Inorganic Chemistry with Doc M.
Fall Semester, 2012
Day 22. Organotransition Metal Chemistry I: The 18-electron rule

Name(s):	Element:

Topics:

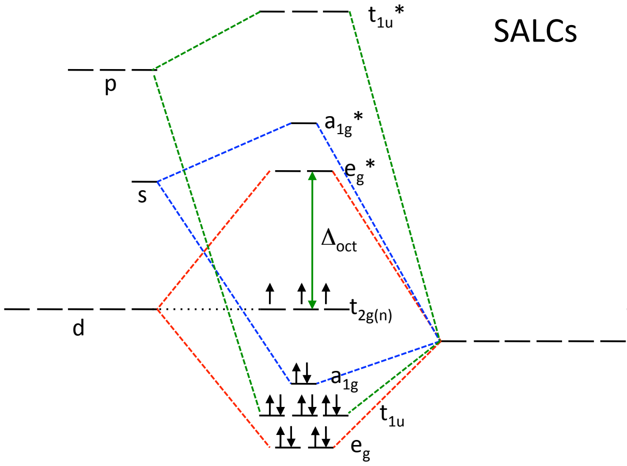
1. π-Back-bonding and the octahedron MO diagram
2. The Eighteen Electron Rule
3. Functional Groups

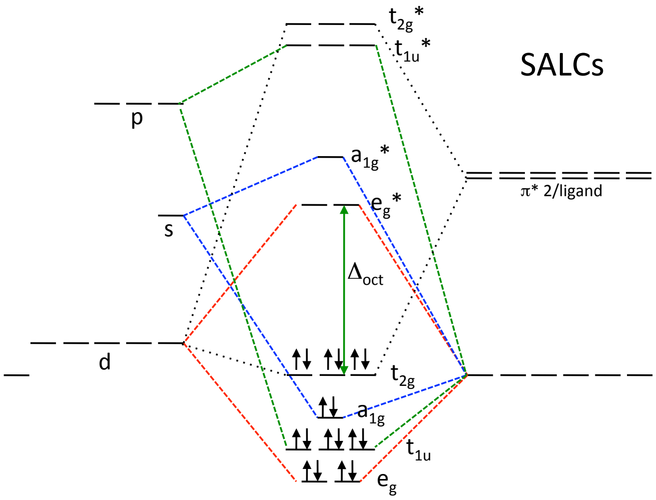
1. π-Back-bonding.

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 p-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 π-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.

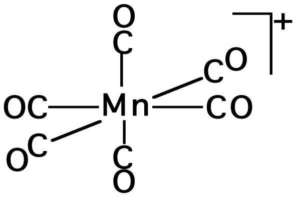
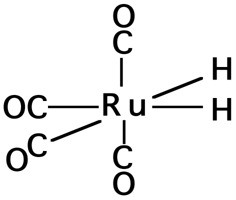
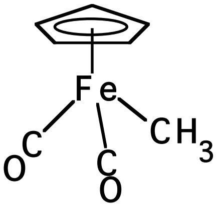
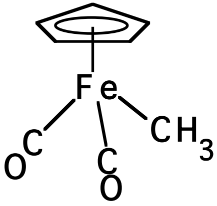
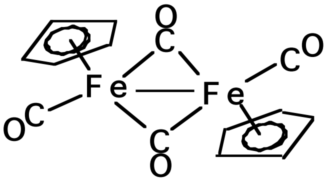
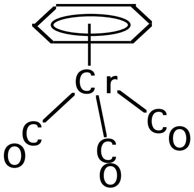
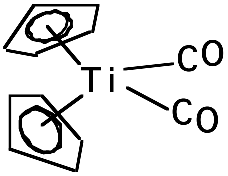
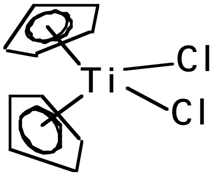
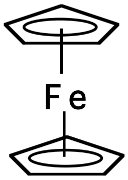
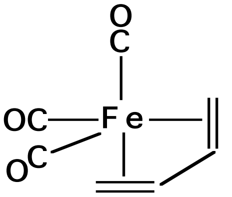
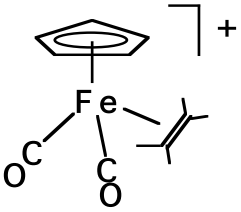
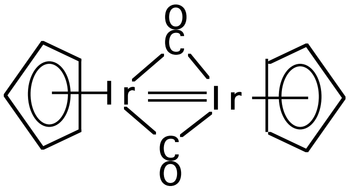
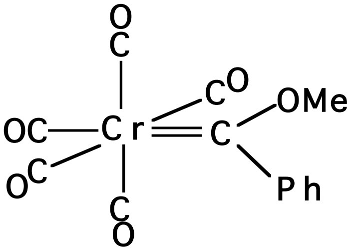
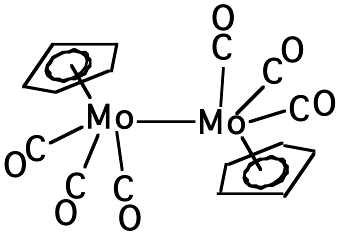
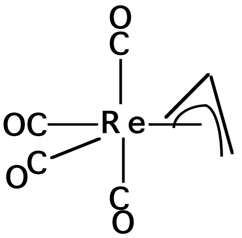
The MO diagram below left shows the σ-donation that occurs between an octahedral set of ligands and the ligand σ-SALC orbitals. The π*-SALC orbitals that will be used for π-back bonding are added in the figure at right. They are labeled as "π* orbitals" and consist of two such orbitals from each of the 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. The other nine π-SALC orbitals are non-bonding. Because the t_{2g} orbitals are now bonding, and lower in energy, they should populated, leading naturally to 18 electrons.

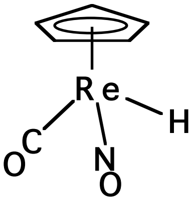
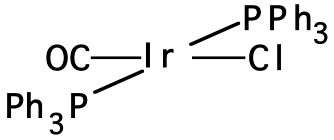
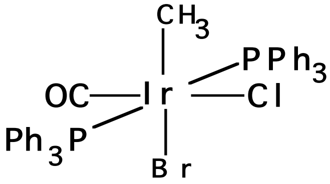
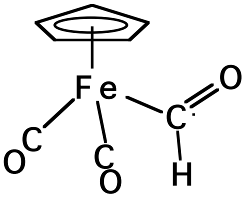
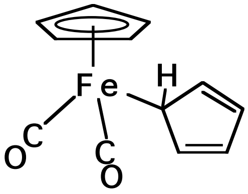
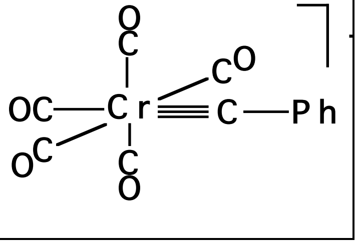




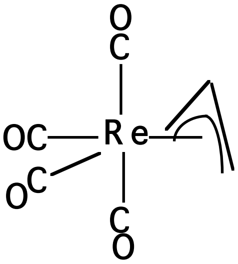
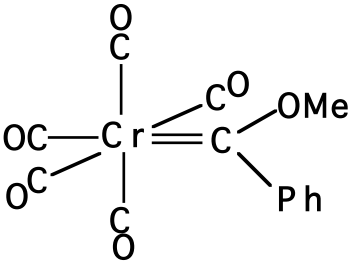
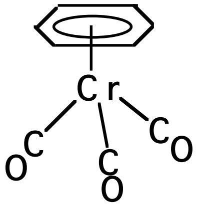
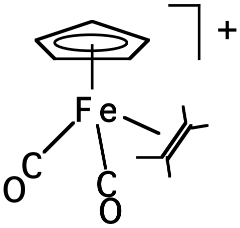
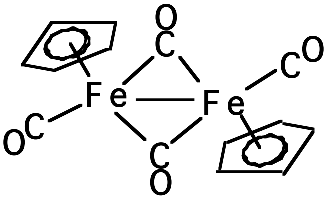
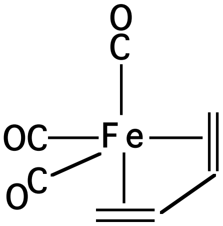
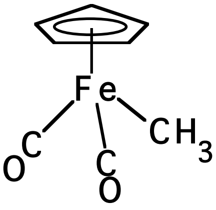
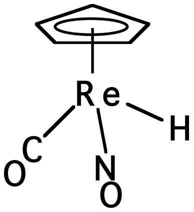
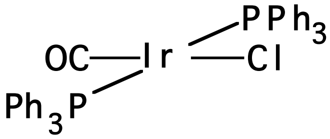
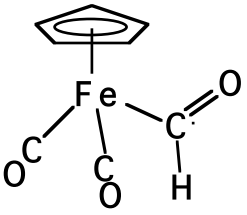
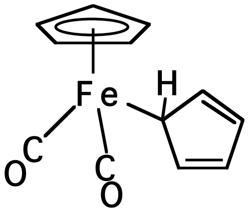
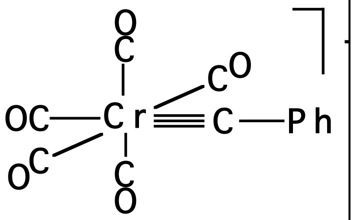
Sketch one of the three t_{2g} molecular orbitals — the sketch should include one SALC consisting of four CO π^* orbitals and one of the t_{2g} orbitals from the metal.

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

3. 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) (p-C_5H_5)$Fe(CO)_3$
   (e) (p-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 p-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: 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

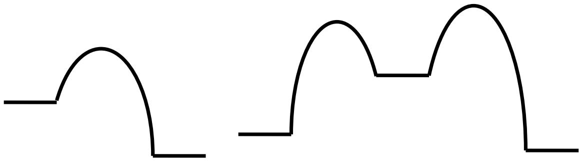
Row 5:
Cr(CO)5(COMePh): Cr(0) has 6e + 5 COs for 10e + two electrons from carbene = 18e
count each Mo separately. Cp = 5 + Mo(0) is 6e + 6 for COs + 1e for Mo-Mo bond = 18e
Re(CO)4(C3H5): Re(0) has 7e + 4 COs worth 8e + three pi electrons from pi-manifold of allyl group

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

Answers to Day 21.

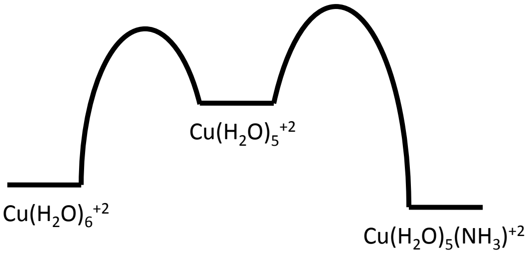
A. Background/review



B. Substitution reactions mechanisms: octahedral complexes

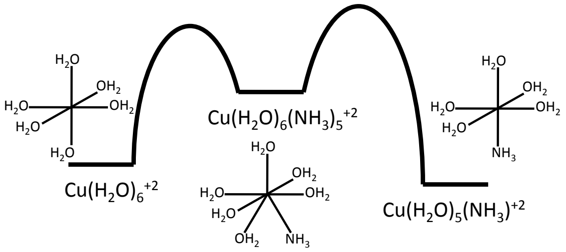
1. $Cu(H_2O)_6^{+2}(aq) + NH_3(aq) \rightarrow Cu(H_2O)_5(NH_3)^{+2}(aq) + H_2O(aq)$
   $Co(H_2O)_6^{+2}(aq) + NH_3(aq) \rightarrow Co(H_2O)_5(NH_3)^{+2}(aq) + H_2O(aq)$
   $Ni(H_2O)_6^{+2}(aq) + NH_3(aq) \rightarrow Ni(H_2O)_5(NH_3)^{+2}(aq) + H_2O(aq)$

2. a. Dissociative mechanism.



Step 1. $Cu(H_2O)_6^{+2}(aq) \rightarrow Cu(H_2O)_5^{+2}(aq) + H_2O(l)$ slow step
Step 2. $Cu(H_2O)_5^{+2}(aq) + NH_3(aq) \rightarrow Cu(H_2O)_5(NH_3)^{+2}(aq)$
rate = $k[Cu(H_2O)_6^{+2}(aq)]^1$

2b. Associative mechanism.



Step 1. $Cu(H_2O)_6^{+2}(aq) + NH_3(aq) \rightarrow Cu(H_2O)_6^{+2}(NH_3)(aq)$ slow step
Step 2. $Cu(H_2O)_6^{+2}(NH_3)(aq) + \rightarrow Cu(H_2O)_5(NH_3)^{+2}(aq) + H_2O(l)$
rate = $k[Cu(H_2O)_6^{+2}(aq)]^1[NH_3(aq)]^1$

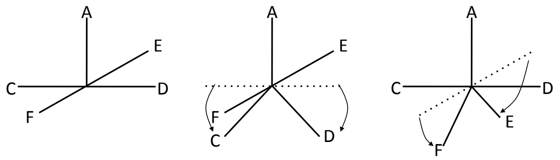
C. Factors affecting reaction mechanisms. 1.

	ΔH^{act}	ΔS^{act}
Associative mechanism, A	> 0	> 0
Dissociative mechanism, D	< 0 (probably)	< 0

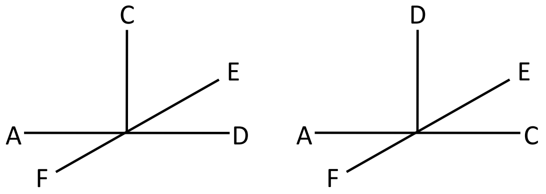
2. Large ligands would prefer D mechanism; 3. Ignoring CFSE arguments for the moment, one would expect that larger oxidation states make better Lewis acids and have a stronger attraction for Lewis bases. Better Lewis acids would seem to prefer the associative mechanism; 4. CFSE Considerations. a. CFSE for d^3 in a square pyramidal geometry is $-1.0\Delta_o$, $0.2\Delta_o$ less stable than it is for the octahedron; b. CFSE for d^3 in a pentagonal bipyramidal geometry is $-0.774\Delta_o$, $0.426\Delta_o$ less stable than it is for the octahedron. CFSE calculations for d^4(assume all are high-spin): Octahedral d^4: CFSE = $-0.6\Delta_o$; square pyramidal d^4 CFSE = $-0.914\Delta_o$; pentagonal bipyramidal d^4 :CFSE = $-0.492\Delta_o$

5. The terms **stable** and **unstable** refer to thermodynamics. Stable compounds have large negative free energies; 6. An associative route would go through an octahedral intermediate.

D. Stereochemistry of Reactions 2.



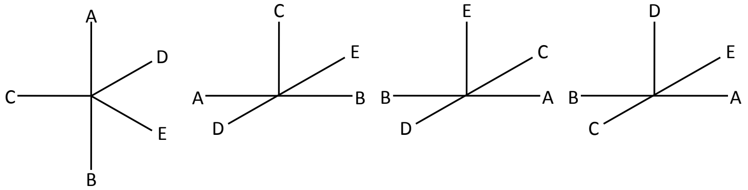
3. Looking at the first trigonal bipyramid above (middle drawing), ligands A, C, and D are equatorial. Each of these three ligands could become the axial ligand when the tbp returns to sq py. If A is axial, we get the original structure, shown above at left. If C or D becomes axial, we get these two, respectively:



4. trigonal bipyramidal d^3: CFSE = -0.626Δ_o; square pyramidal d^3: CFSE = -1.00Δ_o; therefore a preference for the latter; trigonal bipyramidal d^4: CFSE = -0.708Δ_o; square pyramidal d^4: CFSE = -0.914Δ_o; again a preference for the latter, however the difference is much smaller. For ballpark figuring, Δ_o is about 200 kJ/mol for a substance that absorbs at 600 nm (an example absorbance), so a difference in CFSE of 0.1Δ_o corresponds to about 20 kJ/mol.

E. Pseudorotation in trigonal bipyramid complexes

1. Starting with the trigonal bipyramid shown below left, each of the equatorial positions (C, D, E) could become axial. This leads to the following three square pyramids. Note: There is a specific stereoisomer (enantiomer) that results from each possibility starting with the original tbp drawing. For example, if C before axial, the view down the C axis would yield AEBD when viewed clockwise. The enantiomer (ADBE) could not be formed from the Berry conversion.



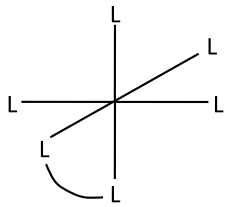
2.	A	B	C	D	E
Axial	3/5	3/5	2/5	2/5	2/5
Equatorial	2/5	2/5	3/5	3/5	3/5
Total	1	1	1	1	1

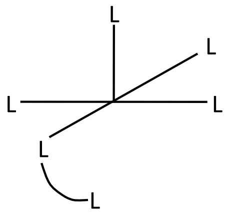
No, additional cycles are necessary to average all 5 positions. In fact, it will take 5 cycles to completely and evenly average all five groups.

F. The Chelate Effect.

All three reactions will have $\Delta H = 0$ and $\Delta S > 0$

2. When one leg of a chelate dissociates, the other end still holds the chelate in the neighborhood and significantly increases the chances that the loose end with re-associate:





G. The Trans Effect (Substitution Reactions of Square Planar Complexes).

$Pt(NH_3)_4^{+2} + 2\ Cl^- \rightarrow \rightarrow$ *trans*-$Pt(NH_3)_2(Cl)_2$

$PtCl_4^{-2} + 2\ NH_3 \rightarrow \rightarrow$ *cis*-$Pt(NH_3)_2(Cl)_2$