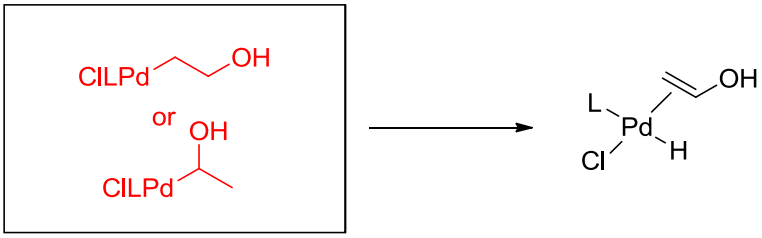
Organometallic Chemistry Name:____Rick Parry_____
Problem Set #2
Due: Sept. 20, 2011

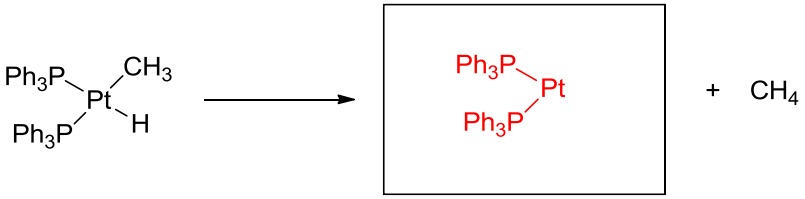
Questions 1-4: Provide the products or reagents to complete the following reactions and identify them by the type of reaction occurring. *CHE-334 students need to answer 8 of 11 and CHE-534 students need to answer 10 of 11.*

1. Reactions of metal-alkyls

a) beta-hydride elimination

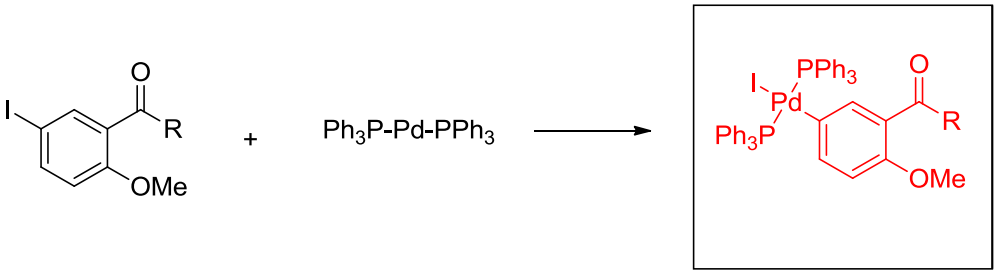


b) reductive elimination

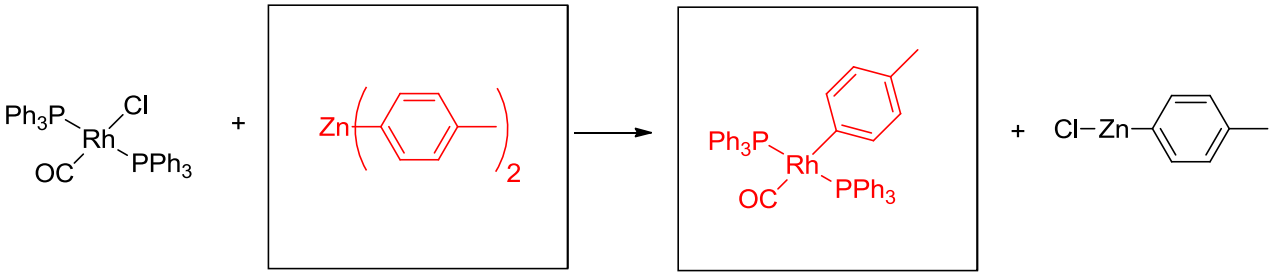


2. Synthesis of metal-alkyls

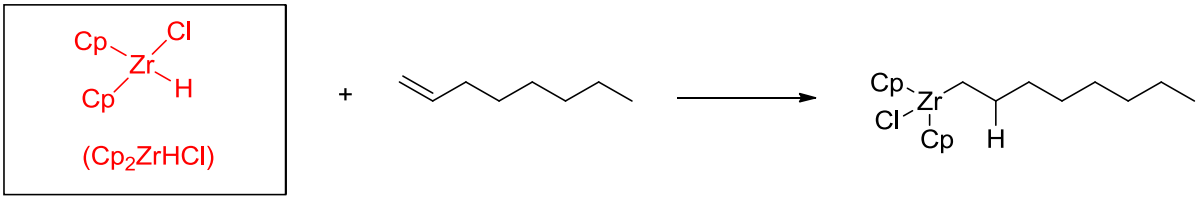
a) oxidative addition



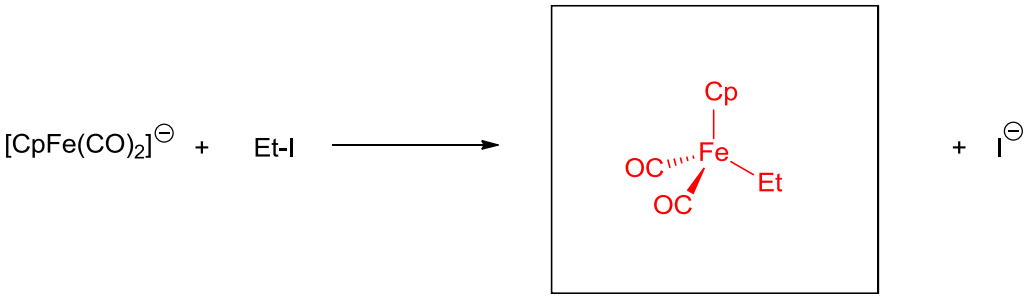
b) transmetallation



c) 1,2-insertion

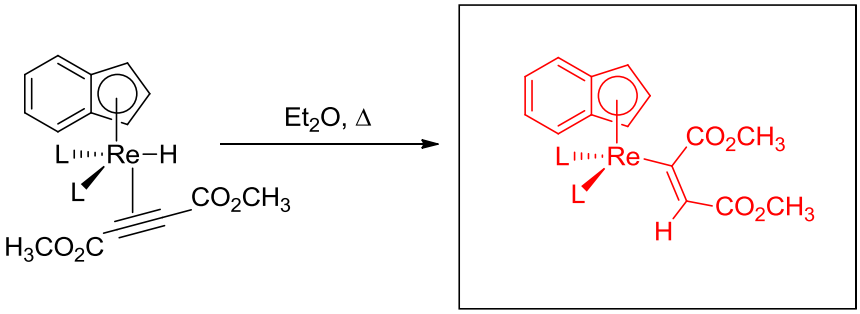


d) electrophilic attack of M

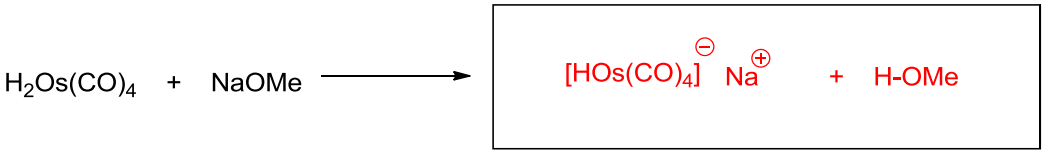


3. Reactions of metal-hydrides

a) 1,2-insertion

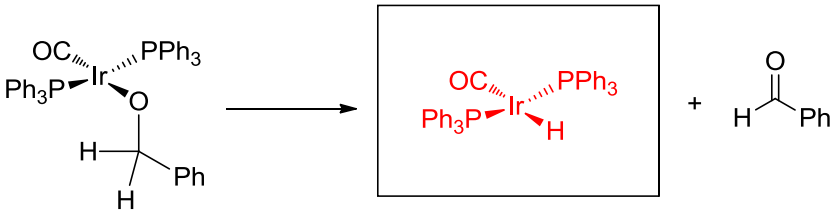


b) deprotonation

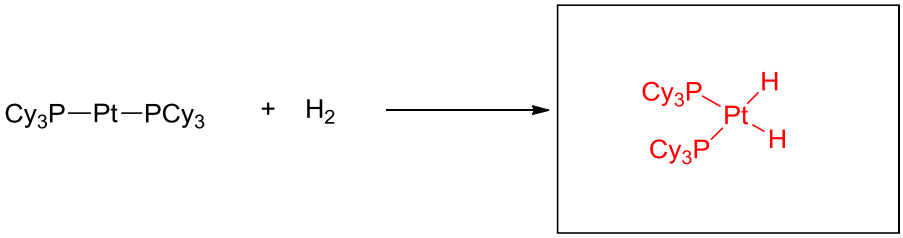


4. Synthesis of metal-hydrides

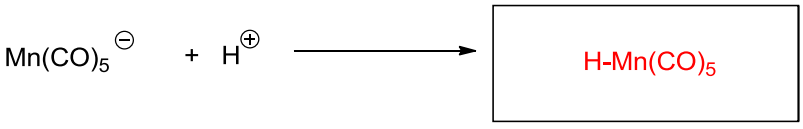
a) beta-hydride elimination



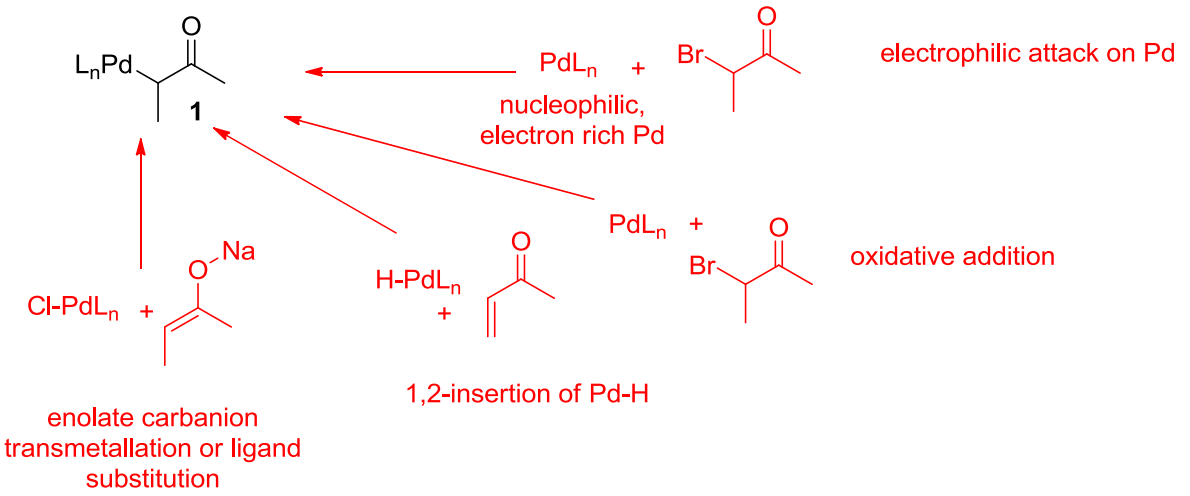
b) oxidative addition of hydrogen gas



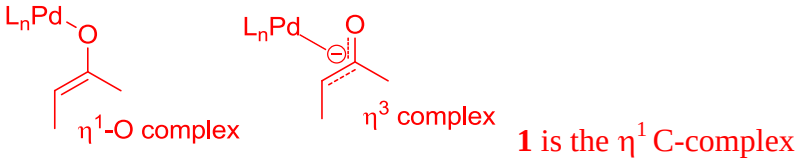
c) protonation



5. Transition metal enolate complexes like **1** have been a very active area of research for the last decade. They are basically just metal-alkyl complexes. Suggest a method for the synthesis of a metal-enolate complex such as **1**. *CHE-334 students should suggest one method and CHE-534 students should suggest 3 different methods.*



6. The metal-enolate complex can actually exist in three possible isomers or forms. All three isomers are based on the resonance forms of an enolate structure. Two of these isomers are η^1 complexes and one is an η^3 complex. Complex **1** is one of the η^1 complexes.
a) *Both CHE-534 and CHE-334*: Draw the other η^1 complex and the η^3 complex.



b) *CHE-534 only:* Choose two of the complex isomers and explain what factor might favor the formation of one over the other. Factors that might be considered include early vs. late transition metals, hard-soft acid-base effects, ligand effects (strongly π basic or π acidic, sterically demanding), coordination number, etc.

The η^1 O-complex would be favored by:
-hard acid metal (high oxidation state and/or early transition metal)
-electron withdrawing ligands, i.e. strong backbonding ligands. This would allow the strongly π basic O ligand's electron density to be delocalized.
-steric crowding from ligands or substituents on the enolate
-high coordination number on metal

The η^1 C-complex would be favored by:
-soft acid metal (low oxidation state, late transition metal)
-less substitution at C
-low coordination number on metal

-small spectator ligands

The η^3 complex would be favored by:
-low coordination number on metal (coordinatively unsaturated)
-small spectator ligands