). The overlapping generates an apparent quartet pattern. For $F_2BrP \cdot BH_3$ and $F_2IP \cdot BH_3$ only the broad 1:1:1:1 quartet is visible (J_{HB} = 117 Hz). The ^{11}B spectrum of $F_2ClP \cdot BH_3$ and $F_2BrP \cdot BH_3$ appears as a 1:3:3:1 quartet (J_{BH} = 105 Hz) with each member further split into a doublet (J_{BP} = 27 for X = Cl, 19 Hz for X = Br). This doublet fine structure was not resolved in $F_2IP \cdot BH_3$ at −80°. The ^{19}F spectrum for complexes with X = Cl, Br, or I consists of a doublet (J_{FP} = 1350 Hz), each member of which is split into a 1:3:3:1 quartet (J_{FPBH} = 20 Hz). The ^{31}P spectrum for complexes with X = Cl, Br, or I showed a widely spaced triplet (J_{PF} = 1350 Hz) with no resolvable fine structure using the equipment available to us. The foregoing nmr patterns provide unequivocal evidence for an ethane type structure with a direct B–P bond.

Since the paramagnetic term is believed to dominate ^{11}B chemical shifts,[30,31] the ^{11}B nucleus should become *less shielded* as electron donation to boron *decreases*. The observed ^{11}B chemical shifts of the halodifluorophosphine–borane(3) complexes show this trend clearly. Only $\delta(^{11}B)$ of $F_2HP \cdot BH_3$ is out of line, a fact which might be interpreted as suggesting that the unusual stability of $F_2HP \cdot BH_3$ may indeed be due to an added attraction between hydridic and protonic hydrogens.

To the extent that chemical shift data for protons attached to boron are controlled by the diamagnetic term, one would expect *increasing* base strength of the ligand to be associated with more effective transfer of electron density to the borane hydrogens or *increasing* ^1H shielding with *increasing* ligand base strength. This expected trend is seen in the $\delta(^1H)$ data of the halodifluorophosphine–borane(3) complexes. This trend is not easily understandable in terms of a hyperconjugation model which would suggest *greater* deshielding of the B–H protons in $F_3P \cdot BH_3$ compared to $F_2IP \cdot BH_3$. Once more $F_2HP \cdot BH_3$ is out of line with the predicted trend in chemical shifts (this most stable member of the series should have the largest upfield

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(25) J. P. Pasinski and R. L. Kuczkowski, *J. Chem. Phys.*, **54**, 1903 (1971).

(26) R. T. Paine and R. W. Parry, *Inorg. Chem.*, **11**, 268 (1972).

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(28) R. C. Taylor and T. C. Bissott, *ibid.*, **25**, 780 (1956).

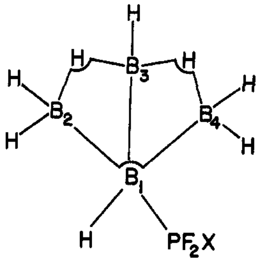
(29) R. J. Wyma, Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1964.

(30) J. W. Emsley, J. Feeny, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1965.

(31) G. R. Eaton and W. N. Lipscomb, "Nmr Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

shift in $\delta(^1H)$). The observed, marked downfield shift suggests some deshielding of the B–H protons, perhaps through the electrostatic attraction to the P–H hydrogen mentioned above. Trends in chemical shift values for ^{19}F and ^{31}P are more complex and will be considered when more data are available.

The nmr spectra of $F_2XP \cdot B_4H_8$ (X = F, Cl, Br, I) are similar to spectra obtained for $F_3P \cdot B_4H_8$[18,32] and $(CH_3)_2NF_2P \cdot B_4H_8$.[33] The structure of the latter has been determined by X-ray diffraction[34] and is schematically represented below. The ^{11}B spectrum of each complex shows a low-field multiplet and a high-field triplet of area ratio 3:1. The low-field multiplet is composed of an overlapping doublet (J_{B_3H} = 122–136 Hz) and triplet (J_{B_2H,B_4H} = 123–136 Hz) in an area ratio of 1:2. The high-field triplet is assigned to B_1. The triplet for B_1 is currently interpreted in terms of a near equivalence in the coupling constants J_{B_1H} and J_{B_1P}.[33] Apparent equivalence of coupling constants has been noted before in selected boron–phosphorus coordination compounds.[33,35,36] The spectra leave little question relative to the gross structural features of $F_2XP \cdot B_4H_8$ compounds. It is interesting that the correlation between complex stability and J_{BP} noted for borane(3) complexes is not clearly apparent in the data available here for the B_4H_8 system. Similarly there is no relationship between ν(B–H) and complex stability. The latter fact is expected since five of the six nonbridging B–H units are well removed from the coordination site.



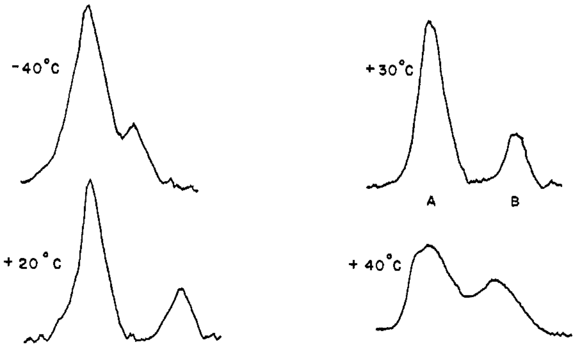


Figure 2.—Temperature dependence of upfield members of the pair of doublets in the ^{19}F nmr spectrum of $F_2ClP \cdot B_4H_8$.

The ^{19}F spectrum of each tetraborane(8) complex (X = F, Cl, Br, I) consists of a pair of widely spaced doublets (J_{FP} = 1260–1360 Hz) with a small chemical shift difference between members of the doublets. Somewhat related behavior was found for $(CH_3)_2NF_2P \cdot B_4H_8$ by Centofanti and Parry[33] and was interpreted in terms of two structural isomers which become identical as the temperature is increased. Only a single doublet was observed for $F_2HP \cdot B_4H_8$,[33] a fact which suggested only a single structure.

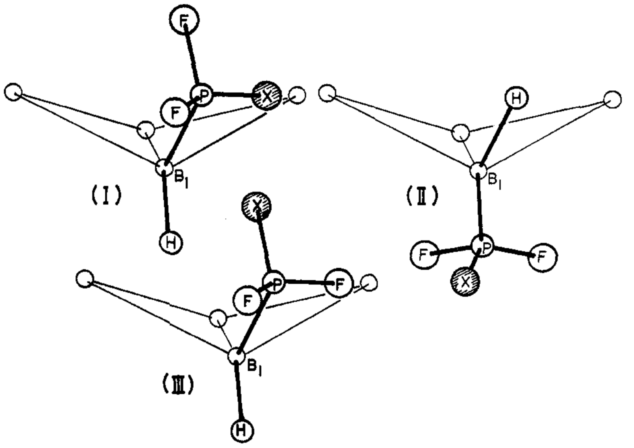
The ^{19}F pairs of doublets of $F_2XP \cdot B_4H_8$ (X = F, Cl, Br, I) show marked temperature dependence in the range −40 to +40°. (See Figure 2.) Peak separations Δ_{AB} and relative peak areas I_A/I_B for the $F_2ClP \cdot B_4H_8$ upfield members are shown as a function of temperature in Table I. The peaks collapse above 40° into a very broad signal. The temperature changes are reversible except for some nonreversible decomposition of the complex which begins above +30°.

TABLE I

TEMPERATURE DEPENDENCE OF THE ^{19}F NMR SPECTRUM OF $F_2ClP \cdot B_4H_8$

Temp, °C	Δ_{AB}, Hz	I_A/I_B	Temp, °C	Δ_{AB}, Hz	I_A/I_B
−40	46.2	4.0	+20	84.8	2.6
−20	55.7	3.3	+30	76.9	2.5
0	67.6	2.9	+40	~60	. . .

Three possible geometrical isomers are shown schematically here. Structure I represents the known solid-state structure of $(CH_3)_2NPF_2 \cdot B_4H_8$ which places the phosphorus in the "up" position with respect to the borane V-shaped cage. Structure II exchanges the terminal hydrogen and phosphorus positions on B_1 so the phosphorus is in the "down" position. Structure III represents a phosphorus "up" structure similar to I, but III places the X substituent in the proximity of the borane cage, whereas I has the substituent pointed directly away from the cage. Interconversion of isomers seems to be best represented by a model involving a I ⇄ III process, which relates isomers by a simple rotation of the ligand about the B–P coordinate bond. Clearly $F_2HP \cdot B_4H_8$ exhibits no isomers, and in terms of the I ⇄ III model, F_2HP must either experience no restriction to rotation or it is locked into a single conformation and cannot rotate at all. The remaining complexes, where X = $(CH_3)_2N$, F, Cl, Br, or I, apparently experience restricted rotation as evidenced by the *pair* of doublets in the ^{19}F spectrum. If steric factors (nonbonded repulsions) are responsible for the restricted rotation, then the rotation should become increasingly difficult in the order H < F < Cl < Br < I < $N(CH_3)_2$ and the coalesence temperature should increase in the same order. Unfortunately de-



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[34] M. D. La Prade and C. E. Nordman, *ibid.*, **8**, 1669 (1969).

[35] J. G. Verkade, R. W. King, and C. W. Heitsch, *ibid.*, **3**, 884 (1964).

[36] A. B. Burg and H. Heinen, *ibid.*, **7**, 1021 (1968).

composition of the samples in the vicinity of the coalescence temperature has prohibited verification of this series.[37]

Interconversions involving structure II, *e.g.*, a I ⇄ II process, would depend on the folding motion of the B_4H_8 cage along the B_1–B_3 bond (B_2 and B_4 moving up and down). This is plausible, but it provides no explanation for the lack of isomers in $F_2HP \cdot B_4H_8$ unless the proposed electrostatic attractions prevent the folding.

Acknowledgments.—We gratefully acknowledge support from the National Science Foundation through Grant GP-14873 and from the Petroleum Research Fund through Grant PRF-2089-A3. We also thank the National Aeronautics and Space Administration for a traineeship to R. T. Paine, 1966–1969.

(37) It should also be noted that electrostatic repulsion–attraction forces may be important in the I ⇄ III process. Interaction between protonic P–H and hydridic hydrogens of the tetraborane(8) group could well create "locked" conformation, structure III, for $F_2HP \cdot B_4H_8$. Electrostatic *repulsions* between the B_4H_8 cage and X for the ligand might be expected to decrease in the order: F > $(CH_3)_2N$ > Cl > Br > I.

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Magnetic Resonance Spectra of Octaborane(12), Octaborane(18), and 2-[2′-Pentaboran(9)yl]pentaborane(9)

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Proton and boron-11 nmr spectra of B_8H_{12}, B_8H_{18}, and 2,2′-$(B_5H_8)_2$ obtained at 51.7 kG are presented and discussed in terms of their structural significance.

Introduction

Until the advent of spectrometers employing superconducting magnets, proton magnetic resonance spectra of boron hydrides have been of only secondary value in structure elucidation.[1] The small range of chemical shifts and consequent overlap of the ^{11}B–H quartets, as well as the interference from the ^{10}B–H septets and nuclear quadrapole broadening from both isotopes (80% ^{11}B, $I = {}^3/_2$; 20% ^{10}B, $I = 3$), have limited pmr studies to the smaller symmetric hydrides. Recent studies have shown the value of reexamining the pmr spectra of all boron hydrides at higher field strengths.[2-4] In addition to assigning all the proton resonances of B_4H_{10}, B_6H_{10}, and B_6H_{12}, these studies proved that such spectra can differentiate between equatorial and axial $-BH_2$ proton resonances and separate signals arising from magnetically distinct bridge protons. Here we have extended these observations to the pmr spectra of three of the newer boron hydrides.

Experimental Section

Octaborane(12) and octaborane(18) were prepared by standard synthetic methods.[5,6] The 2-[2′-pentaboran(9)yl]pentaborane(9),[7] 2,2′-$(B_5H_8)_2$, was prepared by reaction of diborane and pentaborane(9) in a hot-cold circulating system.[8] All materials were of normal isotopic distribution (80% ^{11}B; 20% ^{10}B) and were purified by standard high-vacuum techniques.

Proton and boron spectra were recorded on a Varian Associates HR-220 spectrometer using standard Varian low-temperature accessories. Proton spectra were referenced to tetramethylsilane (δ 0.0 ppm) as an external standard.

Boron-11 spectra were frequency swept at 70.6 MHz with a commercially available Varian Associates probe. Chemical shifts were obtained using an external sample of boron trifluoride–diethyl etherate and are referred to $BF_3 \cdot O(C_2H_5)_2 = 0$ ppm. Spectra of B_8H_{18} and 2,2′-$(B_5H_8)_2$ were poorly resolved; however, dilution of these samples with carbon disulfide resulted in pmr spectra of better resolution.

Results and Discussion

Octaborane(12).—The recent suggestion[9] (based on an accidentally overlapped low-field ^{11}B nmr spectrum) that liquid B_8H_{12} exists as a mixture of eight tautomers to give apparent C_{4v} symmetry is untenable in light of the high-field spectra presented here (Figure 1). The 220-MHz pmr spectrum of B_8H_{12} (Figure 2) displays, in order of decreasing field strength, *two* nonequivalent bridge resonances, each of intensity 2, two quartets, each of intensity 2, and an interesting quartet with skewed appearance of intensity 4. This low-field quartet arises from the low-field doublet of intensity 4 in the boron-11 spectrum arising from the 3, 5, 6, and 8 boron atoms.[10] The apparent equivalence of these four boron atoms and the attached terminal protons may result either from accidental overlap at the field strengths employed or from a dynamic process occurring in B_8H_{12} which effectively raises the C_s symmetry observed in crystalline B_8H_{12}[11] to C_{2v} for liquid B_8H_{12}. A dynamic process could consist of rapid tautomerism

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(1) (a) R. Schaeffer, "Progress in Boron Chemistry," Vol. 1, H. Steinberg and A. L. McCloskey, Ed., Macmillan, New York, N. Y., 1964, p 422; (b) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

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(7) All boron cage nomenclature and numbering orders are those set forth under the new rules which appeared in *Inorg. Chem.*, **7**, 1945 (1968). Here we prefer the shortened name 2,2′-decaborane(16) or the formulation 2,2′-$(B_5H_8)_2$.

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(10) The assignments of the ^{11}B nmr resonances are supported by 19.3-MHz spectra of labeled B_8H_{12} prepared from μ-4,6,8-$KB_9H_6D_8$: P. C. Keller, unpublished results; P. C. Keller, *Inorg. Chem.*, **9**, 75 (1970).

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