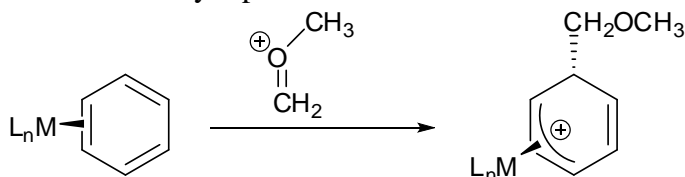


Problem Set #6

Due: Nov. 13, 2008

1. The following reaction was recently reported in the literature.



a) What reaction type is shown? (1 pt.)
electrophilic addition

b) The choice of ML_n was key to the success of the reaction. The authors used $[Os(NH_3)_5]^{2+}$ as one metal complex that bound tightly to benzene and facilitated the reaction shown above. Suggest characteristics of $[Os(NH_3)_5]^{2+}$ that make it work well in this reaction. (3 pts.)

The amine ligands are strong σ donors and are incapable of engaging in π backbonding. This adds electron density to the Os and leaves the Os d_π electrons free to backbond with the benzene π system. The Os complex then activates the benzene as a nucleophile, thereby promoting the donation of benzene's π electrons.

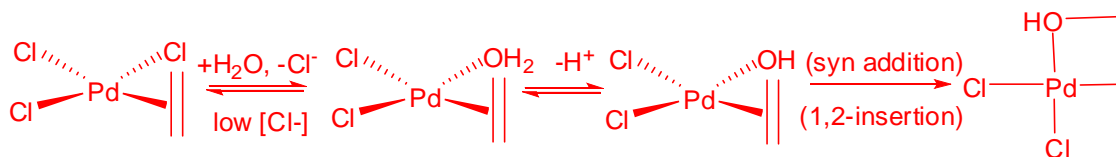
W. D. Harman et al. *Chem. Rev.* **1997**, 97, 1953-78.

c) The authors made Re(I) and W(0) complexes with benzene and anticipated that these complexes would be even more stable than the Os(II) complex. Why do you think they believed this? (3 pts.)

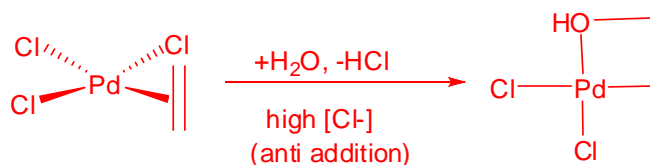
The Re(I) and W(0) complexes have the same number of electrons as Os, but have a lower oxidation state. With a lower oxidation state, the nucleus of the metal will have a weaker hold on the d electrons. Therefore the Re(I) and W(0) d_π electrons will be more available to engage in backbonding with the benzene π system. With greater backbonding, there will be a more stable coordination bond to the benzene ligand. W. D. Harman et al. *JACS* **2004**, 126, 13572-6.

2. The Wacker reaction or process entry on Wikipedia shows two possible mechanisms for the Pd-catalyzed combination of ethylene and water. After viewing the mechanism at the website (http://en.wikipedia.org/wiki/Wacker_process), identify the difference between the two methods. (3 pts.)

One mechanism (below), at low $[Cl^-]$, involves initial coordination of H_2O and subsequent intramolecular, syn nucleophilic addition of OH to the ethylene bound to the Pd.

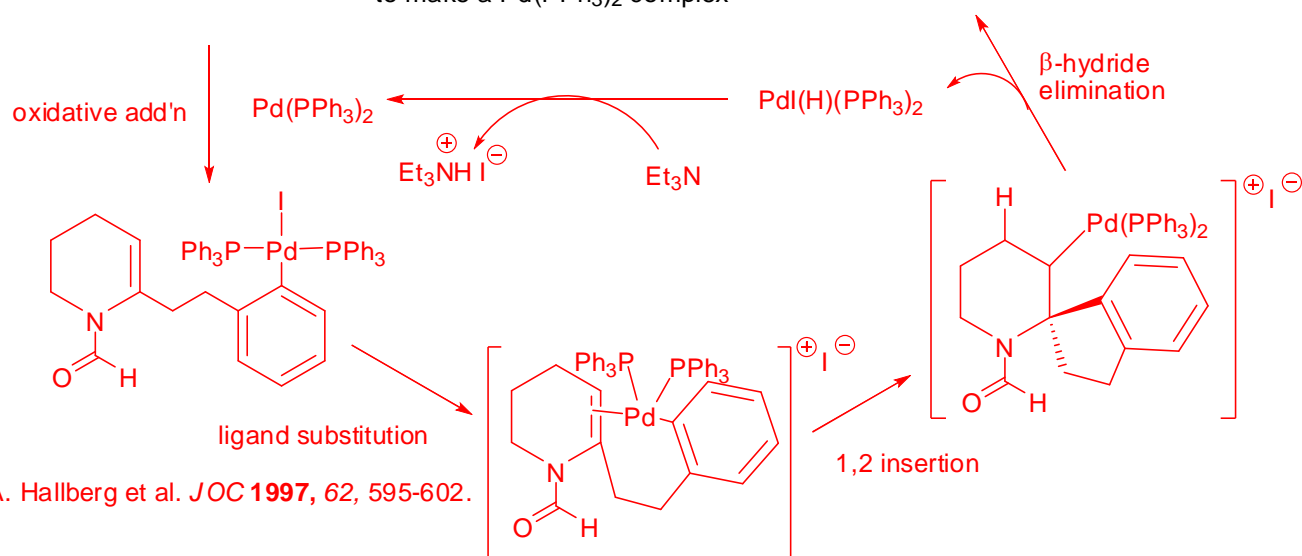
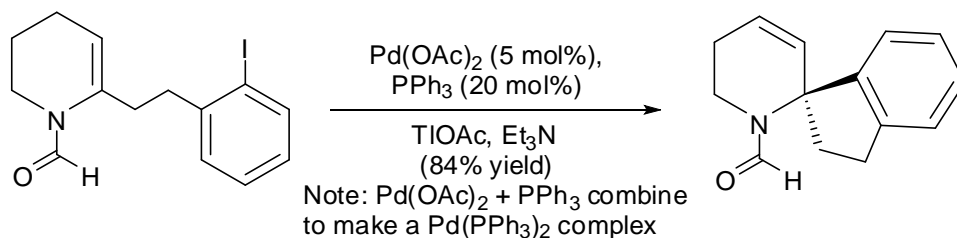


A second mechanism (below), at high $[Cl^-]$, has the same product formed from an intermolecular, anti nucleophilic addition of H_2O on the ethylene bound to the Pd.



3. Propose a mechanism or catalytic cycle for the following reactions. Be sure to identify the reaction type in each step of your mechanism. (5 pts. each)

a)



b)

