

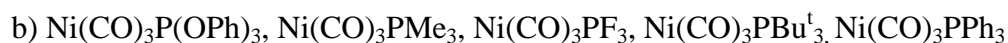
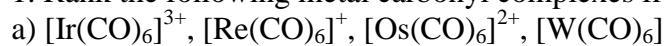
## Organometallic Chemistry

Name: \_\_\_\_\_

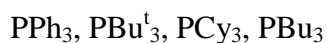
### Problem Set #3

Due: Sept. 29, 2011

1. Rank the following metal carbonyl complexes from lowest IR  $\nu_{\text{CO}}$  to highest. Explain your rationale.

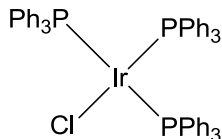


2. Rank the following phosphine ligands from smallest to largest.

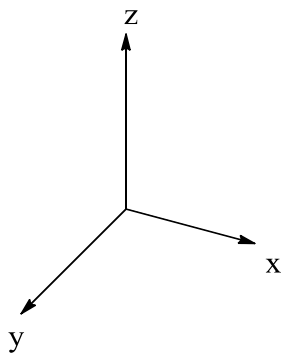


3. Cyclopentadienyl anion (Cp) ligands can have  $\eta^1$ ,  $\eta^3$  or  $\eta^5$  complexes with metals. Draw all three depictions with a generic  $\text{ML}_n$  group. List the number of electrons donated under each circumstance and the coordination number of the ligand in each type of hapticity.

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 reacts and undergoes 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.



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

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



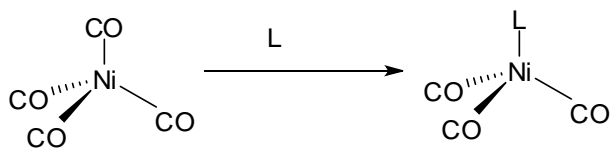
The researchers found the following order of phosphine reactivity:  $\text{PMe}_3 > \text{PBu}_3 > \text{P}(\text{OMe})_3 > \text{PPh}_3$

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

b) What is the rate law for the reaction?

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

8. Thermodynamic parameters for the reaction shown below were as follows:  $\Delta H \approx 25$  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.