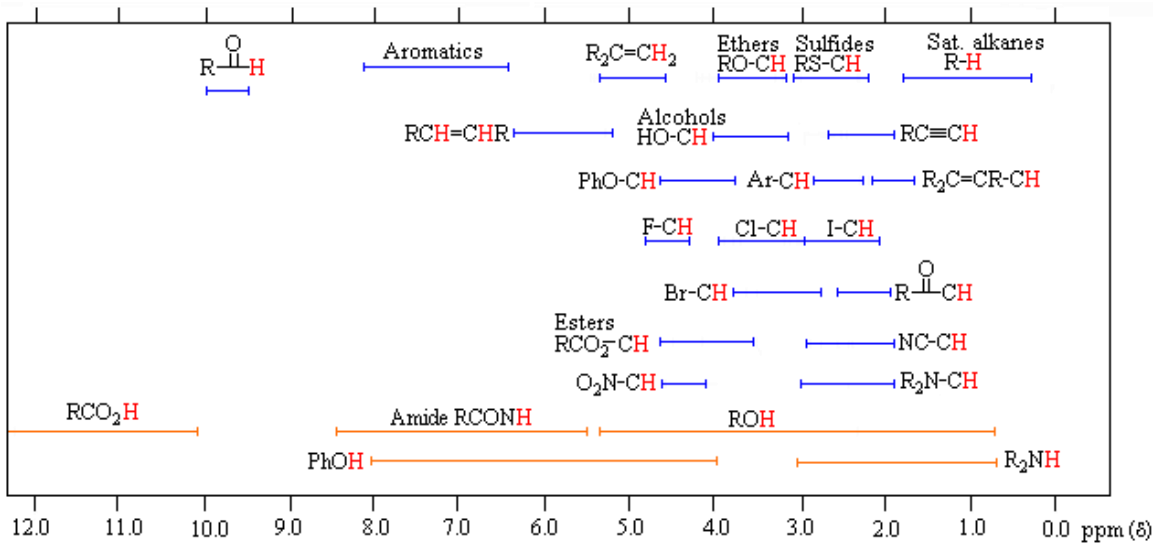
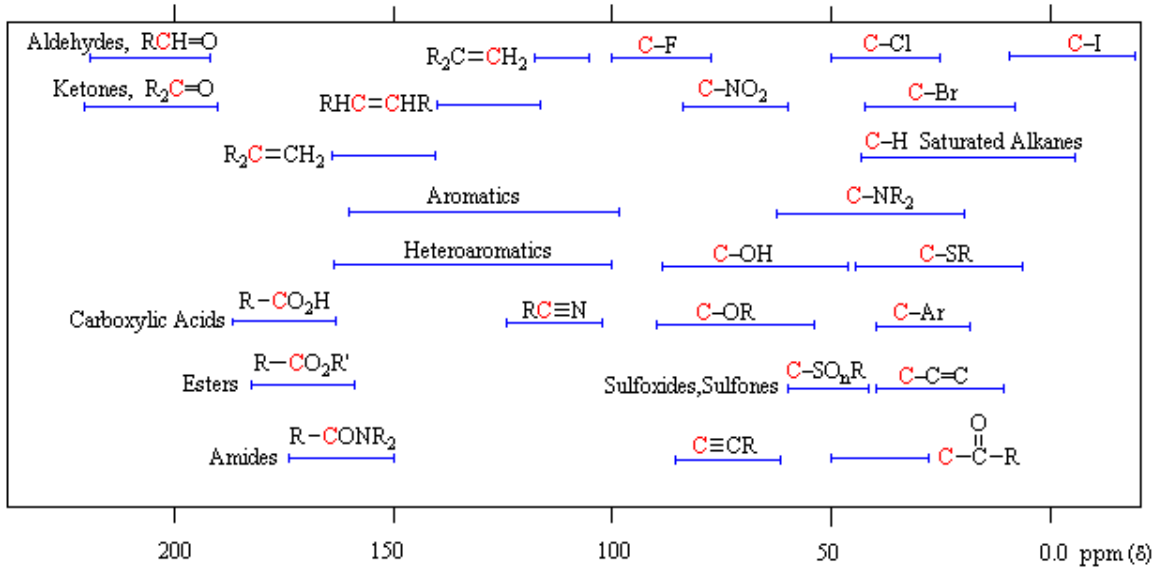
Organometallic Chemistry Name:_____
CHEM 534
Exam 2
November 25, 2008
Prof. Malachowski

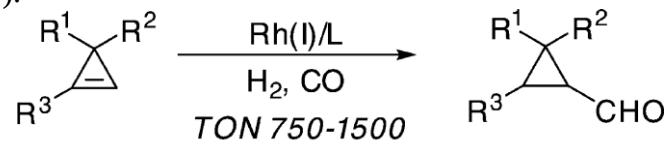
^{1}H NMR chemical shifts



^{13}C NMR chemical shifts



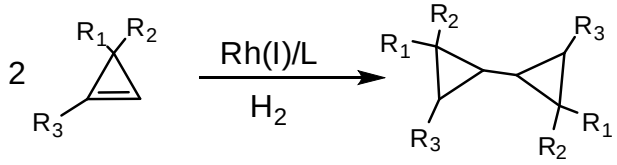
1. The following reaction was reported in the *Journal of the American Chemical Society* (Michael Rubin et al., **2008**, *130 (41)*, 13804–13809).



yields 54-91%
ees up to 83%

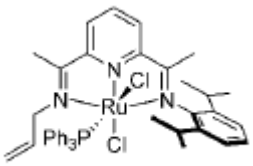
a) Suggest a mechanism for the reaction and identify the reaction type for each step. (7 pts.)

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.)

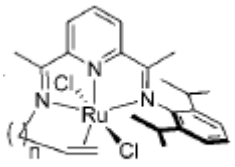


_____/10 pts

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



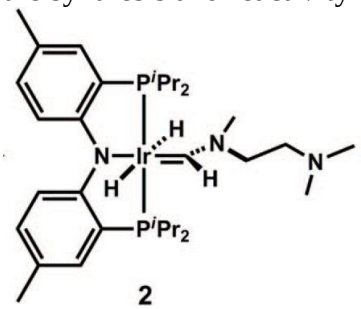
6a



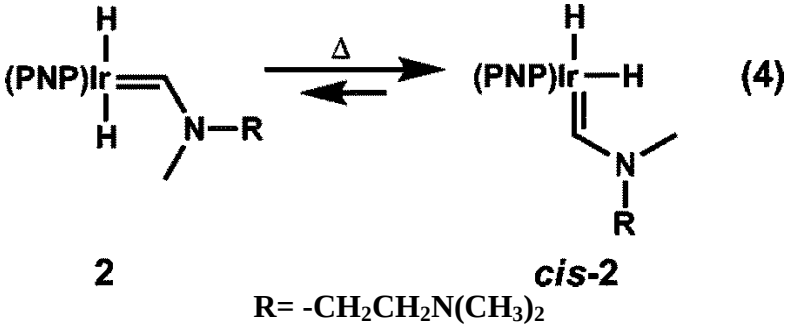
7b-d

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.)

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



2



2 ***cis*-2** **(4)**

R= -$CH_2CH_2N(CH_3)_2$

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

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

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.)

_____/15 pts

d) The authors explained the reluctance of **cis-2** to undergo this subsequent decomposition reaction based on a consideration of resonance forms of **cis-2** (or **2**). Draw two resonance forms of **cis-2** below. (4 pts.)

e) The authors believe that the resonance forms suggest a distribution of electron density that deters the decomposition reaction in part c. Explain their reasoning. (3 pts.)

4. Choose either a metal-(η^3-allyl cation) complex or a metal-(η^6-benzene) complex and answer the following questions.

a) Draw a MO interaction between a π^* orbital of the ligand and a filled d_π orbital of the metal. (5 pts.)

b) Show the interaction between a π orbital of the ligand and an empty d_σ orbital of the metal. (5 pts.)

_____/17 pts

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

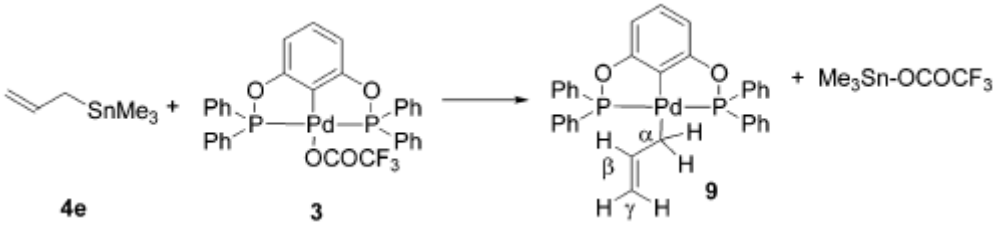
$$Pd(PPh_3)_2 + Ar\text{-}Br \rightarrow (Ph_3P)_2Pd(Ar)Br$$

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

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

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.)

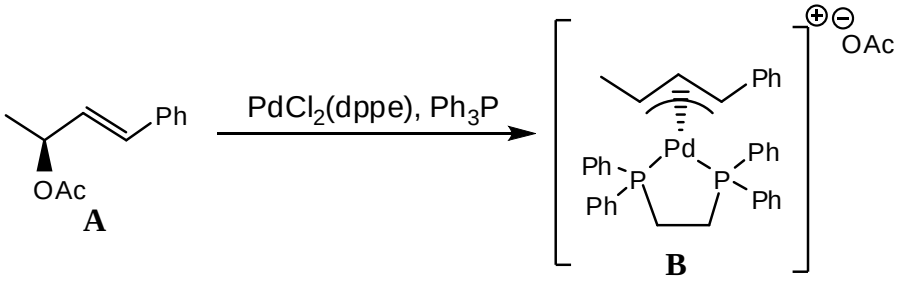
6. There has recently been considerable interest in pincer complexes such as the Pd complexes **3** and **9** shown below (the Ir complex in question 3 is also a pincer complex). These complexes were reported in a recent edition of *the Journal of the American Chemical Society*. (Kálmán J. Szabó et al.,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



4e **3**

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.

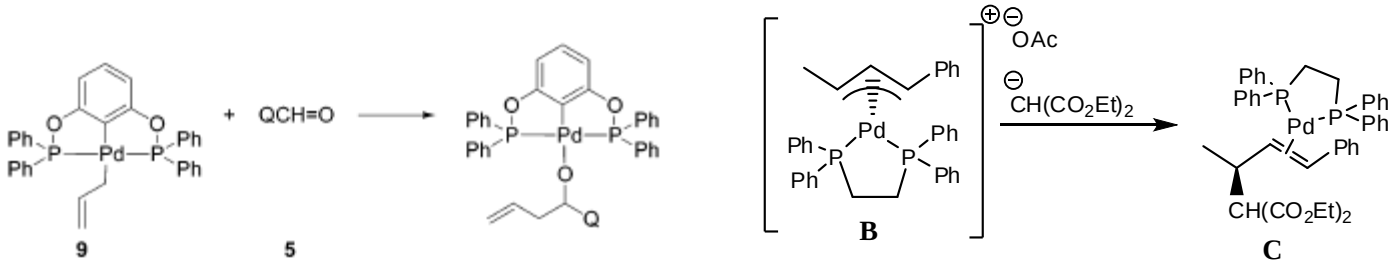
_____/14 pts.



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.)

b) The authors confirmed the allyl complex **9** by analyzing its ^{1}H NMR spectrum. They reported a doublet of triplets (dt) for the CH_2 signal in **9**. Explain this pattern by identifying all the coupling partners. Use coupling constant nomenclature, i.e. $^{\#}J_{XY}$, to describe the coupling constants present. (4 pts.)

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



Q=alkyl, aryl, etc.

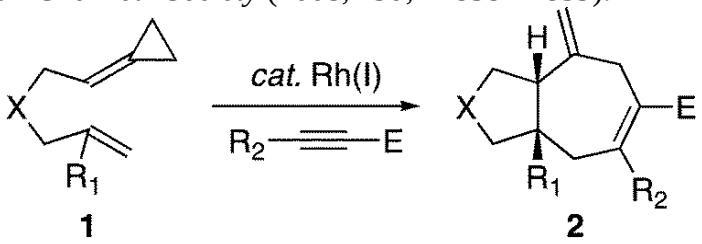
What type of reaction is represented in the reaction of complex **9** with the generic aldehyde? (3 pts.)

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

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.)

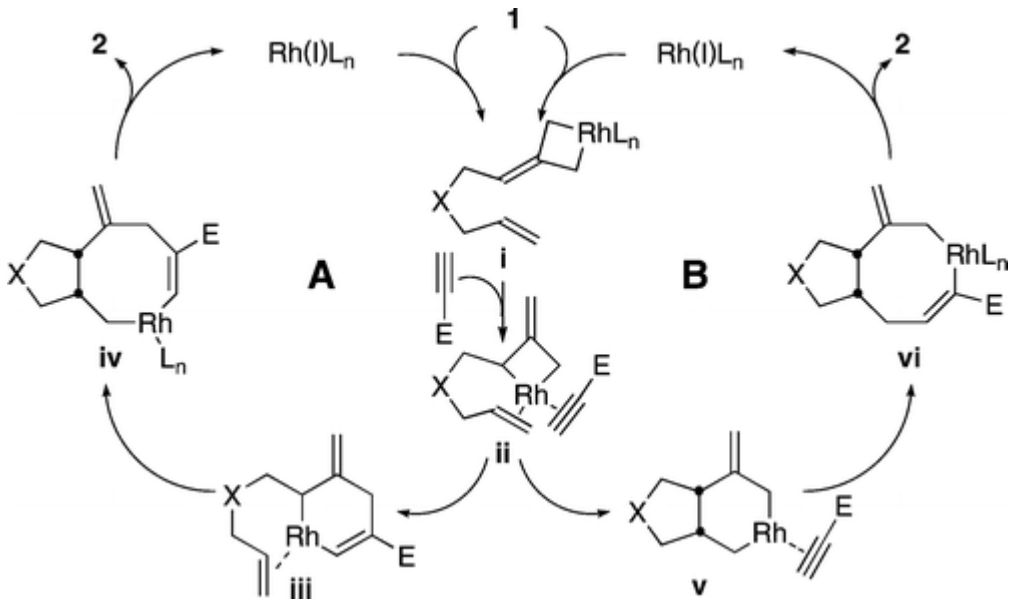
_____/16 pts

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).



1 **2**

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: _____

b) i to ii (actually two steps) _____

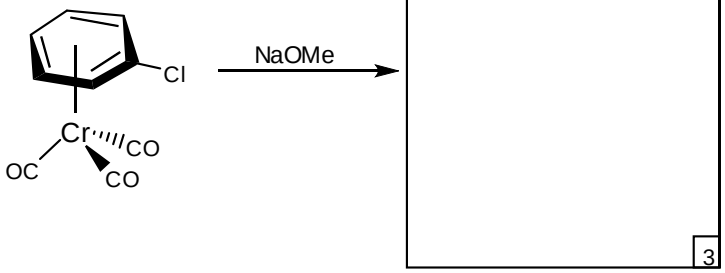
c) ii to iii: _____

d) iii to iv: _____

e) iv to 2: _____

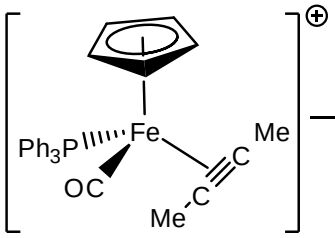
8. Answer the following questions by providing the necessary information.

a)



_____/13 pts.

b)

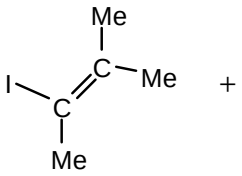


$LiMe_2Cu$

3

c)

2



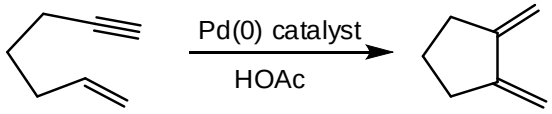
+

2

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

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

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.)



_____/15 pts.