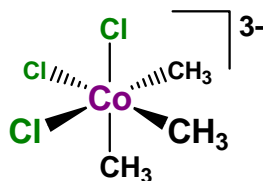


EXAM # 1 – Feb 15, 2007

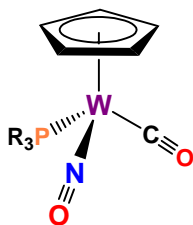
Please answer all questions!

Check this box if you want your graded test put out
in the public boxes outside Prof. Stanley's office:

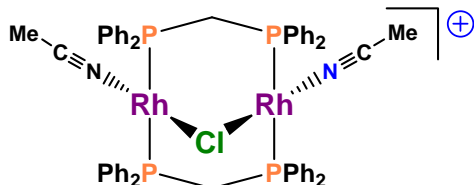
1. (60 pts) Sketch out the structure of the following transition metal complexes as accurately as possible and clearly show the electron counting (including the oxidation state of the metal center and ligand charges if present). You don't have to draw out phenyl rings on ligands (e.g., for PPh₃).



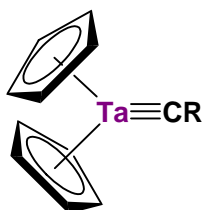
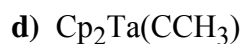
Co(+3)	d6
3CH ₃ ⁻	6e-
3Cl ⁻	6e-
<u>Total</u>	<u>18 e-</u>



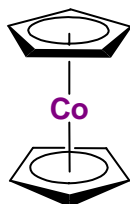
W(0)	d6
Cp ⁻	6e-
NO ⁺	2e-
PR ₃	2e-
CO	2e-
<u>Total</u>	<u>18 e-</u>



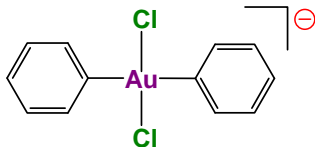
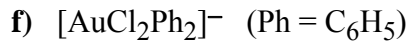
Rh(+1)	d8
μ-Cl ⁻	2e-
2PR ₃	4e-
N≡CR	2e-
<u>Total</u>	<u>16 e-</u>



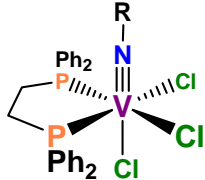
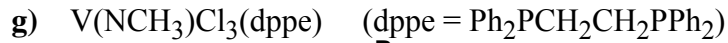
Ta(+5)	d0
2Cp ⁻	12e-
≡CR ³⁻	6e-
<u>Total</u>	<u>18 e-</u>



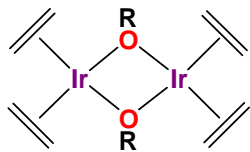
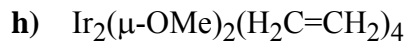
Co(+2)	d7
2Cp ⁻	12e-
<u>Total</u>	<u>19 e-</u>



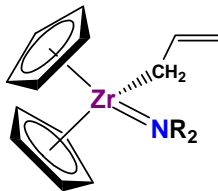
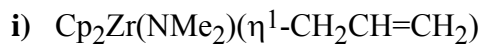
Au(+3)	d8
2Ph ⁻	4e-
2Cl ⁻	4e-
Total	16 e-



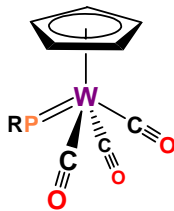
V(+5)	d0
3Cl ⁻	6e-
dppe (2PR ₃)	4e-
≡NR ²⁻	6e-
Total	16 e-



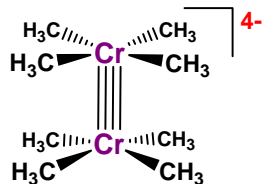
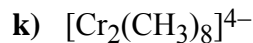
Ir(+1)	d8
2μ-OR ⁻	4e-
2H ₂ C=CH ₂	4e-
Total	16 e-



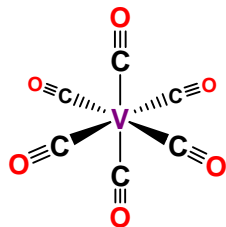
Zr(+4)	d0
2Cp ⁻	12e-
NR ₂ ⁻	4e-
η ¹ -allyl	2e-
Total	18 e-



W(+4)	d2
Cp ⁻	6e-
PR ²⁻	4e-
3CO	6e-
Total	18 e-

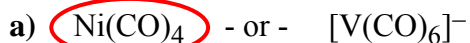


Cr(+2)	d4
4CH ₃ ⁻	8e-
4Cr-Cr	4e-
Total	16 e-



V(0)	d5
6CO	12e-
Total	17 e-

2. (30 pts) For each of the following pairs of complexes, which will have the **highest** average CO infrared stretching frequency? Circle your choice and briefly explain your reasoning.

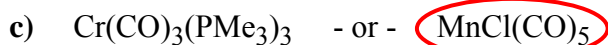


The **least** electron-rich metal will π -backbond the **least** with the CO ligands and have the **highest** CO stretching frequency

V is very electropositive and in a very electron-rich -1 oxidation state, so it will π -backbond the most and have the lower CO stretching frequency. Although Ni has more d electrons (d^{10}), it is considerably more electronegative and will have the higher CO stretching frequency.



The Nb complex is d^0 and can not π -backbond, so it will automatically have the higher CO stretching frequency. The V complex is d^2 with good donor ligands and can π -backbond reasonably well.



The Cr complex has 3 strong PMe_3 σ -donors and only 3 CO ligands. So the Cr will be more electron-rich than the Mn(+1) complex that has a poor chloride donor and 5 π -backbonding CO ligands. Mn is also more electronegative than Cr.



The Rh complex has a cationic charge that will contract the metal d orbitals, poor σ -donors (phosphite and chloride), and the phosphite ligands can also compete for the π -backbonding. This makes the Rh complex the more electron-poor and the one with the higher CO stretching frequency. The Zr complex is d^2 and in a rather low oxidation state (likes to be +4 and d^0). The Cp anions are strong donors and the CO ligands will be strongly π -backbonding to the Zr center.



Both complexes are cationic, but the Ir has 4 strong donor groups and only 2 CO ligands. So it will be more electron-rich and do more π -backbonding giving a lower CO stretching frequency.



The Mo complex has two strong donating dmpe ligands (alkylated phosphines) and only 2 CO ligands. So it will be more electron-rich and the CO π -backbond more. The lower electronegativity of the W is a minor factor easily overridden by the ligand effects.

3. (20 pts) Consider the isocyanide ($C\equiv NR$, sometimes called isonitrile) and nitrile ($N\equiv CR$) ligands that are isomers of one another.

a) (10 pts) Sketch out a Lewis dot diagram for each showing the location of the lone pair(s) and any formal charges based on organic valence conventions.

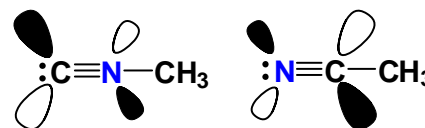


b) (5 pts) Which ligand is the better σ -donor? Why?

$C\equiv NR$ is the better σ -donor because the carbon atom has the lone pair of electrons and it is less electronegative than the N atom in the nitrile. This will make the lone pair have a higher energy (better donor) and greater extent giving better overlap with the metal d orbital.

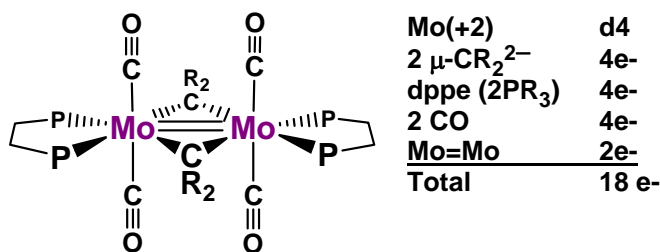
c) (5 pts) Which ligand is the better π -acceptor? Why?

$C\equiv NR$ is the better π -acceptor because the empty π^* orbital has greater orbital extent on the carbon atom due to the carbon atoms lower electronegativity. This allows the isocyanide π^* -orbital to have better overlap and bonding with the filled metal d orbital.

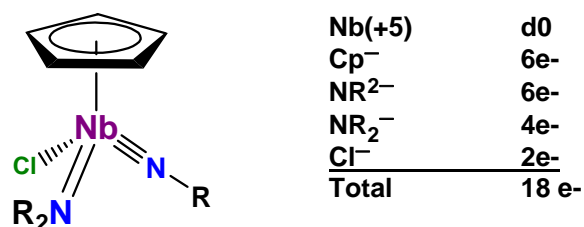


4. (40 pts) Sketch out a neutral 18-electron structure showing the geometry about the metal center as accurately as you can at this point in the course for the following metals and ligands. Use **at least one metal and each type of ligand shown**. Try to keep your structure as simple as possible (bimetallic complexes are OK, nothing higher). Clearly show your electron counting. Ligands are shown without charges, please indicate the proper ligand charge and metal oxidation state in your electron counting.

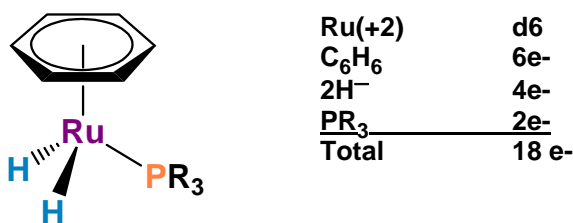
a) Mo, $\mu\text{-CR}_2$, dmpe, CO



b) Nb, NMe, NMe₂, Cp, Cl



c) Ru, C₆H₆, H, PMe₃



d) Mn, CH₃, CO

