

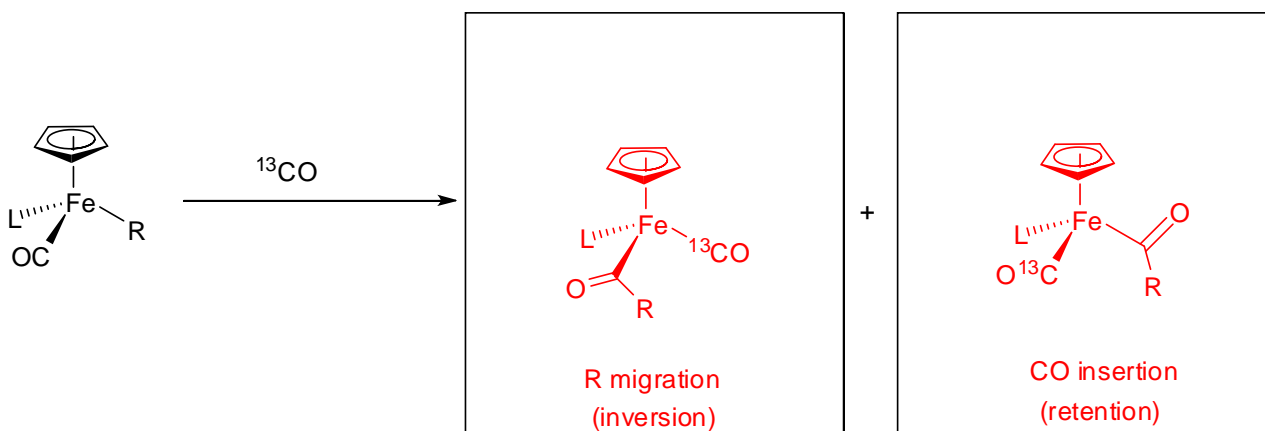
Problem Set #5

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).



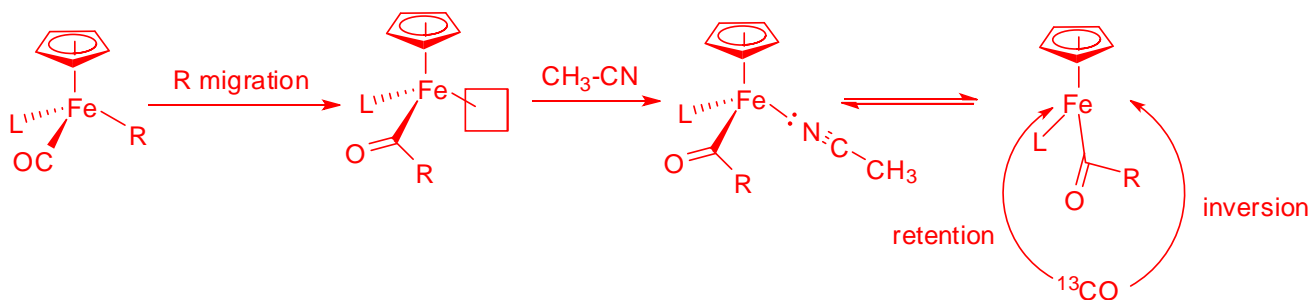
R migration represents an inversion of the stereochemistry at Fe, while CO insertion retains the Fe's stereochemistry from the substrate.

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)

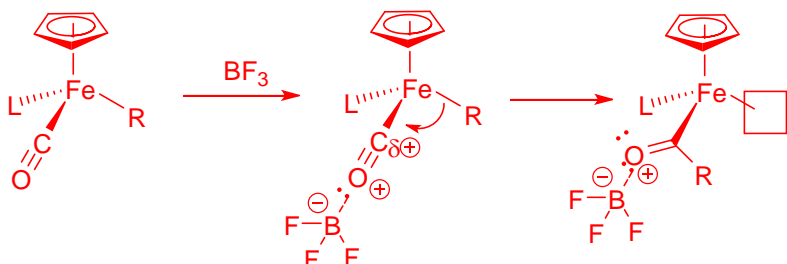
c) Propose one possible effect of coordinating solvents that explains the result in that experiment.

The coordinating solvents might become an Fe ligand before ^{13}CO binds, thereby extending the lifetime of an Fe intermediate. If ^{13}CO does not immediately bind, then the Fe metal complex might have time to lose the solvent "placeholder" and become trigonal planar. Once trigonal planar, then the ^{13}CO can enter from either face resulting in both inversion and retention products.



Alternatively, the coordinating solvent could just add from the face opposite the open ligand site. This would lead to an inversion process. An equilibration as shown above would allow an achiral trigonal planar intermediate to form which would scramble the stereochemical event.

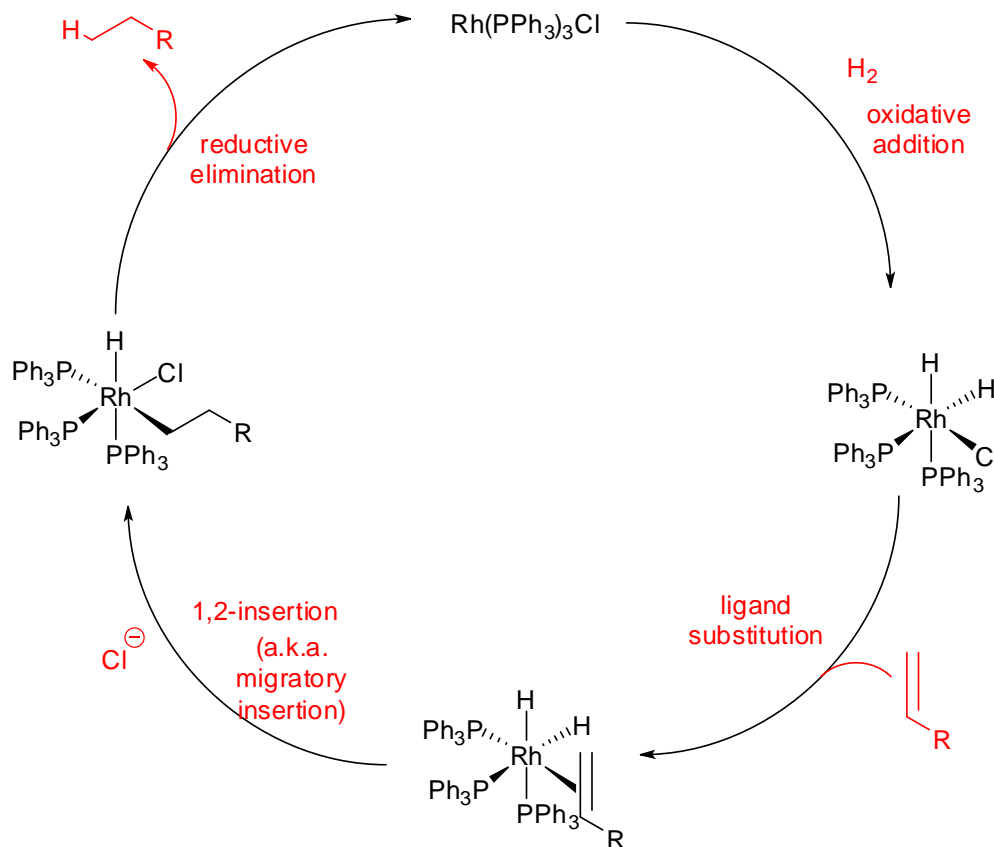
d) The authors of this study used BF_3 to accelerate the 1,1-insertion process. Show with a chemical picture and offer a short description about the role of BF_3 in accelerating the insertion process.



The Lewis acid BF_3 might coordinate with the O of CO making the C more electrophilic. This electrophilic C would be more susceptible to R (Nu) migration.

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.

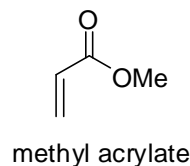
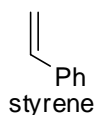
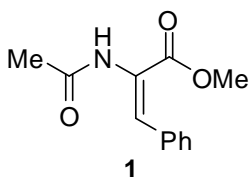
a) Complete the catalytic cycle for alkene hydrogenation by $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ by providing reagents and names for the mechanistic steps in the catalytic cycle.



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.

Cationic Rh would be less capable of conducting an oxidative addition because as a cationic complex it is more electron deficient and therefore less capable of being oxidized. Consequently, it chooses to add the alkene ligand and more electron density before engaging in an oxidative addition with H_2 . With the more electron releasing alkyl phosphine ligands, the Rh has enough electron density to engage in the oxidative addition process before adding the alkene ligand.

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_{eq} . What makes **1** so much better? Propose a method of **1** binding to a Rh complex that supports your suggestion.

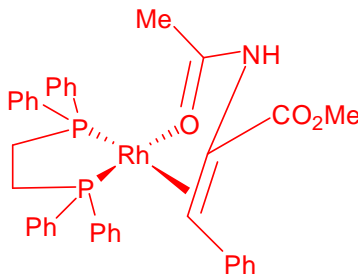


$$K_{\text{eq}} (\text{M}^{-1}) = 5.3 \times 10^3$$

$$20$$

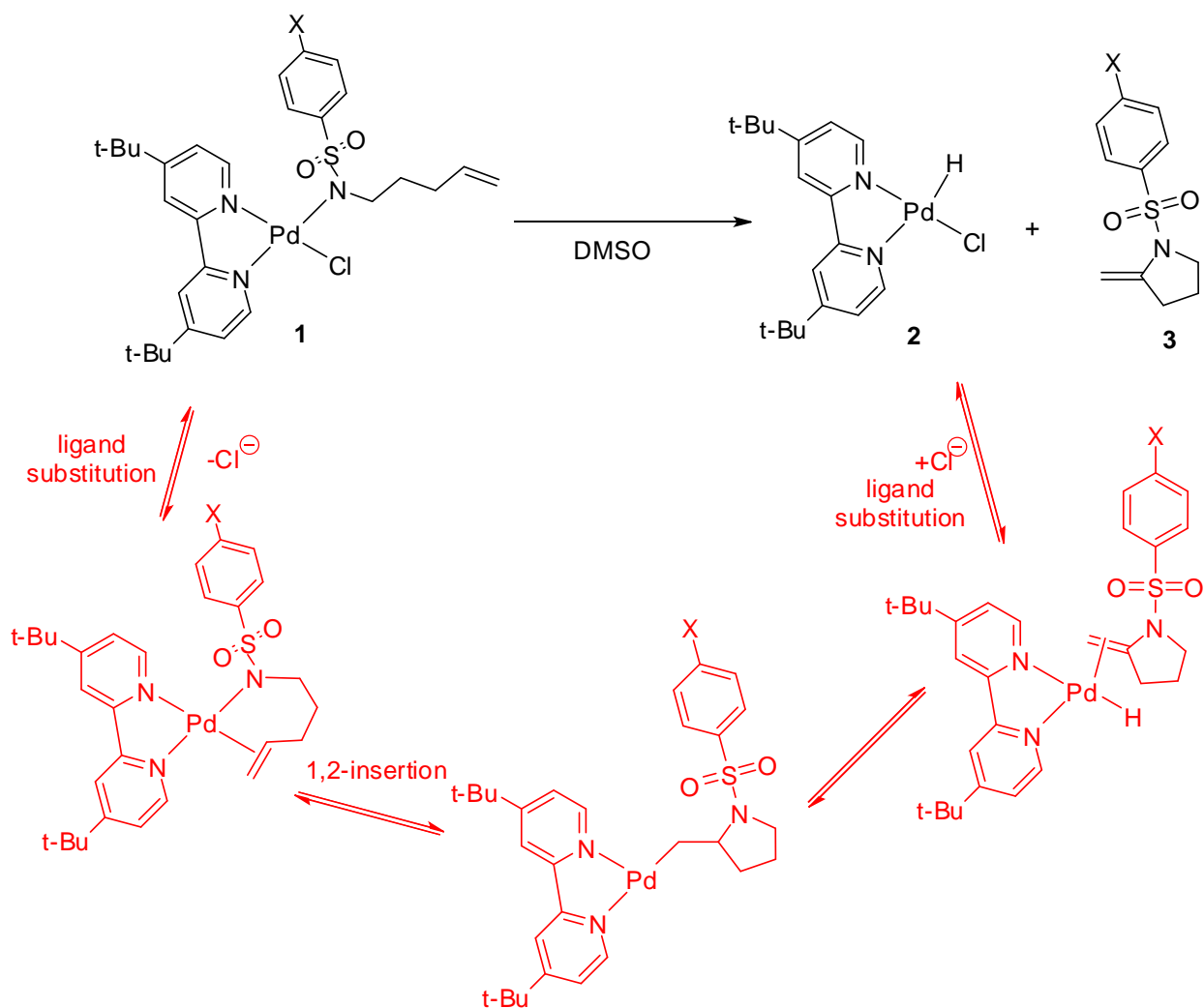
$$3$$

1 can coordinate to $[\text{Rh}(\text{DIPHOS})]^+$ as a bidentate ligand through the alkene and the amide oxygen (shown below) and therefore has a more favorable interaction with the Rh metal.



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 Cl^- inhibited the reaction.



Paul B. White and Shannon S. Stahl, *J. Am. Chem. Soc.*, Article ASAP (DOI: [10.1021/ja208560h](https://doi.org/10.1021/ja208560h))

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 = -NO₂. What does this say about the role of the N-SO₂Ar group in the reaction?

Since the methoxy and methyl groups are both electron releasing groups and the nitro group is an electron withdrawing group, the experimental results showing a faster reaction with the electron releasing groups suggest the reaction depends on the nucleophilicity of the N-SO₂Ar. That is, the N-SO₂Ar group attacks the alkene like a nucleophile.