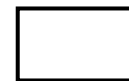
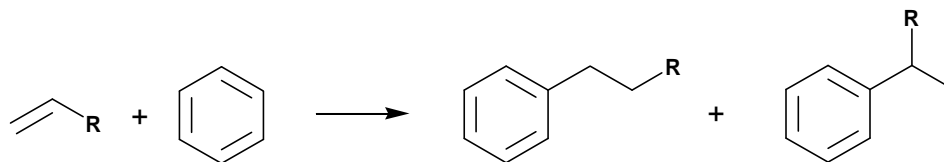


Homework # 4 -- Due: May 1, 2007

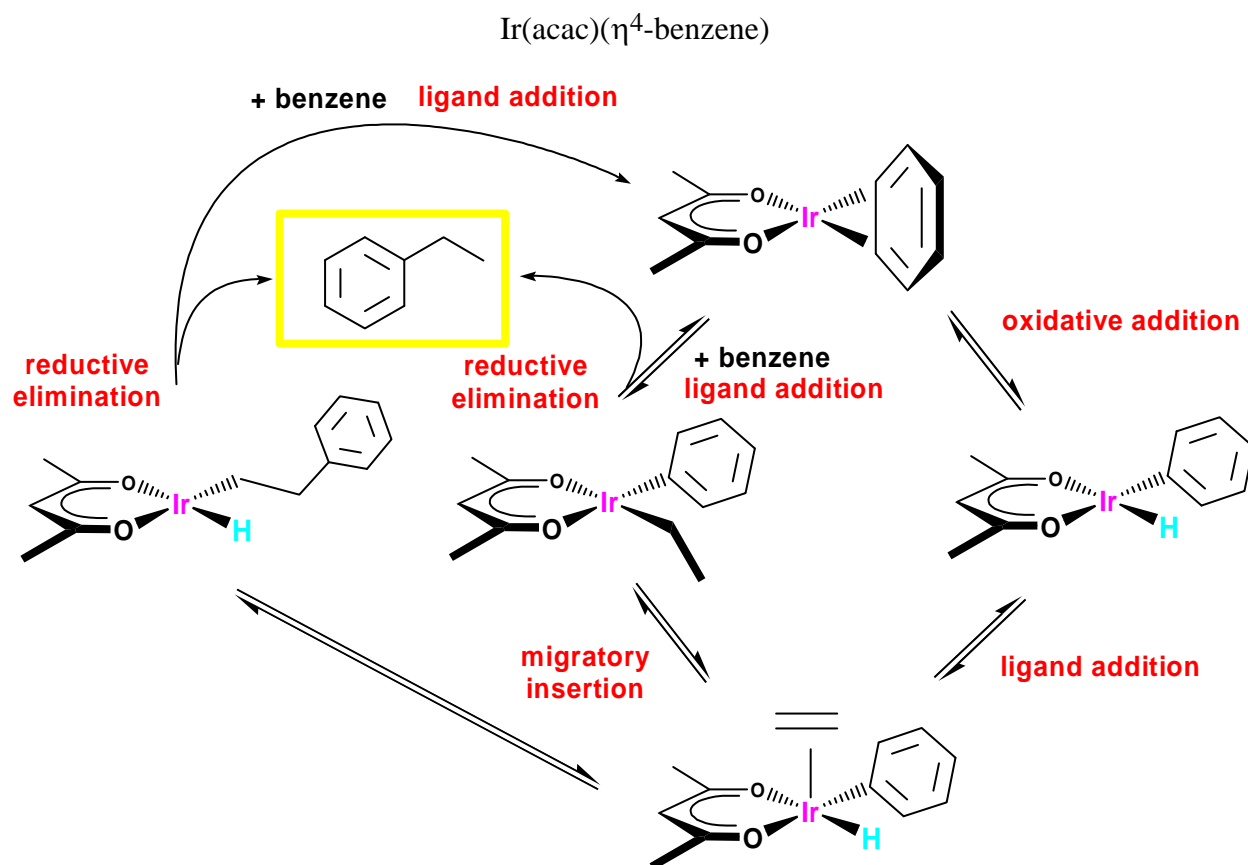
Check the box to the right if you want your graded homework to be placed out in the public rack outside Prof. Stanley's office. Otherwise you will have to pick up your homework from Prof. Stanley in person:



1. (20 pts) Write out a catalytic cycle for the hydrophenylation of alkenes to produce alkylated arenes:



The starting catalyst is shown below and you are to use benzene as the arene and ethylene (ethene) as the alkene. The catalysis proceeds by the following reaction steps: 1) arene C-H oxidative addition, 2) alkene addition, 3) migratory insertion, 4) reductive elimination. The exact ligands involved in step 3 is not specified, you are to choose the most likely ligands to do this reaction. Ligand dissociation of the initial ligands is allowed if necessary, but I have not indicated when this may (or may not) happen. Clearly sketch out each metal complex with proper geometries. [Periana et al., *JACS*, **2000**, *122*, 7414-7415]



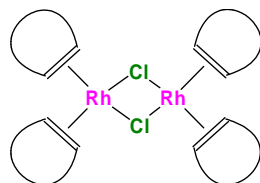
Note that there are two possible migratory insertions and both are acceptable and of similar likelihood. I have a moderate preference for the migratory insertion of the alkene and hydride due to easier movement of the hydride and its spherically symmetrical s orbital that can overlap well with the alkene. The phenyl ring, however, also has a π -system "sticking out" that can also overlap reasonably well with the alkene to do the migratory insertion.

Read the attached paper from the *Journal of the American Chemical Society* and answer the following questions about it.

2. (10 pts) The catalyst precursor used is listed as $[\text{RhCl}(\text{coe})_2]_2$. What is coe? Sketch out the structure of $[\text{RhCl}(\text{coe})_2]_2$ – you can abbreviate the coe ligand as:

coe = cyclooctene

traditionally $[\text{RhCl}(\text{coe})_2]_2$ is not written out as $\text{Rh}_2(\mu\text{-Cl})_2(\text{coe})_4$ because it falls apart quite easily to make reactive 14e- monometallic complexes.



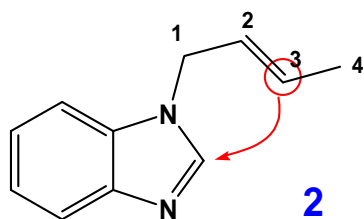
no Rh-Rh bonding due to d^8 square planar configuration that is happy with 16e- count

3. (15 pts) From Table 2 calculate the following:

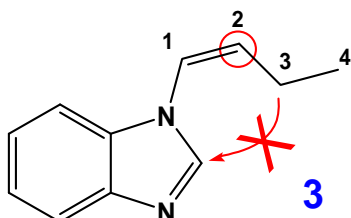
- a) maximum # of turnovers (TON): 10 (2 Rh centers, see note below)
- b) average turnover frequency (TOF hr^{-1}) for entry # 1 (assume 85% conversion to product) = 0.42 hr^{-1}
- c) using the last catalytic run from Table 1, calculate the average TOF for this run = 1.23 hr^{-1}

- a) 5 mole % catalyst refers to the amount of catalyst precursor relative to the amount of reactant (substrate). So if one has 1 mole (or equivalent) of reactant then there is 0.05 moles (or equivalents) of catalyst precursor. # of TO = $1/0.05 = 20$ TO. BUT, each catalyst precursor has TWO Rh centers and falls apart to generate TWO monometallic catalyst complexes. Thus the 5 mole % is actually 10 mole % on a Rh basis. The authors MIGHT have accounted for this in their catalyst mole % figure, so we will accept 10 or 20 as the answer. If so this will also double the answers listed for b) and c).
- c) the yield was 86% with 10 mole % catalyst (but 2 Rh equivalents), so there were 4.3 TO's over 3.5 hours (TOF = $4.3/3.5 \text{ hr} = 1.23 \text{ hr}^{-1}$)

4. (10 pts) In the scheme on the first page, column 2, substrate 1 can be isomerized to 2 or 3. Clearly, 1 can be converted to the product 4. Can 2 or 3 directly cyclize to form 4? Explain your answer for 2 and 3.

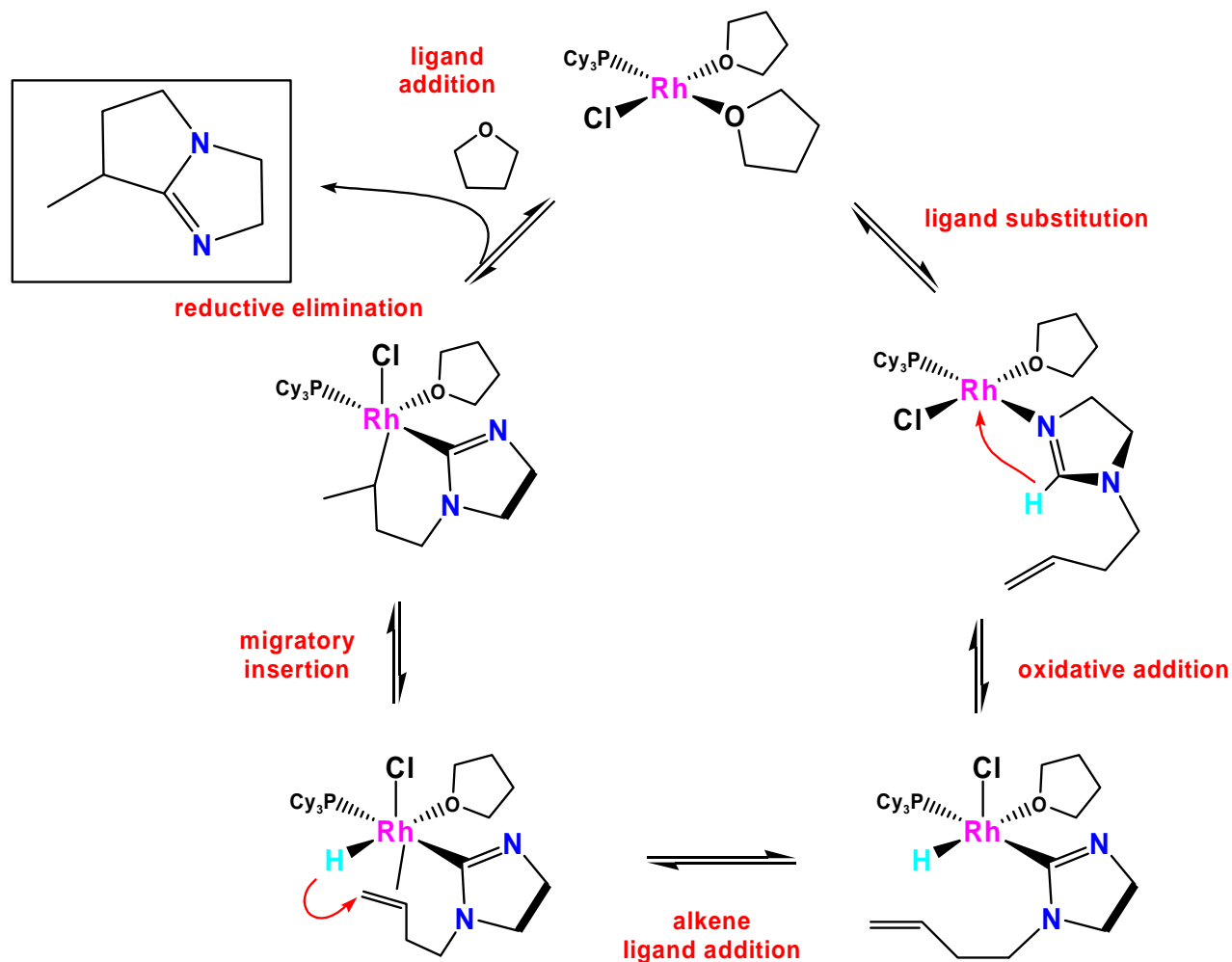


YES, substrate # 2 can ring close to form the desired product 4. So long as there is a double bond at carbon 3, this carbon atom will have the reactivity to ultimately do the ring closing to form product 4.



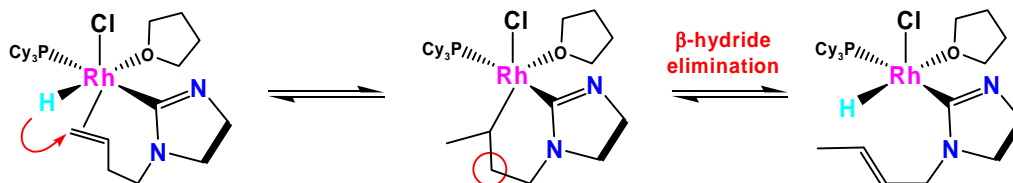
NO, substrate # 3 does NOT have double bond character at carbon 3 needed to perform the eventual ring closing. Carbon 2 might be able to couple, but this would form a 4-membered (and more strained) ring system that is NOT product 4.

5. (25 pts) Sketch out a catalytic cycle for **1** being converted to **4** (no isomerization). You only have to draw the imidazole ring and N-alkenyl group on **1**. Start with the catalyst shown below. The first step is coordination of **1** via the less substituted N lone pair. The second step is C-H bond activation (but label this with the more correct mechanistic term) of the adjacent C-H bond. Based on this information, complete the cycle. Clearly label each step with what is mechanistically happening.



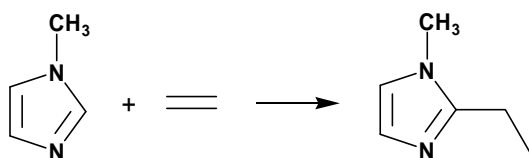
The oxidative addition of the C-H bond to the Rh breaks the weaker Rh-N bond to generate the 16e- Rh(+3) complex. After the alkene ligand adds, the migratory insertion must proceed to give the branched alkyl product with the 6-membered "chelate" ring. The somewhat more stable 6-membered ring system formed, relative to the 7-membered ring that would form if the migratory insertion went the other way, is probably the driving force for this.

6. (10 pts) At what point in the catalytic cycle is the alkene isomerization discussed in question # 4 (and the paper) most likely to happen. Sketch out the isomerization of **1** to **2** and label each step (once again, you don't have to draw out the arene ring on **1** and **2**).

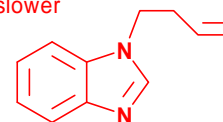


The alkene is isomerized by performing a β -hydride elimination from the circled carbon atom in the middle structure shown above. This moves or isomerizes the double bond. This is clearly happening as a side reaction in the catalysis since the authors do report the formation of **2** and traces of **3**. Isomer **3** is more difficult to make since this involves forming a somewhat more strained 5-membered ring and doing the proper β -hydride elimination from that.

7. (5 pts) Given the catalytic conditions (temp, catalyst loading, TOF), do you think the following similar reaction is likely to be catalyzed by the best catalyst discussed in this paper? Fully discuss.



The coupling reaction of ethylene and imidazole should be much slower and more difficult to do relative to the "linked" reactant molecules that the authors used in this paper.



The tethering of the alkene group onto the imidazole substantially increases the odds (kinetic probability) of it reacting with the metal center in the short period of time that the imidazole ring has oxidatively added to the Rh center. Remember that the reverse alkyl-hydride reductive elimination reaction to kick off the free imidazole can and is happening all the time, otherwise the authors could observe the carbon-bound imidazole C-H oxidative addition product via NMR. Attaching a reactive group onto the substrate makes it a lot easier to coordinate to the metal and this is analogous to the chelate effect that we have discussed many times in class. So the above reaction should go much more slowly.

8. (5 pts) The authors add some excess PCy_3 , but I've only drawn the catalyst with one PCy_3 ligand. Why didn't I use two PCy_3 ligands on the catalyst?

Two PCy_3 ligands would make the catalyst way too sterically hindered to do this reaction. It is typical to add a little extra phosphine ligand to maintain at least one coordinated phosphine ligand which generates the active catalyst. At the rather high reaction temperature of 160-180 °C (fairly high for a homogeneous catalyst) there will be a fair bit of phosphine ligand dissociation, even for a strongly donating alkylated phosphine ligand like PCy_3 . Adding some excess phosphine ligand will help push the equilibrium back towards the mono-phosphine Rh complex.