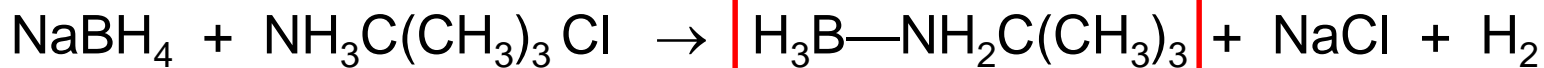


Due by 2 PM Thurs., 2/26: Prelab

Due by 5 PM Thurs., 3/5:

Modeling Lab Informal Report (Answers to Questions)
Borane-Amine Formal Report

In Lab this Week:



- I. Product Characterization (do this first)
- II. Modeling Lab
 - A. Part A: Borane-Amine
 - B. Part B: Metal Arene

Modeling Chemical Reactions: Frontier Molecular Orbitals

As we will see shortly in CHEM 530, molecular orbital diagrams can be extremely complex, even for molecules as “simple” as the adduct you synthesized. **How many MOs should $\text{H}_3\text{B—NH}_2\text{C}(\text{CH}_3)_3$ have?**

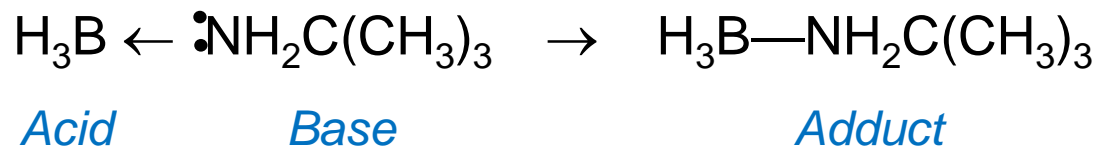
For n valence orbitals (the basis set), there will be n MOs

Each C, N, and B uses its 2s and three 2p orbitals; each H uses its 1s

$6(4) + 14(1) = 38$ valence orbitals \rightarrow **38 MOs for the adduct**

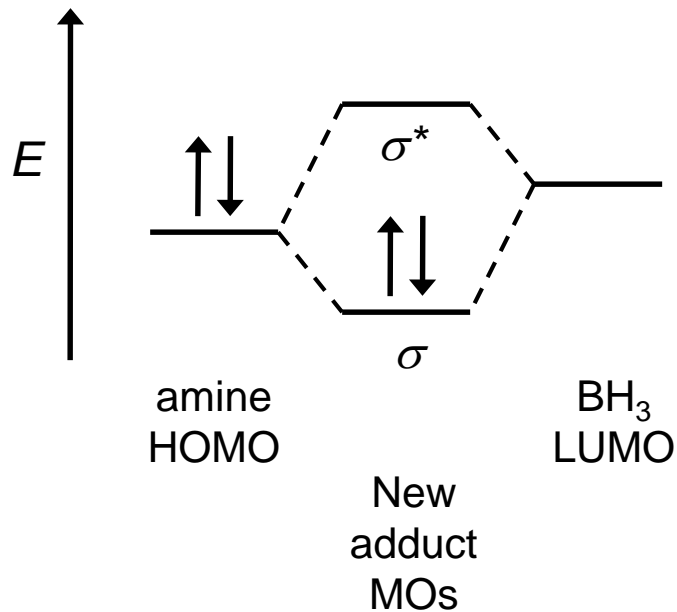
Instead of constructing the entire MO diagram, we will focus on the borane and amine MOs involved in the reaction:

The amine HOMO interacts with the borane LUMO.



FMO Interaction in the Borane-Amine Adduct

You will build BH_3 and $\text{NH}_2\text{C}(\text{CH}_3)_3$, calculate the appropriate MOs and diagram their interaction.




Include:

- MO energies (also, sketch roughly to scale)
- Sketches of all four MOs, showing regions of different sign and areas of overlap
 - How must the FMOs on the reactants overlap to form the new bonding and antibonding (σ) MOs in the adduct?

An Overview of Modeling Tools

“Molecular modeling” encompasses three types of calculations:

Molecular Mechanics	<i>Classical</i>	<i>Can handle many atoms; provide results for further optimization</i>
Semi-empirical	<i>Quantum</i>	<i>More approximations, aided by empirical data</i>
<i>ab initio</i>	<i>Quantum</i>	<i>Fewest approximations H-like orbitals, LCAO approx.</i>

Increasing
Cost


Which of these employ quantum mechanics?

*If quantum methods (recognizing wave-particle duality) are required to describe electron behavior, **how and why** do we use classical MM methods?*

*What is the difference between *ab initio* and semi-empirical calculations?*

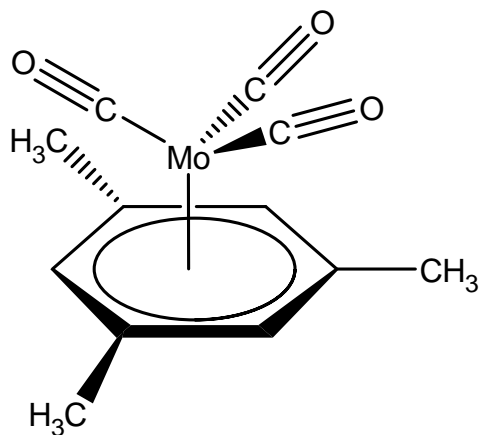
*Why are approximations needed? If *ab initio* calculations employ the fewest approximations, why not use these methods at all times?*

Our Modeling Exercise: Borane-Amine

- I. Model the FMOs involved in the formation of the borane-amine adduct
 - ❖ Build the reactants; use Molecular Mechanics to obtain an initial geometry optimization
 - ❖ Further optimize geometry and calculate FMOs using the Semi-Empirical AM1 method
 - ❖ Generate an MO diagram for the interaction of these FMOs

- II. Predict the IR spectrum of the adduct, for comparison to experiment
 - ❖ Build the adduct; use MM and AM1 methods to optimize geometry and calculate vibrational modes
 - ❖ Animate the vibrations in the calculated IR spectrum to identify predicted frequencies for the functional groups in your adduct.
 - ❖ Use these data to aid in assigning peaks in your experimental spectrum

Metal-Arene $[1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3]\text{Mo}(\text{CO})_3$



An **organometallic** compound:
contains **metal-carbon bonds**

Metal-ligand complexes can be viewed
as **Lewis acid-base adducts**:

Metal: Lewis acid (e⁻ acceptor)

Ligands: Lewis bases (e⁻ donors)

Ligands donate e⁻ to form M-L
coordinate covalent or **dative** bonds.

“Electron Counting” in Organometallic Compounds

The 18-electron “Rule:” Many stable organometallic compounds have 18 total valence electrons around the metal.

– counting metal valence e- and e- donated by ligands

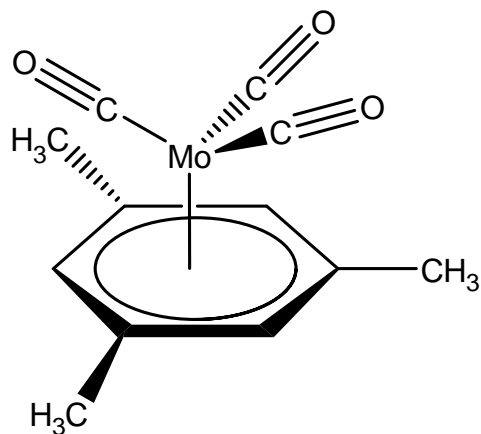
What is “special” about 18 electrons? Think about the “octet rule” . . .

18 electrons represents a filled noble gas core for a transition-metal atom. (e.g., $4s^2 3d^{10} 4p^6 = [\text{Kr}]$)

Counting electrons:

- 1) Determine the charge on the metal and its total number of valence electrons
- 2) Add up the number of electrons donated by the ligands
 - a. Lone-pair and/or π electrons can be donated

Counting Electrons in $[1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3]\text{Mo}(\text{CO})_3$



1) Determine the charge on Mo and its total # of ve-

a. Consider **charges on ligands**: CO and mesitylene are both neutral molecules. . . .

Mo is neutral (0 oxidation state)

b. Determine total # of Mo valence e-

$[\text{Kr}] 5s^2 4d^4 - 6$ valence e- (“d⁶”)

2) Add up the number of e- donated by the ligands:

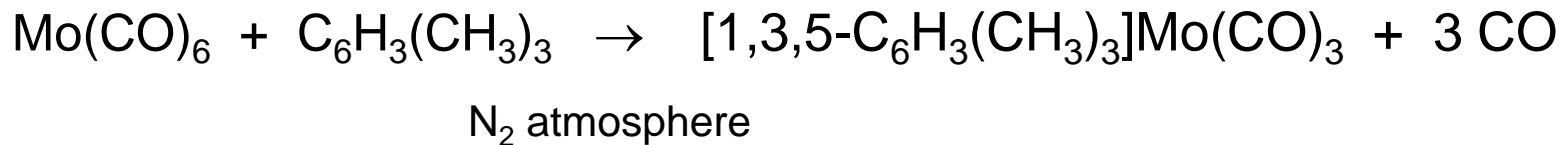
CO ligands: Each donates 2 electrons

$\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3$: Donates 6 electrons (from 3 π bonds)

Coordinated
through 6 atoms

6 Mo valence e- + 6 + 3(2) e- donated by ligands = 18 e- total

(Synthesis) and Characterization of [1,3,5-C₆H₃(CH₃)₃]Mo(CO)₃



In part, characterization will focus on IR spectroscopy and CO stretches:

CO peaks are distinctive in IR spectra of organometallic compounds, occurring in a fairly empty region of the spectrum. ~1850-2125 cm⁻¹

CO peaks observed in the IR (number, intensity, frequency) are sensitive to molecular geometry (i.e., symmetry) and ligand-metal electronic interactions.

When you synthesize the product next week, you will measure its IR spectrum, from which you can calculate the OC-Mo-CO angle.

Modeling Part B: $[1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3]\text{Mo}(\text{CO})_3$

- I. Use Spartan (molecular mechanics and semi-empirical PM3 calculations) to optimize the geometry of the product
 - A. Calculate the OC-Mo-CO bond angles, for comparison to the angles determined next week from your measured IR spectrum
 - B. Predict the IR spectrum, identify CO stretches and determine their frequencies (cm^{-1}); compare to your measured spectrum
 1. You will also be able to predict the number of CO stretches (but not their frequencies) using Group Theory.

Reports Due Thurs., 3/5

- 1) Requested printouts and answers to questions in modeling exercises (See “To be turned in” sections) to Dr. Lammi

- 2) Formal report on the borane-amine synthesis to Dr. Hanna
 - a. Include the portion of the modeling exercise related to the IR spectrum of the adduct