Experiment 4:
The Borane-Amine Adduct

Text #4

CHEM 531

Reminders

- Due this Thursday (2/19):
  - Report: Experiment 3
    - Electrolytic Synthesis of $K_2S_2O_8$
  - Prelab: Experiment 4
    - Borane-Amine Synthesis
- Due in two weeks (3/5):
  - Report: Experiment 4
    - Borane-Amine Synthesis
  - Report: Experiment 5
    - Molecular Modeling (Borane-Amine Complex)
  - Prelab: Experiment 6
    - Metal-Arene Complex (Text #16)

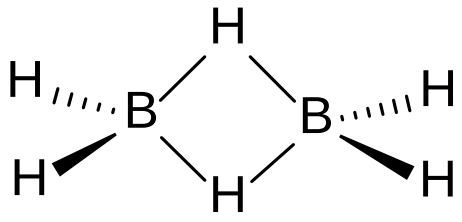
Borane (BH_3)

- In principle prepared by reduction of BX_3:

$$BCl_3 + LiAlH_4 \longrightarrow B_2H_6 \ (+ AlCl_3 + LiCl)$$

$$BF_3 + NaBH_4 \longrightarrow B_2H_6 \ (+ NaBF_4)$$

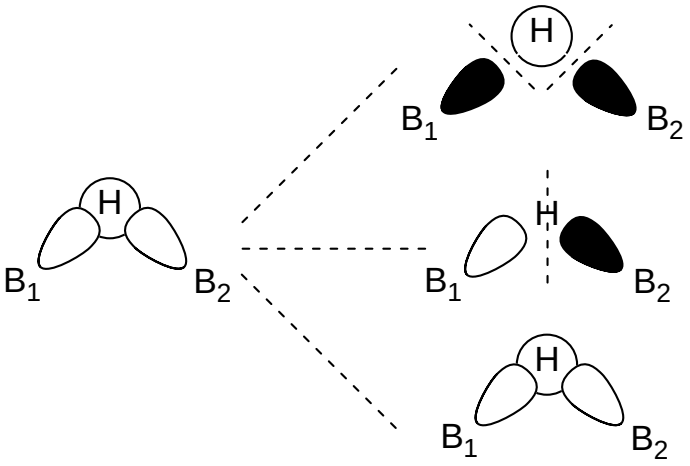
  - Only B_2H_6 (diborane) can be isolated



$$\rightleftharpoons \quad 2\ BH_3 \qquad (K \sim 1 \times 10^{-5})$$

Diborane (B_2H_6) Structure

- "Bridging" B-H-B links
  - 3-center, 2-electron bonds
  - Boron is approximately sp^3



$\Psi_3^*(BHB) = 0.5\Phi(B1) + 0.5\Phi(B2) - 0.707\Phi(H)$ (Antibonding)

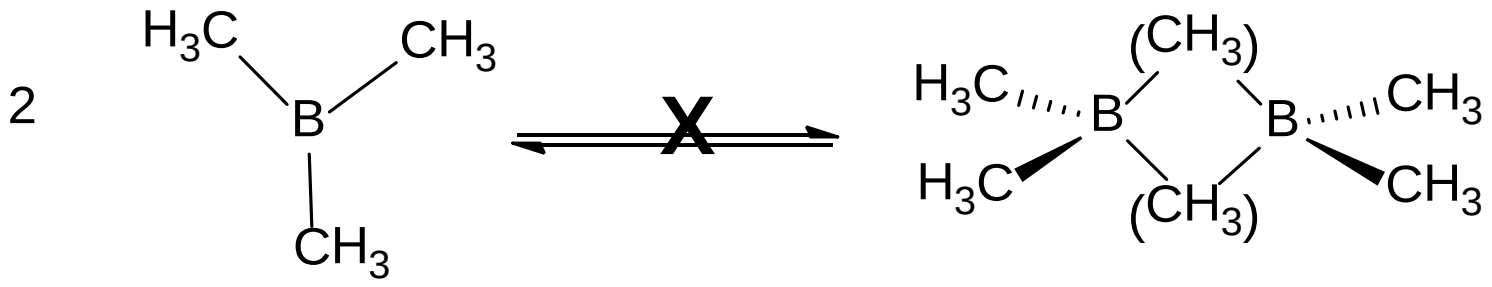
$\Psi_2(BHB) = 0.707\Phi(B1) - 0.707\Phi(B2)$

$\Psi_1(BHB) = 0.5\Phi(B1) + 0.5\Phi(B2) + 0.707\Phi(H)$ (Bonding)

Trimethylborane (Me_3B)

- No tendency to dimerize

- Why not?



Stabilization of Borane

- Borane is a useful reagent
  - Diborane is a gas at room temperature
    - Flammable
- Stabilized by formation of Lewis Acid-Base Adducts

Lewis acid: *an electron acceptor*

Lewis base: *an electron donor*

Much broader definition than Brønsted-Lowry

$$BH_3 + NH_3 \rightarrow BH_3 : NH_3$$

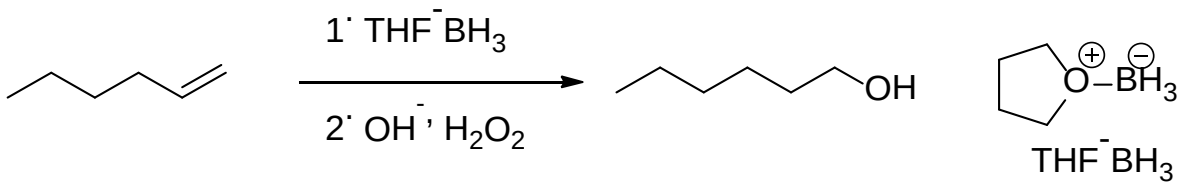
Acid *Base* *Adduct*

$H_3B \leftarrow :NH_3$

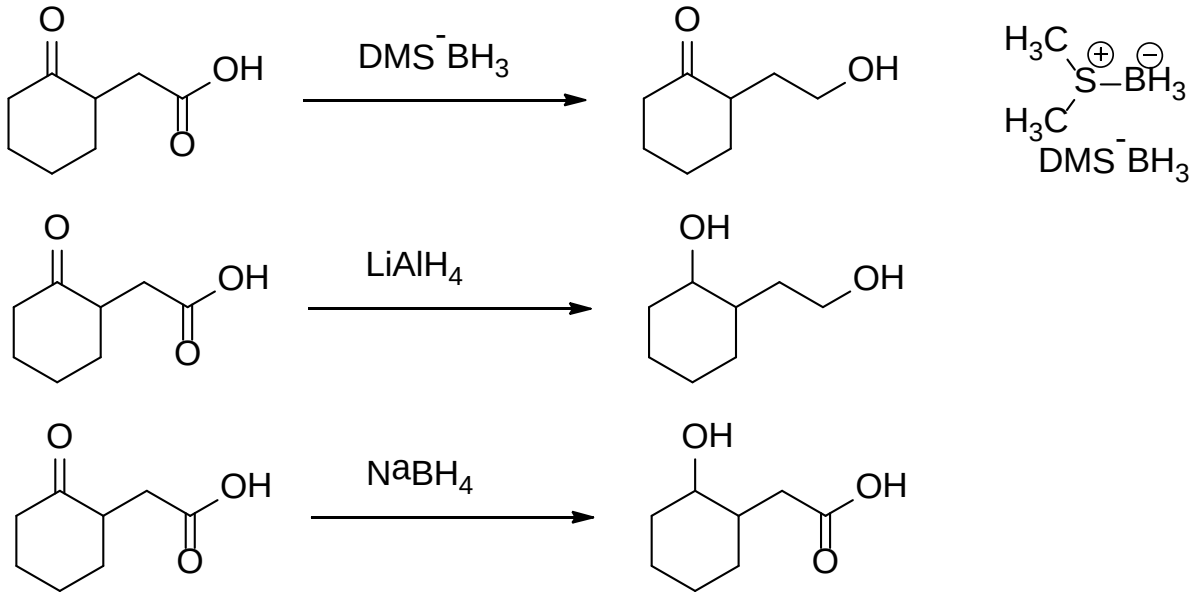
$H_3\overset{\ominus}{B}—\overset{\oplus}{N}H_3$

Borane Adduct Applications

- Hydroboration-oxidation



- Selective reduction



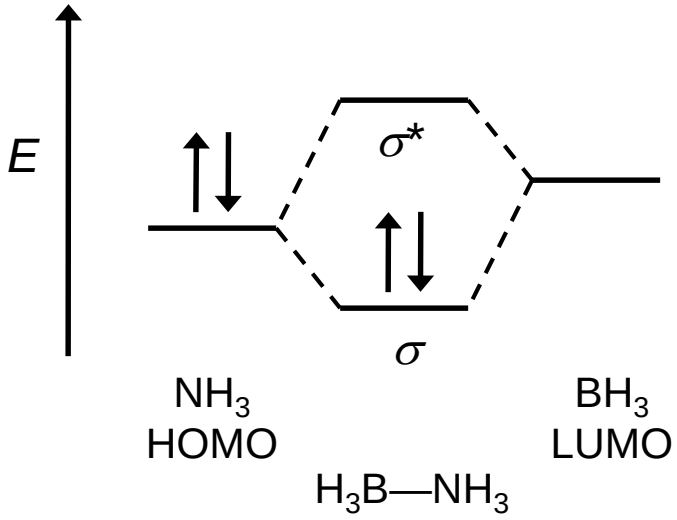
Adduct Formation: Frontier Molecular Orbitals

The key interaction in Lewis acid-base adduct formation may be simply viewed as involving overlap of frontier molecular orbitals on the reactants. (You will model this interaction next week for your reaction.)

Which HOMO and which LUMO must interact?

*The base **donates electrons**. Its HOMO must be involved.*

*The acid **accepts electrons** into its lowest lying empty orbital (LUMO).*

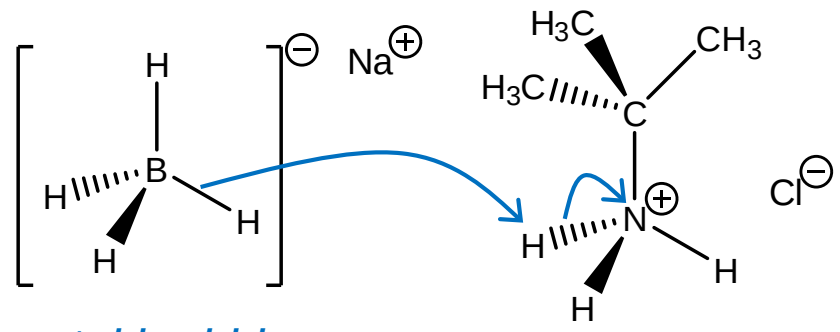


*When two orbitals interact, two new orbitals are formed, the **bonding** and **antibonding** MOs.*

Electrons are placed into MOs according to the same rules for atomic orbitals.

Reaction of Interest

$$NaBH_4 + NH_3C(CH_3)_3Cl \rightarrow H_3B{-}NH_2C(CH_3)_3 + NaCl + H_2$$



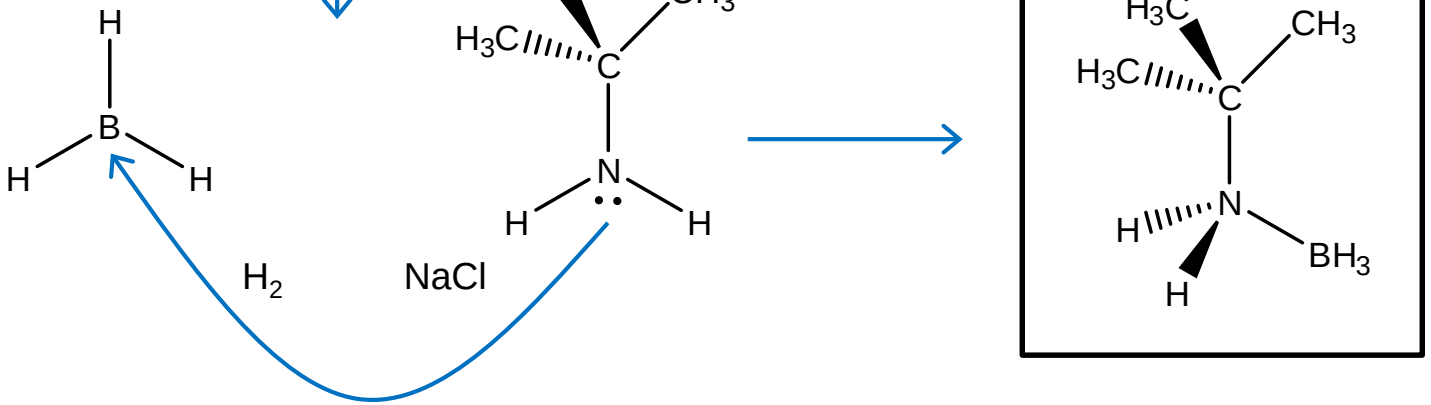
metal hydride ("M^+H^-")

Why use $NaBH_4$ as a source of BH_3?

More convenient, less dangerous than B_2H_6

How does this base compare to NH_3?

Better e- donor; sterics could be hindering for some reactions.



H_2 NaCl

Product Characterization (to be completed 2/17)

1) Yield and Percent Yield

2) Melting Point

How can you use melting point to qualitatively determine purity?

For a pure substance, complete melting occurs over a narrow range of T.

What if your product does not melt completely below 200°C?

Contamination by NaCl – ionic compounds melt at much higher temps.

3) IR Spectroscopy

What functional groups do you expect?

B-H, N-H, N-C, C-C, C-H, B-N

Which functional group is most diagnostic of product formation?

(You will predict its characteristic frequency via modeling.)

B-N – diagnostic of new boron-nitrogen bond not found in reactants

Procedural Notes

1. We will work at **1/3 SCALE** to minimize waste. You may add slightly more THF if required to dissolve starting materials.

2. $NH_3\,C(CH_3)_3Cl$ is commercially available, so we will **not** synthesize it. The synthetic procedure to make the adduct begins on p. 51.

3. **Apparatus:** We will use 100-mL round-bottom flasks with magnetic stir bars. (The mechanical stirrer and drying tube are not required.) Set up **under benchtop hood** (H_2 evolved.)

4. React as long as possible (1.5-2 hrs?), allowing ~30 min. for filtration, etc.

Procedural Notes, continued

5. **Product recovery:** Your product is **in solution in THF!!** This means that you need to **save the filtrate**. Collected solids may be discarded.

   a) Make sure your filter flask is clean.
   b) Use the fritted glass filter. Crystals may pass through filter paper.
   c) Do not allow water to be pulled into filter flask.
      - ***Disconnect vacuum hose from flask first!!!***
        - *Then turn off water*

   d) Dry the THF solution with sodium sulfate

Procedural Notes, continued

5. We will use **rotary evaporation** to collect your borane—amine adduct.

   Rotate the flask under reduced pressure (often with heating) to evaporate solvent, leaving solid product.

   How does reduced pressure help?

   Boiling occurs when solvent's $P_{vapor} = P_{atmosphere}$ By reducing "atmospheric" pressure, a lower vapor pressure is required, which can be achieved at a lower temperature.

6. **Characterization** – yield, melting point, IR – will be completed next week.

   a) Note: For easier yield determination, it will help if you obtain the **mass of your clean, dry round-bottom flask** prior to beginning work this week.

Formal Report Due Thurs., 3/5

- You will write a formal report for this experiment, following the general format described previously.

- **In addition to the borane—amine synthesis**, your report should also include the results and a discussion of the **related modeling exercises** to be completed next week.

- More detail about the modeling will be provided next week.