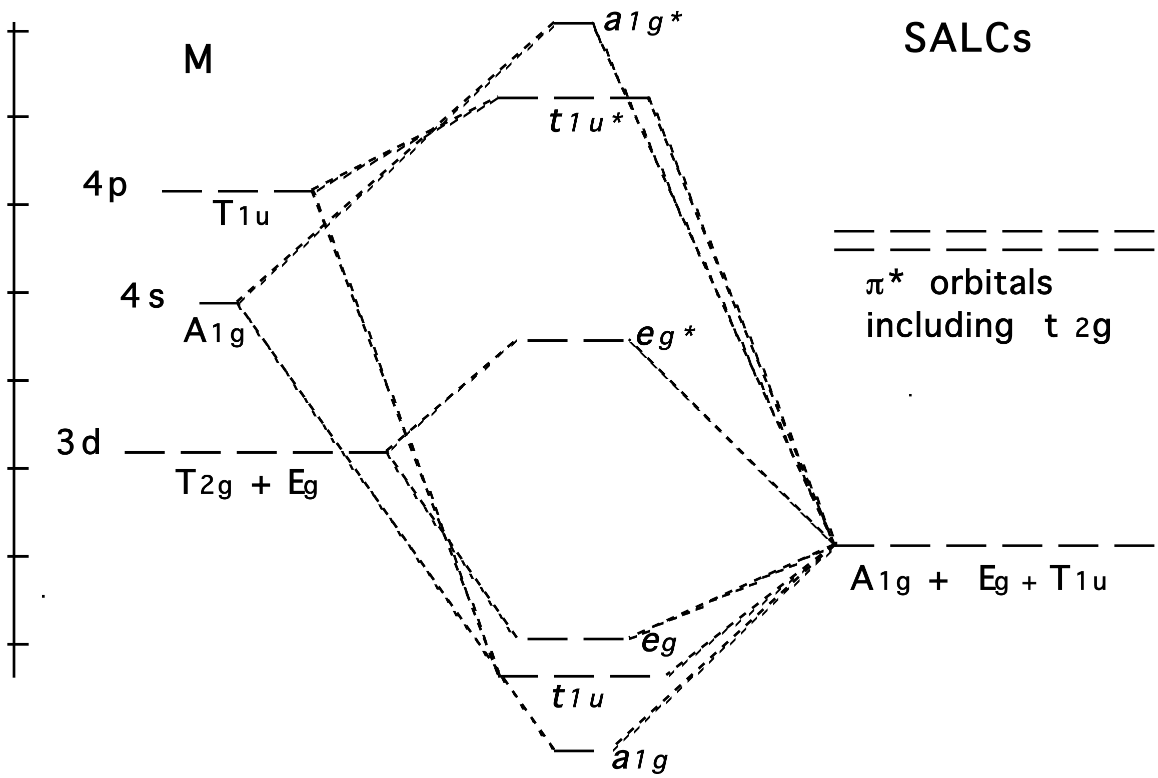
Inorganic Chemistry with Doc M. Group: ______________________

Fall Semester, 2007 Names: ______________________

Day 21. Organotransition Metal Chemistry I: The 18-electron Rule

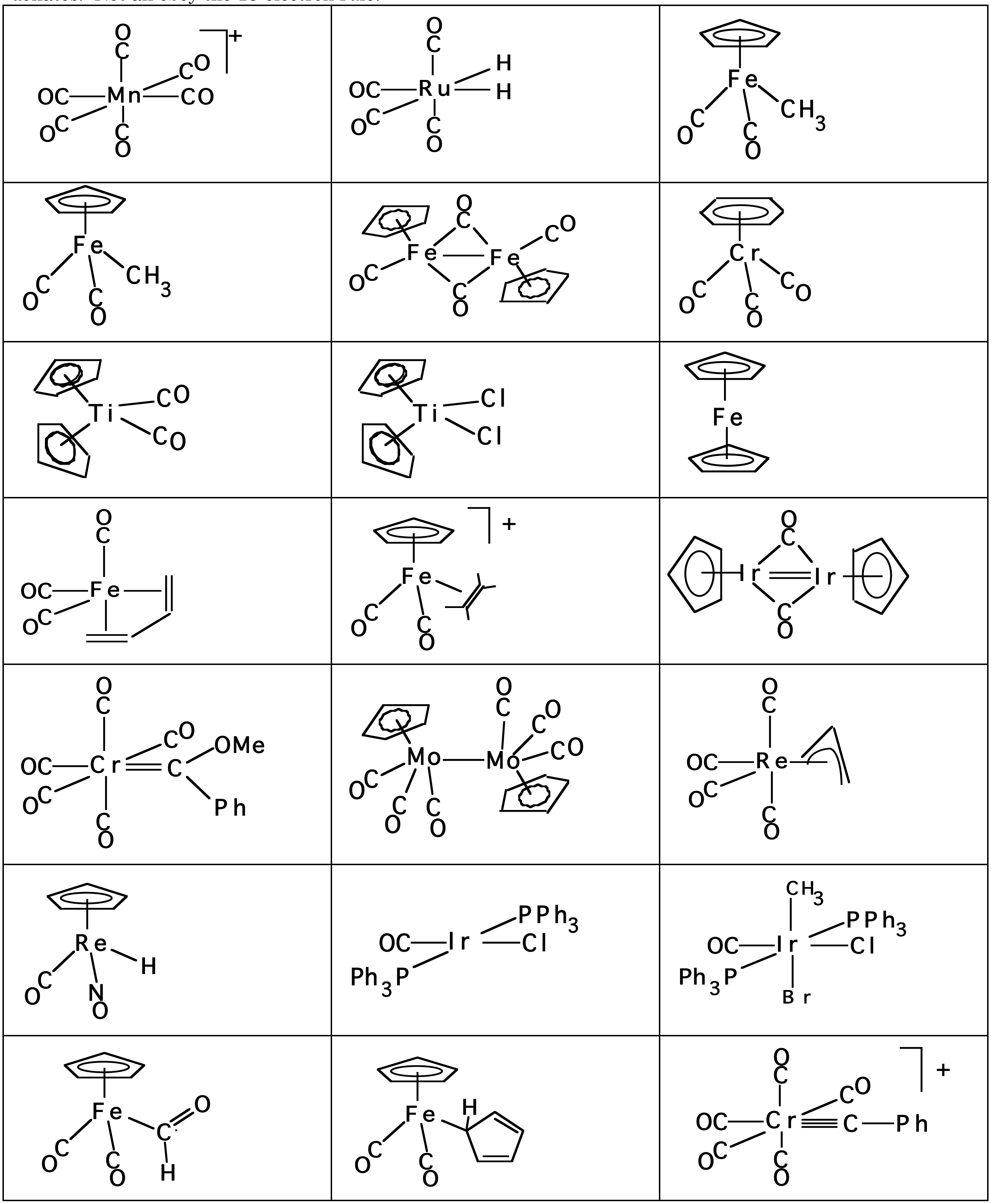
1. π-Back-bonding. π-Back bonding can occur between any metal with electrons to share (low oxidation state) and any ligand with symmetry-allowed empty orbitals. Sketch the σ-donation and the π-back bonding that occurs between a transition metal and a carbon monoxide ligand. Repeat this for a transition metal and a PF_3 ligand. Lots of ligands have orbitals that are symmetry-allowed for □-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.

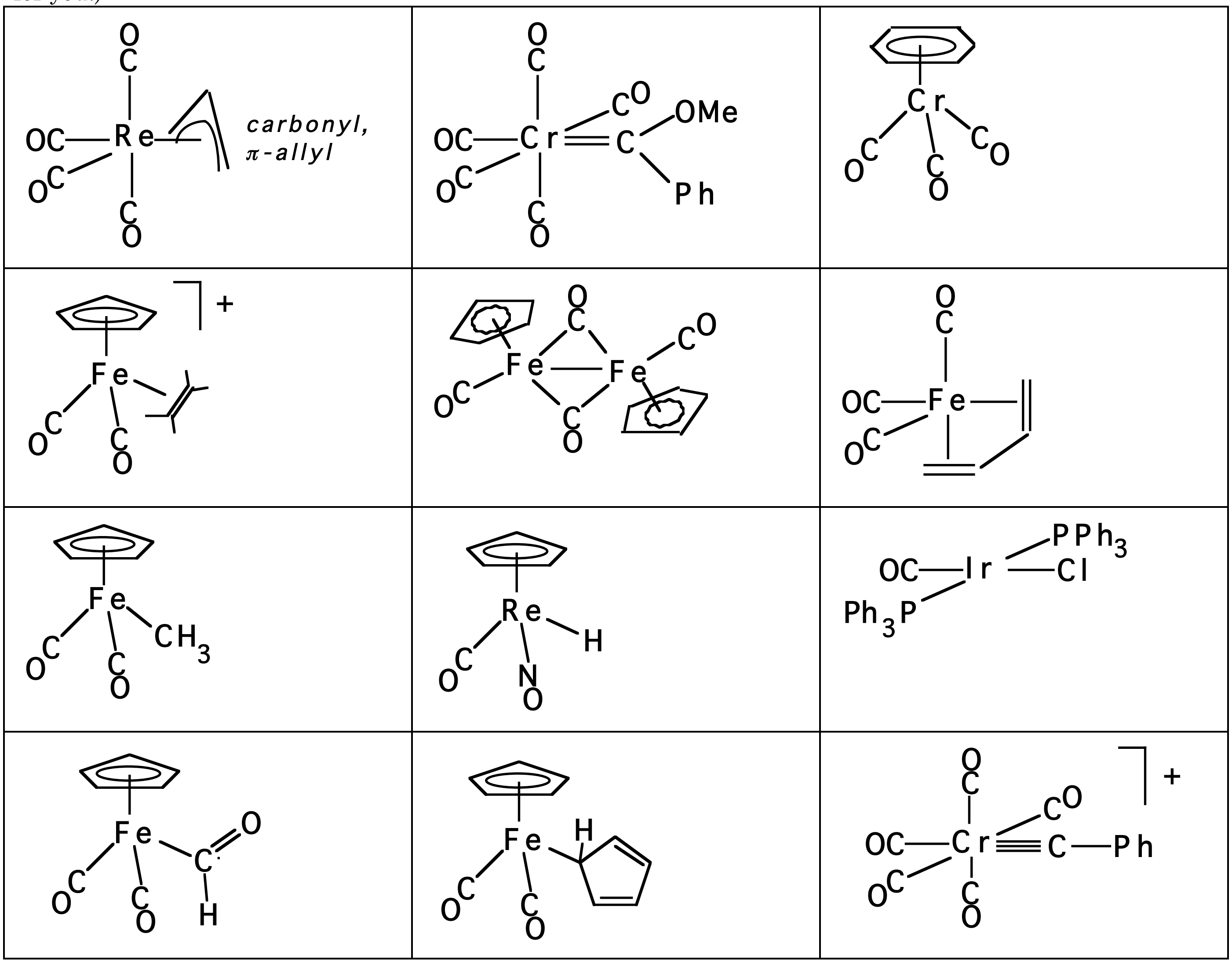


Sketch one of the three t_{2g} molecular orbitals — the sketch should include one SALC consisting of four CO π* orbitals and one of the t_{2g} orbitals from the metal.

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.)



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