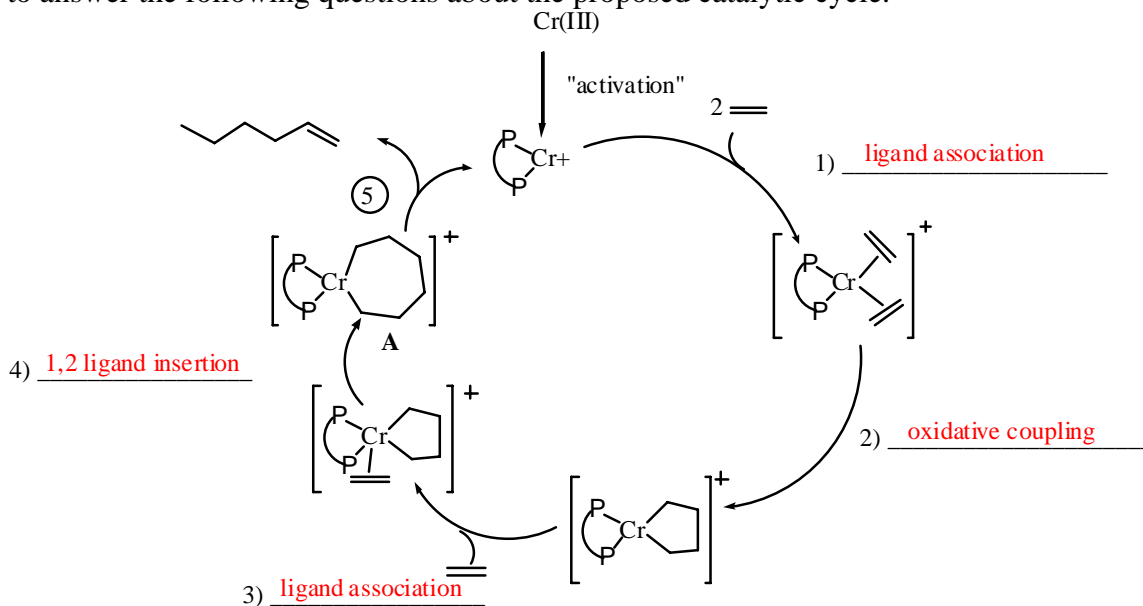


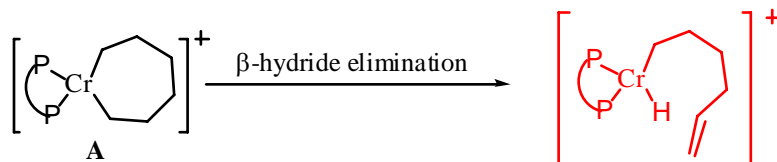
Answers to Prof. Malachowski's portion of the 2004 final exam

1. An important area of research interest is the identification of catalysts for the polymerization of ethylene. Chromium catalysts have recently been reported as efficient for the synthesis of 1-hexene. Shown below is a proposed catalytic cycle for this trimerization process as published in a recent literature article. Use our class discussions to answer the following questions about the proposed catalytic cycle.



a) Based on our class discussions of organometallic reactions, label steps 1-4 with the reaction type.

b) The last step, 5, lacks detail as drawn, but details have recently emerged from mechanistic studies. Step 5 actually involves two reactions. The first is a  $\beta$ -hydride elimination. Draw the product of a  $\beta$ -hydride elimination of intermediate A in the space below.



c) What type of reaction would then take your intermediate to the final products, 1-hexene and the Cr-bisphosphine catalyst?

*reductive elimination*

*References: A. Bollmann et al. JACS 2004, 126, 14712 and J. E. Bercaw et al. JACS 2004, 126, 1304.*

d) What are the formal oxidation states of chromium in the catalytic cycle as drawn?

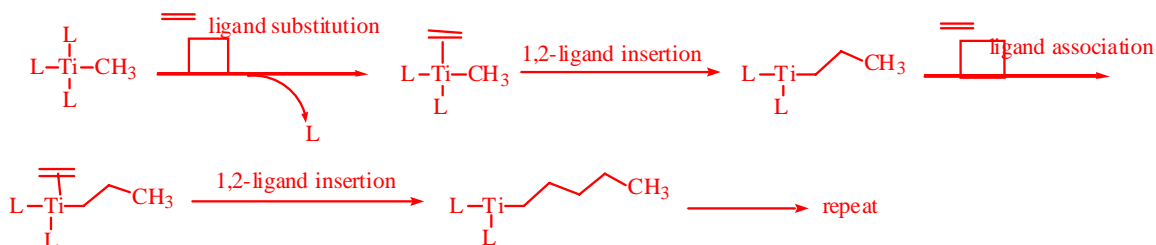
*Chromium enters the catalytic cycle by being reduced from +3 to +1. The first intermediate after step 1 is also +1, but then the chromium becomes +3 during the oxidative cyclization (step 2). All subsequent intermediates are +3 until the reductive elimination that releases the 1-hexene and returns the chromium to +1.*

2. Polymerization of ethylene and other simple alkenes is an enormously important area of organometallic chemical activity as it is the source of polymers used in a range of applications. One of the most famous catalytic process for polymerization is the Ziegler-Natta process. This reaction uses high valent forms of titanium or zirconium as the catalyst.

a) Why might a high valent, early transition metal be more likely to make polymers instead of a trimer such as 1-hexene shown for chromium-catalyzed ethylene polymerization?

*With little or no d electrons, high valent titanium and zirconium compounds can't easily cause  $\beta$ -hydride elimination which leads to termination of the growing chain. The chromium complexes used in the synthesis of 1-hexene are primarily  $d^3$  and therefore more likely to cause  $\beta$ -hydride elimination, thus terminating the polymerization process.*

b) One of the major controversies in organometallic polymerization is the mechanism of the reaction. There are primarily two proposed mechanisms. One mechanism suggests that the polymerization occurs via metallacycle intermediates as shown in the 1-hexene synthesis, while a second suggests polymerization occurs through a 1,2-ligand insertion. Using a hypothetical  $L_3Ti-CH_3$  organometallic catalyst, sketch a series of reactions that show how the ethylene polymerization would proceed without metallacycle intermediates.

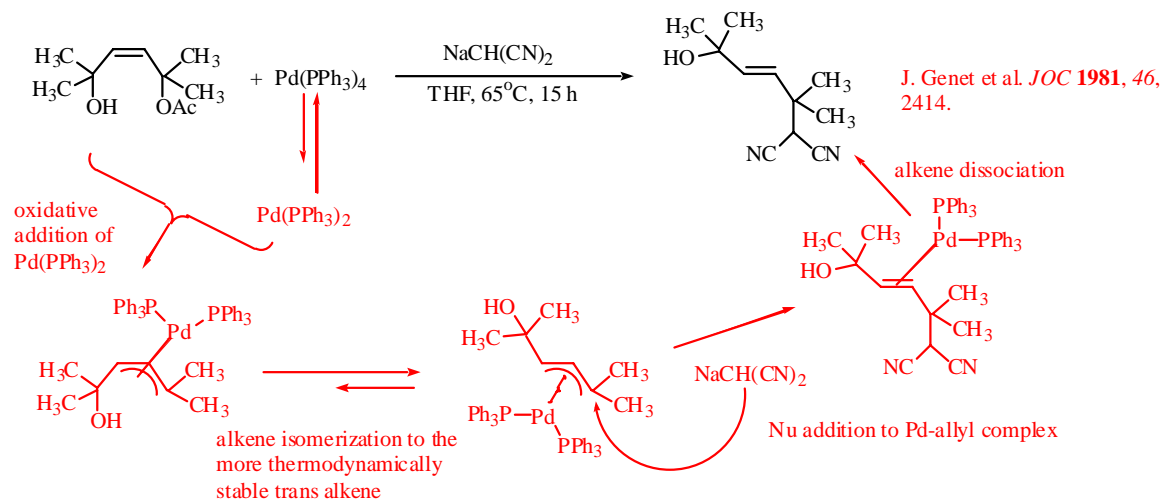


c) The Ziegler-Natta polymerization is a heterogeneous catalytic process. What does this mean and what implications does this have for determining the mechanism of the reaction?

*A heterogeneous catalytic process means that the catalyst is in a different phase (solid, in this case) and the substrate or starting materials are in another phase (liquid and gas in this case). Heterogeneous reactions are not amenable to*

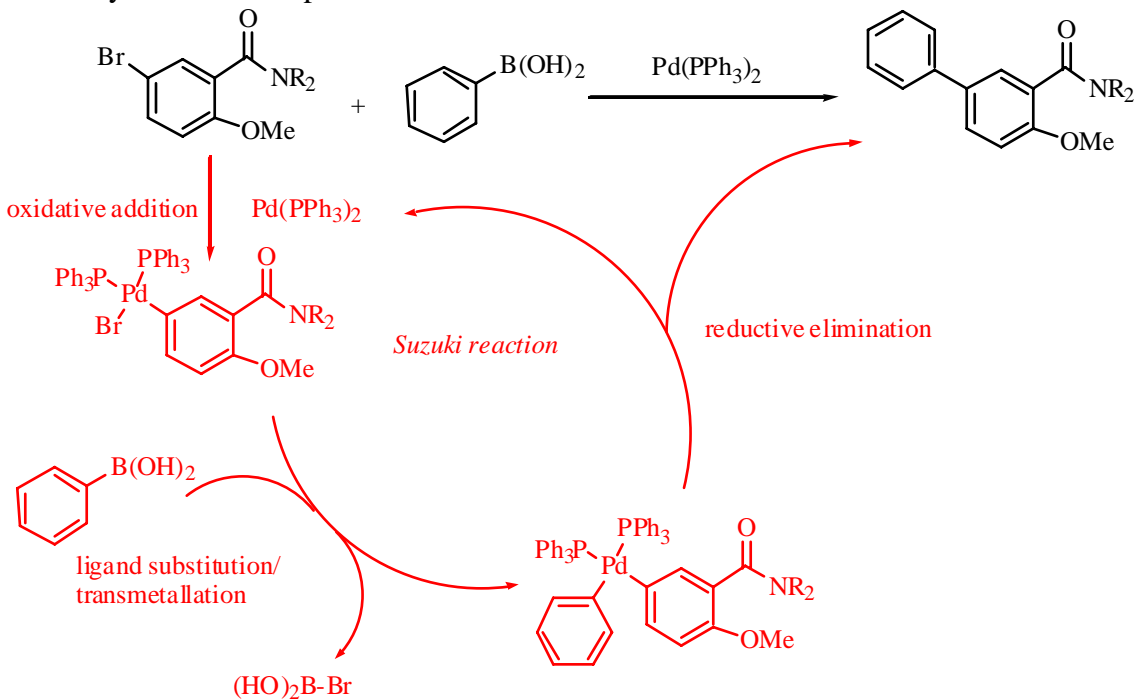
analysis as most spectroscopic and other analytic tools are much less effective in heterogeneous systems.

3. Suggest a mechanism for the following reaction. Show all important intermediates and electron flow arrows where appropriate. Your mechanism should explain why the alkene is isomerized in the reaction process. Hint: a Pd- $\eta^3$ -allyl complex is an intermediate.

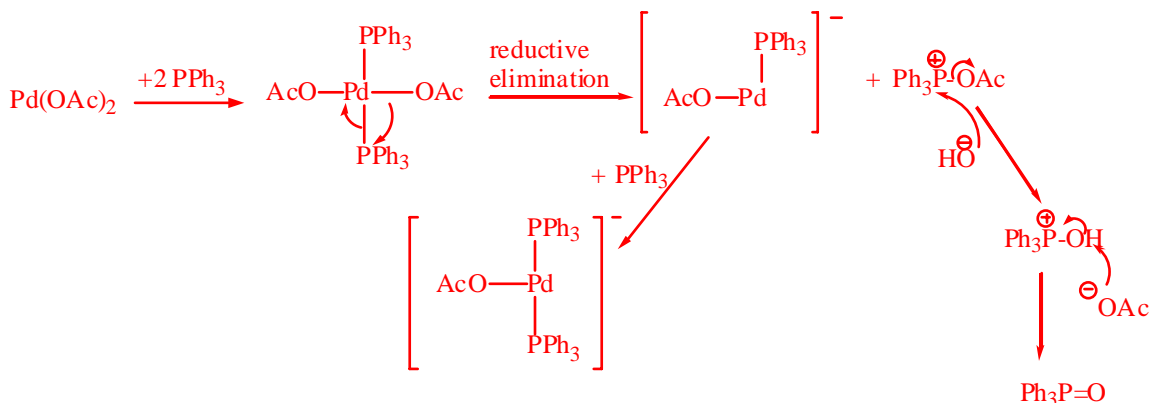


4. A couple weeks ago, I ran the following reaction in lab to make the biaryl product shown.

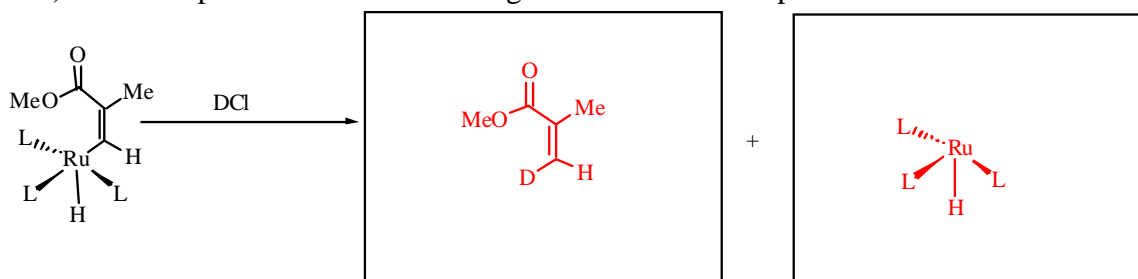
a) Identify the name and type of reaction shown and show a "textbook" catalytic cycle for the synthesis of the product.



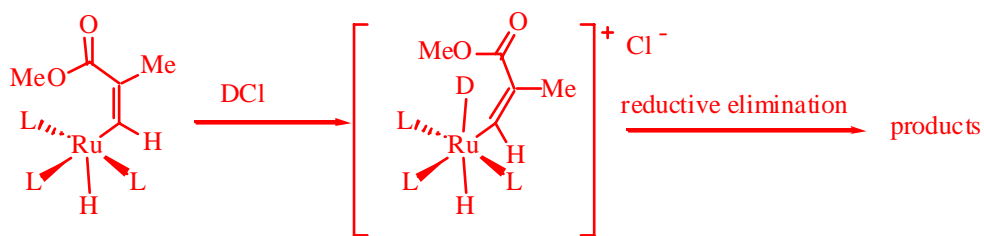
b) I actually added Pd(OAc)<sub>2</sub> and PPh<sub>3</sub> (3 eq.) to get to the catalytically active Pd(PPh<sub>3</sub>)<sub>2</sub>. This is a key, but overlooked and misunderstood step. Suggest a mechanism for this reaction. Hint: the actual catalytic Pd complex may be Pd(PPh<sub>3</sub>)<sub>2</sub>(OAc)<sup>-</sup>, the reaction is run in an aqueous solution and Ph<sub>3</sub>P=O is a side product.



5. a) Draw the products of the following reaction in the box provided.



b) Suggest a reasonable mechanism for the reaction leading to the products that you have drawn.



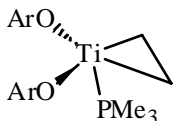
c) Why

doesn't a reaction occur without the addition of DCl?

*The initial ruthenium complex is not coordinatively saturated and therefore is less prone to reductive elimination of ligands. In addition, the protonation/deuteration of the Ru complex makes the Ru more electron deficient and therefore more prone to reductive elimination.*

6. The titanacyclopentane article that we discussed in class on Tuesday, December 7 reported the titanacyclopentane below and offered characterization information in the experimental section.

a)  $^1\text{H}$  NMR information provided for this compound showed four signals:  $\delta$  7.36-6.87, 1.72, 0.51, 0.22 ppm. Assign these four signals to protons in the structure.



*7.36-6.87 aromatic protons; 1.72  $\text{CH}_2$  nearest to  $\text{PMe}_3$ ; 0.51  $\text{CH}_2$  protons farthest from  $\text{PMe}_3$ ; 0.22  $\text{PMe}_3$  protons.*

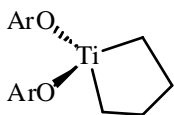
b) The paper also reported the following splitting information: a) 1.72, triplet of doublets; b) 0.51 triplet; c) 0.22 doublet. Explain the splitting pattern seen for these three signals by identifying coupling constants.

*1.72 triplet of doublets due to large three bond coupling to  $^{31}\text{P}$  and two smaller three bond couplings to each adjacent  $\text{CH}_2$  proton.*

*0.51 triplet due to two three bond couplings to each adjacent  $\text{CH}_2$  proton. The distal location of this  $\text{CH}_2$  relative to the  $^{31}\text{P}$  leads to a weak and imperceptible three bond coupling to the phosphorus.*

*0.22 doublet is the result of a two bond coupling to the  $^{31}\text{P}$ .*

c) The related titanacyclopentane shown below did not show any clear splitting patterns (all signals were reported to be broad). Suggest an explanation for this result.



*The titanacyclopentane ring was fluxional at the temperature and on the time scale of the  $^1\text{H}$  NMR experiment. The titanacyclopentane ring has little flexibility and therefore showed a more static structure.*