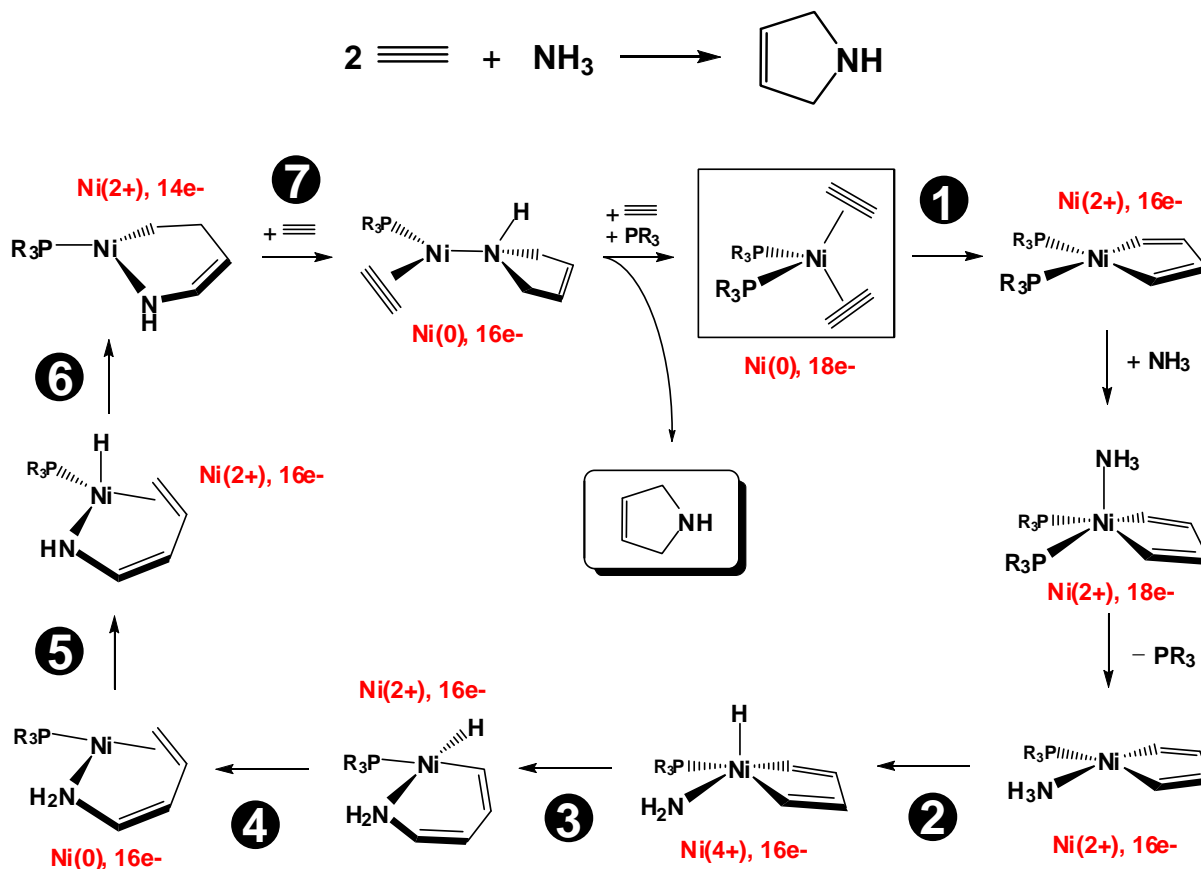


## FINAL EXAM -- May 2007

Check this box if you want your graded test put out in the public boxes outside Prof. Stanley's office:

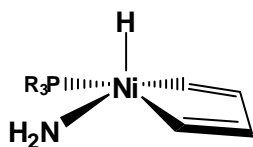
1. (50 pts) Consider the cyclohydroamination reaction and catalysis cycle shown below:



a) (40 pts) Label the indicated reaction steps below (no explanation required). There are two steps for 7, the order of those may or may not be important.

- (1) **oxidative coupling** [two alkynes, Ni(0) to Ni(2+)]
- (2) **oxidative addition** [N-H bond, Ni(2+) to Ni(4+)]
- (3) **reductive elimination** [ $\text{NH}_2^-$  and  $\text{CH}=\text{R}^-$ , Ni(4+) to Ni(2+)]
- (4) **reductive elimination** [ $\text{H}^-$  and  $\text{CH}=\text{R}^-$ , Ni(2+) to Ni(0)]
- (5) **oxidative addition** [N-H bond, Ni(0) to Ni(2+)]
- (6) **migratory insertion** [ $\text{H}^-$  and alkene to form alkyl]
- (7a) **reductive elimination** [ $\text{NH}^-$  +  $\text{CH}_2\text{R}^-$ , Ni(2+) to Ni(0), product coordinated due to N lone pair]
- (7b) **alkyne ligand addition**

- b) (10 pts) One of the reaction steps in the catalytic cycle generates a complex that is very unusual for Ni but considerably more likely for Pd or Pt. Identify the complex (draw out the structure) and indicate what is unusual about it and why it would be more likely with Pd or Pt.

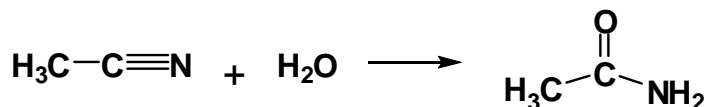


Ni(4+), 16e-

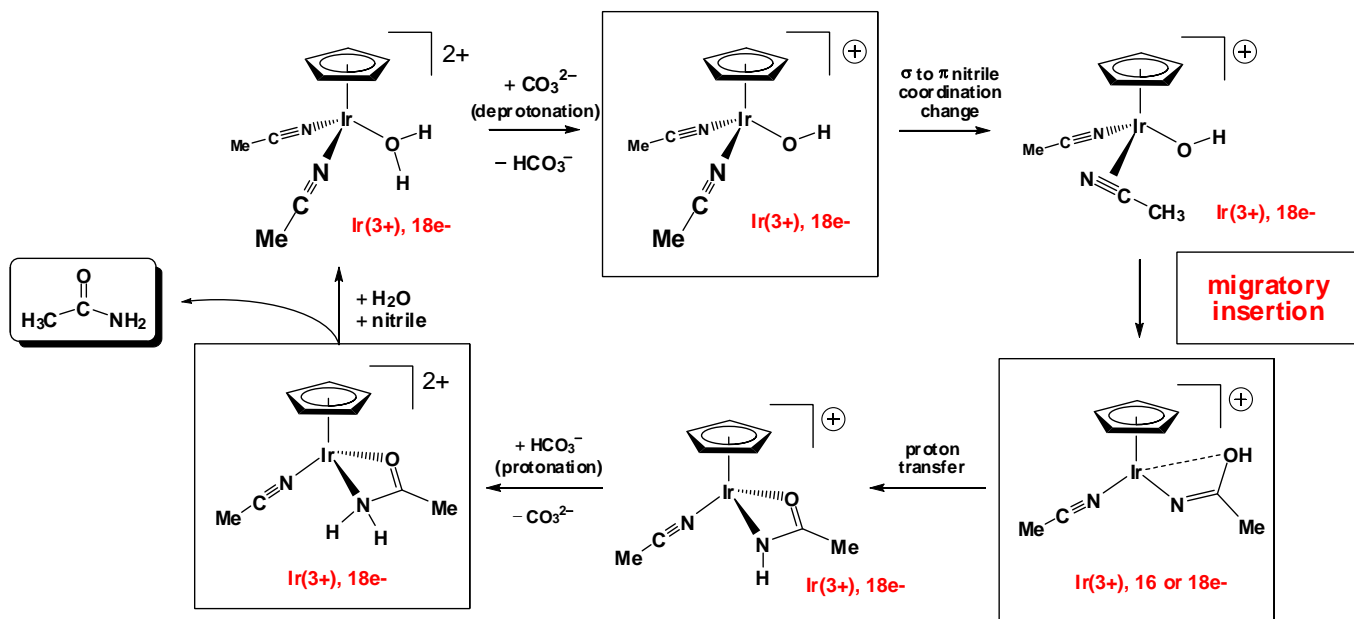
4+ is a very high and unusual oxidation state for Ni, which rarely goes above 2+. This is due to the higher electronegativity of Ni relative to Pd and Pt, both of which can readily form the 4+ oxidation state (d<sup>6</sup> octahedral complexes) because of their lower electronegativities.

Everyone got credit for this question (unless you didn't write anything down).

2. (50 pts) The hydration of acetonitrile to produce organic amides is shown below.



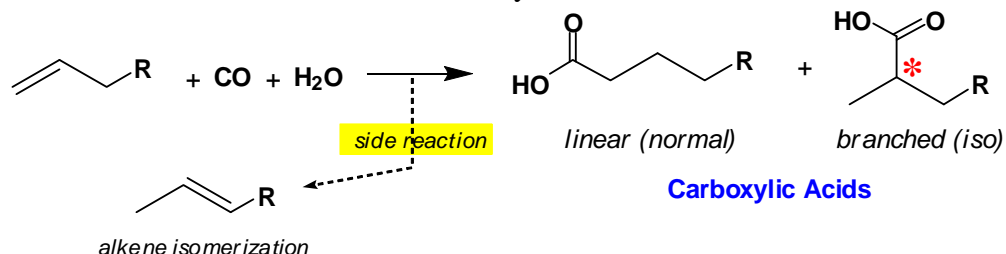
- a) (40 pts) Identify the one boxed mechanistic step in the catalytic cycle and draw in the three missing boxed catalyst complexes for the steps shown. You may use Cp for cyclopentadienyl. Make sure you keep proper track of the charge(s) on the complexes drawn!



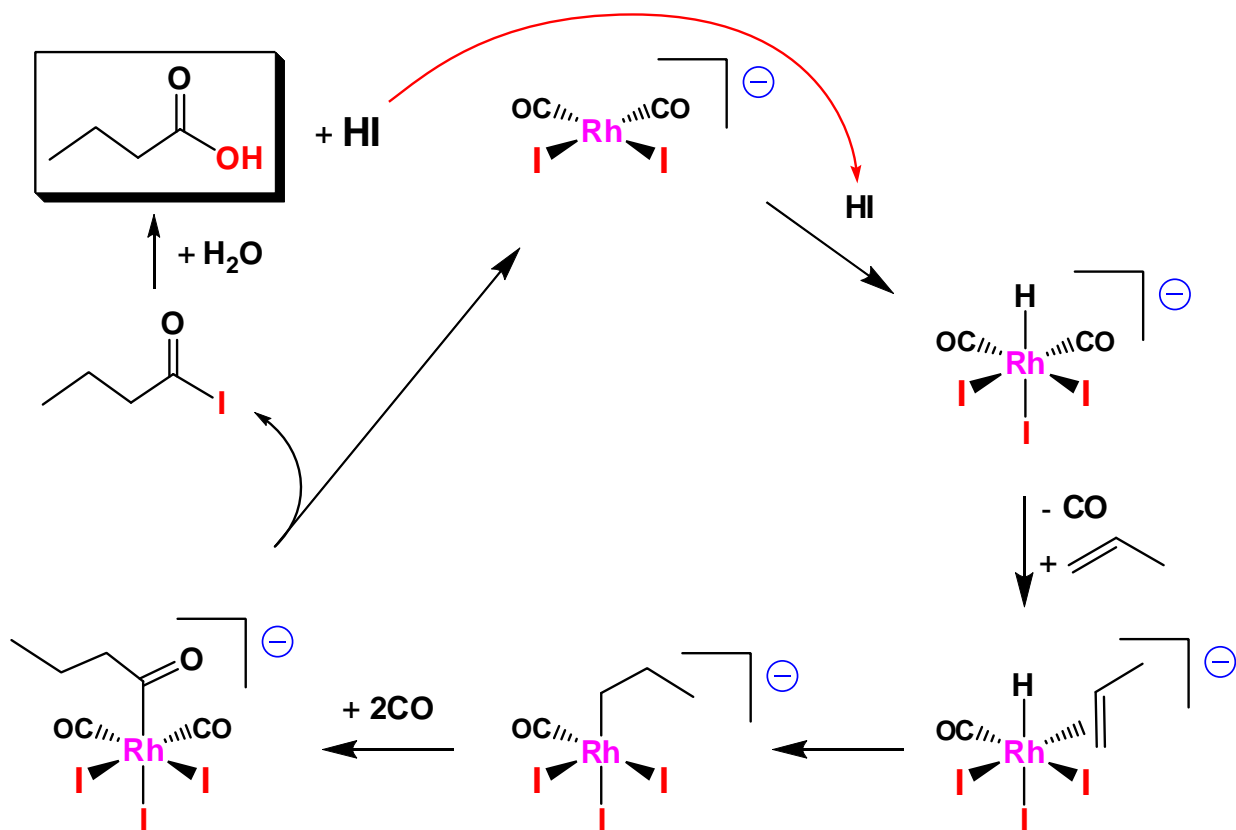
- b) (10 pts) Neutral catalysts do not work well for this reaction. Why?

The cationic charge is important to enable the hydrolysis (deprotonation) of coordinated water to form the more reactive hydroxide ligand that can do the migratory insertion with the nitrile. Neutral metal complexes won't drain enough electron density from the weakly coordinated water ligand to allow deprotonation by a weak to moderate base like carbonate. Strong bases generally won't work here because they will not release the H<sup>+</sup> needed towards the end of the catalytic cycle.

3. (50 pts) Hydroxycarbonylation (also referred to sometimes as hydrocarbonylation) is the catalyzed reaction of alkenes, CO and water to make carboxylic acids:



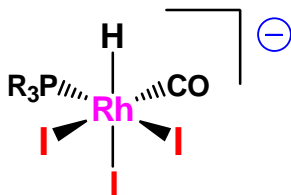
a) (25 pts) Sketch out a catalytic cycle for this using the Monsanto/BP catalyst  $[\text{RhI}_2(\text{CO})_2]^-$  and propylene ( $\text{CH}_3\text{CH}=\text{CH}_2$ ) as your alkene to make the linear carboxylic acid product. HI is a co-catalyst as in the Monsanto acetic acid process. The reactions steps in the proper order are as follows: **1)** oxidative addition of HI, **2)** CO ligand substitution of propylene (clearly indicate whether this is an associative or dissociative ligand substitution rxn; this is also the rate-determining reaction step), **3)** migratory insertion, **4)** another migratory insertion and ligand addition, **5)** reductive elimination of acyl iodide and regeneration of starting  $[\text{RhI}_2(\text{CO})_2]^-$  catalyst. In a separate step outside the Rh cycle the acyl iodide reacts with water to produce the final product and regenerate what species that re-enters the catalytic cycle?



When water reacts with the acyl iodide it regenerates HI, the co-catalyst for the reaction.

- b) (10 pts) This catalyst system has poor linear to branched carboxylic acid selectivity (about 1:1). What would be the effect of replacing a carbonyl ligand with one  $P(i\text{-Pr})_3$  ligand ( $i\text{-Pr}$  = iso-propyl)? Consider the effect on both the rate of catalysis and selectivity to the linear carboxylic acid. Clearly explain your reasoning.

Everyone got credit for this question (unless you didn't write anything down).

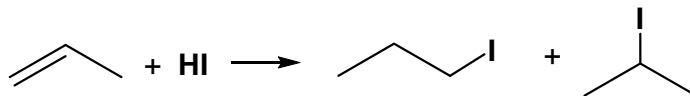


**Rate effect:** Replacing one of the CO ligands with a strong donating alkylated phosphine will make the Rh even more electron-rich. This will increase substantially the  $\pi$ -backbonding with the last remaining CO ligand and make its dissociation far slower. This should dramatically slow down the coordination of the alkene and slow the rate of catalysis. The one compensating factor could be that the more electron-rich metal will now be more likely to dissociate an iodide ligand. The *trans*-effect will specifically

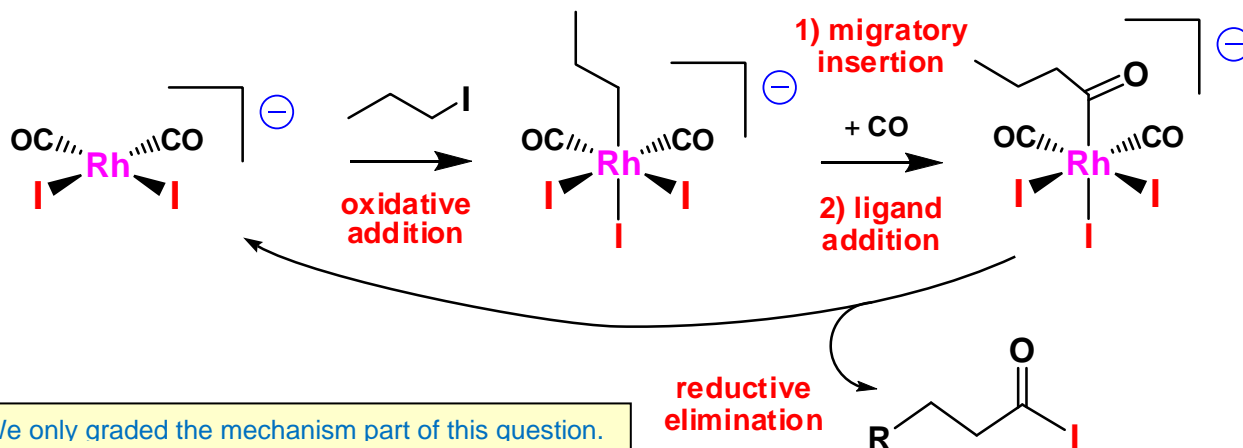
favor dissociating the iodide *trans* to the phosphine and coordination of the alkene at this site, which is cisoidal to the hydride to perform the migratory insertion rxn.

**Selectivity:** The bulkier phosphine should generally favor the hydride-alkene migratory insertion to produce the less hindered linear alkyl product, which will then go on to form the linear acyl iodide and carboxylic acid. Note, however, that the magnitude of the selectivity effect may well depend on exactly where the phosphine is coordinated and how the alkene is oriented to the Rh-H bond and the phosphine directing effect. For example, if the iodide ligand *trans* to the phosphine dissociated, the *trans* phosphine would have essentially no steric effect on the coordinating alkene for the migratory insertion step.

- c) (15 pts) It is known that HI can react directly with an alkene to produce an alkyl iodide:



Sketch out and label the reaction steps showing how  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$  could react with the  $[\text{RhI}_2(\text{CO})_2]^-$  catalyst to produce the acyl iodide intermediate (not the entire cycle). Briefly discuss how (if) this would affect the catalytic reaction.

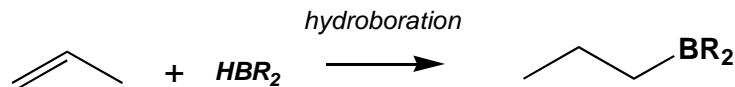


We only graded the mechanism part of this question.

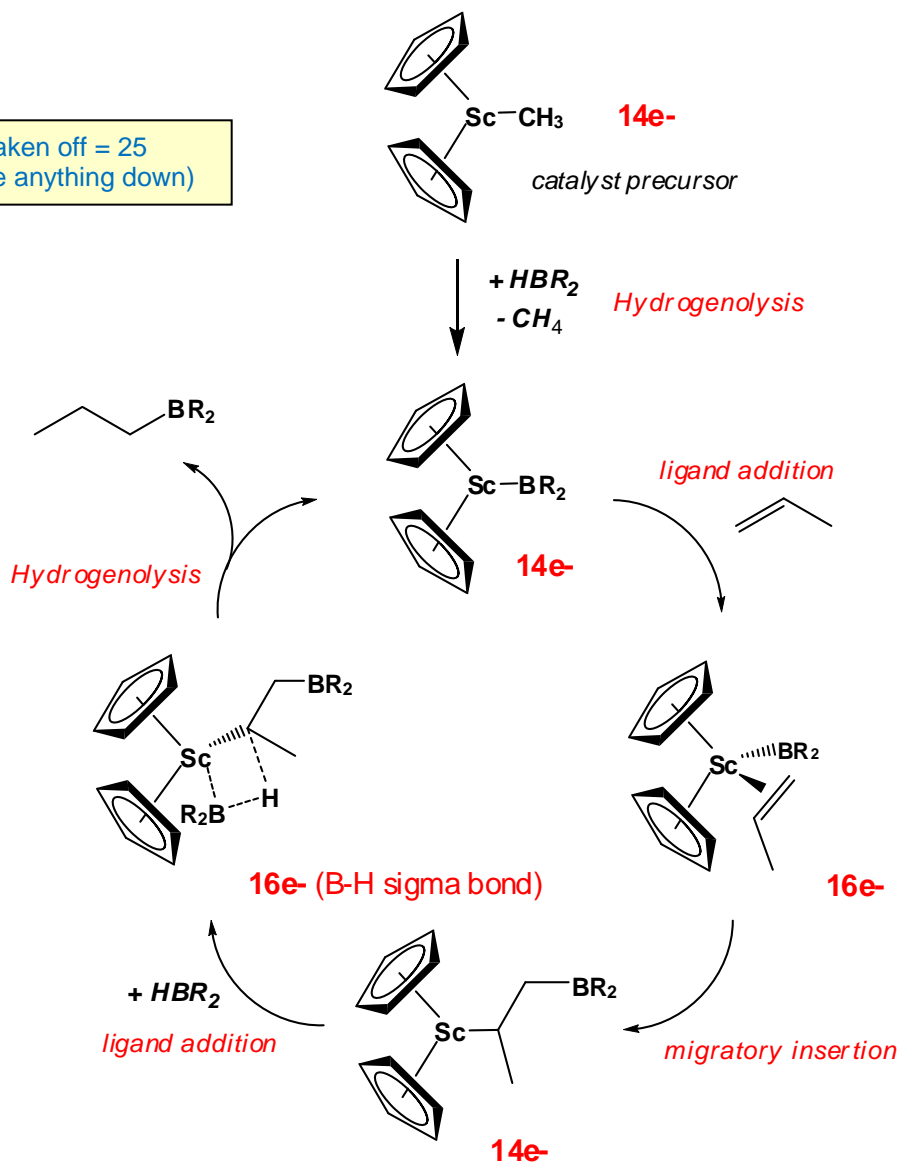
This could actually speed up the rate of catalysis as the oxidative addition step is not dependent on an empty coordination site opening up on the catalyst as is necessary for the alkene coordination and subsequent reaction.

**Extra:** The bad aspect overall is the preferred formation of the branched alkyl iodide (2-iodopropane) that would react to make the branched carboxylic acid, a generally non-desirable product.

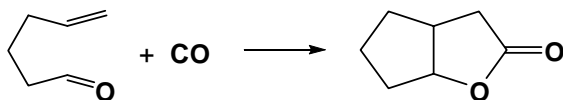
4. (50 pts) Sketch out a reasonable catalytic cycle for the following reaction and clearly label each step. Make sure that the # of ligands on the catalyst and the electron-counting is OK. Indicate the electron-count for each metal complex (but do NOT show the detailed electron-counting). Use the catalyst precursor complex shown at the top of the catalytic cycle to generate your active catalyst by reaction with  $\text{HBR}_2$  (R = non-bulky alkyl group) to eliminate  $\text{CH}_4$  (don't forget to label what this step is called).



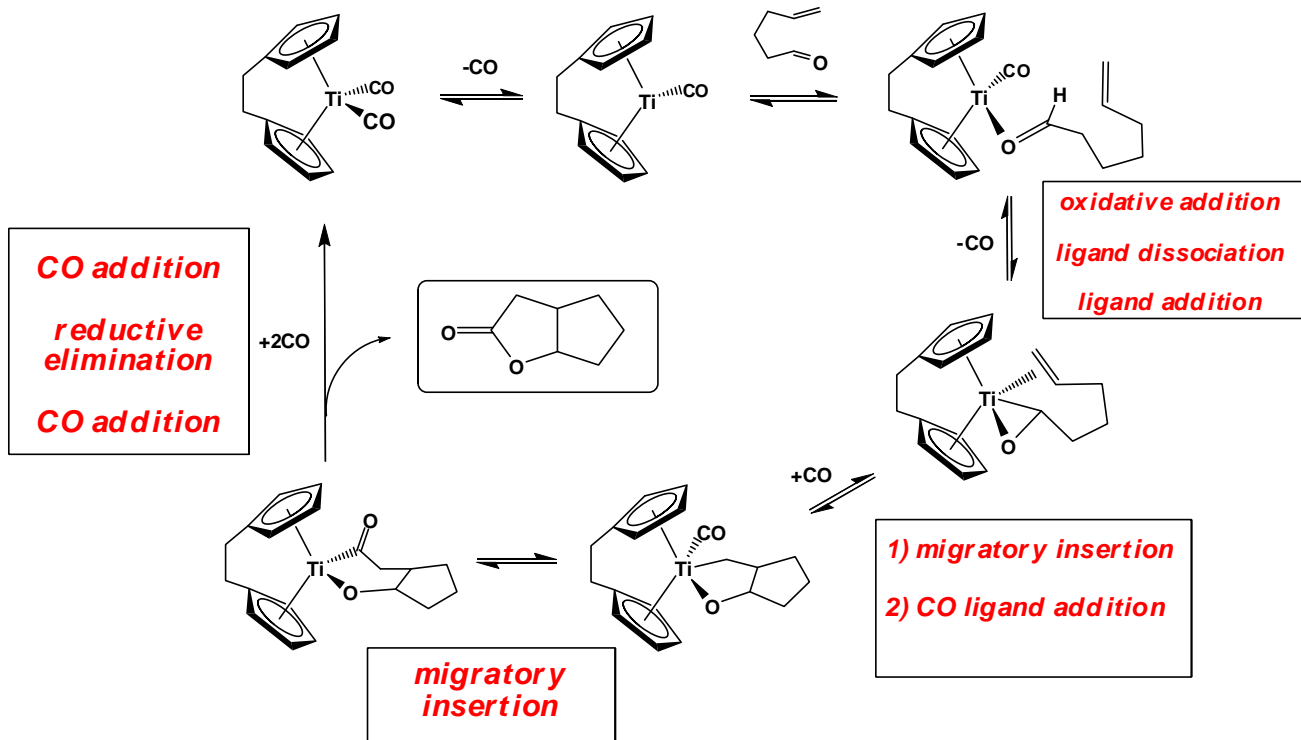
Maximum points taken off = 25  
(unless you didn't write anything down)



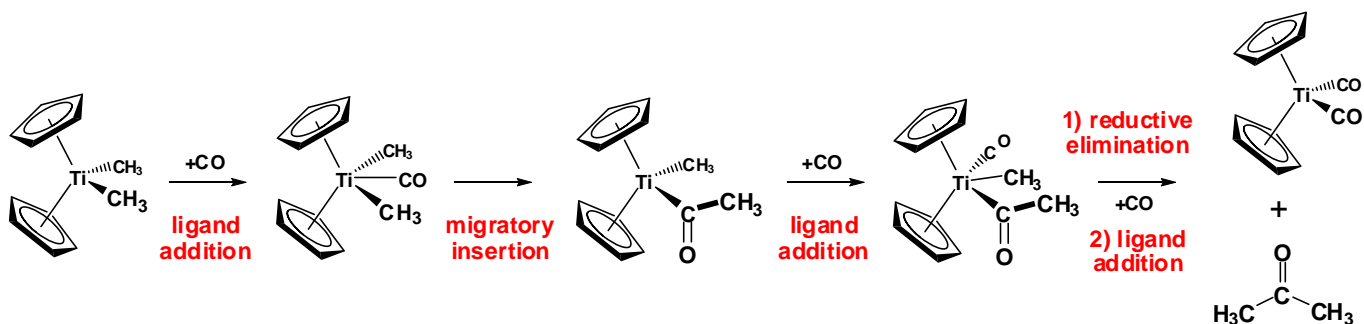
5. (50 pts) Bill Crowe's research group (LSU Chem) has studied the following cyclocarbonylation rxn.



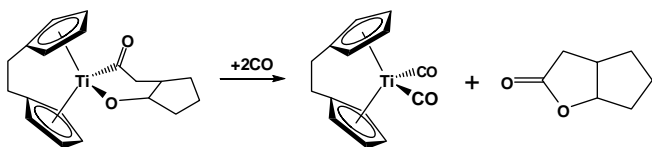
a) (30 pts) Label the boxed reaction steps in my proposed catalytic cycle (there may be more than one reaction occurring in each step, if the order is important label them 1), 2), etc.).



b) (15 pts) One might start with  $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$  and react it with excess CO to produce the active  $\text{Cp}_2\text{Ti}(\text{CO})_2$  catalyst and acetone ( $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ ). Clearly sketch out and label the reaction steps to accomplish this. You don't have to draw out the Cp rings on the complexes (use Cp).



c) (5 pts) This rxn is not really catalytic as the following reaction step is extremely slow and difficult. Why? (briefly but clearly explain)



Full credit, unless you didn't write anything down.

The reductive elimination to take  $\text{Ti}(4+)$ ,  $d^0$ , to  $\text{Ti}(2+)$ ,  $d^2$  is difficult due to the low electronegativity of early transition metals and their preference for high oxidation states. This specific rxn will be especially difficult because of the extremely strong Ti-OR bond, more so than that shown above in part b) involving weaker Ti-alkyl, acyl bonds.