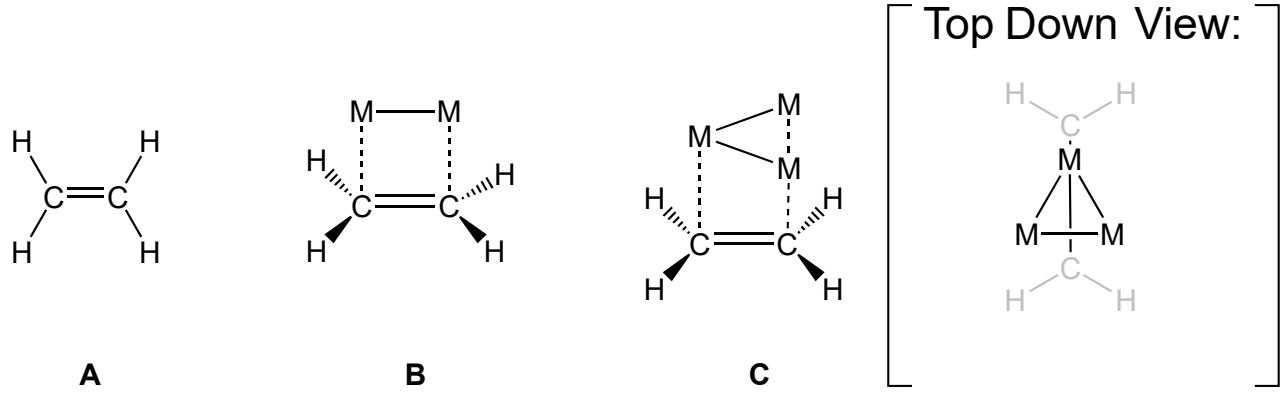
2017 Ch112 − Problem Set 2
Due: Thursday, October 19 – before class

Problem 1 (2 points)

The MO diagrams of complicated molecules can be constructed from the interactions of molecular fragments. The point groups of isolated fragments are often of higher symmetry that the actual molecule. It is useful to analyze the fragment in a lower symmetry point group that is a subgroup of the actual point group of the fragment. Consider the coordination of ethylene to M_2 and M_3 moieties, as shown below.

1) For molecules A, B, and C, list the symmetry operations and point groups.



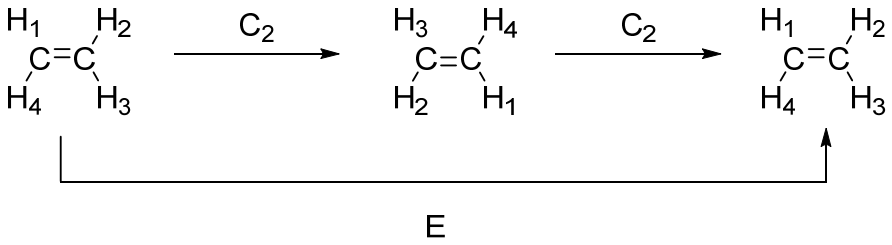
Consider the following multiplication table for C_{2v}, filled in according to the products of operations:

$\underline{\text{Operation}_{\text{cell}}} = \underline{\text{Operation}_{\text{column}}} \times \underline{\text{Operation}_{\text{row}}}$

You will find that all possible products of operations (or squares of operations) are also operations that are members of this group (C_{2v}). Note that C_{2v} is an Abelian group (multiplications of operations are commutative).

C_{2v}	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

2) We can obtain new characters corresponding to D_{2h} by adding additional operations to the C_{2v} point group, a subgroup of D_{2h}. Expand the multiplication table to D_{2h}. Use ethylene to visualize four operations as shown in the example below.



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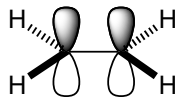
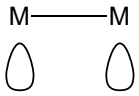
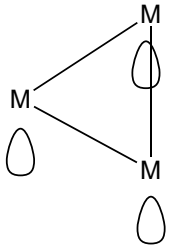
D_{2h}	E	C_2	σ_v	σ_v'	?	?	?	?
E	E	C_2	σ_v	σ_v'				
C_2	C_2	E	σ_v'	σ_v				
σ_v	σ_v	σ_v'	E	C_2				
σ_v'	σ_v'	σ_v	C_2	E				
?								
?								
?								
?								

3) Analyze the interaction between ethylene and the M_2 and M_3 fragments. For each metal, consider only a single orbital of sigma symmetry as basis set for interactions. For ethylene only consider the HOMO and LUMO. Draw the SALCs of the M_2 and M_3 fragments that have the correct symmetry to make bonds with the ethylene HOMO and LUMO, respectively. Indicate if these SALCs are σ acidic/basic or π acidic/basic.

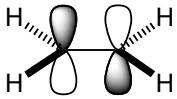
binding with HOMO:

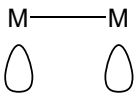


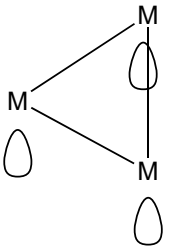




binding with LUMO:







Problem 2 (3 points)

1) Consider an octahedral metal complex ML_6. Show an MO diagram taking into account σ interactions only (including 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).

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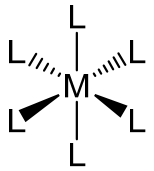
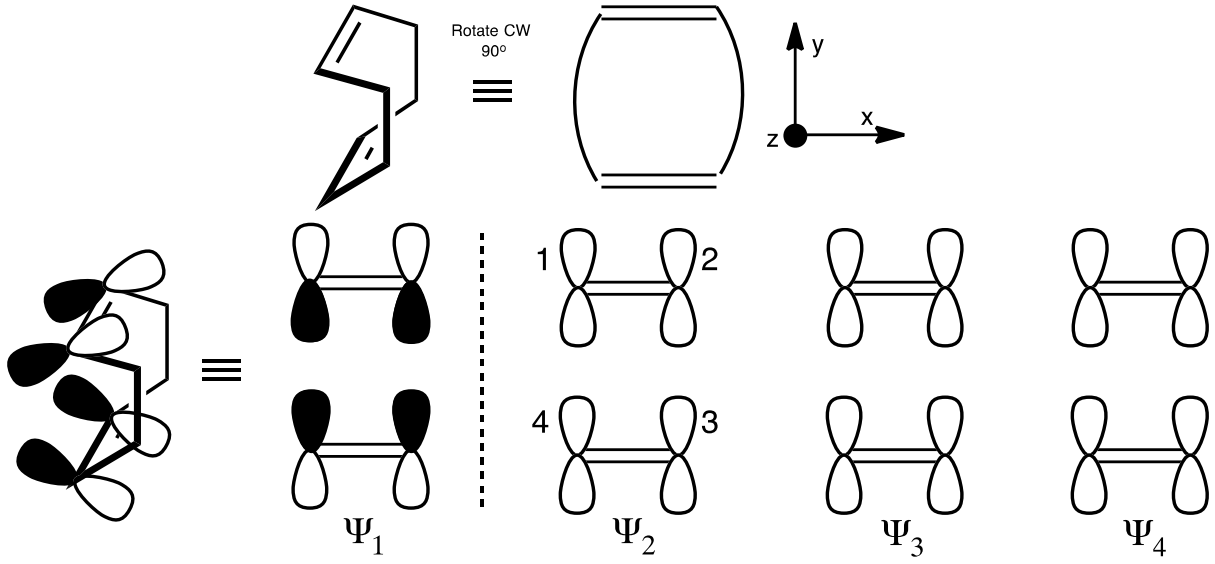


2) Now consider the substitution of two L ligands on the metal complex for 1,5-cyclooctadiene (COD) as shown in the following reaction scheme. First derive the MO diagram of the isolated fragment COD.

i) What is the point group of COD?
ii) Using the four p orbitals on each of the sp^2 hybridized carbon atoms as the basis set, generate a reducible representation Γ_{4p}. Express Γ_{4p} as a sum of irreducible representations, derived either by inspection or mathematically.
iii) Find the normalized wavefunctions for the four SALCs, using the projection operator to determine its coefficients. Use the following diagrams of the p-orbitals to represent the SALCs graphically and provide normalized wavefunctions for each. An example is shown below to highlight the selected view. Assign Mulliken symbols to each SALC.
iv) The SALCs derived above correspond to the MOs for the π system of COD. Assume that, because the double bonds are not conjugated, there is only a small energy difference compared to isolated double bond interactions. Sketch the MO diagram for the π system of COD, populate with electrons and include Mulliken symbols. Indicate the character of the MOs (bonding, antibonding) with respect to the interaction between adjacent carbon atoms.



3) Assuming that L and each olefin of COD have similar σ-donating properties, develop a simplified MO diagram of the ML_4(COD) complex. Begin with the orbitals of d-parentage from the diagram you derived in part 1 and interact this set with the appropriate COD SALCs. Assume that the energy of the metal-based d-orbitals is between the π-bonding and the π-antibonding orbitals of COD. Label the parentage of the d-orbitals, considering the given coordinate system, fill with electrons (keeping a d-electron count of 6), and indicate the character of the MOs (σ/π/δ etc. and bonding/non-bonding/antibonding) with respect to M-olefin interaction.

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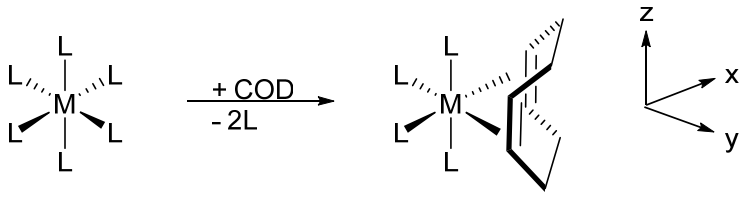
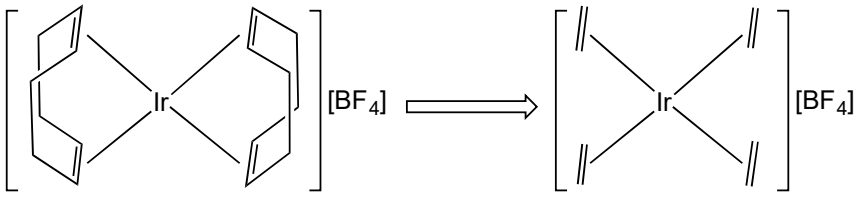


Problem 3 (4 points)

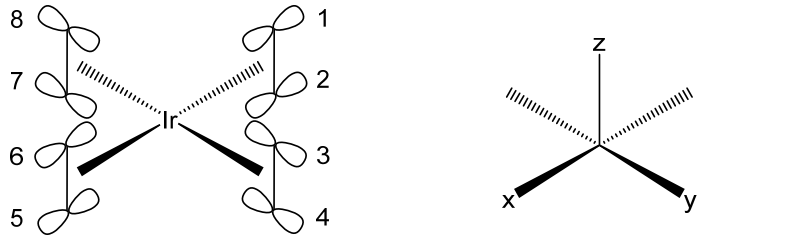
Iridium bis-(cyclooctadiene) tetrafluoroborate, $[Ir(COD)_2][BF_4]$, has a square-planar coordination environment around iridium. For the purposes of this exercise, consider the hypothetical tetra-ethylene complex $[Ir(C_2H_4)_4][BF_4]$ instead.



$Ir(COD)_2(BF_4)$, view along its principal C_n Hypothetical $Ir(C_2H_4)_4(BF_4)$ molecule

1) Give the oxidation state, d-electron count, and valence electron count for $[Ir(C_2H_4)_4][BF_4]$.

2) Assign the point group of the $[Ir(C_2H_4)_4]^+$ cation, and determine the reducible representation for the basis set consisting of the eight carbon 2p orbitals in the π-system of the four ethylene molecules. Each C(2p) orbital has been numbered as shown below:



Side-on view. C(2p) orbitals of ethylene π-system

coordinate system for this problem

3) Reduce the representation in part 2 to a sum of irreducible representations.

4) Sketch all ethylene-based SALCs and assign Mulliken symbols. For each SALC, indicate whether it will act as a Lewis acid or base. Use the figures provided below. It may be helpful to consider the frontier orbitals of each ethylene in your analysis.

5) For a SALC of A_{2u} symmetry, apply the projection operator on p_1 to determine the normalized wavefunction in terms of p_1, p_2,…,p_7, p_8.

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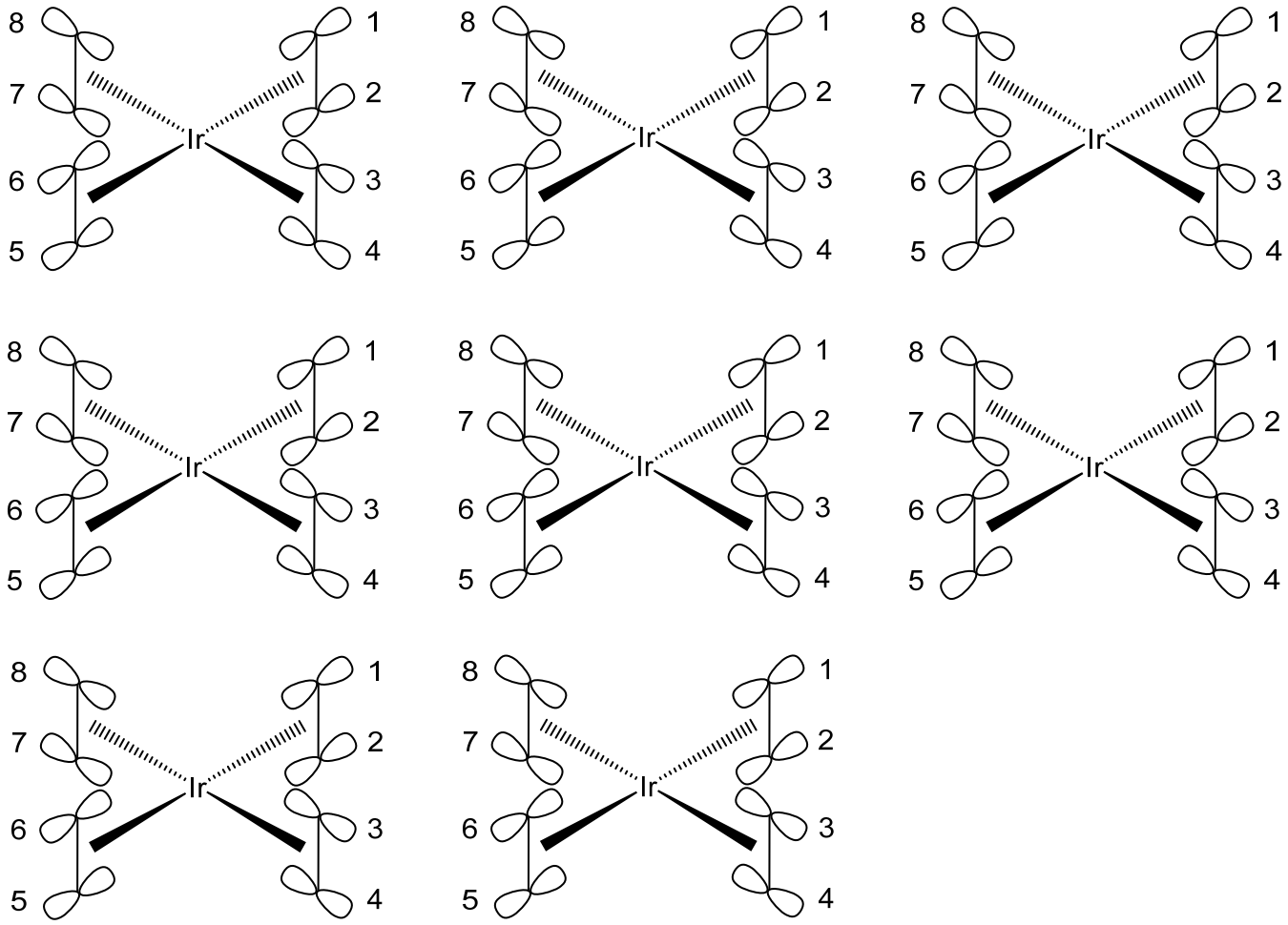
6) Provide normalized wavefunctions for all SALCs, by inspection. For each degenerate set, show that contributions from p_1 and p_2 are equal. Verify that atomic orbital p_1 is used fully in the derived SALCs. Show that two SALC of your choice are orthogonal.

7) Show an MO diagram of $[Ir(C_2H_4)_4]^+$. For Ir, consider a basis set consisting of Ir(5d), Ir(6s), and Ir(6p) orbitals. Populate with electrons, label with Mulliken symbols, and indicate the type of metal-ligand interaction (bonding/antibonding/non-bonding, σ/π/δ). Label the d-orbitals with their parentage (d_{z2}, d_{xy}…etc).

8) Sketch the HOMO−1, HOMO, and LUMO.

(For part 5)



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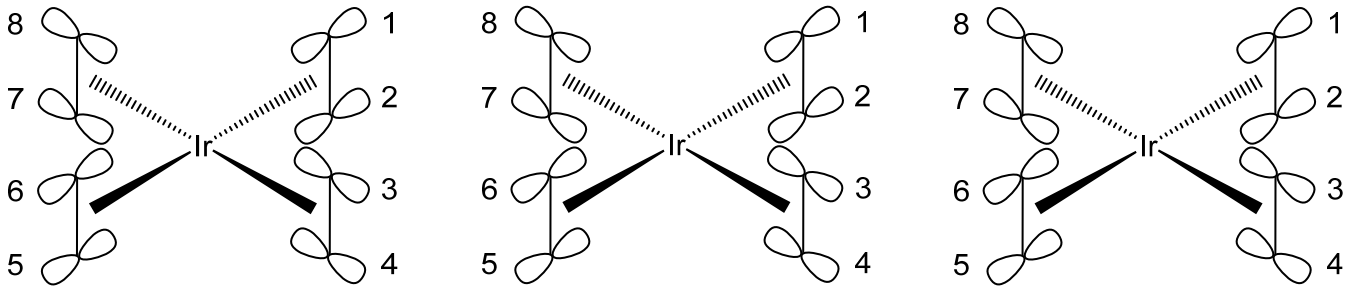
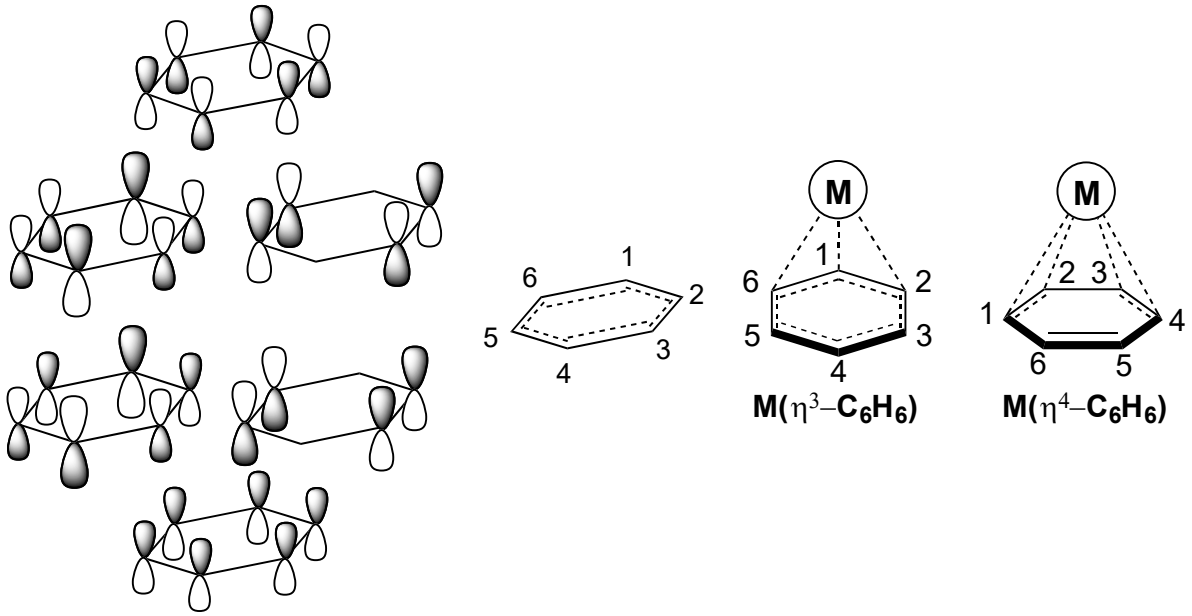
(For part 8)



Problem 4 (1 point)

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^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.

2. 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.