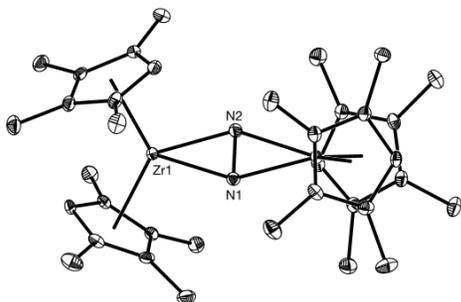


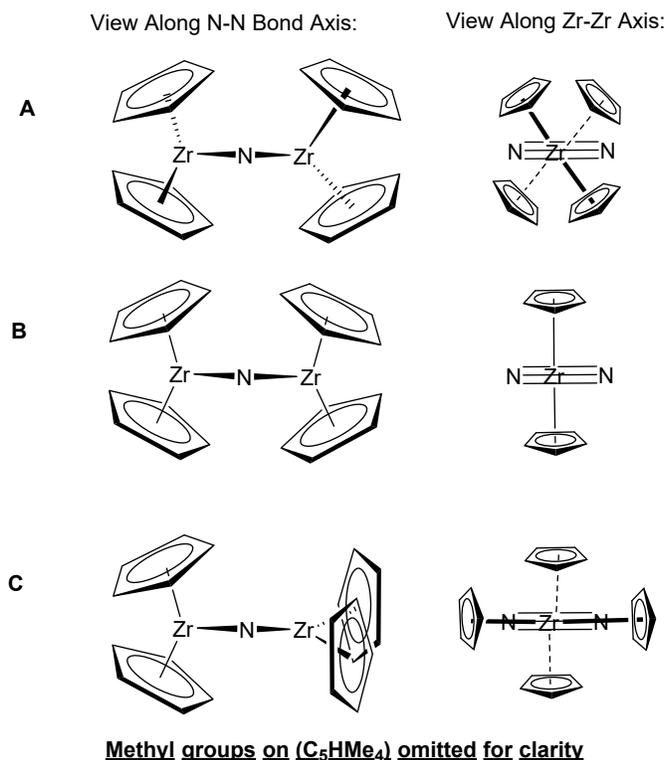
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 Due: Thursday, Oct. 26 – before class

Problem 1 (4 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).

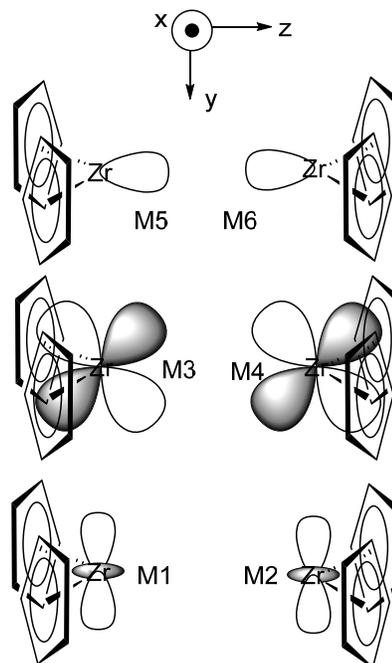


1. Determine the point group of these three structures (A, B, and C), ignoring the methyl groups on the Cp rings.

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

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



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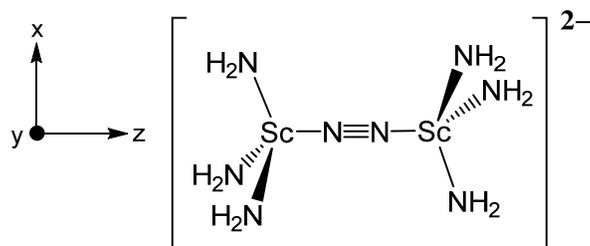
each MO with respect to axis defined by the two Zr atoms, and whether each MO is bonding, non-bonding, or anti-bonding with respect to the Zr-N<sub>2</sub> interaction. Populate the diagram with electrons. Indicate the orbital(s) responsible for the elongation of the N-N distance.

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 (3 points)

The first rare-earth metal complex with an end-on dinitrogen bridge has been isolated from the reduction of Sc[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> under N<sub>2</sub> (*JACS*, ASAP, DOI: 10.1021/jacs.7b08456). Consider the bridging dinitrogen species in the staggered conformation in which the silylamide ligands have been substituted with simple amide ligands, as illustrated below.



1. Using the MO diagram of the trigonal planar Mo(NH<sub>2</sub>)<sub>3</sub> complex discussed in class, show the d-splitting diagram for the N<sub>2</sub>-free, trigonal planar [Sc(NH<sub>2</sub>)<sub>3</sub>]<sup>-</sup> 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).
2. Starting from the d-orbitals of the trigonal planar [Sc(NH<sub>2</sub>)<sub>3</sub>]<sup>-</sup> complex, derive the d-splitting diagram of the trigonal pyramidal [Sc(NH<sub>2</sub>)<sub>3</sub>]<sup>-</sup> fragment. Clearly show the relative energies of the resulting d-orbitals upon pyramidalization. For the d-splitting diagram of the pyramidal [Sc(NH<sub>2</sub>)<sub>3</sub>]<sup>-</sup> 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).
3. Assign the point group of the Sc<sub>2</sub>N<sub>2</sub> model shown above. Derive the metal based SALCs from the two pyramidal Sc fragments (consider only the d-based orbitals). Sketch all SALCs and indicate their Mulliken symbols and d-orbital parentage from each metal. Full mathematical derivation is not required.

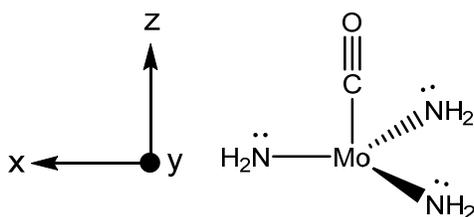
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- Using the SALCs derived above and the frontier orbitals (HOMO-1, HOMO, LUMO) of  $N_2$ , provide a molecular orbital diagram of  $[(NH_2)_3Sc(N_2)Sc(NH_2)_3]^{2-}$ . Populate the diagram with electrons. For each MO, indicate the Mulliken symbol, the axial symmetry with respect to the Sc-N<sub>2</sub>-Sc interactions, and the nature of the interaction (bonding, etc.). Sketch the MOs for all occupied d-based orbitals. Do you expect the compound to be paramagnetic or diamagnetic?
- $[(NH_2)_3Sc(N_2)Sc(NH_2)_3]^{2-}$  loses the  $N_2$  bridge upon brief irradiation with UV-light, leading to the formation of the monomeric  $[Sc(NH_2)_3]^-$  species. By recrystallizing  $[Sc(NH_2)_3]^-$  under  $N_2$ ,  $[(NH_2)_3Sc(N_2)Sc(NH_2)_3]^{2-}$  can be regenerated. Based on these observations, and the MO diagram derived above, provide an explanation for the reversible, weak binding of  $N_2$  in the Sc dimer complex.

### Problem 3 (3 points)

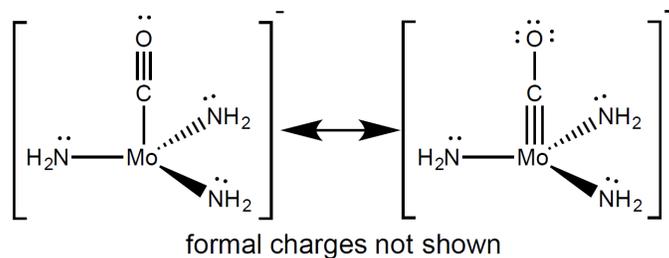
- Derive the full MO diagram of carbon monoxide. Provide qualitatively correct drawings of the frontier orbitals (HOMO-1, HOMO, and LUMO) of CO.
- Consider the interaction between the molybdenum triamide complex  $Mo(NH_2)_3$  shown in class and CO. Using the metal based frontier orbitals of  $Mo(NH_2)_3$  and the frontier orbitals of CO, derive the molecular orbital diagram of  $(CO)Mo(NH_2)_3$  and populate with electrons. For each MO, indicate the axial symmetry with respect to the Mo-CO interactions, and indicate the nature of the interaction (bonding, etc.). Sketch all Mo-CO interactions.



- Consider the one electron reduced complex  $[(CO)Mo(NH_2)_3]^-$  and its two resonance forms. By providing a molecular orbital argument, explain which resonance form is more significant in  $[(CO)Mo(NH_2)_3]^-$ . How does the oxidation state assignment, and d and valence electron count of the metal change in the two limiting cases? Discuss generally what affects the propensity of the metal to bind CO in one vs the other limiting resonance forms (oxidation state, position in the group, in the period, other ligands). Circle the two MOs that determine the character of the interaction.

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4. Sketch the expected product of the reaction between  $[(\text{CO})\text{Mo}(\text{NH}_2)_3]^-$  and  $\text{Me}_3\text{SiCl}$ . Assume the amide ligands are spectators. Is this consistent with the resonance picture obtained from part 3? Explain.
5. Provide the predicted increasing order of the C-O stretching frequencies of compounds analyzed in parts 1, 2, 3, and 4.