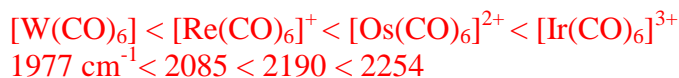


Problem Set #3

Due: Sept. 29, 2011

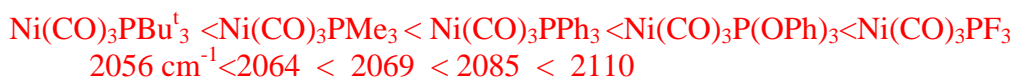
1. Rank the following metal carbonyl complexes from lowest IR ν_{CO} to highest. Explain your rationale.

a) $[\text{Ir}(\text{CO})_6]^{3+}$, $[\text{Re}(\text{CO})_6]^+$, $[\text{Os}(\text{CO})_6]^{2+}$, $[\text{W}(\text{CO})_6]$



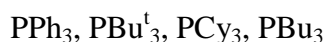
All complexes are d^6 , but with increasing charges on the metal in going from left to right. The more electron deficient the metal, the more electronegative it will become and the less capable of electron donation for backbonding. With less backbonding, the CO bond is made stronger and therefore the $\text{IR}\nu_{\text{CO}}$ stretch is higher.

b) $\text{Ni}(\text{CO})_3\text{P}(\text{OPh})_3$, $\text{Ni}(\text{CO})_3\text{PMe}_3$, $\text{Ni}(\text{CO})_3\text{PF}_3$, $\text{Ni}(\text{CO})_3\text{PBU}^t_3$, $\text{Ni}(\text{CO})_3\text{PPh}_3$

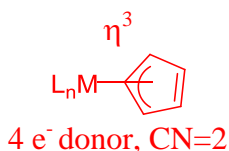
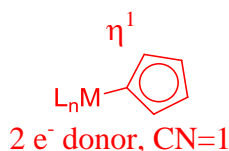


The phosphines directly influence the $\text{IR}\nu_{\text{CO}}$ band with the most electron deficient PF_3 withdrawing the most electron density from the Ni, thereby reducing the backbonding to the CO ligands. With the least amount of backbonding, the $\text{Ni}(\text{CO})_3\text{PF}_3$ carbonyls have the strongest CO bond and therefore the highest ν_{CO} band. The $\text{P}(\text{OPh})_3$ phosphine is also electron deficient due to the electronegative O ligands. The alkyl substituted phosphines are the most electron donating or electron rich with the larger t-butyl ligands having the most electron density to donate.

2. Rank the following phosphine ligands from smallest to largest.

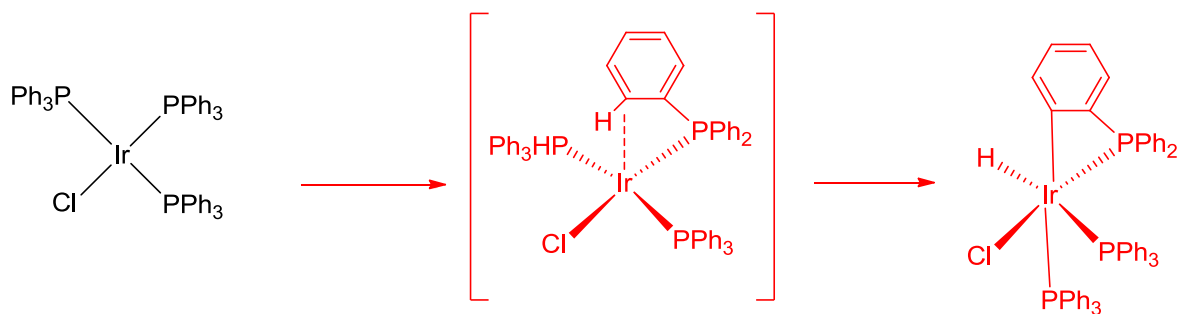


3. Cyclopentadienyl anion (Cp) ligands can have η^1 , η^3 or η^5 complexes with metals. Draw all three depictions with a generic ML_n group. List the number of electrons donated under each circumstance and the coordination number of the ligand in each type of hapticity.

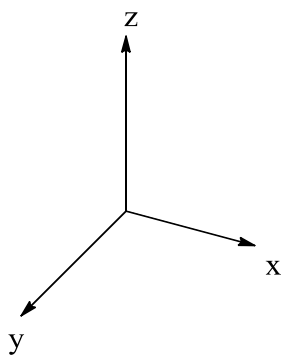


4. *CHE534 students only.* One way that some phosphine-metal complexes can decompose over time is through the formation of agostic interactions. The Ir complex below, $(\text{IrCl}(\text{PPh}_3)_3)$, was an early example of an agostic complex where one aryl C-H bond became involved in an agostic interaction.

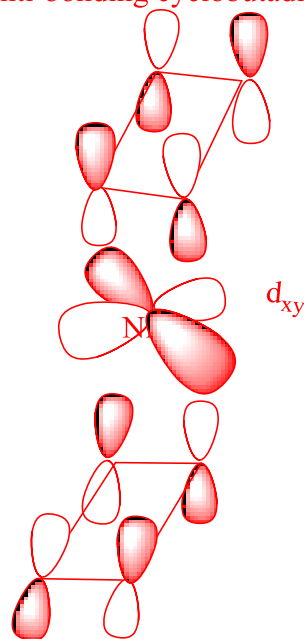
The C-H bond eventually react and undergo an oxidative addition. In the space below, draw the agostic interaction intermediate and the oxidative addition product from such a process.



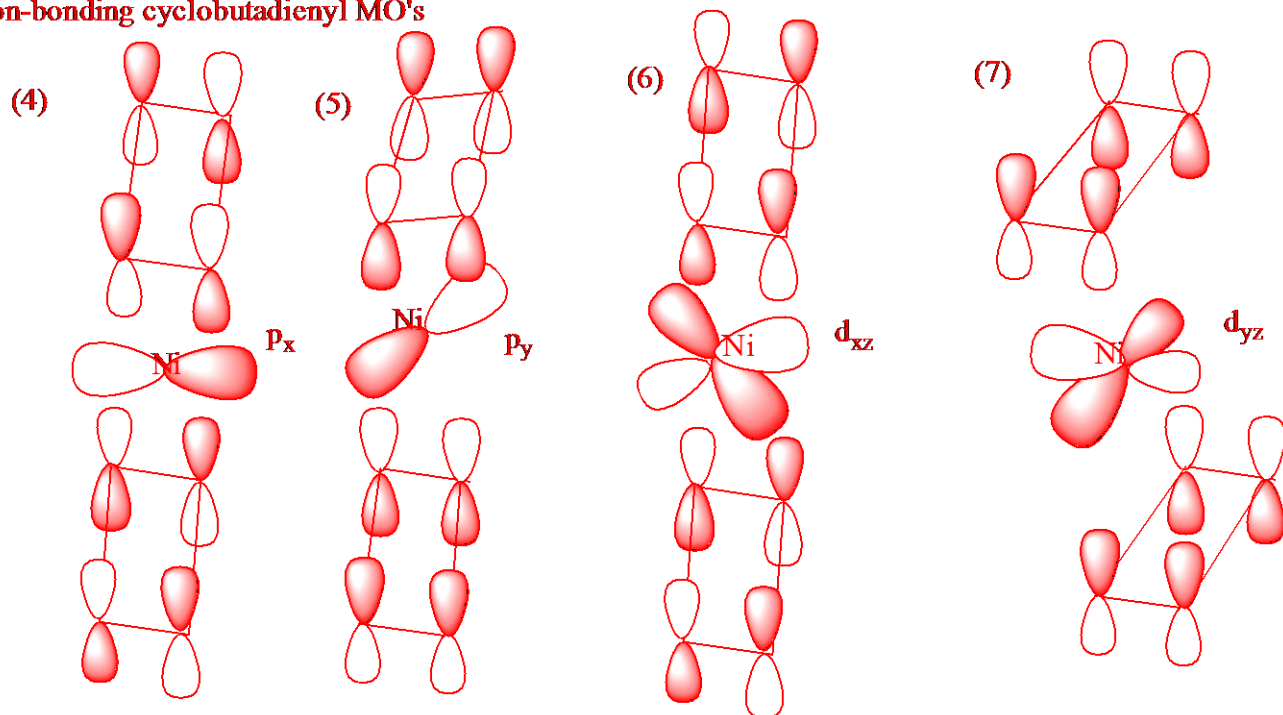
5. Another example of a sandwich complex is $(\eta^4\text{-C}_4\text{H}_4)_2\text{Ni}$. There are a total of eight different possible orbital interactions between the cyclobutadienyl molecular orbitals and s, p or d orbitals of Ni. *CHE334 students draw six and CHE534 students draw all eight.* Note: your picture should show the Ni orbital interactions with BOTH cyclobutadienyl ligands.



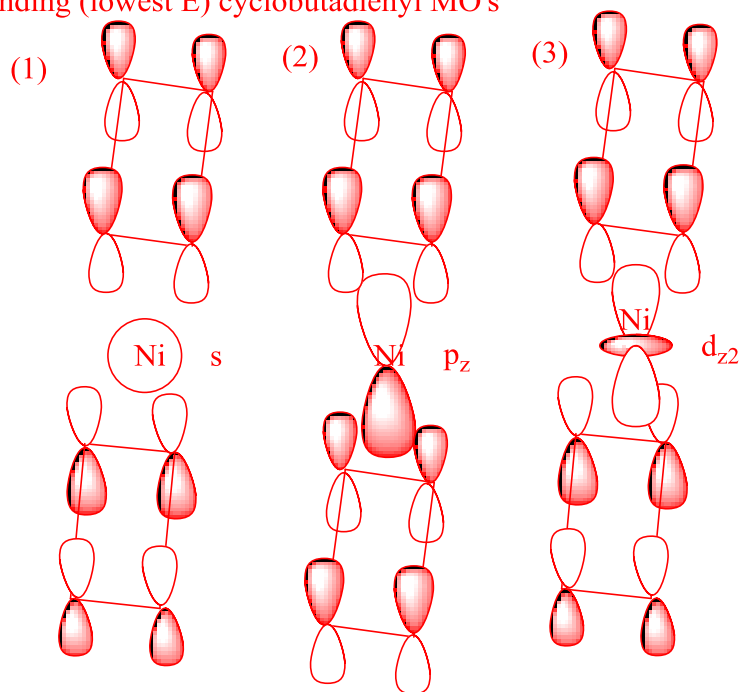
anti-bonding cyclobutadienyl MO



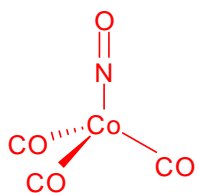
non-bonding cyclobutadienyl MO's



bonding (lowest E) cyclobutadienyl MO's



6. Propose a structure for $\text{Co}(\text{CO})_3\text{NO}$. Provide an oxidation state for the metal and an overall electron count.



Using the ionic electron-counting method, Co is -1 due to the +NO ligand. With NO and the 3 CO's as 2 e- ligands, the metal has a total of 18 e-'s.

7. The substitution of $V(CO)_6$ by phosphine ligands (eqn. 1) was studied and reported in the literature.



The researchers found the following order of phosphine reactivity: $PMe_3 > PBu_3 > P(OMe)_3 > PPh_3$

Qi-Zhen Shi, Thomas G. Richmond, William C. Troglor,*+ and Fred Basolo *J. Am. Chem. Soc.* **1984**, *106*, 11-76

a) What type of reaction is happening? Be as specific as possible.

Associative ligand substitution

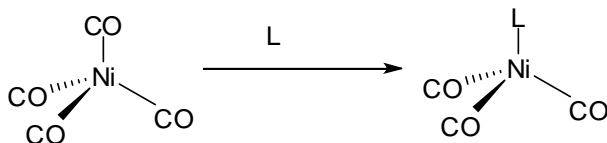
b) What is the rate law for the reaction?

$$\text{rate} = -d[V(CO)_6]/dt = k [V(CO)_6][PR_3]$$

c) In considering the rate differences with the different phosphine R groups, what does this suggest is important to facilitate the reaction?

Phosphines with small alkyl groups are optimal. This suggests the most basic or strongest σ donors with the least steric crowding result in the fastest ligand substitution reaction.

8. Thermodynamic parameters for the reaction shown below were as follows: $\Delta H \sim -25$ kcal/mol and $\Delta S = 13$ eu in hexane solvent.



What do these thermodynamic values tell you about the mechanism of the reaction? Be as explicit as possible.

The enthalpy value is close to the bond dissociation energy of the Ni-CO bond, which must break to initiate a dissociative substitution process. The positive entropy value is also supportive of a dissociative substitution process since such an event converts one molecule into two molecules and creates more freedom of movement in both molecules; both processes create greater disorder.