DISPLACEMENT REACTIONS ON TRIMETHYLAMINE-FLUOROBORANES J. M. VanPaasschen and R. A. Geanangel Chemistry Department, University of Houston

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Recently we reported (1) that the order of methyl proton chemical shifts in trimethylamine adducts of fluorinated boranes suggested that the order of Lewis acid strengths in such compounds was

$$BH_3 \stackrel{\checkmark}{=} BF_3 > BH_2 > BHF_2$$

Since this result was unexpected from considerations of the inductive effect, we have studied the system further, looking at a number of displacement reactions chosen to illucidate relative adduct strengths. The technique used was essentially the same as that used by Shore (2) and Cowley (3) with a weighed quantity of adduct placed in an nmr tube, an equimolar quantity of Lewis acid condensed in along with an appropriate volume of methylene chloride, and the tube sealed under vacuum. The tubes were warmed to room temperature and their proton spectra recorded as soon as practical. Each sample was studied over a period of time until it was certain that no further changes were occuring. The products of such reactions were generally identified by their proton nmr chemical shift and in some cases the identification was confirmed by boron-ll nmr.

One objective of these studies was the preparation of the free acid  $BH_2F$ , which has apparently not been prepared previously, and  $BHF_2$ , for which there are several known preparations. <sup>(4,5,6)</sup> If a straightforward borane displacement reaction is operative, these compounds are expected as products when their respective trimethylamine adducts are treated with a stronger

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borane Lewis acid. Our choice for such an acid, based on the proton nmr chemical shifts of the adducts, was boron trifluoride. The results of our experiments are represented by the equations below:

$$(CH_3)_3NBH_2F + BF_3 \xrightarrow{CH_2Cl_2} (CH_3)_3NBF_3 + [BH_2F]$$

$$(CH_3)_3NBHF_2 + BF_3 \xrightarrow{CH_2Cl_2} (CH_3)_3NBF_3 + [BHF_2]$$

$$(CH_3)_3NBHF_2 + BF_3 \xrightarrow{CH_2Cl_2} (CH_3)_3NBF_3 + [BHF_2]$$

As indicated neither of the fluorinated boranes were obtained by displacement with boron trifluoride at room temperature; instead diborane and boron trifluoride were the observed products. The molar ratios of these products were as expected if the desired boranes had formed but then disproportionated, but we have no direct evidence for their existance as intermediates. Difluoroborane is notorious for such disproportionation and is especially difficult to separate from boron trifluoride. <sup>(6)</sup> Boron tribromide was tried as the displacing acid and the reaction with  $(CH_3)_3NBHF_2$  was run at  $-45^\circ$  in toluene. The volatile products were collected in a trap and then reacted with excess trimethylamine. Again the final products were principally  $(CH_3)_3NBH_3$  and  $(CH_3)_3NBF_3$ with variable proportions of  $(CH_3)_3NBHF_2$  up to about 12%.

The results of the foregoing experiments make it very difficult to assign relative acid strengths between  $BF_3$  and the partially fluorinated boranes since we are depending on the position of an equilibrium to indicate which acid competes more strongly for the base and the disproportionation removes one of the components of the equilibrium. This surely shifts the equilibrium. This surely shifts the equilibrium in a way extraneous to the problem under study. This same situation exists in the reaction between trimethylamine-borane and boron trifluoride which is known to give diborane almost quantitatively. The equilibrium lies almost completely to the right despite the fact that  $(CH_3)_3NBH_3$  and  $(CH_3)_3NBF_3$  appear to have almost equal B-N bond energies. <sup>(7)</sup> Presumably the removal of the intermediate  $BH_3$  by dimerization

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shifts the equilibrium in the observed direction. The same conclusion can be reached by considering the effect of the dimerization energy  $(2BH_3 + B_2H_6)$  on the overall free energy change and equilibrium constant for the displacement reaction. Such reactions cannot, therefore, be used to judge relative acid strengths.

While studying the  $BF_3/(CH_3)_3NBH_3$  reaction by means of proton nmr, we noted that approximately 3 mole%  $(CH_3)_3NBHF_2$  is present in the final reaction solution along with trimethylamine-trifluoroborane. To test whether this partially fluorinated adduct could have arisen form H-F exchange between  $(CH_3)_3$ -NBH<sub>3</sub> and  $(CH_3)_3NBF_3$ , a reaction between these compounds was carried out.

$$(CH_3)_3 NBH_3 + (CH_3)_3 NBF_3 \xrightarrow{35^\circ} No Reaction$$

No exchange was noted under these conditions so a similar reaction containing 1 mole%  $BF_3$  was set up. After 1/2 hour at 25°,  $(CH_3)_3 NBHF_2$  to the extent of about 3 mole% was detected in the reaction mixture. This strongly suggests that hydrogen-fluorine exchange takes place between the free acids rather than the adducts in this system. This is in concurrence with the known preparation of  $BHF_2$  from the reaction of  $B_2H_6$  and  $BF_3$  at elevated temperature in the absence of a solvent. <sup>(6)</sup> That  $BF_3$  in the free state is necessary for the formation of the  $BHF_2$ -adduct is demonstrated by the reaction shown below.

$$(CH_3)_3NBH_3 + (CH_3)_3NBF_3 \xrightarrow{1/2 \text{ mole } \%}_{B_2H_6} No \text{ Reaction}$$
  
 $CH_2Cl_2$ 

Despite the fact that diborane is a Lewis acid, no exchange occurs probably because diborane is too weak to displace  $BF_3$  from its adduct.

It is interesting to consider the results of using diborane as the displacing Lewis acid on the partially fluorinated adducts.

$$B_2H_6 + (CH_3)_3NBHF_2 \xrightarrow{CH_2Cl_2} (CH_3)_3NBH_3 + (CH_3)_3NBF_3 + 10\%(CH_3)_3NBHF_2$$

$$B_2H_6 + (CH_3)_3NBH_2F \xrightarrow{CH_2Cl_2} (CH_3)_3NBH_3 + (CH_3)_3NBF_3 + ^10\%(CH_3)_3NBHF_2$$

The fact that diborane displaces both  $BH_2F$  and  $BHF_2$  but not  $BF_3$  is a probably reliable indication that boron trifluoride is a stronger acid towards trimethylamine than either of the partially fluorinated boranes. It is likely however, that the observed ratio of  $BH_3$ ,  $BF_3$ , and  $BHF_2$  adducts reflects to a large degree the composition of  $B_2H_6$ ,  $BF_3$  and  $BHF_2$  in the gas phase and may not necessarily be significant as regards relative acid strengths.

In an attempt to determine which of the partially fluorinated boranes is the stronger acid towards trimethylamine, we have investigated displacement reactions using free difluoroborane as the competing Lewis acid.

$$BHF_{2} (BF_{3}) + (CH_{3})_{3}NBH_{3} \longrightarrow (CH_{3})_{3}NBH_{3} + (CH_{3})_{3}NBF_{3} + 10\%(CH_{3})_{3}NBH_{2}$$
  
$$BHF_{2} (BF_{3}) + (CH_{3})_{3}NBH_{2}F \longrightarrow (CH_{3})_{3}NBH_{3} + (CH_{3})_{3}NBF_{3} + 10\%(CH_{3})_{3}NBH_{2}F$$

Difluoroborane was prepared using the method described in reference 6, but we were unable to effectively separate the product from substantial quantities of boron trifluoride which were always present. This complicates the interpretation of the foregoing displacement reactions. It is tempting to view the results of the reaction of difluoroborane with trimethylamine-monofluoroborane as indicating that  $BHF_2$  is a stronger Lewis acid in this system than  $BH_2F$ , but in view of the results of the reaction with trimethylamine-borane, it is probably more likely that a gas phase equilibrium with  $B_2H_6$ ,  $BHF_2$ , and  $BF_3$  is once again established and that the composition of this dictates the ultimate composition in the solution.

Thus we conclude that  $BF_3$  is a stronger Lewis toward  $(CH_3)_3N$  than  $BH_2F$ ,  $BHF_2$  and  $B_2H_6$ , but we are unable, through displacement reactions, to determine the order of acidity of the last three compounds. Other studies will be required to confirm among or reject the order suggested by nmr studies. <u>Acknowledgment</u> The authors gratefully acknowledge the support of this work by the Robert A. Welch Foundation.

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