

**Chemistry 652**

**Organometallic Chemistry**

**Midterm Examination, April 9, 2009**

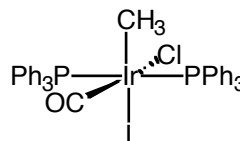
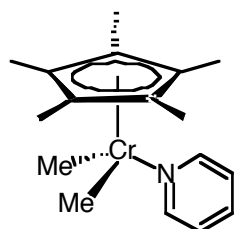
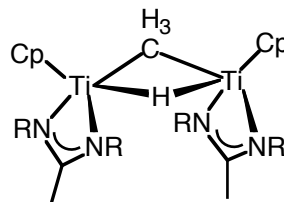
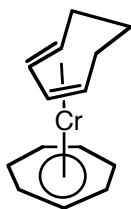
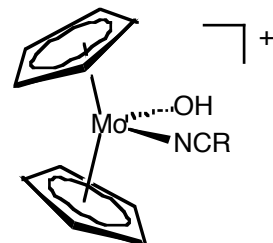
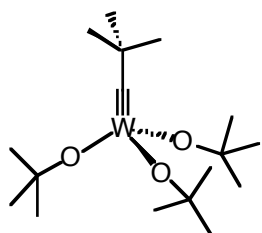
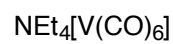
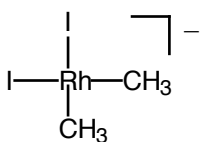
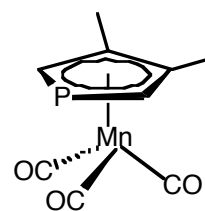
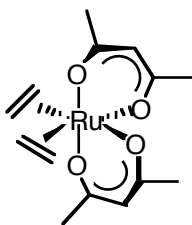
Please write your answers directly in the spaces provided.

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

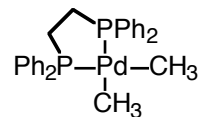
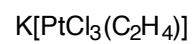
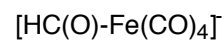
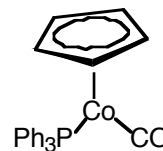
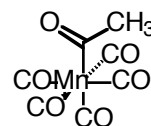


- 1:
- 2:
- 3:
- 4:
- 5:
- 6: \_\_\_\_\_

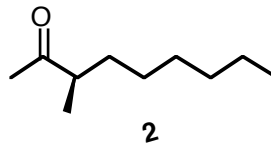
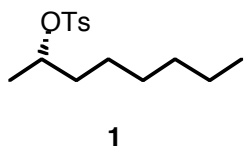
1. (20 pts.) For the following molecules, give the valence electron count and the formal oxidation state of the metal.



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



3. (15 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.

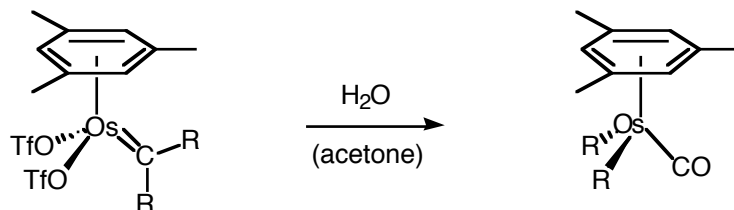


- i) Draw structures of all organometallic intermediates along the reaction pathway.
- ii) Label the reaction type (e. g. 'reductive elimination',  $\beta$ -H-elimination etc.) of each individual reaction step.
- iii) What is the mechanistic implication of this overall transformation for the first step of the reaction sequence?

4. (15 pts.) Describe the experiment that was used by Calderazzo et al. to show that the formation of acetyl manganese pentacarbonyl ( $\text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_5$ ) by an insertion reaction involves migration of the methyl group to a stationary carbonyl ligand (as opposed to the converse). Show how you would prepare the compound(s) needed for the experiment, and clearly identify any assumptions or mechanistic inferences used in the argument.

5. (15 pts.) The compound  $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiCCSiMe}_3)$  (**1**) is a ready precursor of the 'titanocene' fragment. The C-C bond in the coordinated alkyne measures 1.283(6) Å and the C-C-Si angles are 146° and 148°. Explain these structural features within the context of the description of the bonding of alkynes to metal atoms (identify orbitals used in bonding). Draw a Lewis structure that best captures the bonding situation in **1**.

6. (15 pts.) H. Werner et al. have reported the unusual transformation depicted below.



Suggest a mechanism for this unprecedented transformation, drawing structures of all postulated intermediates.

Bonus question (5 points): What is the 'Turing Test' referred to on page 1 of this exam?