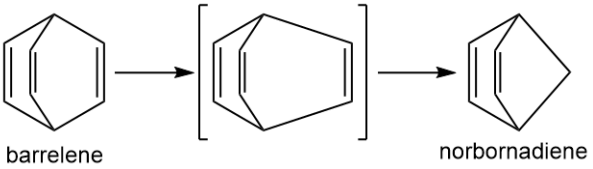
2015 Ch112 − Problem Set 3
Due: Thursday, October 22 – before class

Problem 1 (3 points)

Part A.
In problem set 2, the π-system of bicyclo[2.2.2]octa-2,5,7-triene was analyzed.

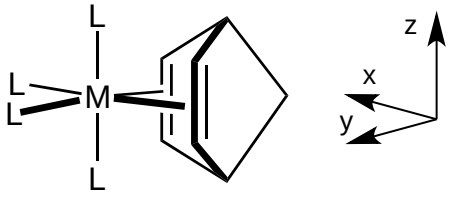


1. Starting from the MO diagram of the π-system of barrelene, show how the energy of each molecular orbital changes for the hypothetical case in which one of the double bonds has been moved away from the other two double bonds to infinity by elongating the connecting two single bonds (see above).

2. When the double bond has been moved to infinity, the remaining system of two double bonds is similar to norbornadiene, a common ligand in organometallic chemistry. *By inspection*, sketch the four MOs of the π-system of norbornadiene. Sketch an MO diagram for the π-system of norbornadiene, and populate with electrons.

Part B.

1. Norbornadiene binds to metal ions as illustrated below. What is the axial symmetry of each of the four orbitals determined above along each axis defined by the metal-ligand bond? For the purpose of this exercise, consider that the double bonds do not interact with each other significantly.



2. Consider a generic octahedral complex ML_6. Show an MO diagram taking into account σ interactions only (showing the derivation is not necessary). For basis set, consider an s orbital for each L, and the s, p, and d orbitals for M. Label with Mulliken symbols. Fill with electrons assuming that the d-count is 6. Clearly label the d orbitals with their parentage (d_{z2}, d_{xy}, etc) and character (bonding, non-bonding, antibonding with respect to the M-L interaction).

3. Substituting norbornadiene for two L ligands, and assuming that L and each olefin moiety of norbornadiene have the same σ-donor properties, provide a simplified MO diagram of the resulting complex starting only with the orbitals of d-parentage from the diagram in part 4. Assume that the energy of the metal-based d orbitals is between the bonding and the antibonding orbitals of norbornadiene. For the purpose of this exercise, consider that the double bonds do not interact with each other significantly. Label the d orbitals with their parentage, assuming the coordinate system above, fill with electrons, and indicate the character of the MOs (σ, π and bonding, non-bonding, antibonding with respect to the M-olefin interaction).

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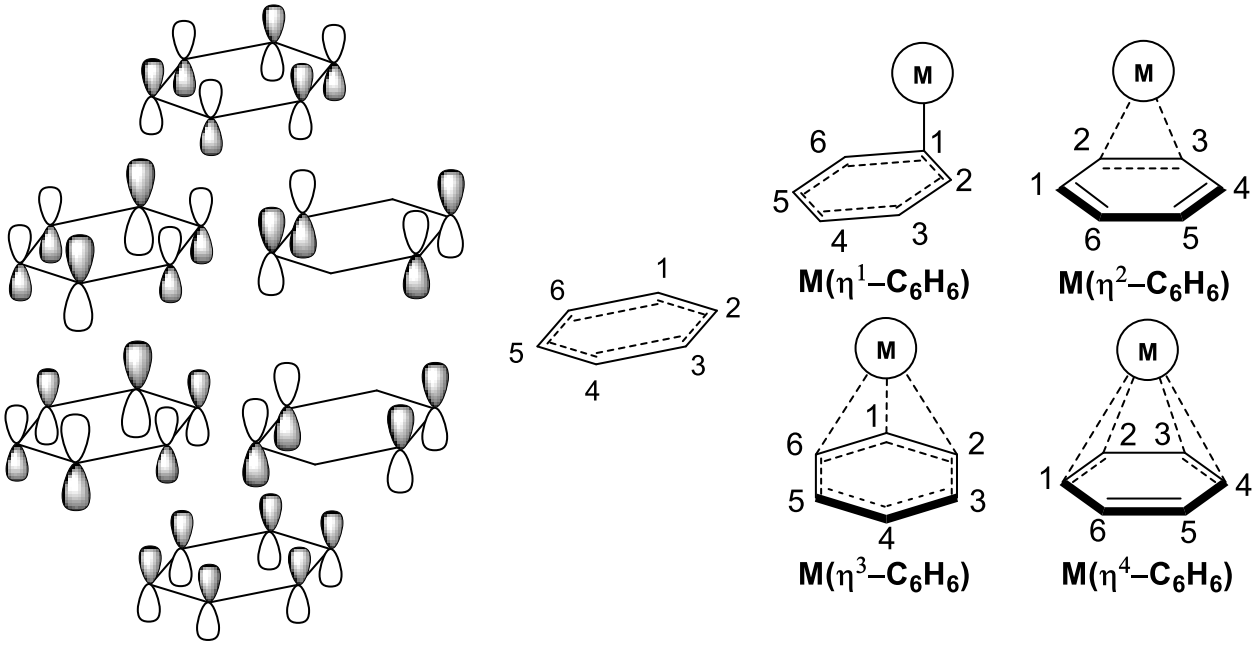
Problem 2 (2 points)

Compounds displaying interactions of metal centers with the π-system of benzene are common in coordination chemistry, including as intermediates for CH activation and cross coupling reactions. Shown below is the molecular orbital depiction of the π-system of benzene, derived in class. Hapticity (η) is defined as the number of contiguous atoms in a ligand interacting with the metal center. Following the numbering scheme provided and assuming that the metal based orbitals fall between the energy of the HOMO and the LUMO of benzene, answer the following questions:



1. Consider the metal ion interacting with benzene in a η^1 fashion. The metal ion has one orbital available along the axis of interaction: σ-acidic (empty). Sketch only the most significant interaction between benzene and the metal ion. Sketch a qualitative MO diagram starting from the one metal orbital and six benzene frontier orbitals.

2. Consider the metal ion interacting with benzene in a η^2 fashion. The metal ion has two orbitals available: one σ-acidic and one π-basic. Sketch only the most significant interactions between benzene and the metal ion. Sketch a qualitative MO diagram starting from the two metal orbitals and six benzene frontier orbitals.

3. Consider the metal ion interacting with benzene in a η^3 fashion. The metal ion has two orbitals available: one σ-acidic and one π-basic. Sketch only the most significant interactions between benzene and the metal ion. Sketch a qualitative MO diagram starting from the two metal orbitals and six benzene frontier orbitals.

4. Consider the metal ion interacting with benzene in a η^4 fashion. The metal ion has three orbitals available: one σ-acidic, one π-basic, and one π-acidic (the two π orbitals are orthogonal to each other). Sketch only the most significant interactions between benzene and the metal ion. Sketch a qualitative MO diagram starting from the three metal orbitals and six benzene frontier orbitals.

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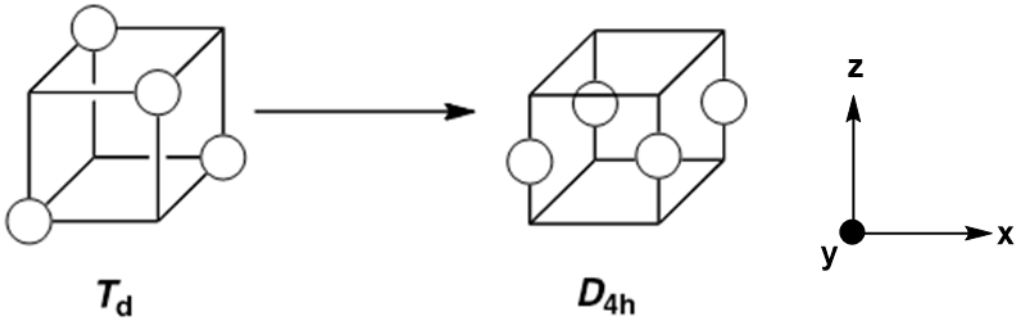
Problem 3 (2 points)

Walsh diagrams provide a convenient method to track the effect of angular distortions on the molecular orbital energies. Molecules with the general formula AH_4 can adopt a number of different geometries. Two of such geometries are shown below, the tetrahedral geometry and the square planar geometry.



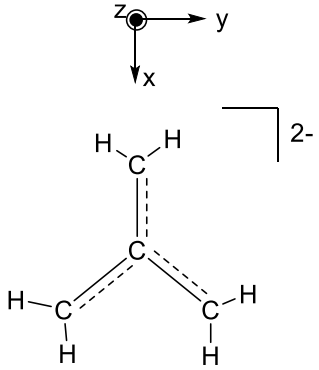
1. Use the given coordinate system. Using the *s* and *p* orbitals on the central atom A, and the *s* orbitals of the four H atoms as the basis set, sketch the molecular orbital diagram of AH_4 in the tetrahedral geometry. Sketch and assign Mulliken symbols for each molecular orbital.

2. Draw a Walsh diagram for the distortion of such a T_d symmetric AH_4 molecule to one with D_{4h} symmetry. Keep the coordinate system the same. This diagram should include the full MO diagram of such a molecule including MO drawings (Mulliken labels are not required). Clearly correlate the molecular orbitals.

3. Based on this diagram, determine which geometry is favored for CH_4 and XeH_4 (model compound for XeF_4). Explain.

Problem 4 (3 points):

1. Trimethylenemethane dianion ($[tmm]^{2-}$) is a planar species exhibiting D_{3h} symmetry. Derive an MO diagram for this ion considering only the four p_z orbitals of $[tmm]^{2-}$. Draw the MOs, indicate Mulliken symbols, and populate the resulting diagram with electrons.



2. Consider a set of three σ-donor ligands, L, arranged in an equilateral triangular fashion, such as shown below. Draw SALCs for this ligand set (L_3), and assign Mulliken symbols according to the point group D_{3h}.

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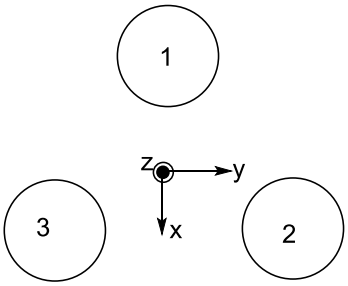
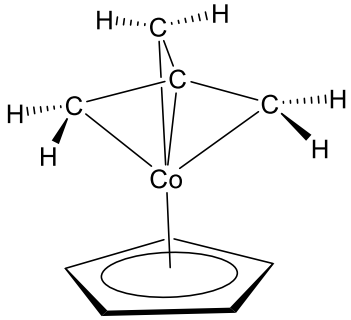
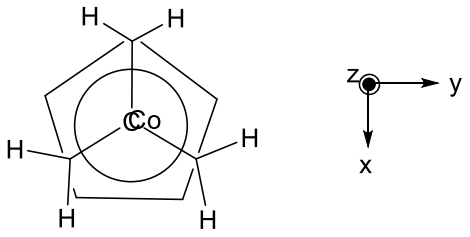


3. Starting from the MCp_2 qualitative MO diagram derived in class, derive the resulting qualitative MO diagram for the [MCp] fragment of C_{5v} symmetry (as if you had removed a Cp anion from the top of the metallocene).
   i. Assign Mulliken symbols to the MOs of your new diagram.
   ii. Clearly indicate the axial symmetry of the MOs (i.e. σ-, π-, or δ-interaction along the z axis, defined as the vector connecting the metal and the centroid of Cp^-).
   iii. Indicate the type of metal-ligand interaction for each MO (i.e. bonding, anti-bonding, or non-bonding).
   iv. Label the d-parentage (d_{z2}, d_{xy}, etc) of the d-based orbitals and clearly indicate their relative energies with respect to the starting diagram of MCp_2.

4. Starting from the MO diagram for the [MCp] fragment derived in part c., derive a new, qualitative MO diagram for the species CoCp(tmm), shown below. Consider only the ligand MOs interaction with the d-based orbitals of the metal center.
   i. Assign the point group of this molecule. What is the d-electron count? What is the metal oxidation state? How many total valence electrons are there?
   ii. Clearly indicate the axial symmetry of the MOs (i.e. σ-, π-, or δ-interaction along the z axis, defined as the vector connecting the metal and the centroid of Cp^-)
   iii. Indicate the type of metal-ligand interaction for each MO (i.e. bonding, anti-bonding, or non-bonding).
   iv. Label the d-parentage (d_{z2}, d_{xy}, etc) of the d-based orbitals and clearly indicate their relative energies.
   v. Populate the MO diagram with electrons



Molecule and coordinate system
viewed from the top-down perspective:



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5. Consider the cationic compound $[CoCp(L)_3]^{2+}$ in which the basis set of SALCs you derived in part (b) are interacting with the [MCp] fragment derived in part (c), according to the structure shown below. Derive a new, qualitative MO diagram for $[CoCp(L)_3]^{2+}$ considering only the ligand MOs interaction with the d-based orbitals of the metal center.
   i Assign the point group of this ion. What is the d-electron count? What is the metal oxidation state? How many total valence electrons are there?
   ii. Clearly indicate the axial symmetry of the MOs (i.e. σ-, π-, or δ-interaction along the z axis, defined as the vector connecting the metal and the centroid of Cp^-)
   iii. Indicate the type of metal-ligand interaction for each MO (i.e. bonding, anti-bonding, or non-bonding).
   iv. Label the d-parentage (d_{z2}, d_{xy}, etc) of the d-based orbitals and clearly indicate their relative energies.
   v. Populate the MO diagram with electrons