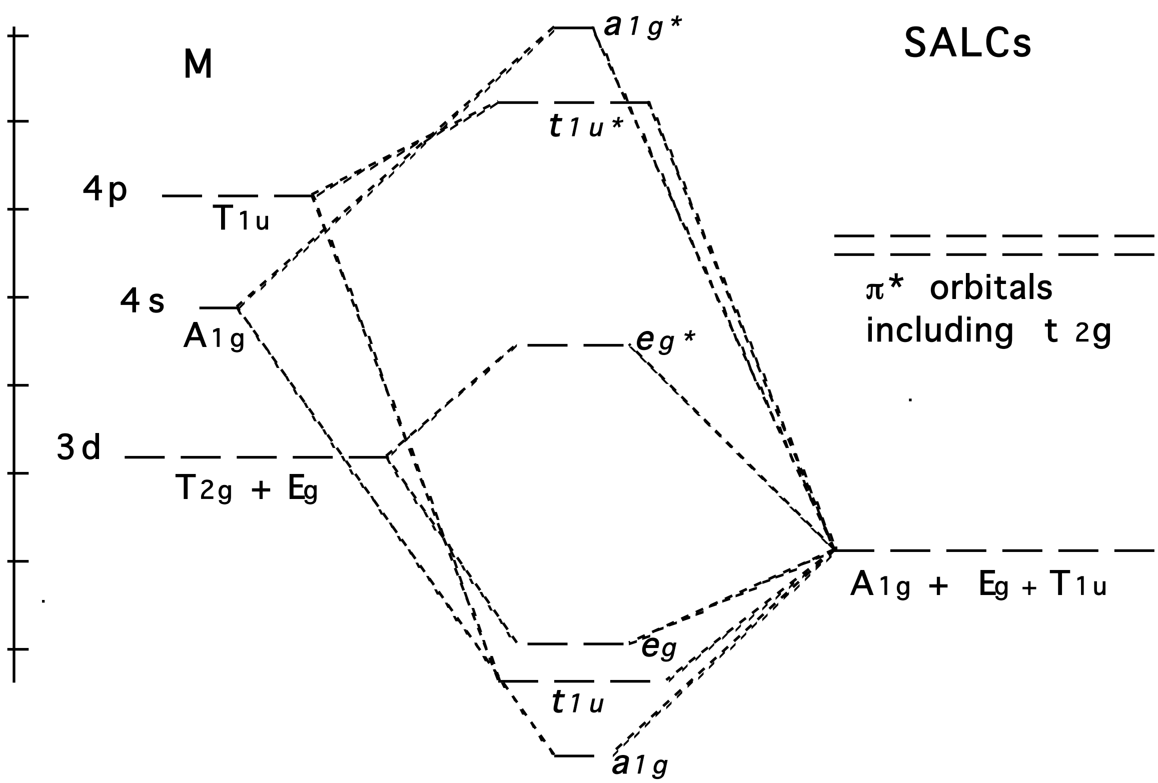
Inorganic Chemistry with Doc M.
Fall Semester, 2009
Day 22. Organotransition Metal Chemistry I: The 18-electron rule

Element team name:

❏ My isotope partner and I worked together.
❏ I worked alone on this assignment.
Your Name(s):

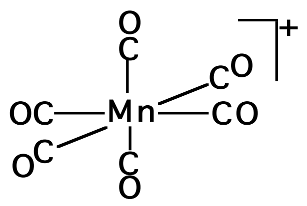
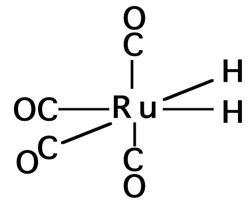
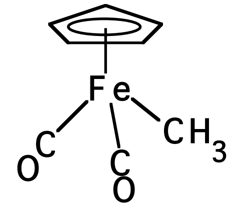
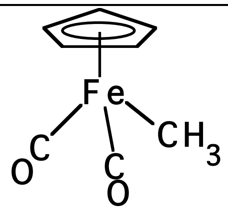
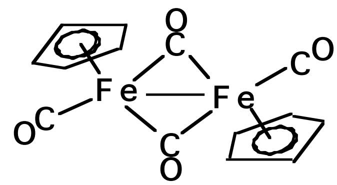
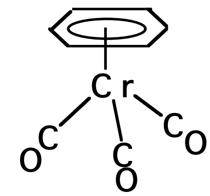
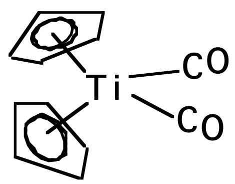
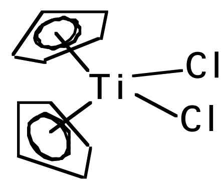
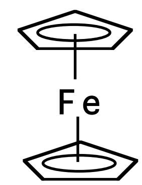
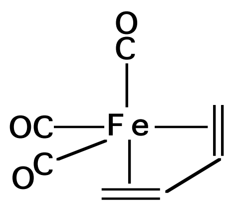
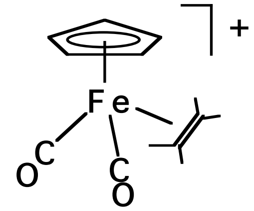
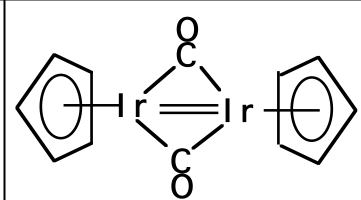
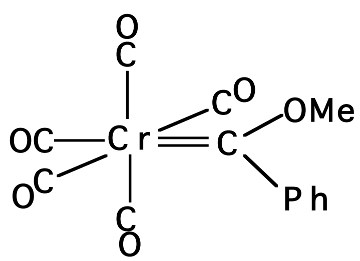
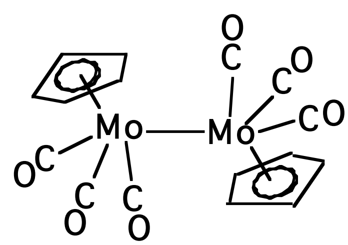
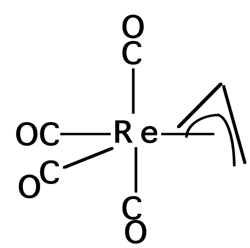
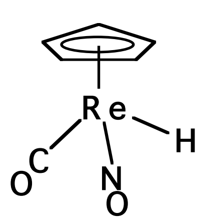
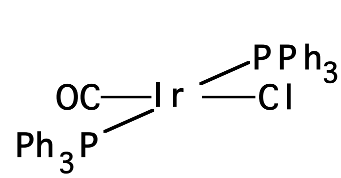
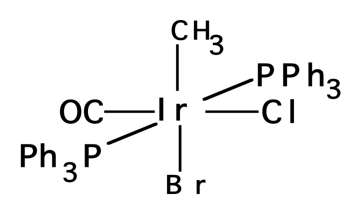
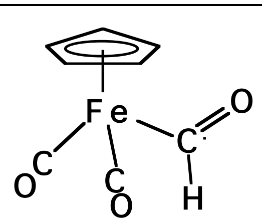
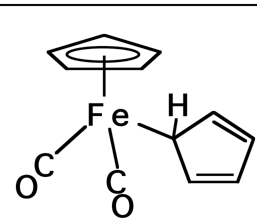
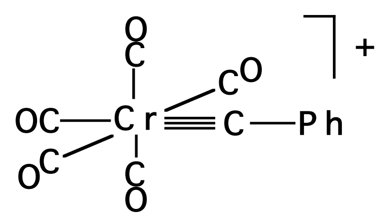
1. π-Back-bonding. π-Back bonding can occur between any metal with electrons to share (low oxidation state) and any ligand with symmetry-allowed empty orbitals. Sketch the σ-donation and the π-back bonding that occurs between a transition metal and a carbon monoxide ligand. Repeat this for a transition metal and a PF_3 ligand. Lots of ligands have orbitals that are symmetry-allowed for p-back bonding, however, the interaction is especially important for these two ligands. In the case of carbon monoxide, few complexes exist in which the metal is in a "high" oxidation state and thus unable to provide electrons for π-back bonding.

The MO diagram below shows the σ-donation that occurs between an octahedral set of ligands and the ligand σ-SALC orbitals. The π-SALC orbitals that will be used for π-back bonding are shown prior to being connected to the metal's orbitals. They are labeled as "π* orbitals" and consist of two such orbitals from each of the ligands. All together the 12 π-SALC orbitals transform in a variety of ways including as t_{2g} — the only one that interests us because its symmetry matches the metals t_{2g} orbitals. Complete the sketch below by connecting three of the π-SALC orbitals with the t_{2g} orbitals from the metal. The other nine π-SALC orbitals are non-bonding. Populate the MO diagram with 18 electrons.

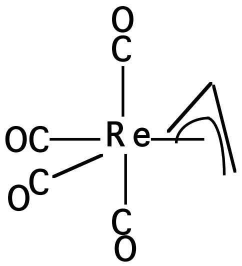
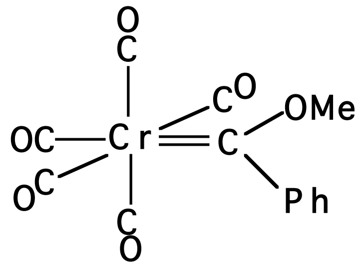
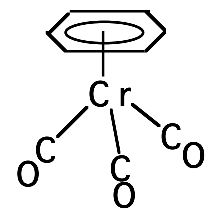
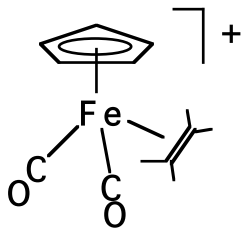
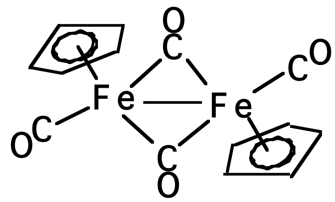
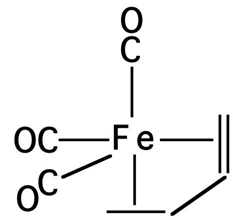
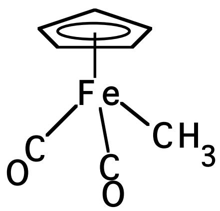
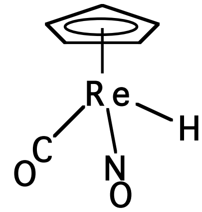
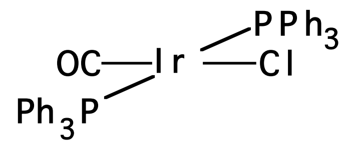
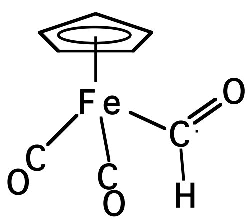
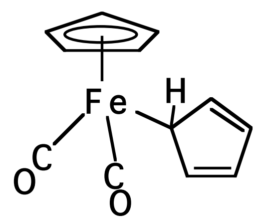
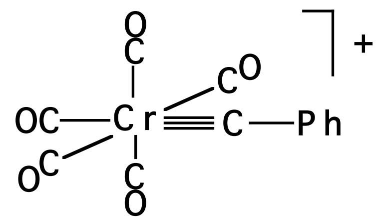


Sketch one of the three t_{2g} molecular orbitals — the sketch should include one SALC consisting of four CO π* orbitals and one of the t_{2g} orbitals from the metal.

2. The 18-electron Rule. Count electrons in the following complexes, indicating how many each ligand donates. Not all obey the 18-electron rule!

2. Functional Groups. Name (list) the functional groups in the following complexes. (The first one is done for you.)

 *carbonyl, π-allyl*		
		
		
		

Review for the standardized ACS final exam.

1. Which of these does not follow the 18-electron rule?
   (a) $V(CO)_6^-$
   (b) $Mn(CO)_6^+$
   (c) $Re(CO)_4^{-3}$
   (d) $(\pi\text{-}C_5H_5)Fe(CO)_3$
   (e) $(\pi\text{-}C_6H_6)_2Zr(CO)$

2. One common form of iron carbonyl is a neutral structure with two Fe atoms joined by a Fe-Fe single bond. Some carbonyls are terminal and others are bridging. What is the formula for this compound?
   (a) $Fe_2(CO)_6$
   (b) $Fe_2(CO)_8$
   (c) $Fe_2(CO)_9$
   (d) $Fe_2(CO)_{10}$
   (e) $Fe_2(CO)_{12}$

3. Which of the following does not form a carbonyl of formula $M(CO)_x$?
   (a) V
   (b) Cr
   (c) Mn
   (d) Fe
   (e) Ni

4. In which of the following is π-back bonding least significant in terms of stabilizing the species?
   (a) $V(CO)_6^-$
   (b) $Cr(CO)_6$
   (c) $Mn(CO)_6^+$
   (d) $W(CO)_6$
   (e) $Ni(CO)_4$

Answers: D, C. C. C

Answers: Topic XI Worksheet

Row 1

Mn(CO)5^+: Mn+ = 6 e + 6 x 2 = 18e
Ru(C)4(H)2: Ru(0) 8e + 8 e from COs + 2 x 1e for Ru-H = 18e
CpFe(CO)2CH3: Cp = 5 + Fe = 8 + 2 x 2 for COs + 1e for Fe-C = 18e

Row 2:
oooops
count each Fe separately. Cp = 5 + Fe(0) is 8e + 2 for terminal CO + 2 x 1e for bridging COs + 1e for bond to the other Fe = 18e
(C6H6)Cr(CO)3: 6e for C6H6 + 6e for Cr(0) + 3 x 2e for COs = 18 e

Row 3
(C5H5)2Ti(CO)2: 10e for two Cps + 4e for Ti(0) + 2 x 2e for COs = 18e
(C5H5)2Ti(Cl)2: 10e for two Cps + 4e for Ti(0) + 2 x 1e for Ti-Cls = 16e
(C5H5)2Fe: 10e for two Cps + 8e for Fe(0) = 18e

Row 4:
Fe(CO)3(C4H6): Fe(0) has 8e + 3 x 2e for COs + 4e from butadiene = 18e
CpFe(CO)2(C2H4)^+: Cp = 5 + Fe^+ = 7 + 2 x 2 for COs + 2e for ethene = 18e
[CpIr(CO)]2: each Ir(0) has 9e + Cp for 5e + 2 bridging COs at 1 e to each Ir + two electrons from other iridium in the double bond = 18e

Row 5:
Cr(CO)5(COMePh): Cr(0) has 6e + 5 COs for 10e + two electrons from carbene = 18e
count each Mo separately. Cp = 5 + Mo(0) is 6e + 6 for COs + 1e for Mo-Mo bond = 18e
Re(CO)4(C3H5): Re(0) has 7e + 4 COs worth 8e + three pi electrons from pi-manifold of allyl group

Row 6:
CpRe(CO)(NO)H: Cp: 5e + Re(0): 7e + CO: 2e + linear-NO: 3e + covalent ReH: 1e = 18e
Ir(PPh3)2(CO)(Cl): Ir: d8 + two phosphines at 2e each + 2e from CO and 1e from Cl = 16e (sq pl)
Ir(PPh3)2(CO)(Cl)(Br)(CH3): Ir: d8 + two phosphines at 2e each + 2e from CO and 1e from Cl + 1e from Br + 1e from CH3 = 18e (sq pl)

Row 7:
CpFe(CO)CHO: Cp has 5 + Fe(0) has 8 + 2e from CO + 1e from sigma bonded formyl = 18e
CpFe(CO)C5H5: pi-Cp has 5 + Fe(0) has 8 + 2e from CO + 1e from sigma bonded Cp = 18e

Cr(CO)5(CPh): Cr(0) has 6e + 5 x 2e from COs + Cr-C triple bond (carbyne) counts as 3e given to Cr = 18e total