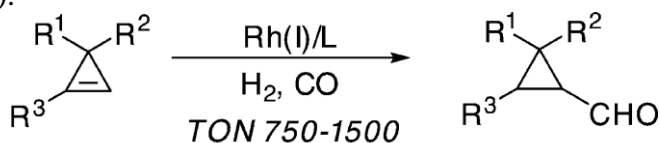




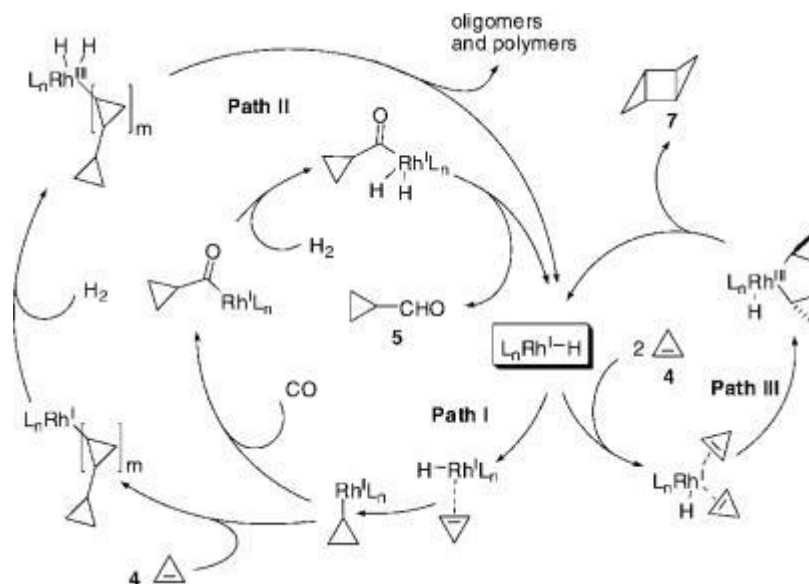
1. The following reaction was reported in the *Journal of the American Chemical Society* (Michael Rubin et al., 2008, 130 (41), 13804–13809).



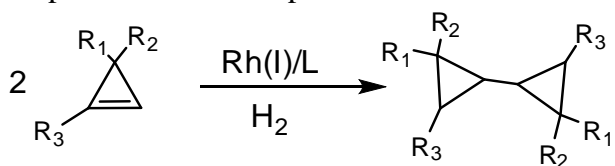
yields 54-91%  
ees up to 83%

a) Suggest a mechanism for the reaction and identify the reaction type for each step. (7 pts.)

Path I below shows the proposed mechanism. The steps are as follows: oxidative addition of H<sub>2</sub> to form the LnRh(I)-H; ligand association with the cyclopropene; 1,2-insertion of Rh-H across the alkene of cyclopropene; association of CO with Rh complex; 1,1-insertion of CO; oxidative addition of H<sub>2</sub>; and reductive elimination of H-C(O)-cyclopropane.



b) One competing process involves the formation of cyclopropyl dimers as shown in the reaction below. Propose a series of steps that allow this to occur and identify the steps in the process. (3 pts.)



Path II or III above. The steps for Path II beginning with LnRh(I)-H are as follows: cyclopropene association; 1,2-insertion of Rh-H across the alkene of cyclopropene; ligand association of cyclopropene; 1,2-insertion of Rh-cyclopropyl across alkene of cyclopropene; oxidative addition of H<sub>2</sub>; reductive elimination of H-cyclopropyl-cyclopropane.

\_\_\_\_\_/10 pts

2. Gerhard Erker and co-workers recently reported in *Organometallics* (Article ASAP) the identification of the two complexes, **6a** and **7b-d**, shown below.

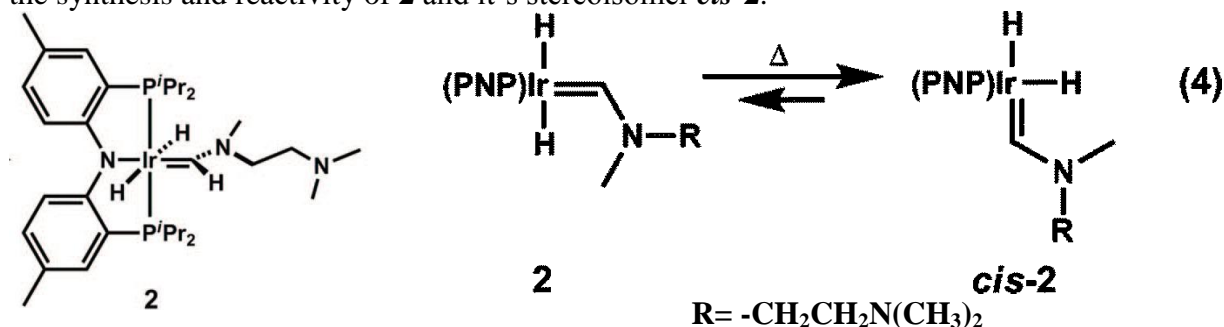


Describe an analytical experiment that would allow you to detect the alkene coordination event in **7b-d**. Be as specific as possible with your experimental details. (6 pts.)

A  $^1\text{H}$  NMR experiment would show an upfield shift in the alkene protons in **7b-d** upon coordination to Ru. The authors of the article actually reported a  $\sim 0.5$  ppm shift from  $\sim 6.0$  in **6a** to  $\sim 5.5$  ppm. A  $^{13}\text{C}$  NMR would experience a similar shift upfield for the carbon signals of the alkene in **7b-d**. The authors actually found a shift from  $\sim 135$  ppm in **6a** to  $\sim 100$  ppm in **7b-d**.

Other experiments that would show the coordination include X-ray crystallography which would show the alkene in close proximity to the Ru.

3. A recent article by Robert Grubbs and co-workers (*Organometallics*, **2008**, 27 (22), 5737–5740) describes the synthesis and reactivity of **2** and its stereoisomer *cis*-**2**.



a) What type of carbene is compound **2**? (3 pts.)

With the heteroatom attached to the carbene carbon, it is a Fischer carbene.

b) What is the typical polarization in the Ir=C bond for this type of carbene? (3 pts.)

The polarization would have a partial positive on the C and a partial negative on the Ir:



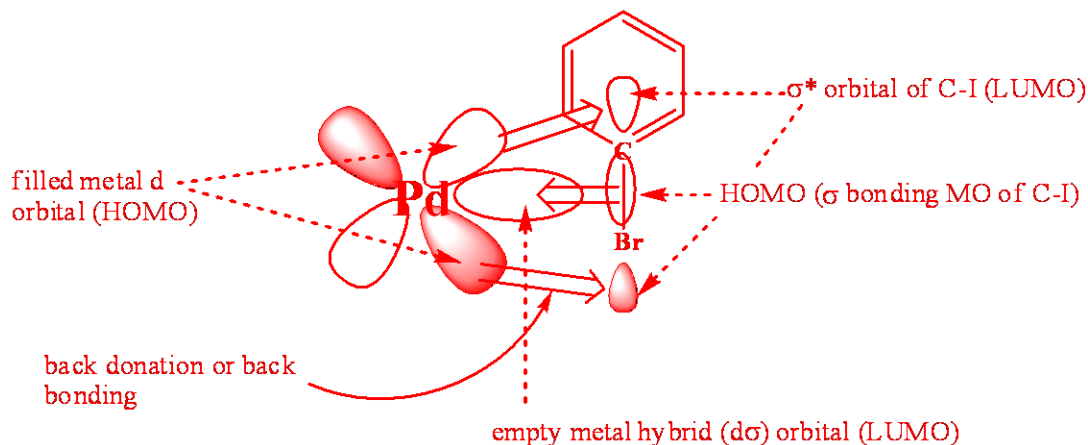
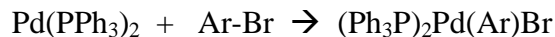
c) The authors were shocked to find that *cis*-**2** was stable. What type of reaction might occur with *cis*-**2** that would lead to its decomposition? (3 pts.)

With the hydride's positioned *cis* to each other in *cis*-**2**, they would be expected to undergo a reductive elimination reaction to release  $\text{H}_2$  and generate  $(\text{PNP})\text{Ir}=\text{CHN}(\text{CH}_3)\text{R}$ .

\_\_\_\_\_/15 pts



5. a) Draw the MO interactions and label them for the following reaction. Assume this is a concerted reaction mechanism. (6 pts.)



b) What is the name of this reaction type? (2 pts.)

This is an example of an oxidative addition.

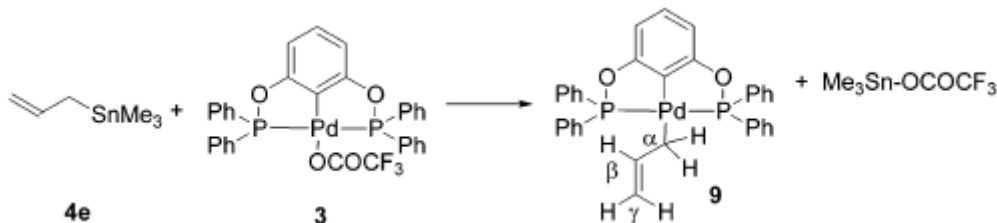
c) What geometry would be expected for the Pd product? Why? (4 pts.)

The  $(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ar})\text{Br}$  will be square planar because it is a  $d^8$  metal and crystal field theory predicts square planar as the most stable electronic arrangement with the fewest electron repulsions.

d) What is the relative position of the Br and Ph groups on the metal in the product immediately after the reaction has occurred? (2 pts.)

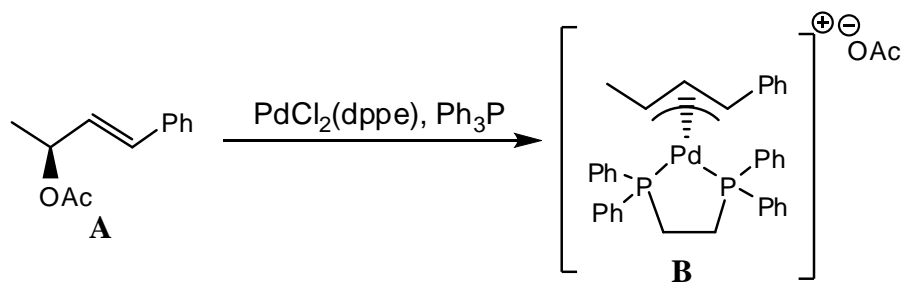
The Br and Ph will initially be cis.

6. There has recently been considerable interest in pincer complexes such as the Pd complexes **3** and **9** shown below (the Ir complex in question 3 is also a pincer complex). These complexes were reported in a recent edition of *the Journal of the American Chemical Society*. (Kálmán J. Szabó et al., **2004**, 126 (22), 7026–7033)



One of the reasons for the interest in the pincer complexes such as **9** is the important difference in their nature and reactivity. Indeed, the allyl complex **9** contrasts with most other allyl complexes that we saw in our class discussions, such as **B** shown below.

\_\_\_\_\_/14 pts.



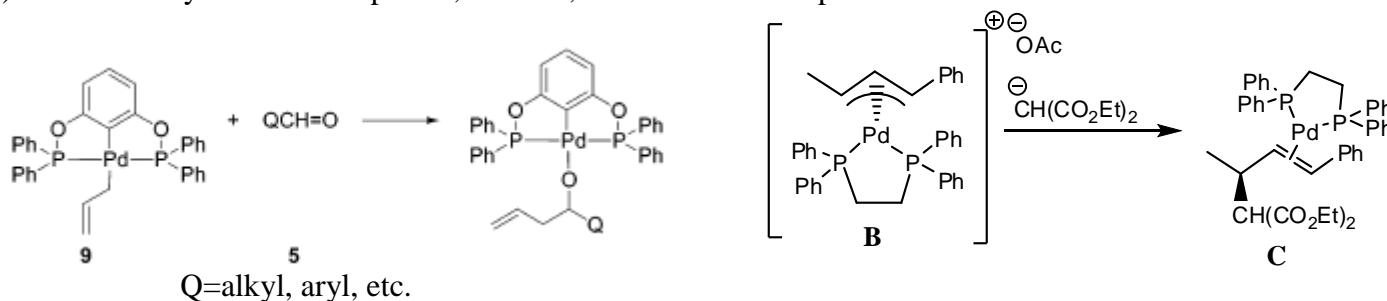
a) Describe the most obvious difference in the nature or structure of the allyl complex in **9** versus that in **B** and briefly explain why you think this difference exists. (3 pts.)

The Pd complex **9** is a  $\eta^1$ -allyl complex, while that in **B** is a  $\eta^3$ -allyl complex. The stable tridentate pincer complex sterically prevents a higher hapticity coordination of the Pd with the allyl group.

b) The authors confirmed the allyl complex **9** by analyzing its  $^1\text{H}$  NMR spectrum. They reported a doublet of triplets (dt) for the  $\text{CH}_2$  signal in **9**. Explain this pattern by identifying all the coupling partners. Use coupling constant nomenclature, i.e.  $^nJ_{\text{XY}}$ , to describe the coupling constants present. (4 pts.)

There are three adjacent atoms that would couple to the  $\text{CH}_2$  signal: the  $\beta$  vinylic  $^1\text{H}$  and the two cis  $^{31}\text{P}$  groups. The vinylic H coupling is represented as  $^3J_{\text{HH}}$  and the cis P couplings would be represented as  $^3J_{\text{HP}}$ . The vinylic coupling is slightly greater (8.4 Hz) than the cis P couplings (5.3 Hz), thereby leading to the doublet of triplets pattern.

c) The reactivity of these complexes, **9** and **B**, also differs. Examples of their reactions are shown below:



What type of reaction is represented in the reaction of complex **9** with the generic aldehyde? (3 pts.)

Complex **9** reacts with aldehydes (an electrophile) in an electrophilic attack or addition. After the reaction, the alkoxide product coordinates to the Pd. This reaction might also be seen as the result of a 1,2-insertion across the  $\text{C}=\text{O}$  bond of the aldehyde.

What type of reaction is represented in the reaction of complex **B** with the malonate anion? (3 pts.)

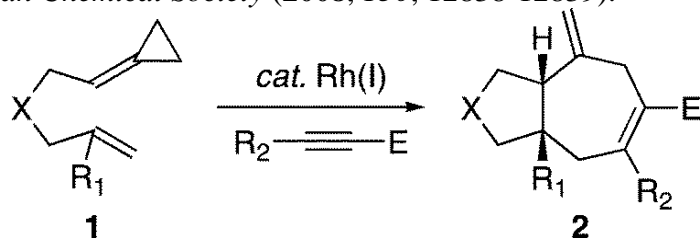
Complex **B** reacts with the malonate anion (a nucleophile) in a nucleophilic attack or addition.

d) One very common reaction in organometallic chemistry is the cross coupling reaction of two alkyl/aryl groups on palladium. Compound **9** has two alkyl/aryl groups on palladium. Why doesn't **9** undergo the final step of a cross-coupling reaction and put these two groups together. What is the name of this final step in cross-coupling reactions and why doesn't it occur in this case? (3 pts.)

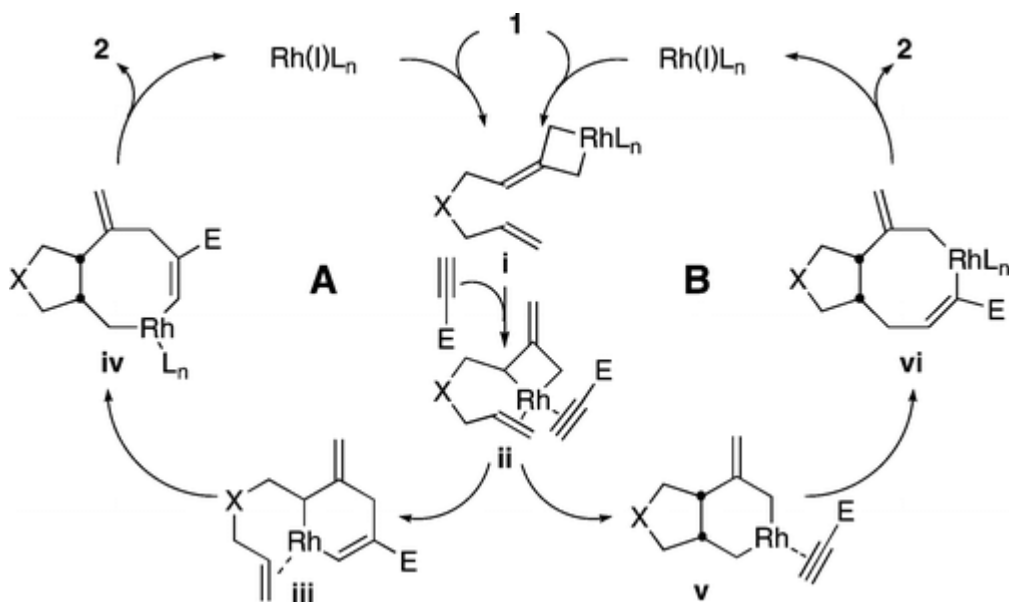
The final step is a reductive elimination of the alkyl and aryl groups. It can't occur in complex **9** because the two groups, the aryl and the allyl in this case, are trans to each other and they must be cis to reductively eliminate.

\_\_\_\_\_/16 pts

7. Problem Set 4 showed parts of the following reaction that was reported by P. Andrew Evans and co-workers in the *Journal of the American Chemical Society* (2008, 130, 12838-12839).



The proposed catalytic cycle ( $R_1, R_2=H$ ) is shown below.



Identify the following steps in the proposed catalytic cycle by their reaction type. (2 pts. each)

a) 1 to i: oxidative addition

b) i to ii (actually two steps) alkyl ligand rearrangement and ligand substitution

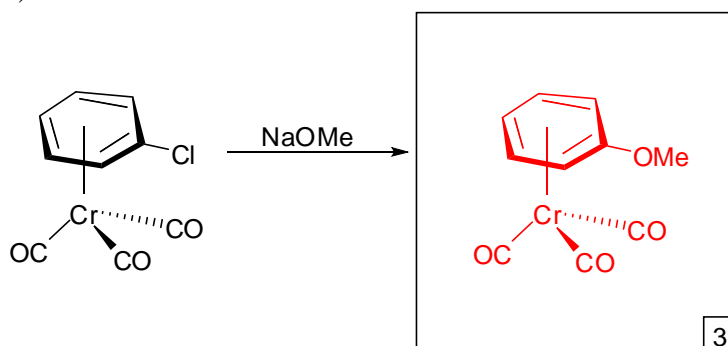
c) ii to iii: 1,2-insertion

d) iii to iv: 1,2-insertion

e) iv to 2: reductive elimination

8. Answer the following questions by providing the necessary information.

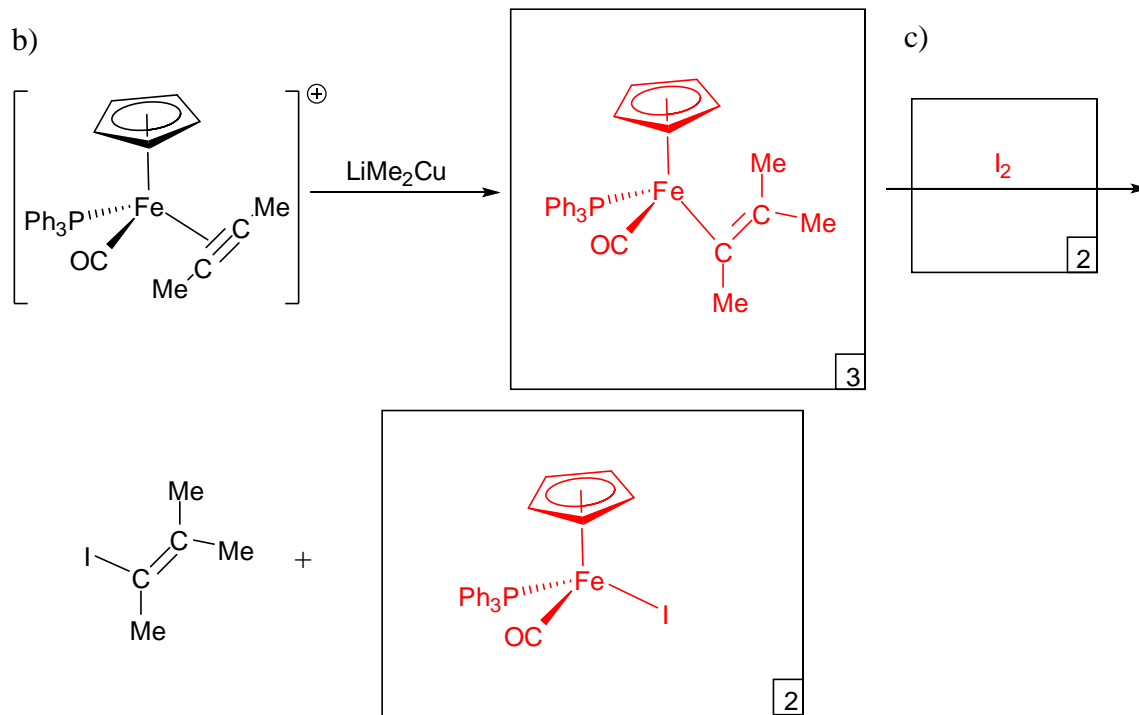
a)



3

Crabtree 4<sup>th</sup> ed. Ch. 8, problem no. 5

\_\_\_\_\_/13 pts.

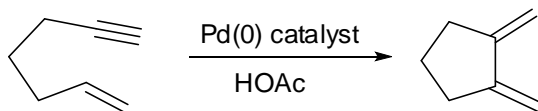


Crabtree 4<sup>th</sup> ed. Ch. 8, problem no. 9

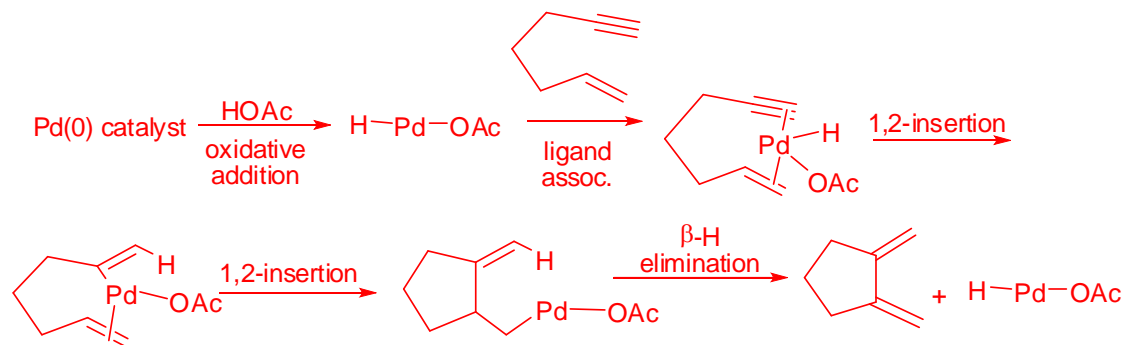
d) What type of reaction is shown in question b? (1 pt.) nucleophilic addition

e) What type of reaction is shown in question c? (1 pt.) electrophilic abstraction

9. Provide two mechanisms for the illustrated transformation. In one mechanism, HOAc oxidatively adds to Pd(0) to generate a palladium hydride; in the other mechanism, HOAc simply serves as the solvent, i.e. it is not involved in the mechanism. Be sure to identify each step by reaction type. (6 pts.)

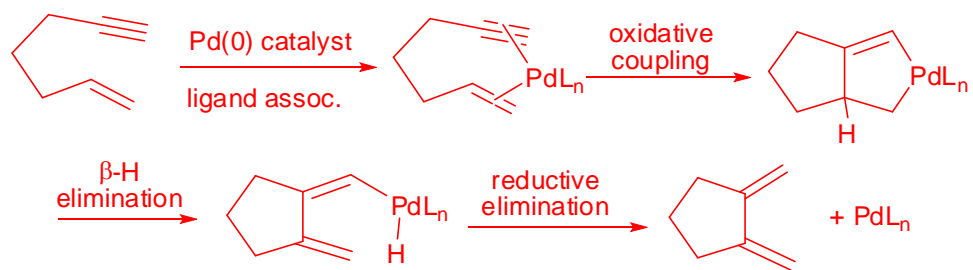


mechanism WITH HOAc involved:



\_\_\_\_\_/15 pts.

mechanism WITHOUT HOAc involved



G. Fu MIT open courseware Fall 2004