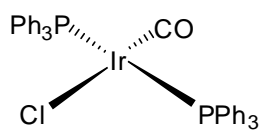
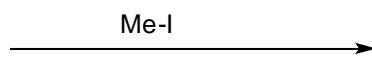


1. Provide the product and the type of mechanism occurring in the reactions below. CHE-334 students do 6 of 8 questions; CHE-534 must complete 7 of 8. (20 pts.)

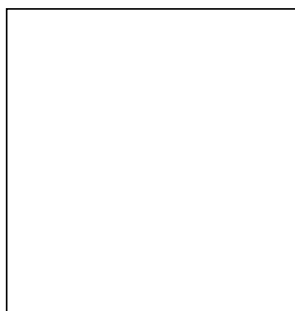
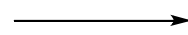
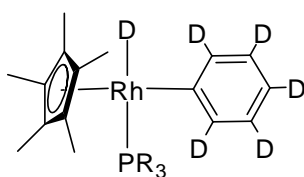
a)



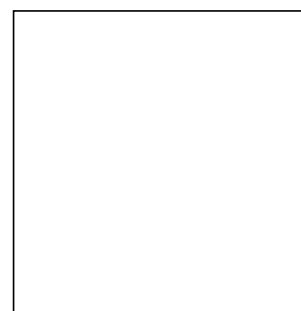
Vaska's complex



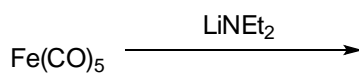
b)



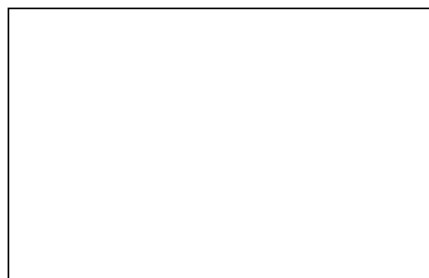
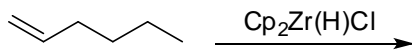
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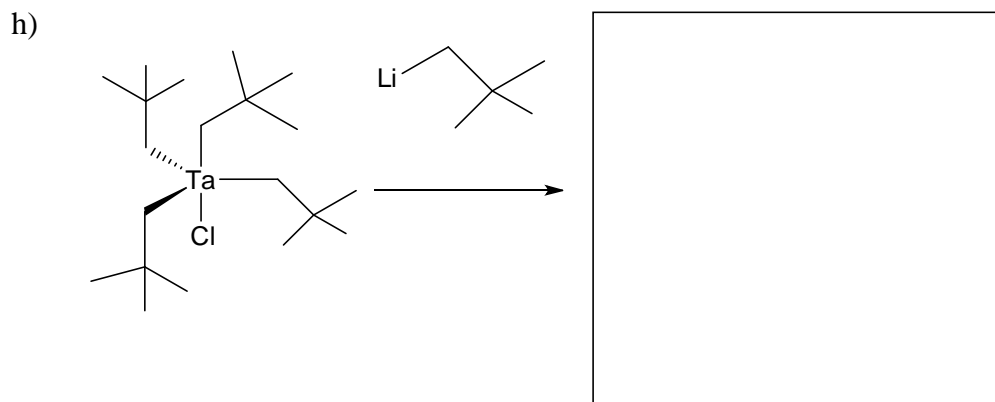
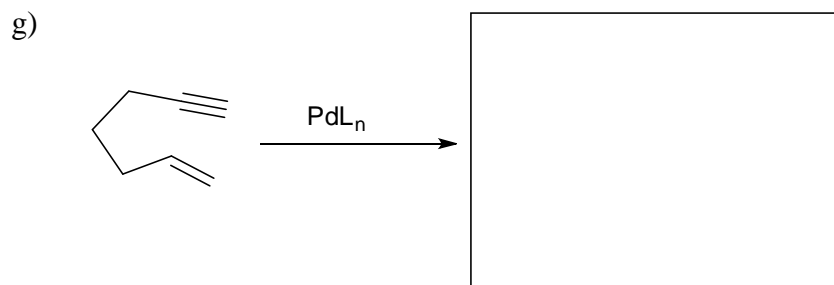
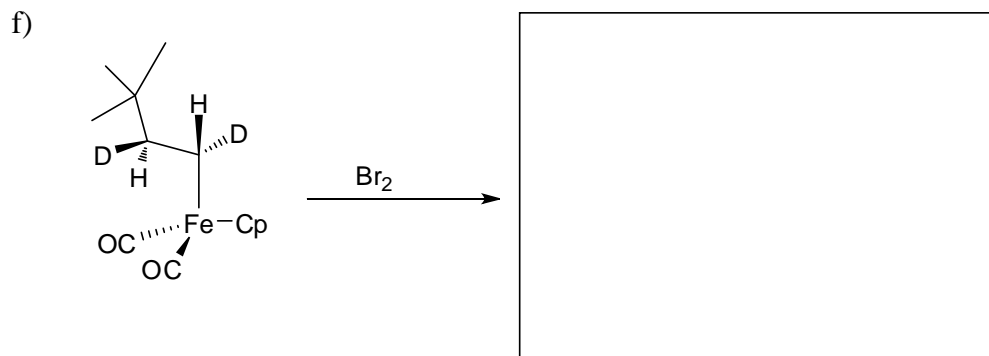
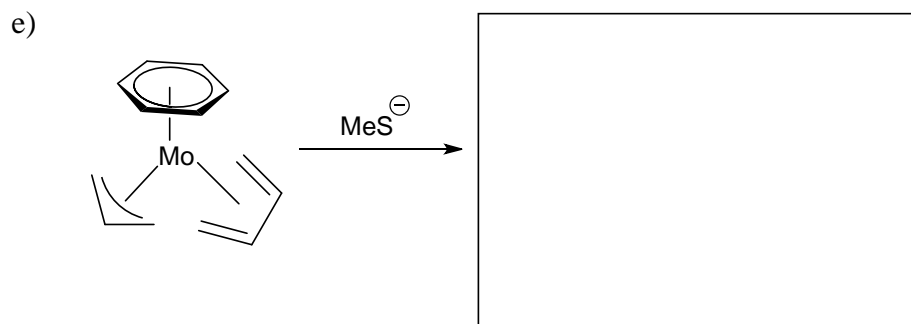


c)



d)

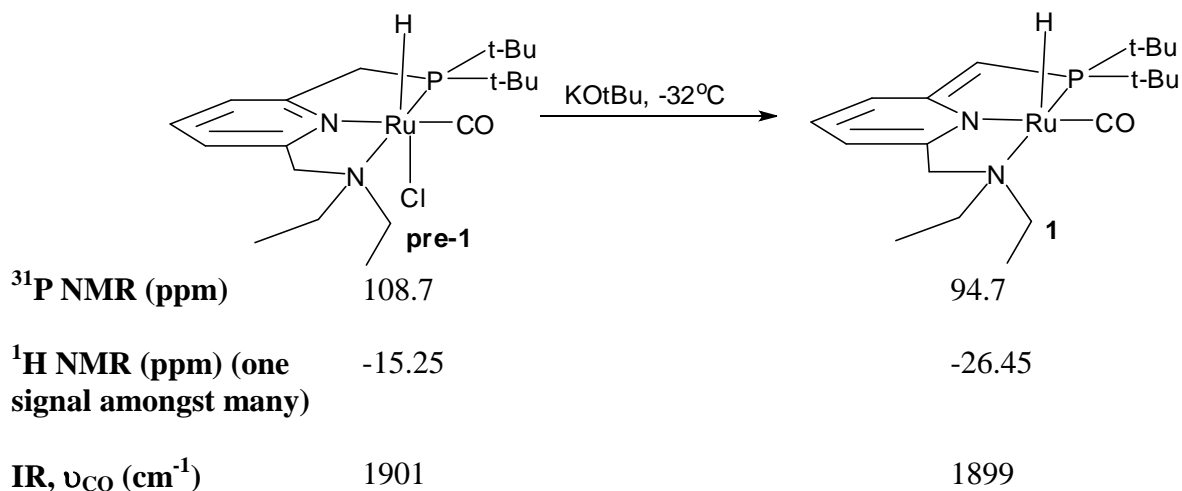




Questions 2-5: CHE-334 must complete 2 of the 4 questions, while CHE-534 must complete 3 of 4 questions. (20 pts. each)

2. While I was in England last spring, David Milstein, a former DuPont researcher currently at the Weizmann Institute of Science in Israel, came to speak. He discussed the chemistry of complex **1** below which he has been exploring for the last decade. Ru complex **1** was synthesized from **pre-1** by reacting with KOt-Bu.

a) Show electron flow arrows that rationalize the formation of **1** from **pre-1**.



A portion of the reported spectroscopic information for compound **pre-1** and **1** is shown above.

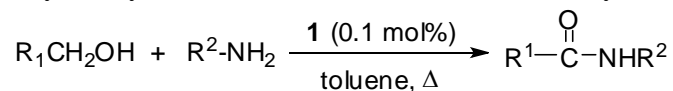
Answer the following questions about the data based on our discussions in the course.

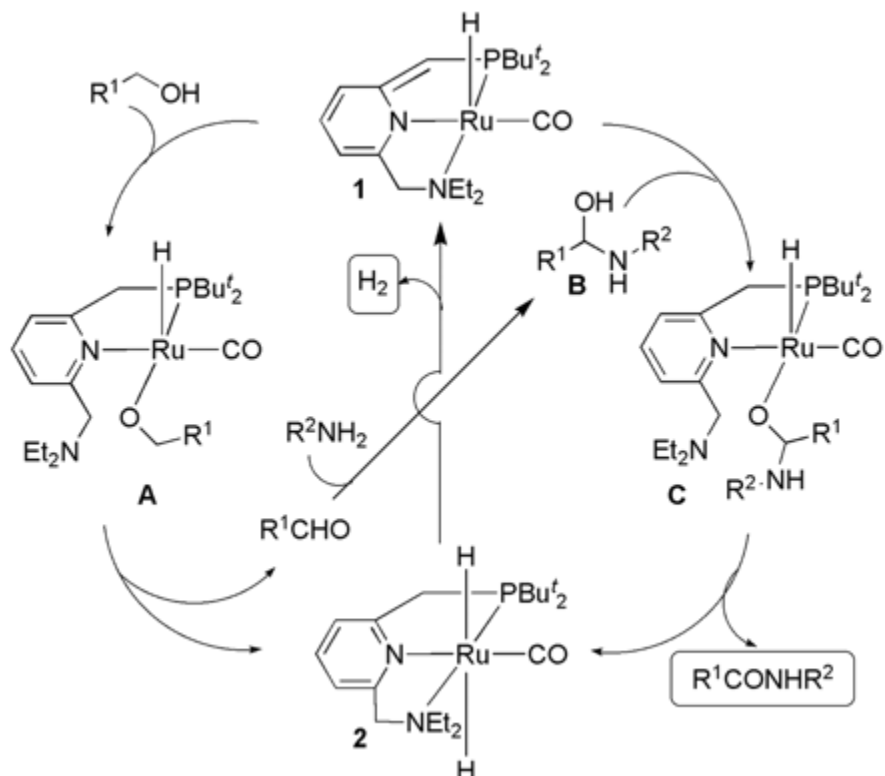
b) Of the 30 or so protons present in **pre-1** and **1**, circle the proton that is most likely responsible for the signal listed, i.e. -15.25 ppm in **pre-1** and -26.45 in **1**.

c) What does the NMR information suggest about the electronic nature of complex **1** and the Ru atom at its core versus complex **pre-1**?

d) Does the IR information confirm this conclusion or does it suggest something else?

3. One of the processes catalyzed by **1** is shown in the reaction and catalytic cycle below.





a) Identify the steps in the catalytic cycle by determining the type of process shown. If more than one fundamental mechanistic process occurs, then list them all in the space provided. (3 pts. each)

<i>Reaction:</i>	<i>Type of process:</i>	<i>Reaction:</i>	<i>Type of process:</i>
1 to A		1 to C	
A to 2		C to 2	
2 to 1 (H ⁺ reagent not shown)			

b) Does the spectroscopic information in the previous problem for **1** (versus **pre-1**) support the type of reactivity seen in the reaction? Be as specific as possible. (5 pts.)

4. One recent challenge that organometallic chemists have overcome is the ability to get aryl chlorides to undergo oxidative addition as easily as their bromide or iodide counterpart. This is important because the chloride derivatives tend to be less expensive and more commercially available. One of the important innovations that was used to accomplish oxidative addition was to use phosphine ligands such as $\text{P}(\text{Cy})_3$ and $\text{P}(\text{t-Bu})_3$ instead of the traditional PPh_3 that was commonly used in earlier versions of the reaction.

a) Draw the molecular orbital interactions that occur in the oxidative addition of $\text{Pd}(\text{P}(\text{t-Bu})_3)_2$ with chlorobenzene. Assume this is a concerted addition. Identify the $d\sigma$, $d\pi$, σ and σ^* orbitals. Label the HOMO and LUMO orbitals of both the metal and the chlorobenzene. Identify the direction of electron donation and backbonding.

b) It is believed that in many oxidative additions, the most active catalytic form of the Pd is a monoligated form, i.e. $\text{Pd}(\text{P}(\text{t-Bu})_3)_2$. Furthermore, as described above, phosphine ligands with cyclohexyl and t-butyl groups were most successful with aryl chlorides. Provide a steric reason and an electronic rationale for the success of these ligands in aryl chloride oxidative additions. In the electronic case, reflect on your answer to part a and be as specific as possible in characterizing the essential interactions that lead to oxidative addition.

5. At -20°C , the ^1H NMR spectrum of the agostic species shown below (**1**) consists of a complex phenyl region (30 H's) and six signals at the following chemical shifts:

peak number	$\delta(\text{ppm})$	peak information
1	2.88	doublet, 1 H
2	2.39	singlet, 3 H
3	1.62	singlet, 3 H
4	0.48	doublet, 1 H
5	-2.23	broad singlet, 3 H
6	-24.65	doublet of doublets, 1 H

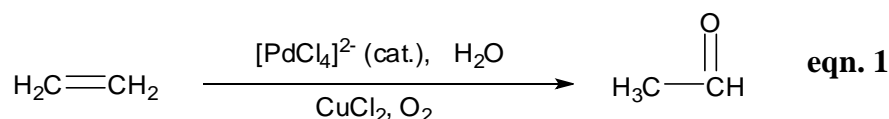
a) Assign the six peaks in the table to protons on complex **1**. Note: peaks 1/4 and 2/3 cannot be definitively assigned to one particular proton, so they may be assigned as a group.

b) Why is peak 6 a doublet of doublets?

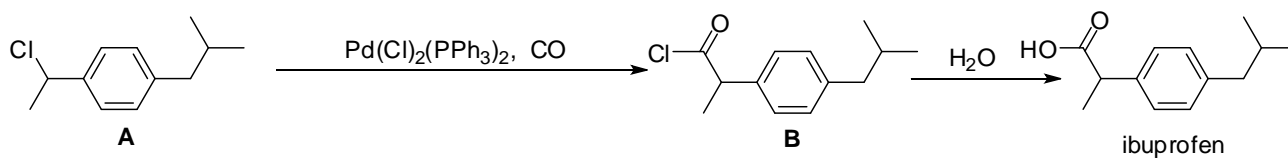
c) Why is the signal at -2.23 ppm a broad singlet? At -80°C , the peak splits into three distinct signals: -9.80 , 0.40 , and 2.71 ppm. Briefly explain what is happening.

Questions 6-8: CHE-334 and CHE-534 must both complete 2 of the 3 questions. (15 pts. each)

6. The Wacker reaction, equation 1 below, is used to manufacture millions of tons of acetaldehyde each year. The mechanism is deceptively complex and is still not fully understood. Nevertheless, it is believed that the key step is a nucleophilic addition. The nature of the nucleophilic addition is dependent on the concentration of chloride ion. Draw the two different nucleophilic addition reactions and indicate which one occurs under high $[\text{Cl}^-]$ and which one under low $[\text{Cl}^-]$. Briefly describe what causes one to be preferred over the other.

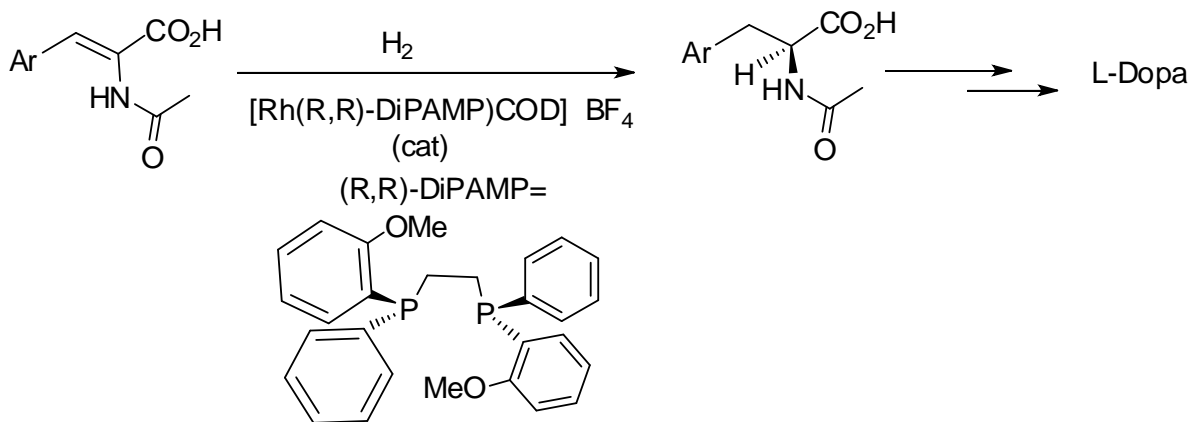


7. The industrial synthesis of ibuprofen is conducted through an efficient three step process called the Boots-Hoechst-Celanese Synthesis. One key catalytic step transforms **A** to **B** as shown below. Based on our class discussions, propose a catalytic cycle that takes **A** to **B**. Draw all intermediates and identify all reaction steps in the process.



8. Building on the work of Sir Geoffrey Wilkinson with Rh catalyzed alkene hydrogenations, William Knowles was able to develop an asymmetric method to make L-Dopa, which is the most commonly used medication to treat Parkinson's disease. The key reaction in the process is shown below. Describe the process by which the hydrogenation occurs. You do NOT need to show the entire mechanism, just

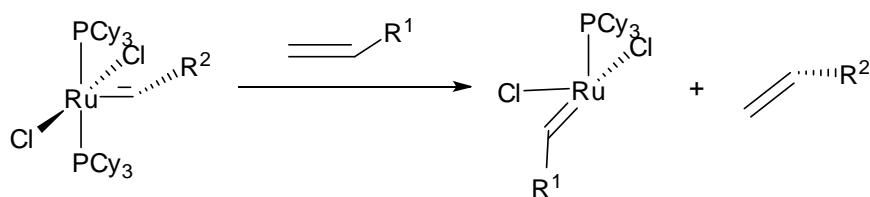
a key intermediate that explains the important bond forming step and the basis of the chiral center formation. You should identify the type of reaction shown. You may abbreviate all ligands or structures as long as the key concepts are conveyed.



Questions 9 and 10: CHE-334 and CHE-534 must both complete 1 of the 2 questions. (10 pts. each)

9. N-Heterocyclic carbenes (NHC's) are revolutionizing ligand design. Draw an N-heterocyclic carbene and briefly describe why they are similar to phosphines and how they differ from phosphines.

10. a) Draw the mechanism of the olefin metathesis process whose reaction is shown below. Show intermediates and label any steps that we have discussed.



b) What is one way in which the outcome of an olefin metathesis reaction can be controlled?