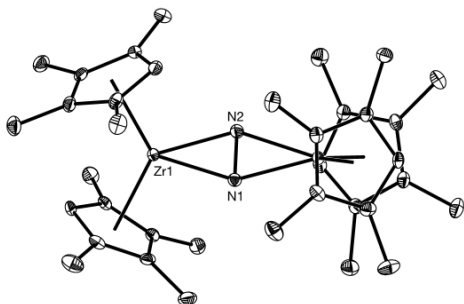


## 2018 Ch112 – Problem set 3

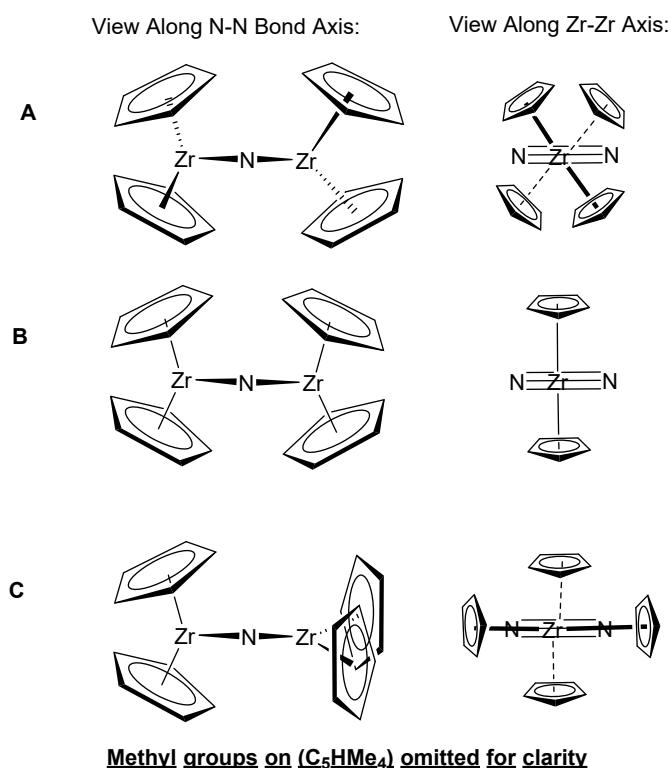
Due: Thursday, Nov. 1 – before class

### Problem 1 (3 points)

In 2004, a bimetallic Zr compound exhibiting side-on  $N_2$  binding was reported by Chirik and coworkers (*Nature*, **2004**, 427, pp. 527-530). The crystal structure of this compound was obtained, and the ORTEP view is shown below.



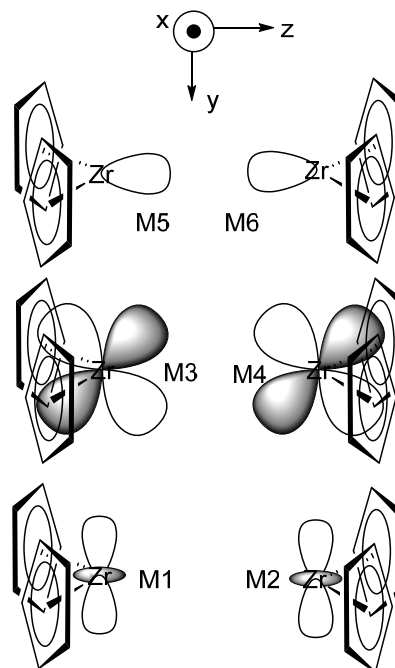
Depending on the relative orientations of the dinitrogen ligand and the two  $(Me_4HC_6)_2Zr$  units that it bridges, several different point groups could be imagined for this molecule. Three examples are shown in the figure to the right (A, B, and C—Example A corresponds to the structure reported by the Chirik group).



$Zr_2$  Frontier MOs (N-N bond along y-axis)

1. Determine the point group of these three structures (A, B, and C), ignoring the methyl groups on the Cp rings.

2. Using structure B, and the point group to which it belongs, derive SALCs for the frontier metal orbitals found in the metallocene wedge. Use the approximation that these are bent  $Cp_2Zr$  fragments, and for your basis set, consider only the three d-orbitals we have described in class, shown to the right, for a total of 6 SALCs. Use the indicated labels (M1-M6) in your derivation of the SALCS using the projection operator. Indicate the Mulliken symbols of each SALC, and write out the normalized wavefunction corresponding to each SALC.



3. Indicate the Mulliken symbols of the five frontier MOs of dinitrogen (HOMO-1, HOMO, LUMO). Derive the qualitative MO diagram corresponding to the interaction between the 6  $Zr_2$  SALCs and the frontier orbitals of  $N_2$ . This should be done using structure B from part 1. Indicate the Mulliken symbols for each MO. Sketch each of the resulting MOs, indicate the axial symmetry of

## 2018 Ch112 – Problem set 3

Due: Thursday, Nov. 1 – before class

each MO with respect to axis defined by the two Zr atoms, and whether each MO is bonding, non-bonding, or anti-bonding with respect to the Zr-N<sub>2</sub> interaction. Populate the diagram with electrons. Indicate the orbital(s) responsible for the elongation of the N-N distance.

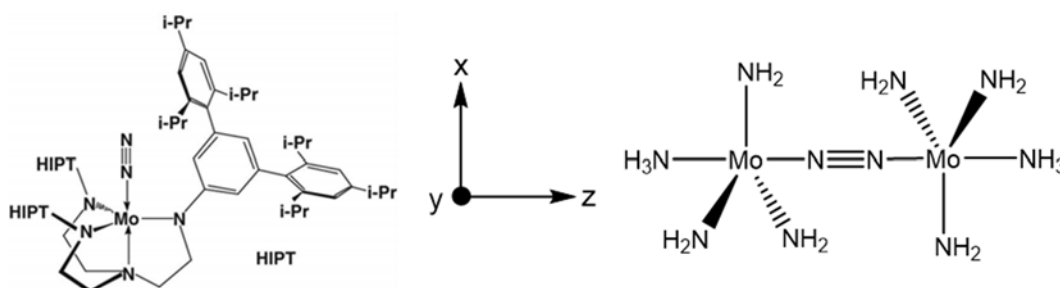
4. Provide an explanation for why the isolated compound (from the *Nature* paper) does not exhibit the conformation of structure B.

5. By inspection, generate SALCs for the frontier orbitals of the two metallocene fragments in the point group of structure C. Derive an MO diagram for the interaction with N<sub>2</sub> and draw the MOs responsible for elongation of the N-N distance. Indicate whether you expect B or C to exhibit the longer N-N distance. Suggest an explanation for why the isolated compound does not exhibit the conformation of structure C.

### Problem 2 (4 points)

#### Part A

Catalytic reduction of dinitrogen to ammonia has been demonstrated at a single Mo center (Schrock *et al*, *Science*, **2003**, 301, 76-78). The structure of the end-on bound dinitrogen complex is shown below, featuring a tripodal ligand with extremely bulky substituents (HIPT). The use of less bulky substituents leads to the formation of the end-on bridging dinitrogen species. Consider the bridging dinitrogen species in the staggered conformation in which the equatorial ligands have been substituted with simple amide ligands, as illustrated below.



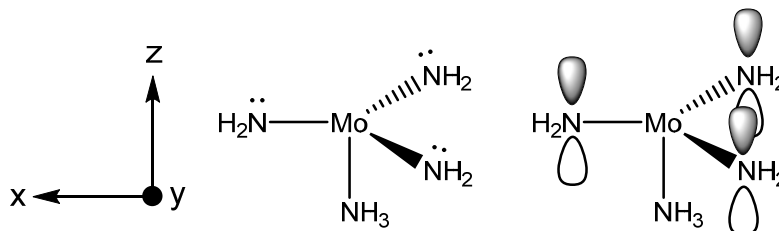
1. Assign the point group of the Mo<sub>2</sub>N<sub>2</sub> model shown above. Using the frontier orbitals of the [(NH<sub>3</sub>)Mo(NH<sub>2</sub>)<sub>3</sub>] fragment discussed in class, derive the metal based SALCs from the two molybdenum fragments (**consider only the d-based orbitals**). Full mathematical derivation is not required. Sketch all SALCs and indicate d-orbital parentage from each metal.
2. Using the SALCs derived from part 1 and the frontier orbitals (HOMO-1, HOMO, LUMO) of N<sub>2</sub>, provide a molecular orbital diagram of the dimeric [(NH<sub>3</sub>)(NH<sub>2</sub>)<sub>3</sub>Mo-N<sub>2</sub>-Mo(NH<sub>2</sub>)<sub>3</sub>(NH<sub>3</sub>)] species. Populate the diagram with electrons. For each MO, indicate the axial symmetry with respect to the Mo-N<sub>2</sub>-Mo interactions, and indicate the nature of the interaction (bonding,

## 2018 Ch112 – Problem set 3

Due: Thursday, Nov. 1 – before class

etc.). Sketch the MOs of all occupied d-based orbitals. Do you expect the compound to be paramagnetic or diamagnetic?

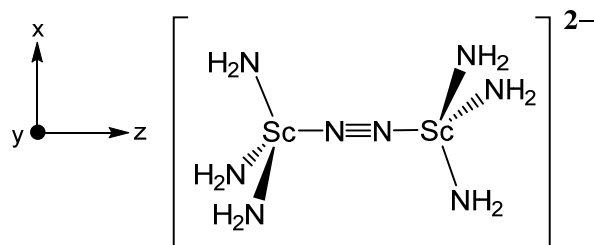
- Consider the hypothetical case in which the lone pairs of the equatorial amide ligands are instead oriented parallel to the z axis as illustrated below. Considering  $\sigma$  and  $\pi$  interactions with the  $\text{NH}_2$  ligands, provide a molecular orbital diagram for this new  $[(\text{NH}_3)\text{Mo}(\text{NH}_2)_3]$  fragment starting from the case where the amide lone pairs are in the xy plane (as shown in lecture). Assume that the order of the energy of the d-based orbitals will not change. Label the frontier orbitals with their d-orbital parentage.



- Perform the same bonding analysis as in part 2 using the metal based frontier orbitals obtained in part 3. Based on analysis, which orientation of the equatorial amide ligand lone pairs would result in a more activated  $\text{N}_2$  ligand? (Parallel to the z axis or parallel to the xy plane?) Provide a molecular orbital argument. Which experimental technique can be used to answer this question? Propose a ligand framework for the equatorial plane donors that would enforce the orientation of the lone pairs of  $\text{NH}_2$  along the z axis.

### Part B

The first rare-earth metal complex with an end-on dinitrogen bridge has been isolated from the reduction of  $\text{Sc}[\text{N}(\text{SiMe}_3)_2]_3$  under  $\text{N}_2$  (Evans *et al*, *JACS*, **2017**, 139, 14861-14864). Similar to part A, consider the bridging dinitrogen species in the staggered conformation in which the silylamide ligands have been substituted with simple amide ligands, as illustrated below.



- Using the MO diagram of the trigonal planar  $\text{Mo}(\text{NH}_2)_3$  complex discussed in class, show the d-splitting diagram for the  $\text{N}_2$ -free, trigonal planar  $[\text{Sc}(\text{NH}_2)_3]^-$  complex. Populate with electrons, and indicate the type of metal-ligand interaction (bonding/antibonding/non-bonding,  $\sigma/\pi/\delta$ ). Label each orbital with their d-orbital parentage ( $d_{z^2}$ ,  $d_{xy}$ ...etc).

## 2018 Ch112 – Problem set 3

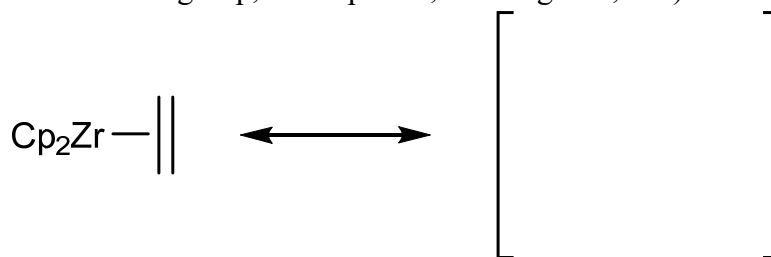
Due: Thursday, Nov. 1 – before class

- Starting from the d-orbitals of the trigonal planar  $[\text{Sc}(\text{NH}_2)_3]^-$  complex, derive the d-splitting diagram of the trigonal pyramidal  $[\text{Sc}(\text{NH}_2)_3]^-$  fragment. Clearly show the relative energies of the resulting d-orbitals upon pyramidalization. For the d-splitting diagram of the pyramidal  $[\text{Sc}(\text{NH}_2)_3]^-$  fragment, populate with electrons, and indicate the type of metal-ligand interaction (bonding/antibonding/non-bonding,  $\sigma/\pi/\delta$ ). Label each orbital with their d-orbital parentage ( $d_{z^2}$ ,  $d_{xy}$ ...etc).
- Derive the metal based SALCs from the two pyramidal Sc fragments (consider only the d-based orbitals). Sketch all SALCs and indicate d-orbital parentage from each metal.
- Using the SALCs derived above and the frontier orbitals (HOMO-1, HOMO, LUMO) of  $\text{N}_2$ , provide a molecular orbital diagram of the dimeric  $[(\text{NH}_2)_3\text{Sc}(\text{N}_2)\text{Sc}(\text{NH}_2)_3]^{2-}$  species. Populate the diagram with electrons. For each MO, indicate the axial symmetry with respect to the Sc-N<sub>2</sub>-Sc interactions, and indicate the nature of the interaction (bonding, etc.). Sketch the MOs of all occupied d-based orbitals. Do you expect the compound to be paramagnetic or diamagnetic?
- The dimeric  $[(\text{NH}_2)_3\text{Sc}(\text{N}_2)\text{Sc}(\text{NH}_2)_3]^{2-}$  species loses the  $\text{N}_2$  bridge upon brief irradiation with UV-light, leading to the formation of the monomeric  $[\text{Sc}(\text{NH}_2)_3]^-$  species. By recrystallizing  $[\text{Sc}(\text{NH}_2)_3]^-$  under  $\text{N}_2$ ,  $[(\text{NH}_2)_3\text{Sc}(\text{N}_2)\text{Sc}(\text{NH}_2)_3]^{2-}$  can be regenerated. Based on these observations, and the MO diagram derived above, provide an explanation for the reversible, weak binding of  $\text{N}_2$  in the Sc dimer complex.

### Problem 3 (3 points)

#### Part A

Consider  $\text{Cp}_2\text{Zr}(\text{C}_2\text{H}_4)$  and its resonance form. How does the oxidation state assignment, and d and valence electron count of the metal change in the two cases? Briefly discuss generally what affects the stability of transition metal complexes in each of the limiting resonance forms (oxidation state, position in the group, in the period, other ligands, etc.).

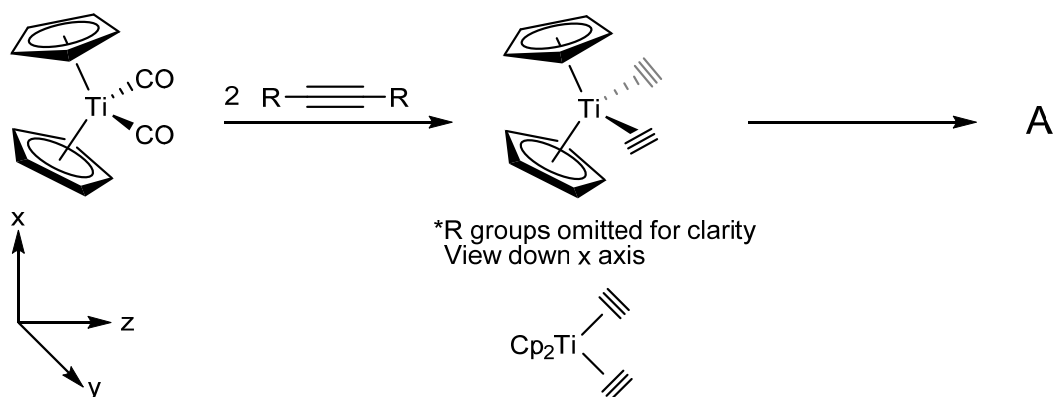


#### Part B

- Consider the following reaction of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  and two equivalents of substituted acetylenes. Provide a molecular orbital diagram of the bis-acetylene adduct, using as basis set the alkyne HOMO and LUMO (only the MOs with lobes pointing toward the metal, not the ones perpendicular to the metal-ligand vector) and the three metal d-based orbitals discussed in class for ansa metallocenes. For each resulting MO, indicate the axial

**2018 Ch112 – Problem set 3****Due: Thursday, Nov. 1 – before class**

symmetry with respect to the Ti-alkyne interactions, and indicate the nature of the interaction (bonding, etc.). Sketch the MOs of all occupied molecular orbitals.



2. Using the frontier orbitals in the previous question, propose a reactivity path and predict the structure of product A.

**Part C**

$\text{Cp}_2\text{ZrH}_2$  reacts with CO to form  $\text{Cp}_2\text{ZrH}_2(\text{CO})$ , while  $\text{Cp}_2\text{ZrCl}_2$  does not react with CO. Provide a molecular orbital explanation for this lack of reactivity.