

Time: 2 hrs.

Chemistry 229

June 21, 1997

Final Examination

Name:

Number:

Score:

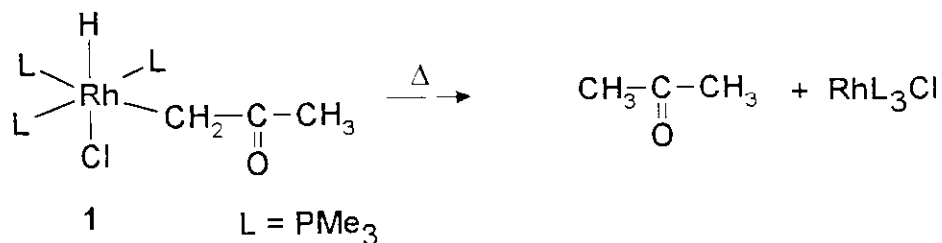
Part One.

Using in each case a maximum of one-half a page, briefly discuss in a general way THREE of the following topics. In your account, you may use non-specific general structures and/or general equations, but in each case, mention at least one specific example. You may answer more than three questions for extra credit, but do so after you're done with the required questions of part two.

1. Two extreme types of carbene ligands: include in your discussion structural features as well as one reaction of complexes containing each type of ligand
2. The rates of H_2 versus D_2 oxidative addition to 16-electron complexes show very small values of k_H/k_D . Discuss the meaning of this small isotope effect in the context of the mechanism. What does this phenomenon have to do with the discovery of η^2-H_2 complexes?
3. Circular dichroism: the interaction of circularly polarized light with chiral compounds, the origin of ORD and CD, positive and negative Cotton effects, and the use of this technique.
4. The chelate and macrocyclic effects: origin of each effect and specific examples of each
5. The outer sphere electron transfer mechanism: mechanism, origin of the activation barrier to electron transfer, the potential energy curves of precursor and successor and the dependence of ΔG^\ddagger on ΔG° (Marcus equation)
6. Cyclopentadienyl sandwich compounds (metallocenes): the π -MO's of each ligand, the resulting metal d-orbital splitting pattern (no explanation necessary), the structure and magnetic behavior of ferrocene and three reactions of this molecule.

Part Two: Do ALL questions.

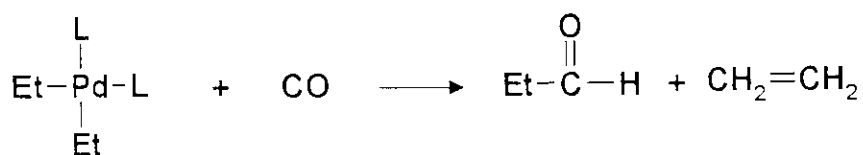
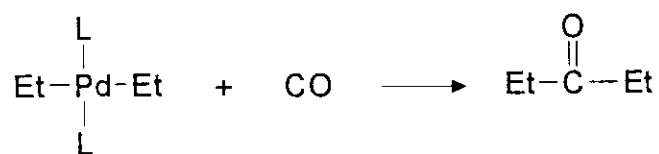
1. The following reaction is observed:



Observations:

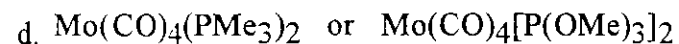
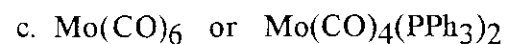
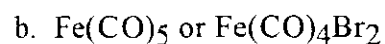
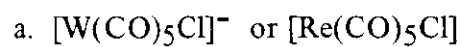
1. When the reaction is carried out with equimolar amounts of L₃ClRh(H)(CH₂COCH₃) and L₃ClRh(D)(CD₂COCD₃), only d₀-acetone and d₆-acetone are observed.
 2. The rate of disappearance of 1 follows first-order kinetics at constant [PMe₃]
 3. The rate decreases when PMe₃ is added, and the value of 1/k_{obs} varies linearly with [PMe₃]
 4. The rate increases when "phosphine sponge" [Rh(acac)(ethylene)₂] is added
 5. A kinetic isotope effect of k_H/k_D = 1.3 is observed for the reaction.
- a. Interpret these observations
 - b. Postulate a mechanism consistent with the above observations
 - c. Derive a rate expression for your mechanism

2. The following reactions are observed:

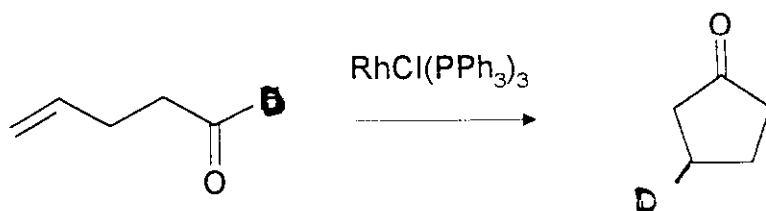


Propose a mechanism (s) to account for the different behavior of the cis and trans isomers.

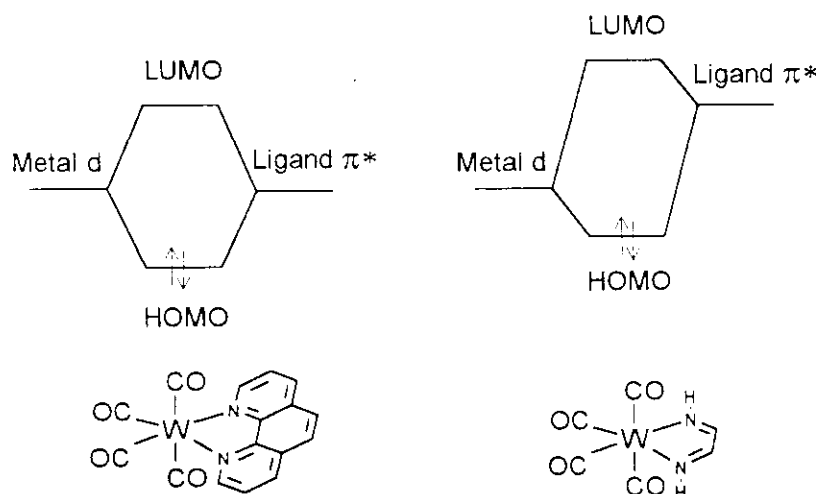
3. Which of the following two complexes has the lower CO stretching frequency in the infrared spectrum? Explain in one sentence.



4. Propose a mechanism to account for the following cyclization. In addition, predict the major side product of this reaction.



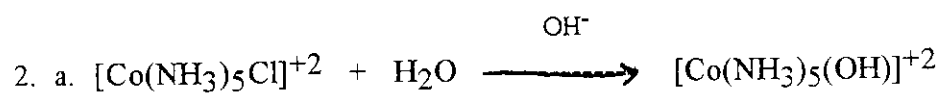
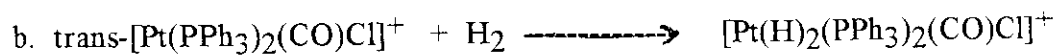
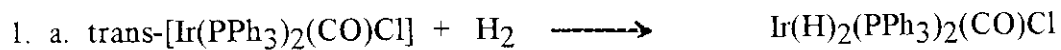
5. The two complexes $[(\text{CO})_4\text{W}(\text{phen})]$ and $[(\text{CO})_4\text{W}(\text{I-Pr-DAB})]$ may be represented by the following MO diagrams for their metal-to-ligand-charge transfer transitions MLCT's.

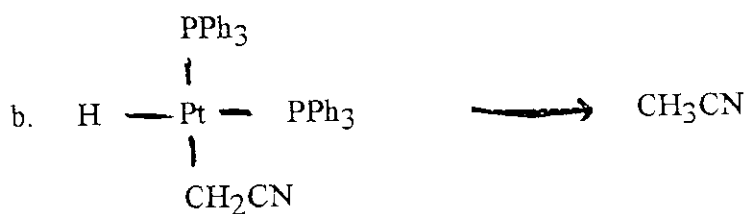
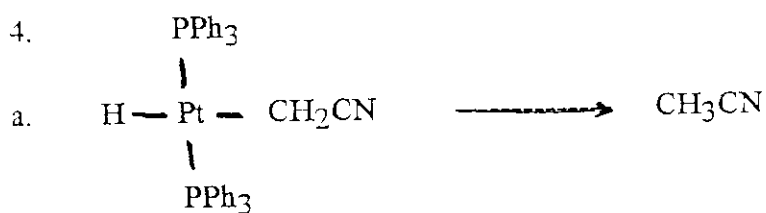
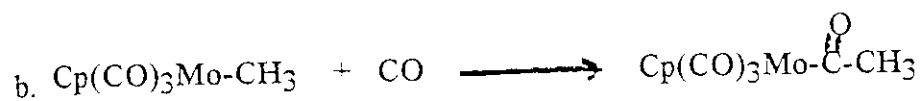
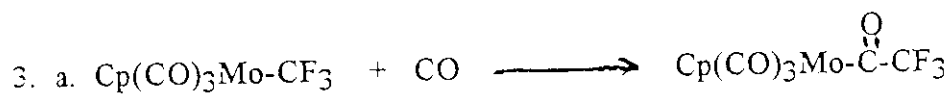
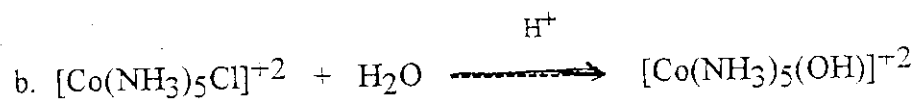


a. Which of the two MLCT bands is more sensitive to solvent polarity? b. Which ligand, phen or DAB is higher in the spectrochemical series? c. How would the sensitivity to solvent polarity (solvatochromism) be affected if the extent of metal back donation is changed (i.e., the CO's are replaced by other ligands)? Explain.

6. At room temperature, the NMR spectrum of $(\text{CO})_5\text{W}=\text{C}(\text{Ph})[\text{N}(\text{CH}_3)_2]$ shows two signals in the N-methyl region. If the sample is heated in the NMR probe, the two signals coalesce and become one signal at 50°C . Explain. (Use back of page, if needed).

7. Circle which reaction is faster. Explain in one sentence.





8. Draw the three highest occupied molecular orbitals of Cp_2V . Deduce the number of unpaired electrons, if any.

9. Two Br^- ligands in $[\text{CuBr}_6]^{-4}$ are found to exchange more easily with the solvent H_2O than the four others. Explain.