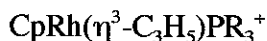
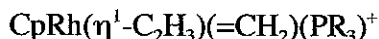
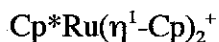
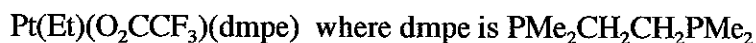
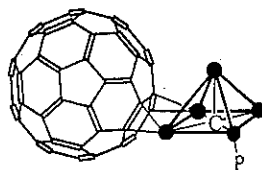


Cumulative Examination in
Inorganic Chemistry
November 3, 2005
J. A. Morrison

1. (20 points) Discuss the chemistry of MIT's Professor Richard R. Schrock. Specifically include the types of complexes that bear his name. Why is his chemistry of contemporary interest?
2. (18 points) For each of the following molecules and ions, give the formal oxidation state, d^n , and the number of electrons in the valence shell of the central atom.



3. (22 points) The product of the reaction between $\text{Os}_5\text{C}(\text{CO})_{14}(\text{PPh}_3)$ and C_{60} is the molecule $\text{Os}_5(\text{CO})_{12}(\text{PPh}_3)(\mu_3\text{:}\eta^2\text{:}\eta^2\text{-C}_{60})$, shown below. First, show that the electron count of the osmium reactant is consistent with a nido-structure. Second, what is the meaning of the $\mu_3\text{:}\eta^2\text{:}\eta^2$ portion of the molecular formula? Third, if Wade's rules are obeyed, what number of electrons must be donated to the cluster by the C_{60} ligand? Fourth, if you were to consider C_{60} alone as a cluster compound, what number of framework electrons do you count and what is the explanation of why this cluster evades the usual counting rules?



4. (20 points). Coordination of CO to bis(pentamethylcyclopentadienyl)ytterbium yielded $\text{Cp}^*_2\text{Yb}(\text{CO})$ and $\text{Cp}^*_2\text{Yb}(\text{CO})_2$. The carbonyl IR stretch in the former was at 2114 cm^{-1} , the CO stretch in the latter was at 2072 cm^{-1} . It is at 2136 cm^{-1} in uncomplexed CO that has been dissolved in methylcyclohexane. Discuss the bonding in these complexes and show that your scheme explains these differences in the CO stretches, particularly the differences between the stretches of the mono- and bis-CO complexes.

Note: Yb is the next to last element on the right side of the lanthanides. It has 16 valence electrons.

Extra credit: The CO stretch of the complex $\text{Cp}^*_2\text{Ca}(\text{CO})$ is found at 2158 cm^{-1} which is higher than that of free CO. Explain.

5. (20 points) For the ethylenes C_2H_4 , C_2Cl_4 , and C_2F_4 , the angle between the substituents is 116.5° , 115.4° and 113.5° , respectively. Explain why these X-C-X bond angles decrease as the substituents are varied. Two common classes of compounds that do not obey the usual VSEPR are the trisilylamines, e.g., $(\text{H}_3\text{Si})_3\text{N}$, which are planar and barium fluoride which is bent--to nearly 90° . Explain each.