CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF UTAH, SALT LAKE CITY, UTAH 84112

Acid-Assisted Base-Displacement Reactions. The Preparation of Halodifluorophosphine- and Carbonyl-Triborane(7) Complexes

BY R. T. PAINE AND R. W. PARRY*[1]

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The base displacement of dimethyl ether from dimethyl ether–triborane(7) is greatly facilitated in special cases if a specific acid such as BF_3 is used to complex the liberated ether. This perturbation of a standard base-displacement reaction has made it possible to prepare and characterize the formerly unattainable triborane(7) adducts: $F_3PB_3H_7$, $F_2ClPB_3H_7$, $F_2BrPB_3H_7$, and OCB_3H_7. Data indicate that the order of base strength toward B_3H_7 as a reference acid is $F_3P > F_2ClP > F_2BrP$. The acid-assisted base-displacement process may well be generally helpful in the preparation of other presently unknown compounds.

The close similarity of F_3PBH_3 and $OCBH_3$ has been recognized for many years. Both F_3PBH_3 and $OCBH_3$ adducts can be prepared by symmetrical cleavage of the B_2H_6 molecule.[2,3] Burg and Spielman[4] were the first to extend the symmetrical cleavage concept to pentaborane(11) utilizing the reaction of B_5H_{11} and CO: $B_5H_{11} + CO \rightarrow OCB_4H_8 + OCBH_3$. It has recently been shown[5] that PF_3 and B_5H_{11} undergo a similar type of symmetrical cleavage process.

Data are available to show that the strength of a boron Lewis acid usually increases with the size of the boron framework.[6] This generalization suggests that B_3H_7 should be a stronger Lewis acid than BH_3. Indeed, considerable evidence in support of this premise is available[7] when nitrogen bases are used as the reference.

In view of the foregoing facts it seemed strange that repeated attempts to prepare $F_3PB_3H_7$ and OCB_3H_7 by symmetrical cleavage of tetraborane(10) or by base displacement from weak-base adducts of triborane(7) were not successful. In an earlier study in this laboratory,[8] the sealed-tube reaction of F_3P and B_4H_{10} at room temperature and at pressures exceeding 5 atm produced F_3PBH_3, B_2H_6, and unidentified volatile materials but no $F_3PB_3H_7$. In the same study,[8] the reaction between NaB_3H_8 and anhydrous HCl in liquid PF_3 at −78° was tried, but no $F_3PB_3H_7$ was identified. More recently Ritter and Deever[9] have studied the reaction of $(CH_3)_2OB_3H_7$ and excess PF_3. Interestingly enough the weak base PF_3, present in large excess, gave rise to degradation of the triborane(7) fragment with formation of the diborane(4) complex $(F_3P)_2B_2H_4$. Up to the present time no attempt to prepare $F_3PB_3H_7$ or OCB_3H_7 had been successful. This paper reports the successful synthesis, in high yields, of $F_3PB_3H_7$, $F_2ClPB_3H_7$, $F_2BrPB_3H_7$, and OCB_3H_7 by a modification of the normal displacement process. The new synthetic procedure, identified as an acid-assisted base-displacement reaction, can be summarized by the equation

$$(CH_3)_2OB_3H_7 + \underset{\substack{\text{or}\\ \text{CO(excess)}}}{F_2XP} + BF_3 \longrightarrow \underset{\substack{\text{or}\\ OCB_3H_7}}{F_2XPB_3H_7} + (CH_3)_2PBF_3$$

This simple perturbation has a dramatic influence on the synthetic utility of the base-displacement process and has interesting implications relative to the mechanistic details of the reaction.

Experimental Section

Equipment.—Standard high-vacuum techniques were used for the manipulation of the volatile compounds. Mass spectra were recorded on a Perkin-Elmer Model 270 mass spectrometer. Infrared spectra were recorded on a Beckman IR 20 spectrometer operating between 4000 and 400 cm^{-1}, with a 70-mm path length gas cell fitted with KBr windows. The nmr spectra were recorded on a Varian HA/HR 100 instrument operating at 32.1 MHz (^{11}B) and 94.1 MHz (^{19}F).[10] An external standard, $(CH_3)_3B$, was used for the ^{11}B nmr spectrum reference, and an internal standard, $CFCl_3$, was used for the ^{19}F nmr reference. The $CFCl_3$ also served as the sample solvent.

Materials.—Tetraborane(10) was prepared by the "hot–cold tube" pyrolysis of diborane(6) as described by Klein, Harrison, and Solomon.[11] The $(CH_3)_2OB_3H_7$ samples were prepared and purified as described by Deever and Ritter.[12] Trifluorophosphine was purchased from Ozark Mahoning Co. and was distilled through a −160° trap before using. The F_2ClP and F_2BrP ligands were prepared and purified by literature procedures.[13]

Reaction of B_4H_{10} with F_2XP.—A 4.2-mmol sample of B_4H_{10} and a 9.0-mmol sample of F_2XP, X = F, Cl, or Br, were condensed into a 7.5-ml Pyrex tube, sealed off under vacuum and then held at 0° for 3–5 days. Each tube was opened through a break-seal and the volatile products were vacuum distilled and retained as follows: $(F_3P)_2B_2H_4$, −126°; $(F_2ClP)_2B_2H_4$ and $(F_2BrP)_2B_2H_4$, −96°; F_3PBH_3, −160°; F_2ClPBH_3 and F_2BrPBH_3, −126°. No triborane(7) complexes were *isolated* from the distillation; however, very small amounts were detected by ^{19}F nmr analysis in the $(F_2XP)_2B_2H_4$ samples. When the same reactions were run in sealed nmr tubes with a 1.5 reactant ratio of B_4H_{10} to PF_2X, small amounts (*ca.* 10%) of triborane(7) complexes were detected by ^{19}F nmr but no diborane(4) complexes. Most of the sample consisted of unreacted B_4H_{10}, PF_2X, and a little B_2H_6.

Reaction of $(CH_3)_2OB_3H_7$ with F_2XP.—A 2.0-mmol sample of $(CH_3)_2OB_3H_7$ was prepared in an nmr tube fitted with a Teflon stopcock. A 2.0-mmol sample of F_2XP, X = F, Cl, or Br, was

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[1] To whom correspondence should be addressed at the University of Utah.

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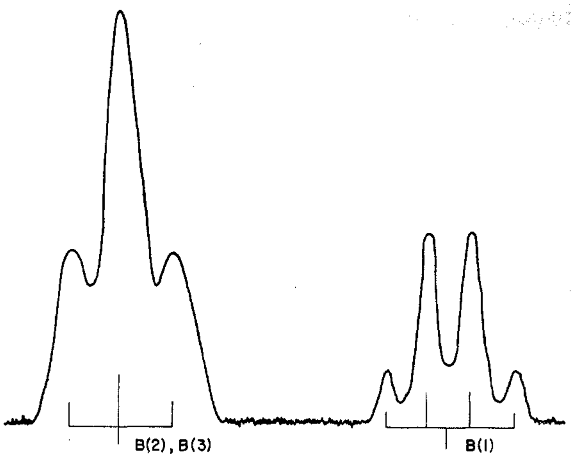


Figure 1.—Schematic representation of the ^{11}B nmr spectrum of the $F_2XPB_3H_7$ complex at −45°.

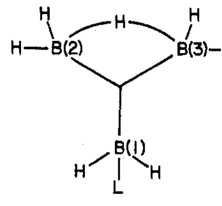
added and the tube was sealed off under vacuum. Each tube was held at 0° for 30 min; each ^{19}F nmr spectrum indicated 20–35% yields of triborane(7) complexes based on peak areas. Long reaction times and/or high ligand concentrations produced significant amounts of diborane(4) complexes. Displacement of $(CH_3)_2O$ was used to estimate the relative base strength of the F_2XP ligands toward B_3H_7.

Acid-Assisted Base-Displacement Reactions.—A 3.2-mmol sample of $(CH_3)_2OB_3H_7$ was prepared in a 10-ml reaction tube fitted with a Teflon stopcock. To the $(CH_3)_2OB_3H_7$, equal amounts (3.0 mmol) of F_2XP and BF_3 were added, the stopcock was closed, and the tube was allowed to warm to about 0° with agitation. The reaction began to occur well below 0° as evidenced by white cloud formation above the liquid phase. The tube was cooled to −78° after approaching 0°, and the warming–cooling cycle was repeated until no further cloud formation resulted (*ca.* five cycles). Vacuum distillation of the volatile products through −78, −126, and −196° retained each $F_2XPB_3H_7$ complex at −126°. The material retained at −78° was analyzed by ^{11}B nmr and found to be $(CH_3)_2OBF_3$. The yields of $F_2XPB_3H_7$ were high (*ca.* 90%). The complexes were characterized chemically through their reaction with an equal amount of $(CH_3)_2NPF_2$. The resulting $(CH_3)_2NF_2PB_3H_7$ was isolated and identified by its ^{19}F nmr spectrum.[14] The OCB_3H_7 complex was prepared in a similar fashion except the reactant ratios were 1.0:1.0:2.0 for $(CH_3)_2OB_3H_7$:BF_3:CO. The yields (*ca.* 60%) were also lower than in the $F_2XPB_3H_7$ system. The excess carbon monoxide did not appear to produce any diborane(4)–carbonyl complex. The OCB_3H_7 was retained at −126° during distillation.

Properties of $F_2XPB_3H_7$ and OCB_3H_7 Complexes.—The infrared spectra of the $F_2XPB_3H_7$ complexes are similar to those of other B_3H_7 complexes.[14,15] The absorptions (cm^{-1}) and tentative assignments are as follows: for $F_3PB_3H_7$: 2550 [ν_{as}(B–H)], 2480 [ν_s(B–H)], 2110, 1570 [bridge modes], 1160, 1050 [$\delta(BH_2)$], 970 [ν_{as}(P–F)], 850 [ν_s(P–F)], 590 [ν(P–B)], 470 [$\delta(PF_2)$], 440 [$\delta(PF_2)$]; for $F_2ClPB_3H_7$: 2590, 2500, 2150, 1610, 1120, 1070, 930, 610, 540 [ν(P–Cl)], 410. (The symbols used above are ν for stretch and δ for deformation. All frequencies are in reciprocal centimeters and the assignments for $F_2ClPB_3H_7$ are the same as those for $F_3PB_3H_7$ except as indicated.) The ^{11}B and ^{19}F nmr spectral parameters are summarized in the order F_2XP, X = F, Cl, and Br, and OCB_3H_7: $\delta(B_2, B_3)$ 98.1, 97.3, 97.3, 95.0 ppm; J(B(2)H, B(3)H) = 113, 113, 113, 140 Hz; δ(B(1)) 139.1, 131.2, 125.7, 142.5 ppm; J(B(1)H = B(1)P) = 102, 90, 90, 124 Hz; δ(F) 59.7, 46.6, 43.1 ppm; J(PF) = 1373, 1332, 1325 Hz. (The spectra were recorded at −45° and the chemical shifts are relative to $(CH_3)_3B$ or $CFCl_3$.) The mass spectra were recorded at 60 eV and the principal peaks are listed here [*m/e* (assignment) relative intensity]: 128 ($F_3PB_3H_7^+$) 1; 128–122 ($F_3PB_3H_x^+$ envelope) 7 for the most intense peak at *m/e* 126; 88 (F_3P^+) 65; 76–67 ($B_6H_x^+$) 8 at *m/e* 74; 69 (F_2P^+) 100; 66–55 ($B_5H_x^+$) 25 at *m/e* 62; 55–44 ($B_4H_x^+$) 23 at *m/e* 48; 50 (FP^+) 79; 40–33 ($B_3H_x^+$) 20 at *m/e* 38; 31 (P^+) 45; 144 ($F_2ClPB_3H_7^+$) 1; 144–139 ($F_2ClPB_3H_x^+$) 9 at *m/e* 141; 104 (F_2ClP^+) 57; 76–67 ($B_6H_x^+$) 10 at *m/e* 74; 69 (F_2P^+) 100; 66–55 ($B_5H_x^+$) 33 at *m/e* 62; 54–44 ($B_4H_x^+$) 28 at *m/e* 48; 50 (FP^+) 81; 40–33 ($B_3H_x^+$) 16 at *m/e* 38; 35 (Cl^+) 42; 31 (P^+) 51; 188 ($F_2BrPB_3H_7^+$) 1; 188–183 ($F_2BrPB_3H_x^+$) 8 at *m/e* 185; 148 (F_2BrP^+) 52; 79 (Br^+) 31; 76–67 ($B_6H_x^+$) 9 at *m/e* 74; 69 (F_2P^+) 100; 66–55 ($B_5H_x^+$) 12 at *m/e* 62; 54–44 ($B_4H_x^+$) 11 at *m/e* 48; 50 (FP^+) 67; 40–33 ($B_3H_x^+$) 6 at *m/e* 38; 31 (P^+) 29.

Results and Discussion

The mass spectra, infrared frequencies, and nmr spectra are analogous to the corresponding data for authentic base–triborane(7) complexes. Some details are of interest. The ^{11}B nmr spectra of the $F_2XPB_3H_7$ complexes are similar and one is shown schematically in Figure 1. This spectrum is consistent with a 1104 framework representation[16] as shown here. The low-field triplet (relative intensity 2) is assigned to the B(2)–BH_2 and B(3)–BH_2 units while the high-field quartet (relative intensity 1) is assigned to B(1). The quartet structure appears to result from coupling constant equivalence $J_{B(1)H} = J_{B(1)P}$. Similar equivalence has been noted before in selected boron–phosphorous compounds.[5,17–21] The ^{11}B nmr spectra are not temperature dependent in the range −40 to +30°. The ^{19}F nmr spectra are similar for each complex and show a widely spaced doublet (J_{PF}) with no currently resolvable fine structure. The ^{11}B nmr spectrum of OCB_3H_7 shows a low-field triplet, assigned to B(2)–BH_2 and B(3)–BH_2 units and a high-field triplet assigned to the B(1)–BH_2 unit, in a 2:1 area ratio.



The use of BF_3 to assist in the preparation of B_3H_7 adducts from $(CH_3)_2OB_3H_7$ appears to be quite obvious in retrospect, yet the earlier data on the reactions of BF_3 with etherate boranes left room for considerable doubt. Deever and Ritter[12] had previously examined the reaction between BF_3 and $(CH_3)_2OB_3H_7$. The products included a complex mixture of boron hydrides including B_4H_{10}, B_5H_9, B_5H_{11}, and B_6H_{12}—products probably resulting from the combination of two B_3H_7 fragments. Therein lies the key to the acid-assisted based-displacement reaction. The ligands PF_2X and CO have been used to "trap" the activated B_3H_7 fragment before the combination reaction can occur. These results suggest a mechanism summarized by the equations

$$(CH_3)_2OB_3H_7 + BF_3 \xrightarrow[\text{determining for } PF_2X]{\text{believed to be rate}} (CH_3)_2OBF_3 + B_3H_7^*$$

$$B_3H_7^* + PF_2X \xrightarrow{\text{fast}} F_2XPB_3H_7$$

$$B_3H_7^* + CO \xrightarrow[\text{determining for CO}]{\text{believed to be rate}} OCB_3H_7$$

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[20] A. D. Norman and R. Schaeffer, *J. Amer. Chem. Soc.*, **88**, 1143 (1966).

[21] A recent observation by Lory and Ritter[14] suggests that second-order factors may be responsible for apparent coupling constant equivalence in the triborane(7) system.

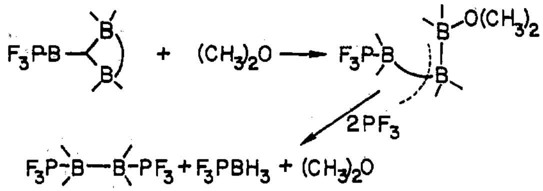
Rapid hydrogen tautomerism in B_3H_7 would make all boron atoms equally available for attack; hence the overall reaction with PF_2X ligands would be expected to proceed rapidly with high yields in agreement with the observations.

Conversely, the unassisted base-displacement reactions proceed much more slowly, with reduced yields and with side reactions. This behavior may be summarized by the equations

$$(CH_3)_2OB_3H_7 \rightleftharpoons (CH_3)_2O + B_3H_7^*$$

$$B_3H_7^* + PF_2X \xrightarrow{\text{fast}} F_2XPB_3H_7$$

The first step is not shifted to the right as in the acid-assisted reaction since the ether is not complexed; therefore, the overall reaction is slower. In addition, the uncomplexed ether is available for subsequent attack on the borane framework of $F_2XPB_3H_7$. This attack may be responsible for the degradation to diborane(4) as outlined by Lory[14] and as indicated schematically here. In the case where the attacking



ligand is carbon monoxide, the relatively low yields seem to indicate that the OCB_3H_7 complex is somewhat less stable or that the CO requires activation before addition to the B_3H_7 fragment.

The proposed mechanistic details are also consistent with the results of the direct reactions between B_4H_{10} and a base. As noted above, excess halodifluorophosphines react with B_4H_{10} in every case to give diborane(4) complexes; however, when B_4H_{10} is in excess, only small amounts of triborane(7) complexes and no diborane(4) complexes are obtained. Apparently the excess base again promotes framework degradation. Lory and Ritter[14] have suggested that B_4H_{10} reacts with $(CH_3)_3N$ to give the stable $(CH_3)_3NB_3H_7$ while PF_3 proceeds on to $(F_3P)_2B_2H_4$ because the $(CH_3)_3N$ stabilizes the B_3H_7 fragment by inductive electron donation toward B(2) and B(3) (the uncomplexed units of the fragment) thereby making them less electrophilic or less open to base attack. The weaker base, PF_3, on the other hand leaves B(2) and B(3) more electrophilic and therefore open to further attack and degradation.

An alternative argument suggests that the base–triborane(7) adduct dissociates and it is the free B_3H_7 fragment which is attacked by F_2XP to produce the B_2H_4 fragment. This argument would also favor stabilization of the B_3H_7 fragment by stronger bases. The question cannot be resolved without more definitive rate data. It is significant that $F_3PB_3H_7$ is rendered less stable by excess F_3P at 0°, suggesting that attack is on the $F_3PB_3H_7$ molecule, since dissociation to give B_3H_7 would be retarded by excess F_3P. This fact would be consistent with the suggestions of Ritter and coworkers.

Relative Stability.—No quantitative measurements of relative stabilities of base–triborane(7) complexes have been accomplished to date; however, a few qualitative estimates are available in the literature. As mentioned above $(CH_3)_3N$ replaces BH_3 in B_4H_{10};[7] hence $(CH_3)_3N$ is a stronger base than BH_3 toward B_3H_7 as a reference acid. The same appears to be true for the bases $(CH_3)_2NPF_2$[14,15] and F_2HP.[14]

Additional qualitative stability information was sought within the $F_2XPB_3H_7$ complexes. The following reaction was used to estimate the relative base strengths of the F_2XP ligands toward B_3H_7

$$F_2XP + (CH_3)_2OB_3H_7 \underset{\text{sealed tube}}{\overset{0°,\ 2\ \text{hr}}{\rightleftharpoons}} F_2XPB_3H_7 + (CH_3)_2O$$

The reactions were carried out in a 1:1 mole ratio of reactants with X = $(CH_3)_2N$, F, Cl, and Br. The resulting mixtures, after 2 hr reaction time, were analyzed using ^{19}F nmr peak areas. The calculated yields of $F_2XPB_3H_7$ follow: X = $N(CH_3)_2$, 97%; F, 35%; Cl, 30%; Br, 20%. True equilibrium is not established in these reactions as evidenced by the small yields of diborane(4) complexes detected by the nmr signal. Nonetheless the reaction does provide a crude test for relative base strength. The yields imply a decreasing trend in base strength for F_2XP toward B_3H_7 in the order X = $N(CH_3)_2 \gg F > Cl > Br$. This order is identical with that observed in gas-phase dissociation studies[5] of borane(3) complexes with the same bases.

Other sometimes useful indicators of relative stability in acid–base complexes such as B–H stretching frequencies, J_{PB} or J_{BH}, and chemical shifts do not appear to be of much help in the triborane(7) system.[5] One trend in chemical shifts may be noteworthy however. The ^{11}B chemical shifts for the base-bonded boron atom (B_1) follow the order: F_2HP, 152;[14] F_3P, 139.1; $(CH_3)_2NPF_2$, 137.2; F_2ClP, 131.2; F_2BrP, 125.7. The downfield shift toward $(CH_3)_3B$ suggests a decreasing electron density at B_1 and hence a weaker P–B coordinate bond. Only $(CH_3)_2NPF_2B_3H_7$ appears to be out of line with the chemical results.

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