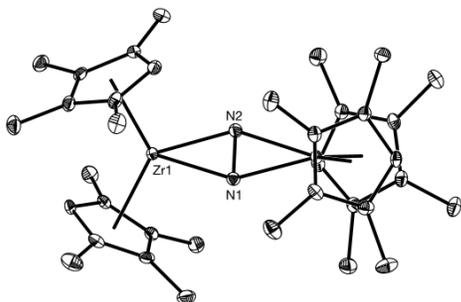


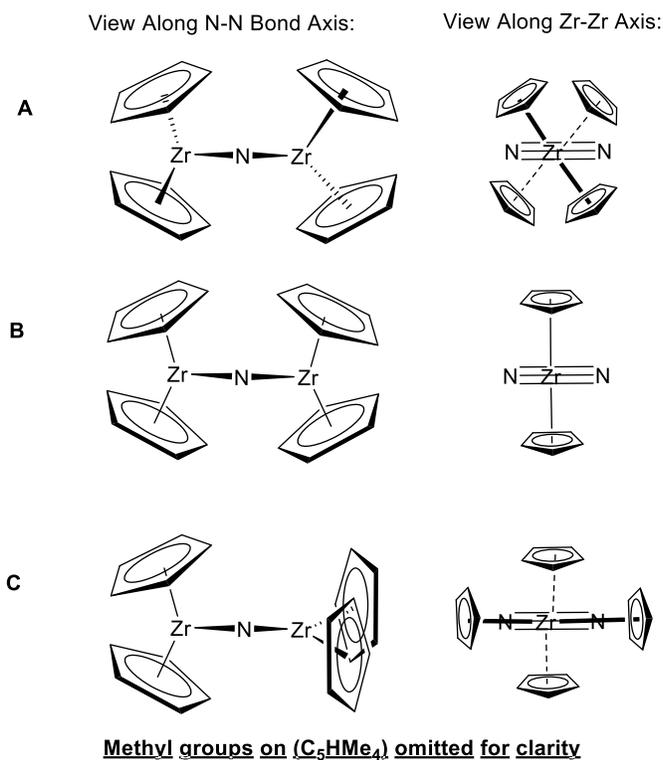
2016 Ch112 – problem set 3
Due: Thursday, Oct. 27 – before class

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).

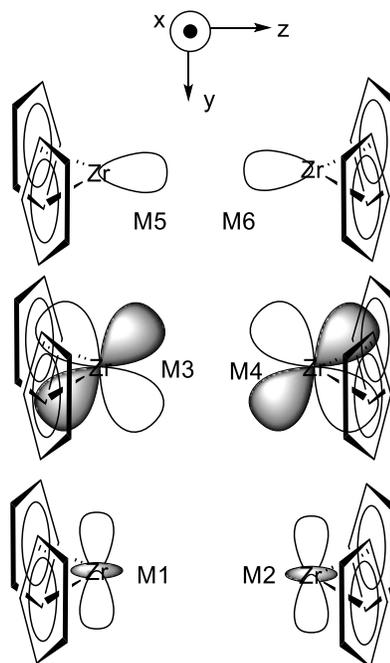


1. Determine the point group of these three structures (A, B, and C), ignoring the methyl groups on the Cp rings.

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

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



2016 Ch112 – problem set 3

Due: Thursday, Oct. 27 – before class

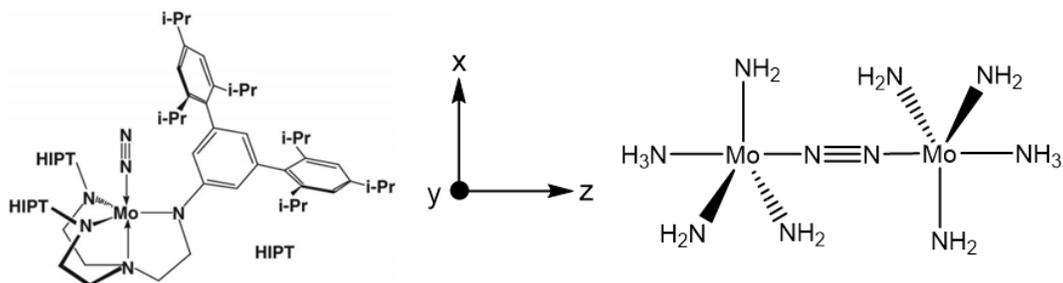
symmetry of each MO with respect to axis defined by the two Zr atoms, and whether each MO is bonding, non-bonding, or anti-bonding with respect to the Zr-N₂ interaction. Populate the diagram with electrons. Indicate the orbital(s) responsible for the elongation of the N-N distance.

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 N₂ 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)

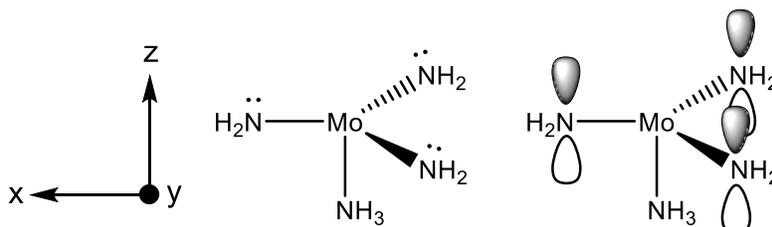
Catalytic reduction of dinitrogen to ammonia has been demonstrated at a single Mo center (Schrock *et al*, *Science*, **2003**, 301, 76-78). The structure of the end-on bound dinitrogen complex is shown below, featuring a tripodal ligand with extremely bulky substituents (HIPT). The use of less bulky 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 Mo₂N₂ model shown above. Using the frontier orbitals of the [(NH₃)Mo(NH₂)₃] 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 N₂, provide a molecular orbital diagram of the dimeric [(NH₃)(NH₂)₃Mo-N₂-Mo(NH₂)₃(NH₃)] species. Populate the diagram with electrons. For each MO, indicate the axial symmetry with respect to the Mo-N₂-Mo 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?

2016 Ch112 – problem set 3**Due: Thursday, Oct. 27 – before class**

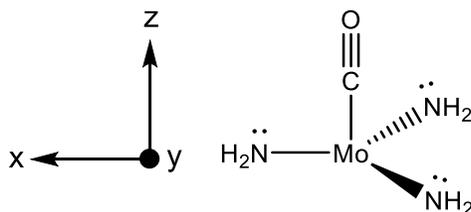
3. Consider the hypothetical case in which the lone pairs of the equatorial amide ligands are instead oriented parallel to the z axis as illustrated below. Considering σ and π interactions with the NH_2 ligands, provide a molecular orbital diagram for this new $[(\text{NH}_3)\text{Mo}(\text{NH}_2)_3]$ 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.



4. 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 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 NH_2 along the z axis.

Problem 3 (3 points)

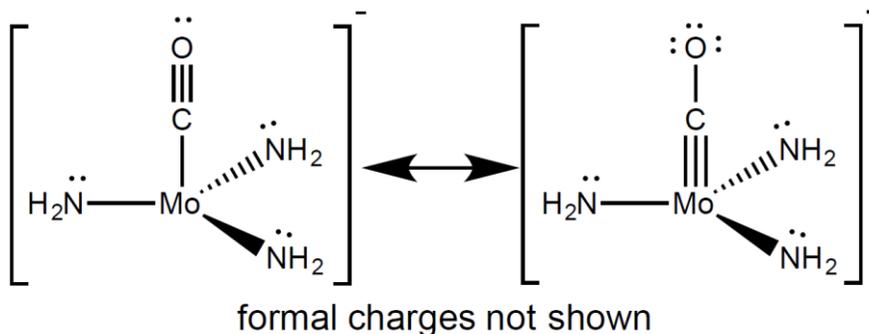
1. Derive the full MO diagram of carbon monoxide. Provide qualitatively correct drawings of the frontier orbitals (HOMO-1, HOMO, and LUMO) of CO.
2. Consider the interaction between the molybdenum triamide complex $\text{Mo}(\text{NH}_2)_3$ shown in class and CO. Using the metal based frontier orbitals of $\text{Mo}(\text{NH}_2)_3$ and the frontier orbitals of CO, derive the molecular orbital diagram of $(\text{CO})\text{Mo}(\text{NH}_2)_3$ 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.



3. Consider the one electron reduced complex $[(\text{CO})\text{Mo}(\text{NH}_2)_3]^-$ and its two resonance forms. By providing a molecular orbital argument, explain which resonance form is more significant in $[(\text{CO})\text{Mo}(\text{NH}_2)_3]^-$. How does the oxidation state assignment, and d and valence electron

2016 Ch112 – problem set 3**Due: Thursday, Oct. 27 – before class**

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.



4. Sketch the expected product of the reaction between $[(\text{CO})\text{Mo}(\text{NH}_2)_3]^-$ and Me_3SiCl . 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.