

# Notes

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## The Lability of a Boron-Nitrogen Bond

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In an effort to find new and convenient synthetic routes to  $\text{BH}_3$  adducts, the reaction of the corresponding  $\text{BF}_3$  adducts with various hydrides was investigated. Lithium hydride and  $\text{CH}_3\text{NH}_2\text{BF}_3$  gave no reaction after 5 days at room temperature. Sodium borohydride with  $\text{CH}_3\text{NH}_2\text{BF}_3$  and lithium borohydride with both  $\text{CH}_3\text{NH}_2\text{BF}_3$  and  $(\text{CH}_3)_2\text{NHF}_3$  gave small traces of the corresponding boranes along with other products.<sup>2</sup> Lithium aluminum hydride and  $(\text{CH}_3)_3\text{NBF}_3$  gave a volatile aluminum product which has not yet been characterized. Only the reaction between  $(\text{CH}_3)_3\text{NBF}_3$  and  $\text{LiBH}_4$  gave significant yields of the desired borane. Although this reaction is presumably general for tertiary amines, it offers little advantage over the method of Schaeffer and Anderson.<sup>3</sup> Nevertheless, the mechanism of this reaction is of some interest and prompted this report.

### Experimental

Reactions were carried out in evacuated sealed tubes, with 20 to 30 ml. of ethyl ether and 1 to 5 mmoles of reactants. Stirring was provided magnetically or by a mechanical shaker. Reactions were run at room temperature, usually for 24 hr. At the end of the reaction period, the tube was opened and checked for noncondensable gases. The contents were filtered, and volatile materials were removed from the filtrate under vacuum, first at  $-45^\circ$  to remove solvent, any  $(\text{CH}_3)_3\text{N}$ , and diborane, at  $25^\circ$  to remove  $(\text{C}_2\text{H}_5)_2\text{OBF}_3$  and  $(\text{CH}_3)_3\text{NBH}_3$ , and at  $60^\circ$  to remove  $(\text{CH}_3)_3\text{NBF}_3$ .

Exchange reactions were conducted between the pairs  $\text{LiBH}_4$  and  $\text{B}_2\text{H}_6$ ,  $(\text{CH}_3)_3\text{NBH}_3$  and  $\text{B}_2\text{H}_6$ ,  $(\text{CH}_3)_3\text{NBH}_3$  and  $\text{LiBH}_4$ ,  $(\text{CH}_3)_3\text{NBH}_3$  and  $\text{B}_2\text{H}_6$ , where one of each pair had been prepared from boron isotopically enriched to 95% in the lighter isotope. The exchanging mixtures were treated in a fashion similar to the preparative reactions. Components were separated and converted to  $(\text{CH}_3)_3\text{NBH}_3$  for isotopic analysis by the B-H splitting pattern in the proton magnetic resonance spectrum. The  $\text{B}^{10}:\text{B}^{11}$  ratio was determined as  $7/4$  of the ratio of the intensity of the outermost member of the H- $\text{B}^{10}$  septet to the intensity of the outermost member of the H- $\text{B}^{11}$  quartet. To test this method of analysis, two samples were prepared by weight from normal and enriched  $(\text{CH}_3)_3\text{NBH}_3$ . The  $\text{B}^{10}:\text{B}^{11}$  ratios observed were 0.69 and 2.5, and the calculated values were 0.71 and 2.8. Also, in the spectrum of normal  $(\text{CH}_3)_3\text{PBH}_3$ , the n.m.r. observed isotopic ratio is 0.23, in good agreement with the accepted  $0.19/0.81 =$

0.23 ratio. Thus the method appears to have an accuracy of  $\pm 10\%$  in the  $\text{B}^{10}/\text{B}^{11}$  range from 0.2 to 3.0 (and presumably to 5.0). Samples of  $(\text{CH}_3)_3\text{NBF}_3$  were checked for isotopic dilution by the methyl splitting pattern, where the  $\text{B}_{\text{NC}}\text{H}$  coupling constant can be observed.<sup>4</sup> With the widespread use of n.m.r., there undoubtedly will be other instances where this quick and convenient method for isotopic analysis will be useful.

### Results and Discussion

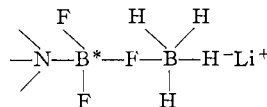
The reaction



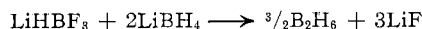
proceeds essentially to completion in 24 hr. Yields between 90 and 95% of  $(\text{CH}_3)_3\text{NBH}_3$ , m.p.  $94-95^\circ$ , were realized when an excess of  $\text{LiBH}_4$  for the above equation was used. The diborane was converted to trimethylamine borane separately and weighed. Yields were of the order 60 to 85% with melting ranges from  $85$  to  $93^\circ$ . Presumably, the inferior purity arose from disproportionation of the diborane before the reaction tube had been opened. (A trace of noncondensable gas always accompanied the formation of diborane.) The precipitate was identified as  $\text{LiF}$  by X-ray powder pattern.

The extended reaction time and the 3:1 mole ratio of reactants are required for complete conversion of the fluoride to the hydride. When reaction periods of up to 4 hr. were used, unreacted  $(\text{CH}_3)_3\text{NBF}_3$  was recovered. If a 1:1 mole ratio of  $\text{LiBH}_4$  to  $(\text{CH}_3)_3\text{NBF}_3$  is used, the product is contaminated with a fuming  $\text{BF}_3$  material which is easily removed by exposure to the atmosphere followed by resublimation.

Two possible mechanisms immediately suggest themselves. The first involves stepwise metathetical exchange of fluoride for hydride ions with the formation of  $\text{LiF}$  and  $\text{B}_2\text{H}_6$  by-products without rupture of the B-N bond. This would be somewhat analogous to the aminolysis of  $\text{F}_3\text{PBH}_3$  where the P-B bond remains intact.<sup>5</sup> The second involves a displacement of  $\text{BF}_3$  by  $\text{BH}_3$  and the subsequent conversion of the  $\text{BF}$  moiety to  $\text{B}_2\text{H}_6$  by reaction with excess  $\text{LiBH}_4$ . Since no  $\text{BH}_3$  (or  $\text{B}_2\text{H}_6$ ) is present initially, a complex of  $\text{LiBH}_4$  and  $(\text{CH}_3)_3\text{NBF}_3$  is postulated such as



which then rearranges to  $(\text{CH}_3)_3\text{NBH}_3$  and  $\text{LiHB}^*\text{F}_3$ . The subsequent reaction



accounts for the observed stoichiometry and the formation of  $\text{LiF}$  instead of  $\text{LiBF}_4$ .

(1) E. I. du Pont de Nemours and Company, Explosives Department, Experimental Station, Wilmington, Del.

(2) While this work was in progress, the reaction between  $\text{NaBH}_4$  and  $\text{CH}_2\text{NH}_2\text{Cl}$  at  $0^\circ$  has been reported to give good yields of  $\text{CH}_2\text{NH}_2\text{BH}_3$ : D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **85**, 395 (1963).

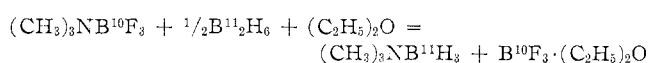
(3) G. W. Schaeffer and E. R. Anderson, *ibid.*, **71**, 2143 (1949).

(4) C. W. Heitsch, to be published.

(5) G. Kodama and R. W. Parry, *J. Inorg. Nucl. Chem.*, **17**, 125 (1961).

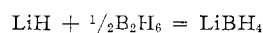
A similar intermediate can be drawn with a hydride ion as the bridging ligand, again rearranging to  $(\text{CH}_3)_3\text{-NBH}_3 + \text{LiHB}^*\text{F}_3$ . This mechanism also involves a transfer of trimethylamine from the labeled to the unlabeled boron. While the single hydrogen bridges are known in other cases,<sup>6</sup> the fluorine bridge should be favored here for steric reasons. It should be easier to develop a coordination member of five for boron with four hydrides and a fluoride than with three fluorides, a hydride, and a trimethylamine. However, the nature of the bridging ligand is unimportant to the argument below.

To test these hypotheses, a series of exchange and tracer studies was conducted. No exchange was apparent between  $(\text{CH}_3)_3\text{NB}^{10}\text{H}_3$  and  $\text{LiB}^{11}\text{H}_4$ . When  $\text{B}^{10}_2\text{H}_6$  and  $\text{LiB}^{11}\text{H}_4$  had equilibrated and had been converted to  $(\text{CH}_3)_3\text{NBH}_3$ , their n.m.r. spectra were identical (see Experimental section). Similarly,  $\text{B}^{11}_2\text{H}_6$  and  $(\text{CH}_3)_3\text{NB}^{10}\text{H}_3$  were found to give a random distribution of isotopes. Moreover, the reaction



goes to completion with only a small (10–50%) excess of  $\text{B}_2\text{H}_6$ .<sup>7</sup>

In the reaction between  $(\text{CH}_3)_3\text{NB}^{10}\text{F}_3$  and  $\text{LiB}^{11}\text{H}_4$ , both boron isotopes were randomly distributed between the amine borane and the diborane products. This gives no indication as to the course of the reaction, since this exchange could occur through the diborane produced. Lithium hydride in large excess was added to another reaction between normal  $\text{LiBH}_4$  and  $(\text{CH}_3)_3\text{-NBF}_3$  enriched in  $\text{B}^{10}$  where the ratio of salt to adduct was 1.2:1. Diborane generated was consumed by the reaction



Thus the quantity of free  $\text{B}_2\text{H}_6$  in the system was kept low and its exchange with other species reduced. In this system the  $\text{B}^{10}:\text{B}^{11}$  ratio in the borane adduct was 1.1, while in the  $\text{LiBH}_4$  it was 1.6. That the  $\text{B}^{10}$  would accumulate in the salt implies that the conversion of  $(\text{CH}_3)_3\text{NBF}_3$  to the borane involves a cleavage of the nitrogen–boron bond, with displacement of  $\text{BF}_3$  by  $\text{BH}_3$  (or  $\text{BH}_4^-$ ) as the more favored of the two reaction paths. There is some mixing of the isotopes. This might arise either from some exchange of  $\text{F}^-$  for  $\text{H}^-$  without cleavage of the B–N bond or from exchange between the diborane and the borane adduct before reaction with  $\text{LiH}$ .

**Acknowledgment.**—The author wishes to thank Dr. R. W. King for his assistance in obtaining n.m.r. spectra. The financial assistance of the Research Corporation is gratefully acknowledged.

(6) D. F. Gaines, *Inorg. Chem.*, **2**, 523 (1963).

(7) Best available values for the heats of association of the  $\text{BH}_3$  and  $\text{BF}_3$  complexes with  $\text{N}(\text{CH}_3)_3$  are about equal [F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958)]. The driving force in this case appears to be the formation of  $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ , which is considerably less dissociated than the corresponding borane.

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## Solvation of Metal Ions in Aqueous Solutions: the Metal–Oxygen Bond

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In the course of a series of studies of complex compound formation in aqueous solutions of strong electrolytes by the Raman spectroscopic method, we have obtained considerable evidence of the formation in solution of aquo–metal ion complexes involving a significant degree of electron sharing in the metal–oxygen bond. The appearance of a vibrational Raman line is dependent upon there being a change in bond polarizability with bond length ( $I \propto (\partial\alpha/\partial r)^2$ ), which in turn depends on a finite electron density in the bond. Thus purely ionic or ion–dipole bonding does not give rise to a Raman line characterizing the bond.<sup>1</sup> Table I lists Raman lines observed from nitrate, sulfate, and perchlorate salts of various metals after the lines due to the oxyanions and to the solvent water have been subtracted.<sup>2–4</sup> In each case the new lines were best observed from very concentrated, near-saturated solutions of the salts listed in Table I. Spectra were obtained using a Cary Model 81 Raman spectrophotometer, with calibrated polarizing screens wrapped around the sample tubes for depolarization measurements.

TABLE I  
LOW FREQUENCY, POLARIZED RAMAN BANDS FROM AQUEOUS  
SALT SOLUTIONS

Salt	Raman line, $\text{cm}^{-1}$
$\text{Cu}(\text{NO}_3)_2$	440
$\text{Zn}(\text{NO}_3)_2$	390
$\text{Hg}(\text{NO}_3)_2$	380
$\text{Mg}(\text{NO}_3)_2$	370
$\text{In}(\text{NO}_3)_3$	410 and 460 overlapping bands
$\text{CuSO}_4$	440
$\text{MgSO}_4$	360
$\text{ZnSO}_4$	400
$\text{Ga}_2(\text{SO}_4)_3$	475, shoulder on 435 $\text{cm}^{-1}$ $\nu_2(\text{E})$ line of $\text{SO}_4^{2-}$
$\text{In}_2(\text{SO}_4)_3$	350–550
$\text{Tl}_2\text{SO}_4$	470
$\text{Cu}(\text{ClO}_4)_2$	440
$\text{Hg}(\text{ClO}_4)_2$	380
$\text{In}(\text{ClO}_4)_3$	ca. 420, shoulder on 465 $\text{cm}^{-1}$ $\nu_2(\text{E})$ line of $\text{ClO}_4^-$
$\text{Mg}(\text{ClO}_4)_2$	360

The new lines were in all cases highly polarized and therefore readily distinguishable from the restricted rotational<sup>4</sup> water band at 450  $\text{cm}^{-1}$ . However, the

(1) J. H. B. George, J. A. Rolfe, and L. A. Woodward, *Trans. Faraday Soc.*, **49**, 375 (1953).

(2) G. Herzberg, "Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand, Princeton, N. J., 1945.

(3) R. E. Hester, Thesis, Cornell University, 1962.

(4) P. C. Cross, J. Burnham, and P. A. Leighton, *J. Am. Chem. Soc.*, **59**, 1134 (1937).