## EXPERIMENT 4

# The Borane–Amine Adduct $BH_3:NH_2C(CH_3)_3$

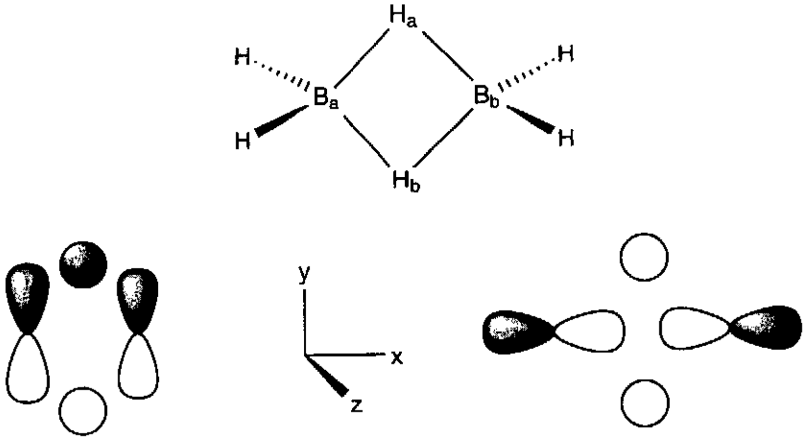
*Note: This experiment requires one 4 hour laboratory period.*

Compounds containing boron and hydrogen adopt unusual structures that are not observed for the hydrides of the neighboring element carbon. Representative compounds include $B_2H_6$, $B_4H_{10}$, $B_5H_9$, $B_5H_{11}$, $B_9H_{15}$, $B_{10}H_{14}$, $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, and many others. Although these species were initially of interest purely for their curious structures, boron hydrides have become important reagents in organic synthesis. Furthermore, the study of their structures provided the foundation for understanding the bonding in metal clusters and carbocations.

Diborane, $B_2H_6$, is the simplest of the boranes. It is most conveniently prepared from the reaction of sodium borohydride, $NaBH_4$ (frequently called sodium tetrahydroborate), with $BF_3$ in ether:

$$3\,NaBH_4 + 4\,BF_3 \longrightarrow 3\,NaBF_4 + 2\,B_2H_6$$

At room temperature, diborane is a gas with the molecular structure shown in Figure 4-1.



$(B_a\,p_y + B_b\,p_y) + (H_a\,s - H_b\,s)$

$(B_a\,p_x - B_b\,p_x) + (H_a\,s + H_b\,s)$

**Figure 4-1**
Structure of $B_2H_6$ and the orbitals involved in B–H–B bonding.

The two bridging H atoms lie above and below the plane described by the four terminal H atoms and the two B atoms. Whereas each terminal H atom bonds to only one B atom, each of the bridging H atoms bonds equally to two B atoms. In diborane there are eight B–H bonds, and one might expect that 16 valence electrons are needed to hold the molecule together (normally, a bond consists of an electron pair). Instead, diborane only possesses 12 valence electrons (3 from each boron and 1 from each hydrogen). How are 12 electrons able to form eight B–H bonds? The answer is related to the presence of the bridging hydrogen atoms. The *s* atomic orbitals on these hydrogen atoms overlap with *p* atomic orbitals from both of the adjacent boron atoms to form "multicenter" molecular orbitals as shown in Figure 4-1. The four electrons in these two multicenter molecular orbitals form four B–H bonds, for an average of only *one* electron per bond. The other eight valence electrons in diborane form the normal two-electron bonds to the terminal hydrogen atoms. Such molecular orbitals, consisting of the simultaneous overlap of several atomic orbitals, are common to most of the boron hydrides.

Although $B_2H_6$ exists largely in the bridged form, it does dissociate to a very small extent to give $BH_3$.

$$B_2H_6 \rightleftharpoons 2\ BH_3$$

Electron acceptors are sometimes referred to as Lewis acids, and electron donors as Lewis bases. Borane, $BH_3$, is a Lewis acid because it has six valence electrons and thus can accept two electrons from other molecules. Borane forms numerous complexes (called adducts) with donor molecules such as amines and phosphines. For example, diborane reacts with trimethylamine as shown

$$B_2H_6 + 2\ N(CH_3)_3 \longrightarrow 2\ BH_3{:}N(CH_3)_3$$

The geometry around both the B and N atoms is approximately tetrahedral, and the structure of the adduct is very similar to that of the all-carbon analogue neopentane, $CH_3{-}C(CH_3)_3$.

Historically, Lewis base adducts of borane were prepared from $B_2H_6$, a substance that inflames in air and is immediately hydrolyzed by water. In addition to these hazards, $B_2H_6$ is exceedingly toxic. For these reasons, a more convenient and less dangerous route to the adducts was sought. It was found that the reaction of $NaBH_4$, which is an air stable solid, with an alkylammonium salt produces the borane–amine adduct under mild conditions:

$$NaBH_4 + NHR_3{}^+Cl^- \longrightarrow BH_3{:}NR_3 + NaCl + H_2$$

The particular reaction to be carried out in this experiment involves *tert*-butylammonium chloride; this salt may be simply prepared by bubbling gaseous

HCl into an ether solution of *tert*-butylamine:

$$NH_2C(CH_3)_3 + HCl \longrightarrow NH_3C(CH_3)_3{}^+Cl^-$$

The borane adduct is formed according to the following equation:

$$NaBH_4 + NH_3C(CH_3)_3{}^+Cl^- \longrightarrow BH_3:NH_2C(CH_3)_3 + NaCl + H_2$$

The product, $BH_3:NH_2C(CH_3)_3$, is a white solid (mp 96 °C) that is stable toward air and water at room temperature. You will measure its IR and $^1H$ nuclear magnetic resonance (NMR) spectra. The $^1H$ NMR spectrum of $BH_3:NH_2C(CH_3)_3$ consists of one sharp peak corresponding to the $-CH_3$ protons at approximately $\delta - 1.2$ relative to tetramethylsilane. The corresponding signals for the protons on the N and B atoms are broadened so greatly by the nuclear quadrupole moments of $^{14}N$ and $^{11}B$ that they may not be visible in the spectrum.

Borane adducts undergo many reactions. For example, the replacement of H by Cl in the $BH_3$ portion of the molecule can be accomplished by reaction with gaseous HCl

$$BH_3:NH_2C(CH_3)_3 + HCl \longrightarrow BH_2Cl:NH_2C(CH_3)_3 + H_2$$

This reaction again illustrates the hydridic, $H^-$, nature of the H atoms attached to the electropositive boron atom. The hydridic H atoms readily combine with protonic, $H^+$, hydrogen atoms to produce $H_2$. The analogous reaction with HF replaces all three hydrogen atoms on the boron

$$BH_3:NH_2C(CH_3)_3 + 3\,HF \longrightarrow BF_3:NH_2C(CH_3)_3 + 3\,H_2$$

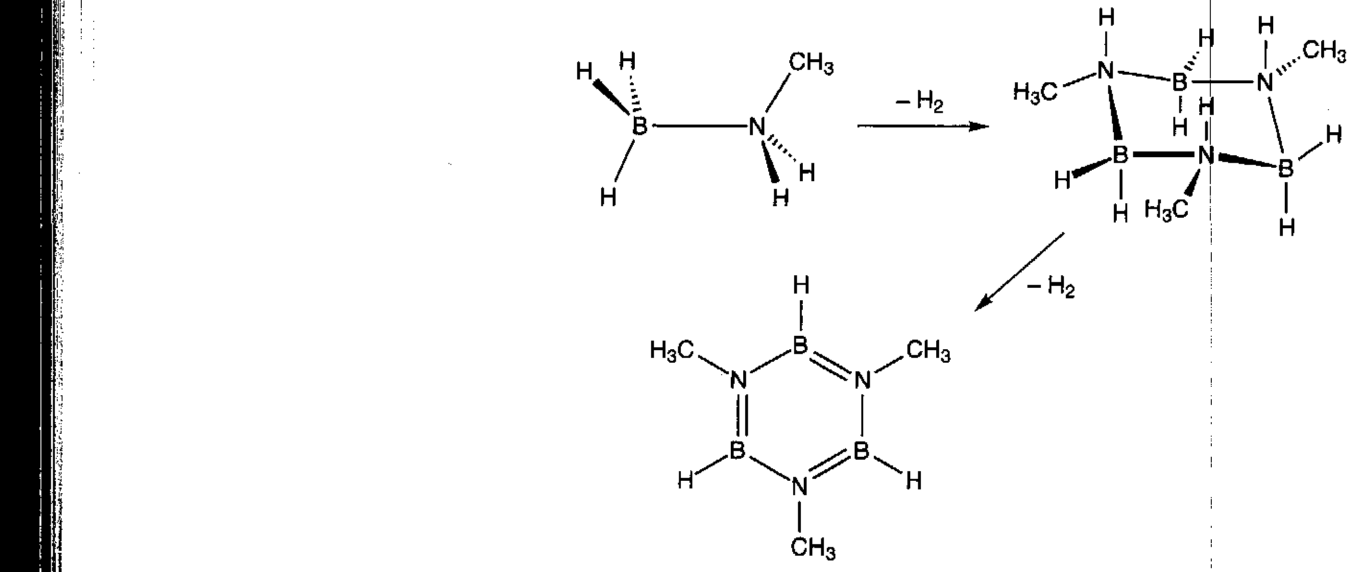
The same adduct can also be prepared directly by treating $BF_3$ with $NH_2C(CH_3)_3$.

Trialkylamine-boranes react with alkenes to form products in which the B and H have added across the double bond

$$BH_3:N(CH_3)_3 + 3\,H_2C{=}CHR \longrightarrow B(CH_2CH_2R)_3 + N(CH_3)_3$$

The trialkylborane $B(CH_2CH_2R)_3$ is a sufficiently weak Lewis acid that it may be liberated from the trimethylamine without difficulty. The ability of a borane to add across the double bond of an alkene in an anti-Markownikov fashion is the basis for the widespread use of boranes in organic chemistry.

Borane-amines lose $H_2$ at high temperatures and generate a variety of products, depending on the particular reactant and the conditions. When the borane-methylamine adduct, $BH_3:NH_2(CH_3)$, is heated to 100 °C, it yields $B_3N_3H_3(CH_3)_3$, which is the B–N analogue of 1,3,5-trimethylcyclohexane. Further loss of $H_2$ occurs at roughly 200 °C to produce the unsaturated cyclic ring compound $B_3N_3H_3(CH_3)_3$ called 1,3,5-trimethylborazole:



The carbon analogue of 1,3,5-trimethylborazole is mesitylene, 1,3,5-$C_6H_3(CH_3)_3$. The parent compound borazole, $B_3N_3H_6$, structurally resembles the isoelectronic compound benzene. For this reason, borazole is sometimes called "inorganic benzene." Like benzene, it has a planar hexagonal structure, and the relatively short B–N bonds indicate the presence of B–N $\pi$ bonding. Despite the physical similarities, benzene and borazole have quite different chemical reactivities. The $\pi$ system of benzene is relatively inert to addition reactions. In contrast, borazole adds hydrogen halides, HX, to give the saturated cyclic aminoborane $B_3N_3H_9X_3$. The susceptibility of borazole to attack is related to the polar nature of the B–N bond.

## EXPERIMENTAL PROCEDURE

*Note*: In contrast to many hydride compounds, such as NaH, $CaH_2$, or $LiAlH_4$, which react explosively with water, $NaBH_4$ is stable in neutral or alkaline aqueous solutions. It rapidly hydrolyzes in acidic solution, however. Fresh $NaBH_4$ should be used in this experiment—old samples of $NaBH_4$ will give inconsistent or poor yields.

### ***tert*-Butylammonium Chloride, $NH_3C(CH_3)_3{}^+Cl^-$**

In a hood, dissolve 2.5 mL (1.7 g, 23 mmol) of 2-amino-2-methylpropane [*tert*-butylamine, $NH_2C(CH_3)_3$] in 20 mL of anhydrous diethyl ether. Cautiously bubble gaseous HCl from a compressed gas cylinder into the solution until precipitation of $NH_3C(CH_3)_3{}^+Cl^-$ is complete. Suction filter the product on a medium frit, wash the solid with a few milliliters of ether, and dry the solid in a vacuum. Determine the yield. Although many alkylammonium chloride salts are very hygroscopic, $NH_3C(CH_3)_3{}^+Cl^-$ is not; it need not be stored in a desiccator except when the humidity is high.

**_tert_-Butylamine-Borane, $BH_3:NH_2C(CH_3)_3$**

Assemble the apparatus shown in Figure 4-2 and lubricate the stirring shaft bearing with glycerin. The drying tube is necessary only if the atmospheric humidity is very high. Add 1.3 g (11.8 mmol) of $NH_3C(CH_3)_3{}^+Cl^-$ and 15 mL of tetrahydrofuran (THF) to the 250-mL three-neck flask. (The THF may be used as obtained commercially unless it contains large amounts of water. Then it should be dried over NaOH and distilled.) To the stirred suspension, add 0.20 g (5.3 mmol) of powdered $NaBH_4$. At this point, $H_2$ gas will be evolved. Add an additional 10–15 mL of THF and continue stirring the solution for about 2 h at room temperature. Filter the solution using a suction filtration apparatus (see Fig. 13-1). After the filtration, disconnect the rubber vacuum tubing from the filter flask *before* the water flow is turned off; this action will prevent water from backing up into the trap. Discard the solid (which contains NaCl and unreacted excess $NH_3C(CH_3)_3{}^+Cl^-$) and keep the solution. Using a rotary evaporator, evaporate the THF solution to dryness. The $BH_3:NH_2C(CH_3)_3$ product that remains in the flask is usually of high purity; determine its melting point to confirm this. If the melting range is less than 4 °C, skip the following recrystallization step. If the melting range is greater than 4 °C, the compound should be recrystallized by dissolving it in a minimum amount (1–2 mL) of toluene and adding 20 mL of hexane until precipitation is complete. Collect the $BH_3:NH_2C(CH_3)_3$ by suction filtration and dry the solid product in air. Redetermine its melting point.

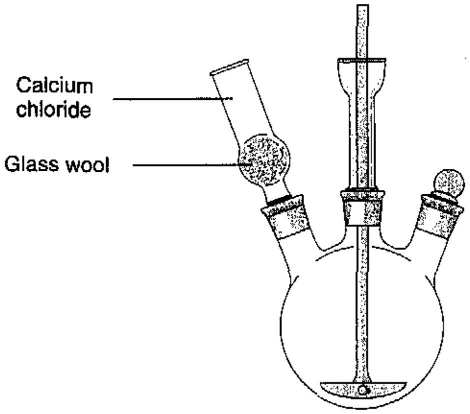


**Figure 4-2**
Apparatus for preparation of $BH_3:NH_2C(CH_3)_3$.

Finally, calculate the yield of product. Measure the IR spectrum of the product in $CHCl_3$ or $CDCl_3$ solution.

## REPORT

Include the following:

1. Percentage yields of $NH_3C(CH_3)_3^+Cl^-$ and $BH_3:NH_2C(CH_3)_3$.
2. Melting point of $BH_3:NH_2C(CH_3)_3$.
3. Infrared spectrum of $BH_3:NH_2C(CH_3)_3$ with assignments to vibrational modes in the molecule. Compare the B–H, C–H, and N–H stretching frequencies and account for their differences.

## PROBLEMS

1. Propose a mechanism for the reaction of $NaBH_4$ with $NH_3C(CH_3)_3^+Cl^-$.
2. Suggest a method of establishing the presence of boron in your product, $BH_3:NH_2C(CH_3)_3$.
3. Earlier it was noted that $B_2H_6$ inflames in air and rapidly hydrolyzes in water. Write balanced equations for these reactions.
4. Write a balanced equation for the hydrolysis of $NaBH_4$ in acidic solution.
5. Draw structures of the following: $NaBF_4$, $NaBH_4$, $B(CH_3)_3$, and $BF_3$.
6. Tetrahydrofuran forms an adduct with $BH_3$, $BH_3$:THF. Draw the structure of this compound. Is there any evidence from this experiment that would suggest that THF coordinates more or less strongly to $BH_3$ than does $NH_2C(CH_3)_3$?
7. Account for the fact that $LiBH_4$ is more soluble in THF than is $NaBH_4$. Would you expect $LiBH_4$ or $NaBH_4$ to give better yields in the present experiment? Why?
8. If you wished to carry out a reaction of the type

$$BH_3:NH_2C(CH_3)_3 + \text{amine} \longrightarrow BH_3:\text{amine} + NH_2C(CH_3)_3,$$

what amine would you choose and what reaction conditions would you use to drive the reaction to completion?

## INDEPENDENT STUDIES

A. Prepare and characterize other amine-borane adducts, such as $BH_3:NH(CH_3)_2$ and $BH_3:N(CH_3)_3$. (Nöth, H.; Beyer, H. *Chem. Ber.* **1960**, *93*, 928. Nainan, K. C.; Ryschkewitsch, G. E. *Inorg. Synth.* **1974**, *15*, 122.)

B. Using your $BH_3:NH_2C(CH_3)_3$, prepare and characterize $BH_2X:NH_2C(CH_3)_3$ (where X = F, Cl, Br, or I). (Nöth, H.; Beyer, H. *Chem. Ber.* **1960**, *93*, 2251. Ryschkewitsch, G. E.; Wiggins, J. W. *Inorg. Synth.* **1970**, *12*, 116.)

C. Prepare and characterize $BH_3$:py (where py = pyridine) and $[BH_2(py)_2^+]I^-$. (Ryschkewitsch, G. E. *J. Am. Chem. Soc.* **1967**, *89*, 3145. Nainan, K. C.; Ryschkewitsch, G. E. *Inorg. Chem.* **1968**, *7*, 1316.)

D. Determine the mass spectrum of $BH_3:NH_2C(CH_3)_3$ and make assignments to all ion fragments.

E. Prepare the interesting tridentate ligand, hydrotris(1-pyrazolyl)borate, $HB(C_3H_3N_2)_3^-$. (Trofimenko, S. *Inorg. Synth.* **1970**, *12*, 102.)

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THIRD EDITION

# Synthesis and Technique in Inorganic Chemistry

## A LABORATORY MANUAL

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