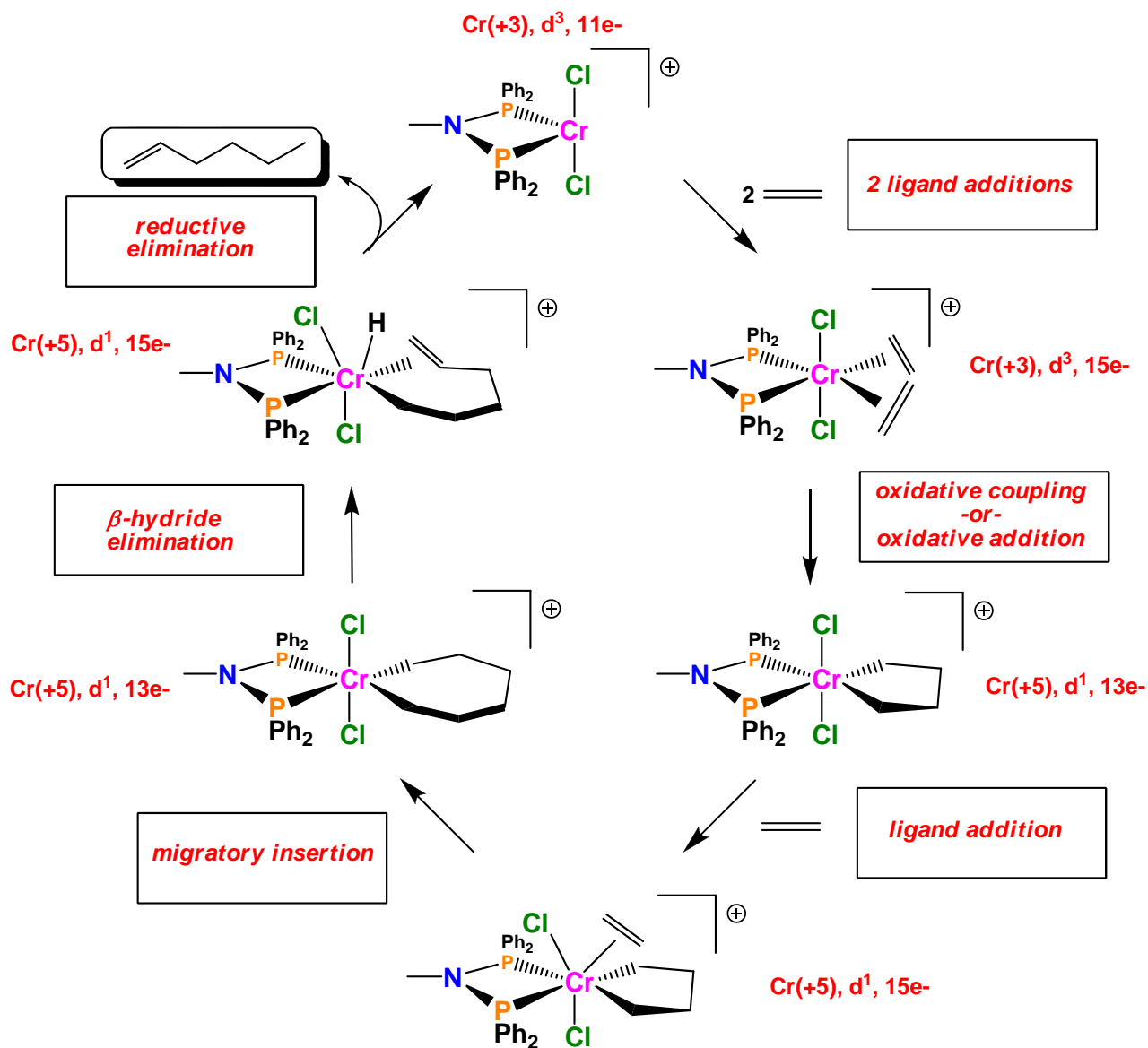


## Homework # 4

Due: Tuesday, April 29, 2008

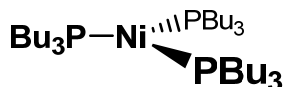
Check the box to the right if you want your graded homework to be placed out in the public rack outside Prof. Stanley's office. Otherwise you will have to pick up your homework from Prof. Stanley in person:

1. (20 pts) Starting with the catalyst shown below (and the first step) sketch out the catalytic cycle for the trimerization of ethylene to make 1-hexene. Clearly label each step.



Read the attached paper from the *Journal of the American Chemical Society* (Shirakura & Suginome, 2008, 130, 5410-5411) and answer the following questions about it.

2. (10 pts) What is the likely nickel catalyst (what the authors refer to as  $\text{Ni}(0)\text{L}_n$ ) that initially reacts with the alkyne? Sketch out this species and indicate its overall electron-count and d-electron count. Use the phosphine ligand that the authors report works best for this catalyst. Briefly discuss why did you chose this compound?



This is the catalyst species that reacts with a  $\text{H-C}\equiv\text{C}$  bond to do the initial oxidative addition reaction. A  $\text{H-C}$  bond is non-electrophilic and requires an empty orbital on the metal in order to initially coordinate before the oxidative addition actually occurs.  $\text{Ni}(\text{PBu}_3)_3$  is a  $\text{Ni}(0)$ ,  $d^{10}$ ,  $16e^-$  species that has an empty coordination site for this.  $\text{Ni}(\text{PBu}_3)_4$ , on the other hand, is an  $18e^-$  species that must first lose a phosphine ligand in order to open up an empty coordination site.  $\text{Ni}(\text{PR}_3)_4$  would be considered the catalyst precursor. Electronically, the  $\text{Ni}(0)$   $d^{10}$  center should not want 4 strongly donating alkylated phosphine donors and will favor dissociation of one to make the more reactive 3-coordinate tris-phosphine compound. The authors add 4 equivalents of  $\text{PBu}_3$  to make sure the Ni centers doesn't become too unsaturated and start decomposing or precipitating metallic nickel. A  $\text{Ni}(\text{PBu}_3)_2$ -type complex doesn't have enough good donors and too low an electron-count ( $14 e^-$ ) to favor the oxidative addition step.

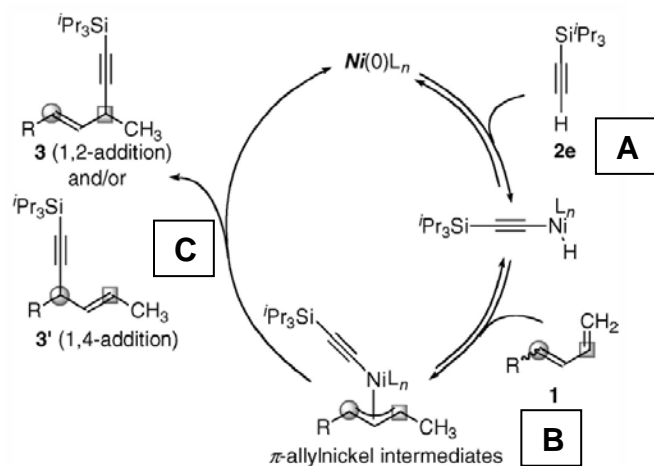
3. (10 pts) From Table 1 calculate the following for entry # 11 (assume 100% conversion to product):

- a) # of turnovers (TON): 10 (10 mole% catalyst = 10 turnovers)  
 b) average turnover frequency (TOF,  $\text{hr}^{-1}$ ) = 2.5  $\text{hr}^{-1}$  (10 turnovers/4 hours)

4. (10 pts) Why doesn't  $\text{P}(\text{O}i\text{Bu})_3$  work as a ligand for this catalytic reaction relative to  $\text{PBu}_3$ ?

$\text{P}(\text{O}i\text{Bu})_3$  is a phosphite ligand and a fairly poor  $\sigma$ -donor and moderately good  $\pi$ -acceptor ligand. The  $\text{PBu}_3$  ligand, on the other hand, is an alkylated phosphine and a very strong  $\sigma$ -donor and poor  $\pi$ -acceptor ligand. This will make the metal center electron-rich enough to favor the  $\text{H-C}\equiv\text{C}$  bond oxidative addition. A secondary reason could be the favorable loss of a  $\text{PBu}_3$  ligand from  $\text{Ni}(\text{PR}_3)_4$  that will generate the active  $\text{Ni}(\text{PBu}_3)_3$  catalyst for the electronic reasons discussed above (see page 4 in Ligand Substitutions and the quiz question asked in class about the electronic factors involved in  $\text{Ni}(\text{PR}_3)_4$  complexes).

5. (20 pts) Label the lettered steps in the authors proposed catalytic cycle (all steps proceeding clockwise). If there is more than one step, list them in the correct order.

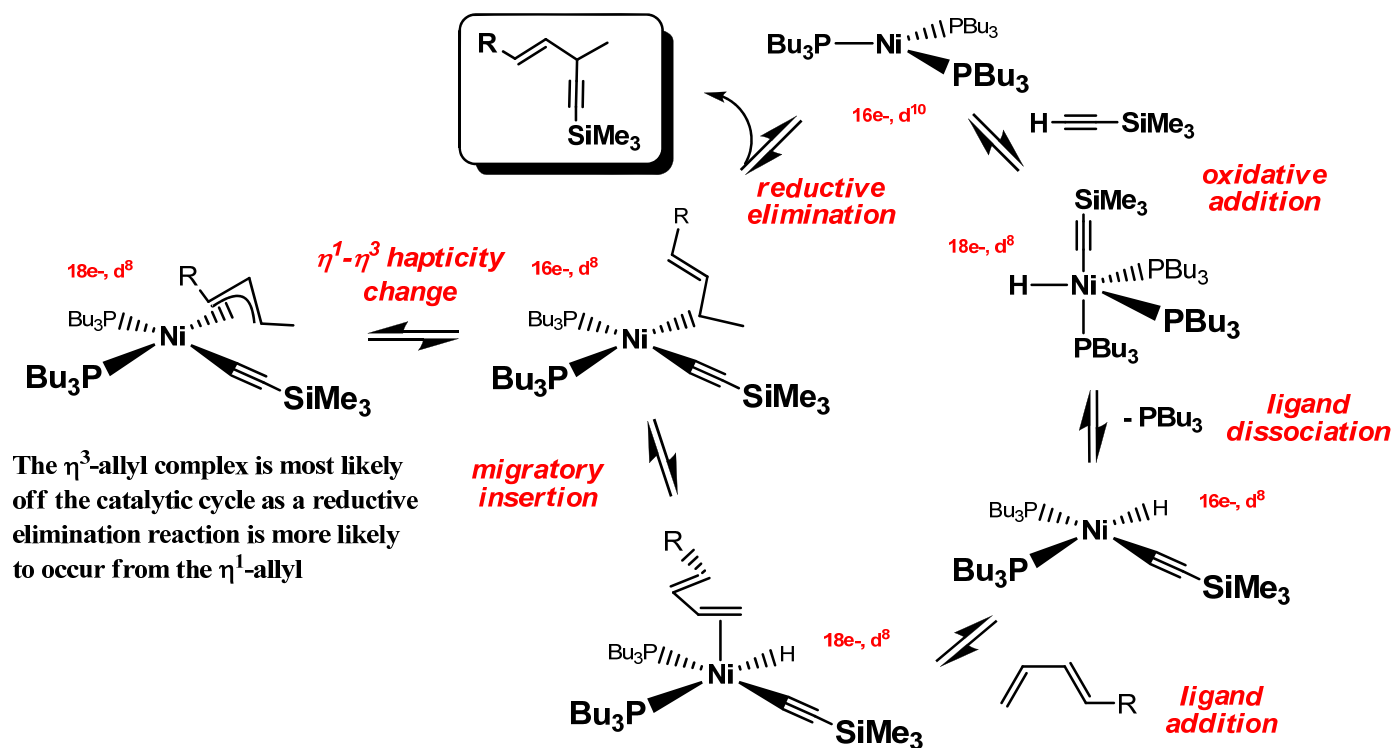


**A =** 1)  $\text{PR}_3$  ligand dissociation (if you think it is  $\text{NiP}_4$ )  
 2) oxidative addition (of alkyne C-H bond)

**B =** 1)  $\text{PR}_3$  ligand dissociation (to give  $16e^-$  complex)  
 2) ligand addition (of one diene double bond)  
 3) migratory insertion (of Ni-H and alkene)  
 4)  $\eta^1$  to  $\eta^3$ -allyl hapticity change

**C =** 1)  $\eta^3$  to  $\eta^1$ -allyl hapticity change  
 2) reductive elimination (of alkynyl and  $\eta^1$ -allyl)  
 3)  $\text{PR}_3$  ligand addition (to regenerate  $\text{NiP}_3$  catalyst)

EXTRA: Shown below is my full proposed catalytic cycle for the abbreviated one shown above.



Notes:

The hydride and anionic alkynyl ligands are about equally likely to do the migratory insertion reaction, but you have to make sure that if you use the alkynyl ligand that you add it to the internal carbon atom of the non-R-group substituted alkene. I used the hydride ligand in my mechanism (as did the authors). But the two  $\pi$ -orbitals on the alkynyl ligand and good overlap with the alkene orbitals makes the alkynyl ligand much better candidate for this relative to a simple alkyl group.

6. (30 pts) Sketch out a catalytic cycle for the dimerization of two of the alkyne reactants to give the side product **4a** (SiMe<sub>3</sub> group). Clearly label each reaction step and show the catalyst complex involved in each step. Start with the catalyst complex shown below (no phosphine ligands involved in this cycle).

