

**Chemistry 652**

**Organometallic Chemistry**

**Midterm Examination, April 1, 2021**

Name: Key

- In a deviation from normal procedure, this is an open textbook/open class notes exam. Specifically, you are welcome to use a periodic table of the elements. During the exam, you may not discuss your work with anybody else, nor may you scour the internet for help!
- If you have a printer, print the exam and put your answers right on it. Alternatively, just write them on a piece of paper (organized by problem no.) and put your name on it. Either way, send a copy/photo/scan (pdf format preferred) of your answers to: [theopold@udel.edu](mailto:theopold@udel.edu)
- The exam is timed. I must receive your answers – electronically – by the end of the class period (i.e., no later than 3:20 PM on April 1, 2021). Points will be subtracted for late submission.

1:

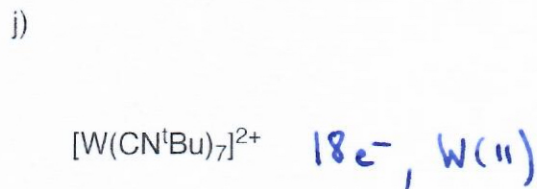
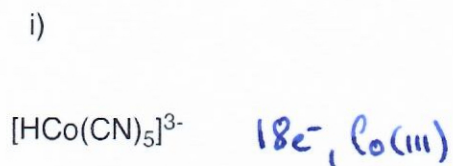
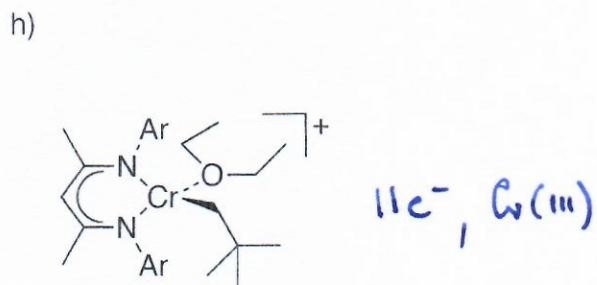
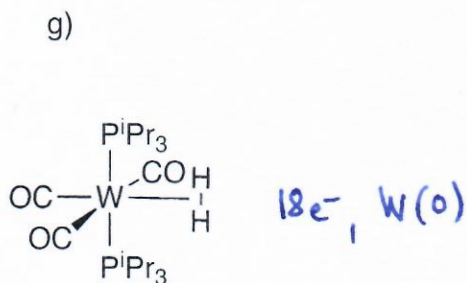
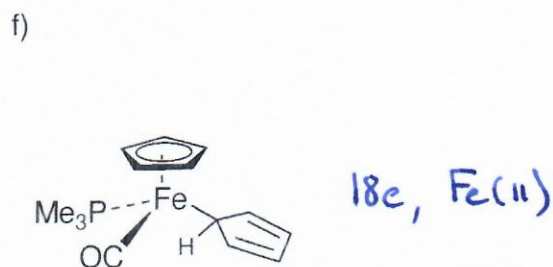
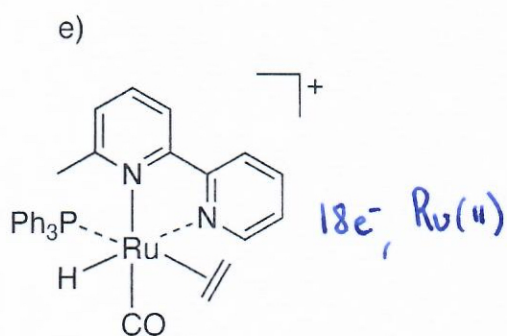
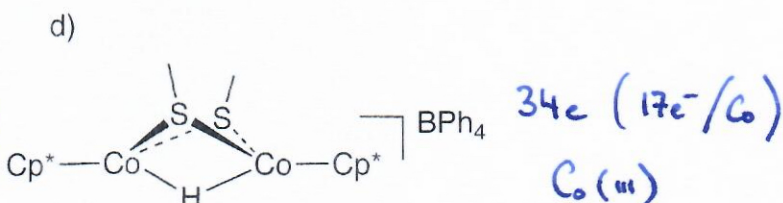
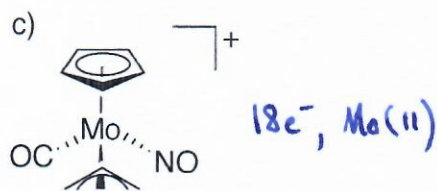
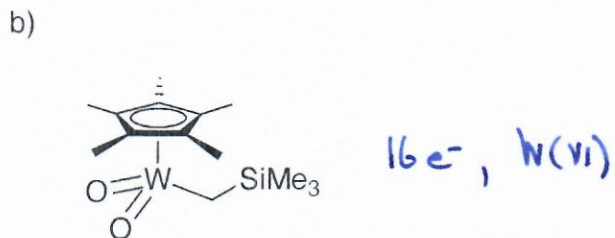
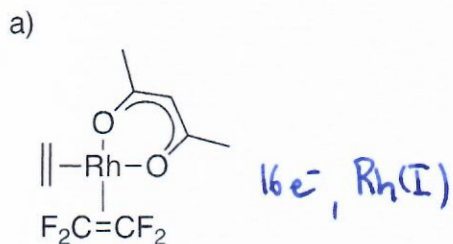
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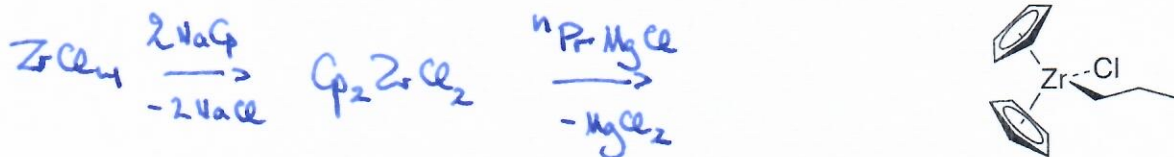
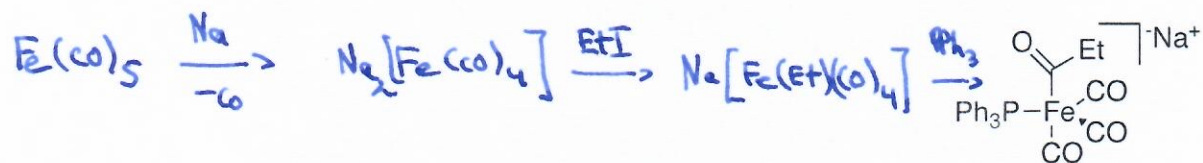
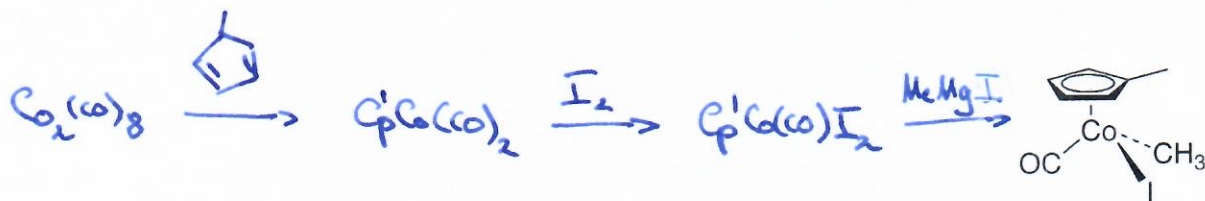
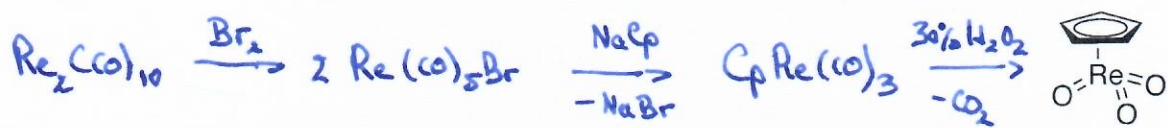
5: \_\_\_\_\_

1. (20 pts.) For the following molecules, give the valence electron count and the formal oxidation state of the metal.

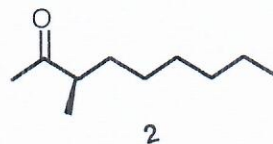
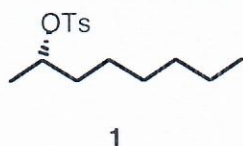


2. (20 pts.) Using only readily available starting materials (i.e. metals, stable metal halides or oxides, or homoleptic carbonyls), as well as organic molecules (including common main group metal alkyls), give plausible synthetic routes to the following organometallic molecules.

The following are illustrative. Other routes are possible.

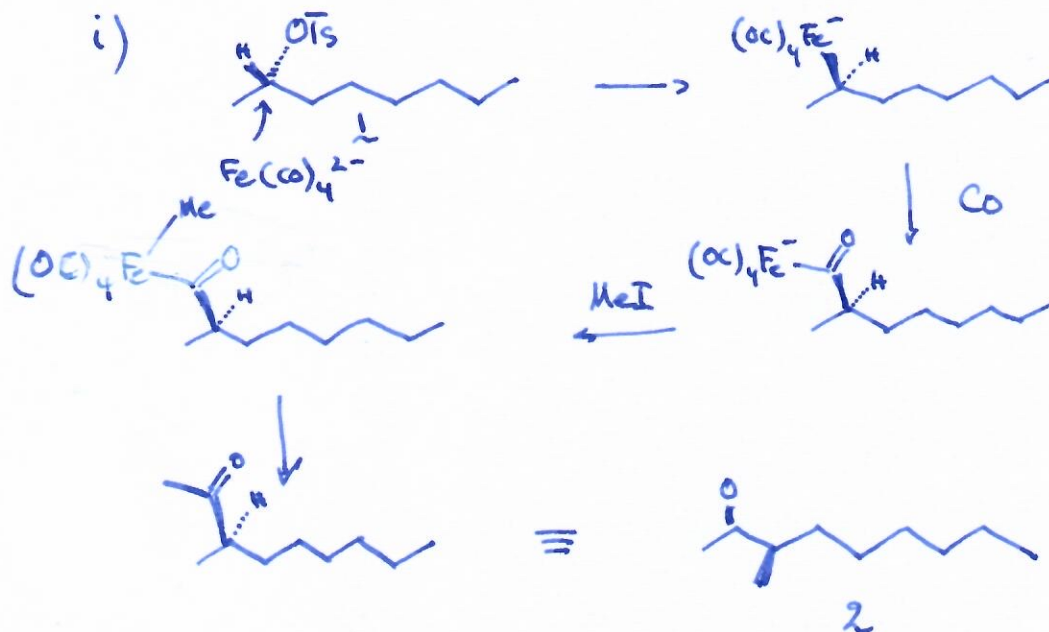


3. (20 pts.) When the product of the reaction of enantiomerically pure (S)-2-octyl tosylate (1) with  $\text{Na}_2[\text{Fe}(\text{CO})_4]$  is treated first with carbon monoxide (CO) and then with methyl iodide (MeI), the organic product is (R)-3-methyl-2-nonanone (2) in 99 % enantiomeric excess.



i) Draw structures of all organometallic intermediates along the reaction pathway, rationalizing this outcome.

ii) What is the mechanistic implication of this overall transformation for the first step of the reaction sequence?



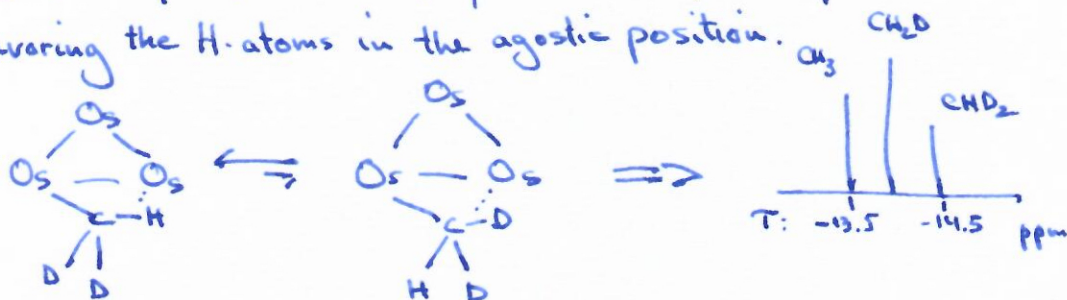
ii) Assuming that the CO-insertion in step 2 proceeds w/ retention of configuration at the migrating carbon, the initial oxidative addition of 1 must go with inversion of configuration. This suggests an  $\text{S}_{\text{N}}2$  type mechanism.

4. (20 pts.) What is meant by the term 'isotopic perturbation of resonance'? Describe a real example from the realm of organometallic chemistry. What is the experimental observation? What is the interpretation in terms of organometallic chemistry?

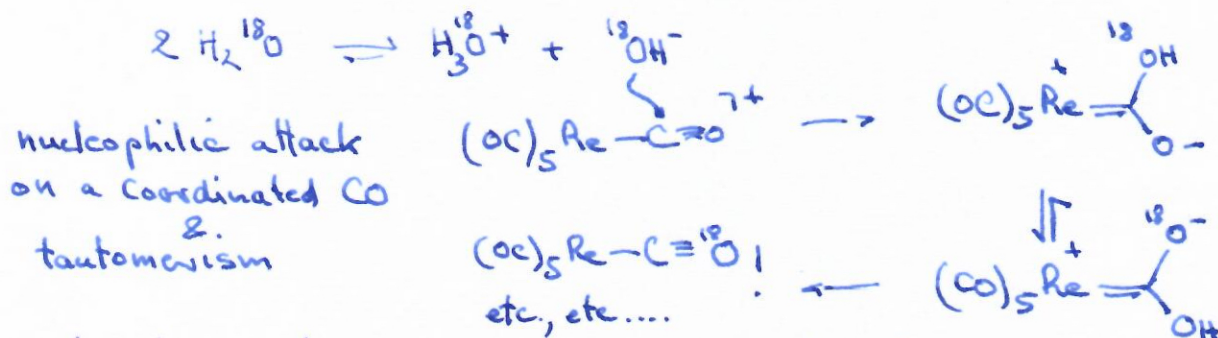
IPeR is an effect of isotopic substitution on the chemical shift of an adjacent nucleus. It is an equilibrium isotope effect

An example referred to in class is Shapley's test for the agostic nature of Me-groups bridging two metals (JACS 1978, 100, 7726)

In  $\mu\text{-H Os}_3(\text{CO})_{10}(\mu\text{CH}_3\text{-}x\text{D}_x)$ , the  $^1\text{H-NMR}$  of the isotopologs exhibit significantly different shifts, because of an equilibrium isotope effect favoring the H-atoms in the agostic position.



5. (20 pts) When  $[\text{Re}(\text{CO})_6]\text{BF}_4$  is recrystallized from  $^{18}\text{O}$  labeled water,  $\text{H}_2^{18}\text{O}$ , the labeled oxygen is incorporated into the CO to give  $[\text{Re}(\text{C}^{18}\text{O})_6]\text{BF}_4$ . Suggest a mechanism to explain this exchange. Why does  $\text{W}(\text{CO})_6$  show no exchange under similar conditions?



$\text{W}(\text{CO})_6$ , being electrically neutral, is less electrophilic and thus less subject to nucleophilic attack.