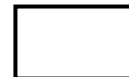


Organometallic Chemistry - 4571

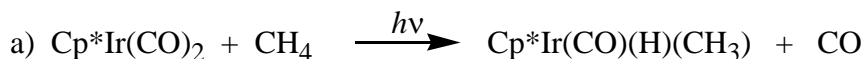
ANSWER KEY

Homework # 3 (Due: Nov 11, 2008)

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:



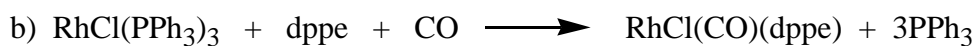
1. (40 pts) Identify the following reactions by their type (migratory insertion, elimination, oxidative addition, reductive elimination, substitution, ligand addition or dissociation, β -hydride elimination, ligand coordination change, etc.). Note that some reactions may have several steps. For reactions with several steps, if the order is important you must list the steps in the correct order.



1) CO ligand dissociation (promoted by photolysis)

2) oxidative addition of methane C-H bond

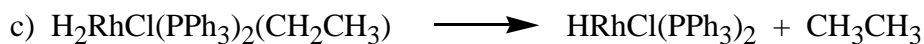
Ir(+1) going to Ir(+3) indicates an oxidative addition rxn. CH_4 is a non-polar substrate and needs an empty orbital on the metal to bind to prior to oxidative addition.



1) PPh_3 substitution with CO

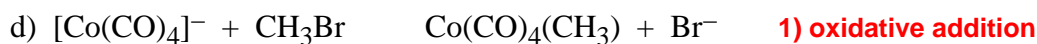
2) two PPh_3 substitutions by dppe (one arm at a time)

The first PPh_3 substitution probably occurs via a dissociative route due to the steric bulk of the 3 PPh_3 groups. The incoming order of CO or dppe is not important.

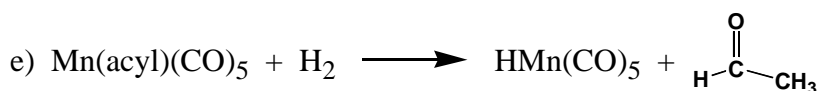


1) reductive elimination

Rh(+4) going to Rh(+2). One could also first have a ligand dissociation of PPh_3 or Cl^- to help promote the reductive elimination rxn. But the dissociated ligand needs to re-coordinate after the reductive elimination.



Co(-1) going to Co(+1) indicates an oxidative addition rxn. CH_3Br is an electrophilic reactive substrate that can react directly with an 18e- metal center via an $\text{S}_{\text{N}}2$ type attack of the metal on the CH_3 -side of CH_3Br . This ejects the Br^- anion that does not coordinate to the metal since it is 18e- and does not need another ligand.



1) CO ligand dissociation

2) oxidative addition of H_2

3) reductive elimination of H^- and acyl-

4) CO ligand addition

This is a bit tricky because there appears to be no change in the oxidation state on the Mn. But the major rxn of H_2 with a d^{2-10} metal is via oxidative addition. You need an empty orbital to do this because H_2 is a non-electrophilic reagent, thus the initial CO ligand dissociation from the 18e- starting complex.



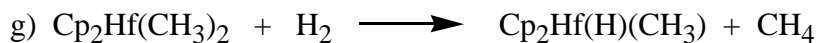
1) η^5 - to η^3 -hapticity (ligand coordination) change

2) CO ligand addition

3) PMe_3 ligand dissociation

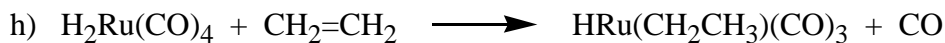
4) η^3 - to η^5 -hapticity change

The indenyl ligand can readily change its hapticity from η^5 to η^3 . This opens up a free coordination site on the metal allowing ligand addition.



1) hydrogenolysis

d^0 metals can NOT do an oxidative addition rxn.



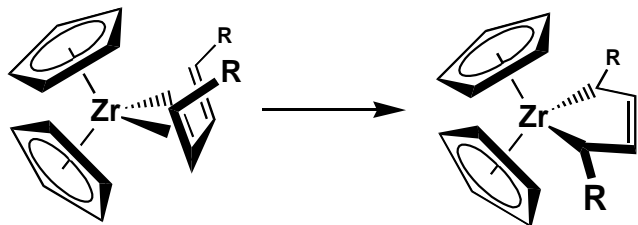
1) ligand dissociation

2) alkene ligand coordination

3) migratory insertion of hydride with alkene

The product is 16e- and would probably need to re-coordinate the dissociated CO (or another ligand) to get back to 18e-.

2. (20 pts) Consider the reaction shown below. Clearly describe what is happening. What kind of electronic effect R groups (electron-withdrawing or electron-donating) on the diene ligand will favor formation of the product? Why?

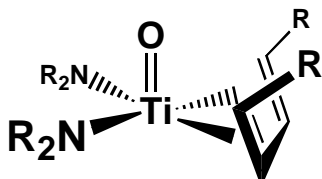


Oxidative Addition

Zr(+2, d^2) is being oxidized to Zr(+4, d^0). The diene ligand is accepting the two electrons from the Zr to become a dianionic ligand. Note that we have broken a bond in the diene (two double bonds down to one double bond).

Electron-withdrawing R-groups on the diene will **favor** the oxidative addition by helping the not very electronegative diene to attract the electrons from the metal. Normally one does not want to have electron-donating ligands on the metal to help favor oxidative addition reactions and putting electron-donating groups on the Cp- rings will help make the metal more electron-rich and make the oxidative addition more facile.

b) Why won't the following complex undergo the same transformation?

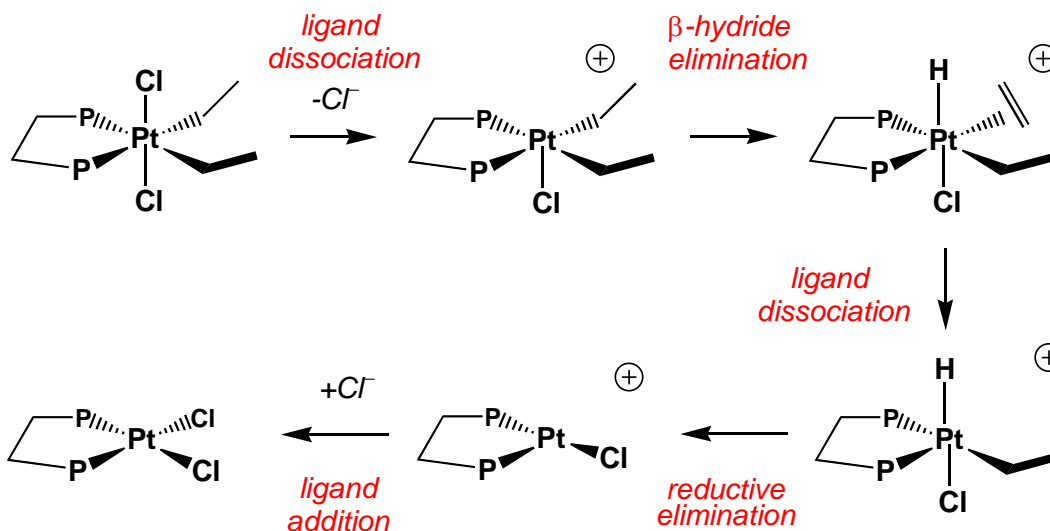


The Ti is in the +4 oxidation state and is already d^0 . A d^0 metal center can NOT do an oxidative addition reaction.

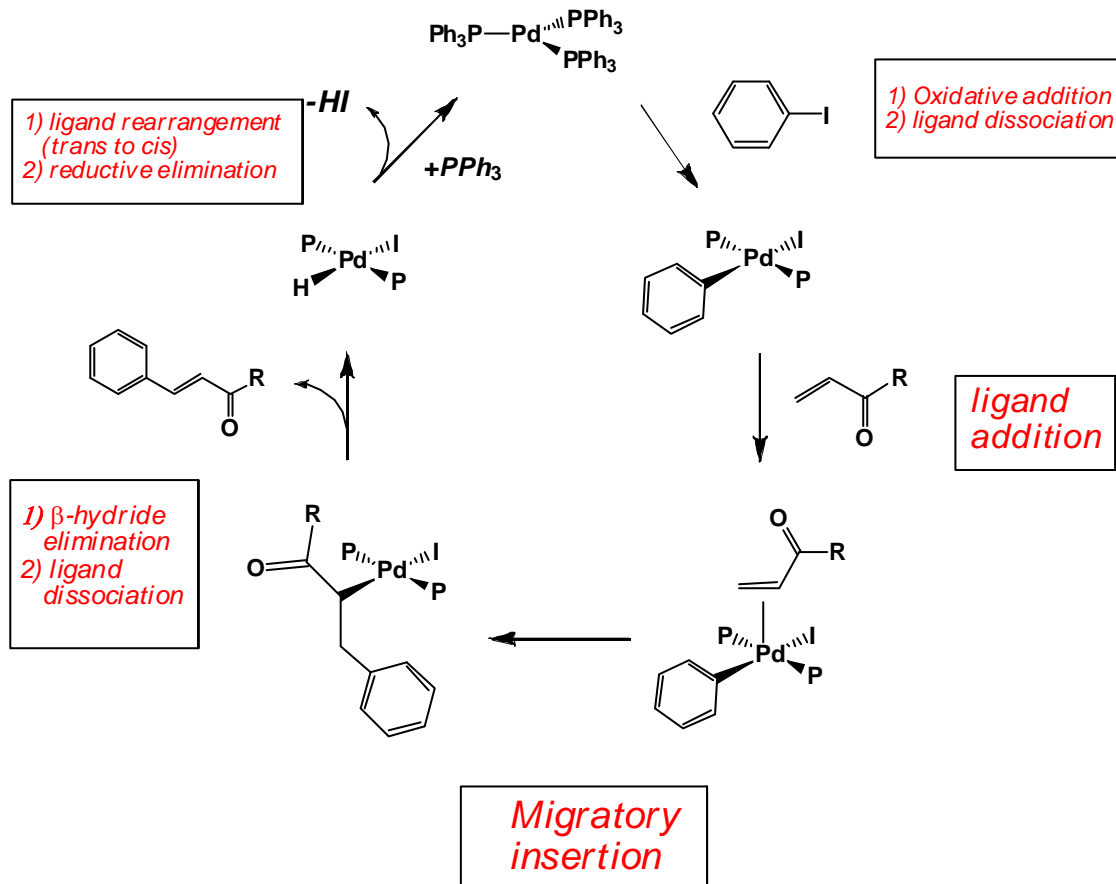
3. (20 pts) Consider the following reaction:



Show in detail each mechanistic step in the conversion to the product species shown. Label and clearly identify each step. The order of the steps may be important – if so list them in the correct order when necessary.



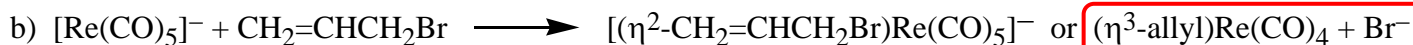
4. (10 pts) Label and clearly identify each step (i.e., migratory insertion, elimination, oxidative addition, reductive elimination, substitution, ligand addition, ligand dissociation, β -elimination, etc.) in the following catalytic reaction (called a Heck arene-alkene coupling reaction). Please write your answer(s) in the box next to the step. If there is more than one step occurring, please list them in the correct order if important.



5. (10 pts) Which of the following products will be the most likely formed from the reaction shown. Circle the best choice and give a brief explanation/justification for your choice.



The starting Os complex is d^0 and can NOT do an oxidative addition reaction. So there is no reaction.



The 18e- Re complex is d^8 and can do a direct oxidative addition reaction with alkyl bromides, which are reactive polar substrates. No empty orbital is needed for this initial rxn. Once the oxidative addition occurs and forms the η^1 -allyl, one gets CO dissociation and a hapticity change from η^1 - to η^3 -allyl.