

**Organometallic Chemistry**

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

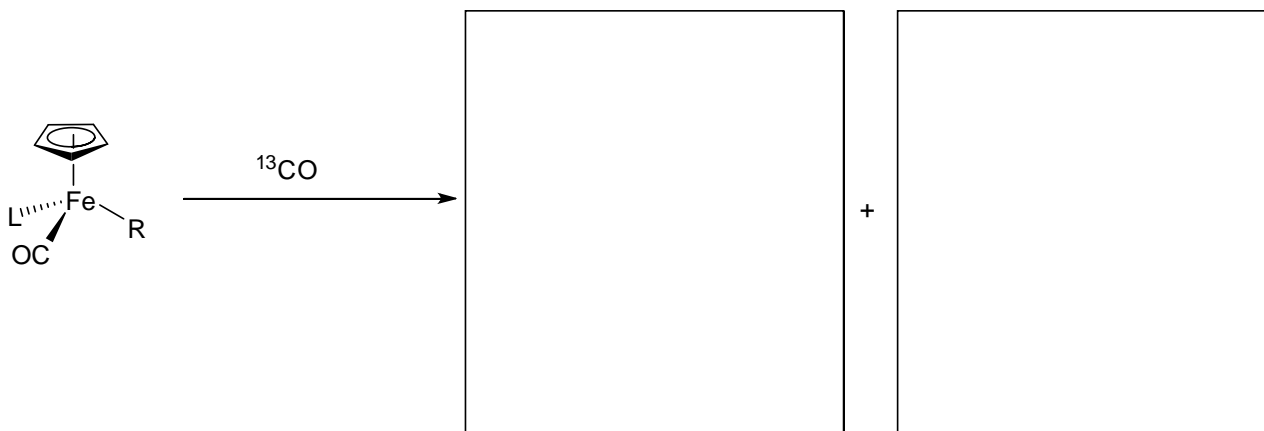
**Problem Set #5**

Due: Nov. 8, 2011

*CHE-334: Complete 2 of 3 questions. CHE-534: Complete all 3 questions.*

1. Another study of 1,1 insertion reactions, much like the  $\text{Mn}(\text{CO})_5\text{C}(=\text{O})\text{Me}$  one described in class, was conducted with the stereogenic metal complex,  $\text{CpFeL}(\text{CO})\text{R}$  (where R=an alkyl group).

a) Provide the two possible products from the two possible reaction paths, R migration and CO insertion. Label each in the answer boxes. Identify each as either an inversion or retention of stereochemistry at the Fe center (based on  $-\text{R}$  and  $-\text{C}(=\text{O})\text{R}$  being roughly equivalent).



The reaction had inversion of stereochemistry when run in a non-coordinating solvent such as nitroethane, but had a mixture of the two possible products when run in coordinating solvents such as hexamethylphosphoramide (HMPA) or acetonitrile.

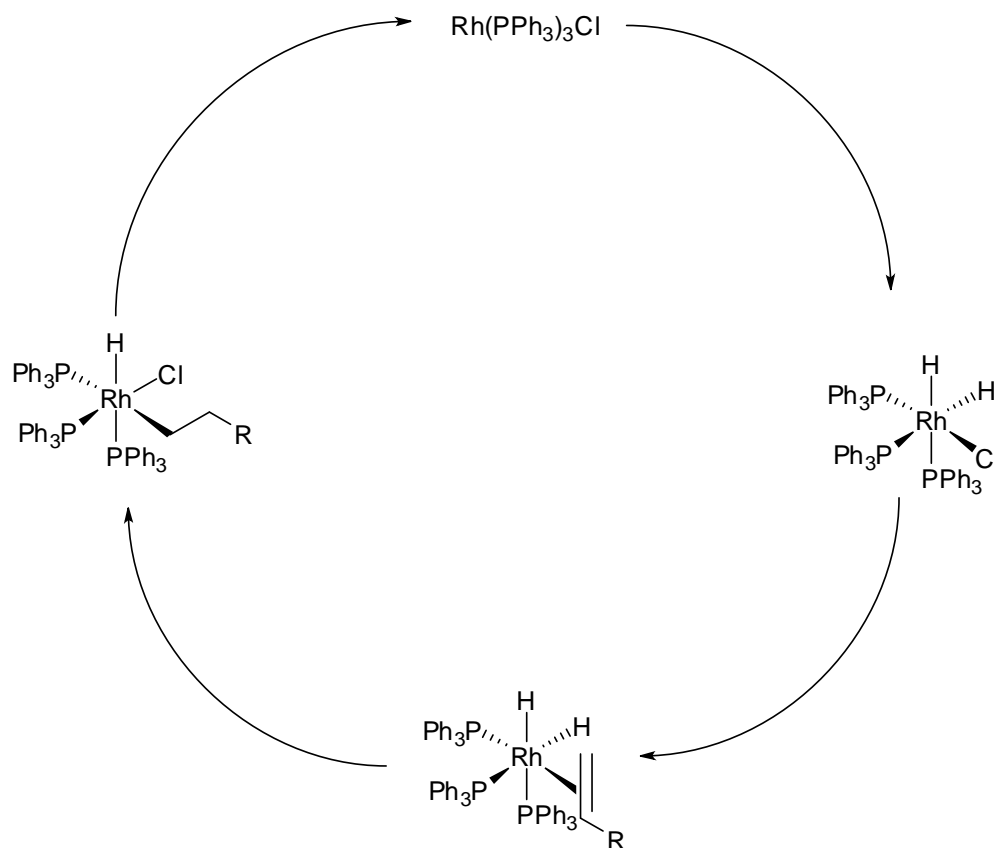
b) Which is the path of 1,1-insertion in nitroethane, R migration or CO insertion? (circle one)

c) Propose one possible effect of coordinating solvents that explains the result in that experiment.

d) The authors of this study used  $\text{BF}_3$  to accelerate the 1,1-insertion process. Show with a chemical picture and offer a short description about the role of  $\text{BF}_3$  in accelerating the insertion process.

2. The Nobel Prize in Chemistry in 1973 went partially to Sir Geoffrey Wilkinson for his work with organometallic complexes. One of the important contributions of Wilkinson was to the catalysis of alkene hydrogenation by rhodium complexes, in particular by  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  which was later known as Wilkinson's catalyst.

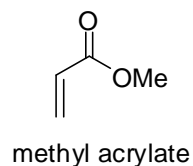
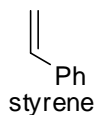
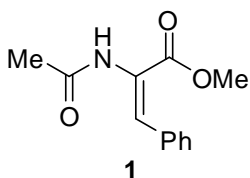
a) Complete the catalytic cycle for alkene hydrogenation by  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  by providing reagents and names for the mechanistic steps in the catalytic cycle.



b) If a cationic Rh complex, such as  $[\text{Rh}(\text{DIPHOS})]^+$  ( $\text{DIPHOS}=\text{Ph}_2\text{P}-\text{CH}_2\text{CH}_2-\text{PPh}_2$ ), is used instead of  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ , then the first two steps of the catalytic cycle are switched in order. However, if alkyl phosphines, e.g.  $(t\text{-Bu})(\text{Me})\text{P}-\text{CH}_2\text{CH}_2-\text{P}(\text{Me})(t\text{-Bu})$ , are used in place of DIPHOS, then there is some experimental evidence suggesting that the catalytic cycle is restored to the same order as with

Wilkinson's catalyst. Explain the changing order of the first two steps depending on the type of Rh catalyst and ligands used.

c) Subsequent work with alkene hydrogenation of more complex alkenes was the basis of another Nobel Prize in Chemistry (2001). One example of a more complex alkene is the cinnamate derivative **1**. Critical to the success of the hydrogenation of **1** is the fact that it is a much better ligand to  $[\text{Rh}(\text{DIPHOS})]^+$  than related alkenes such as styrene and methyl acrylate based on  $K_{\text{eq}}$ . What makes **1** so much better? Propose a method of **1** binding to a Rh complex that supports your suggestion.



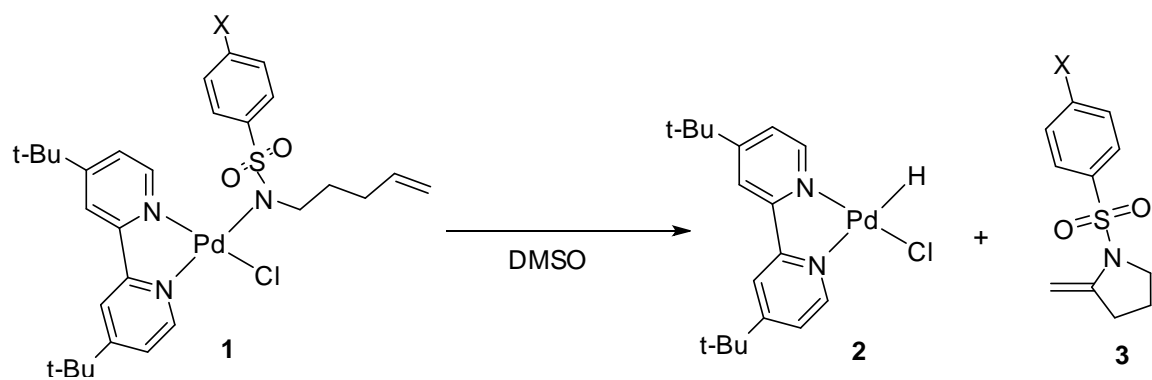
$$K_{\text{eq}} (\text{M}^{-1}) = 5.3 \times 10^3$$

$$20$$

$$3$$

3. The reaction shown below was recently reported in the literature in a study of aminopalladation reactions.

a) Propose a mechanism for this reaction. Note that the researchers reported that the addition of  $\text{Cl}^-$  inhibited the reaction.



b) The researchers studied different X moieties on the tosyl group and the effect they had on the reaction process. When X= -OMe or Me, the reaction was roughly ten times faster than if X= -NO<sub>2</sub>. What does this say about the role of the N-SO<sub>2</sub>Ar group in the reaction?