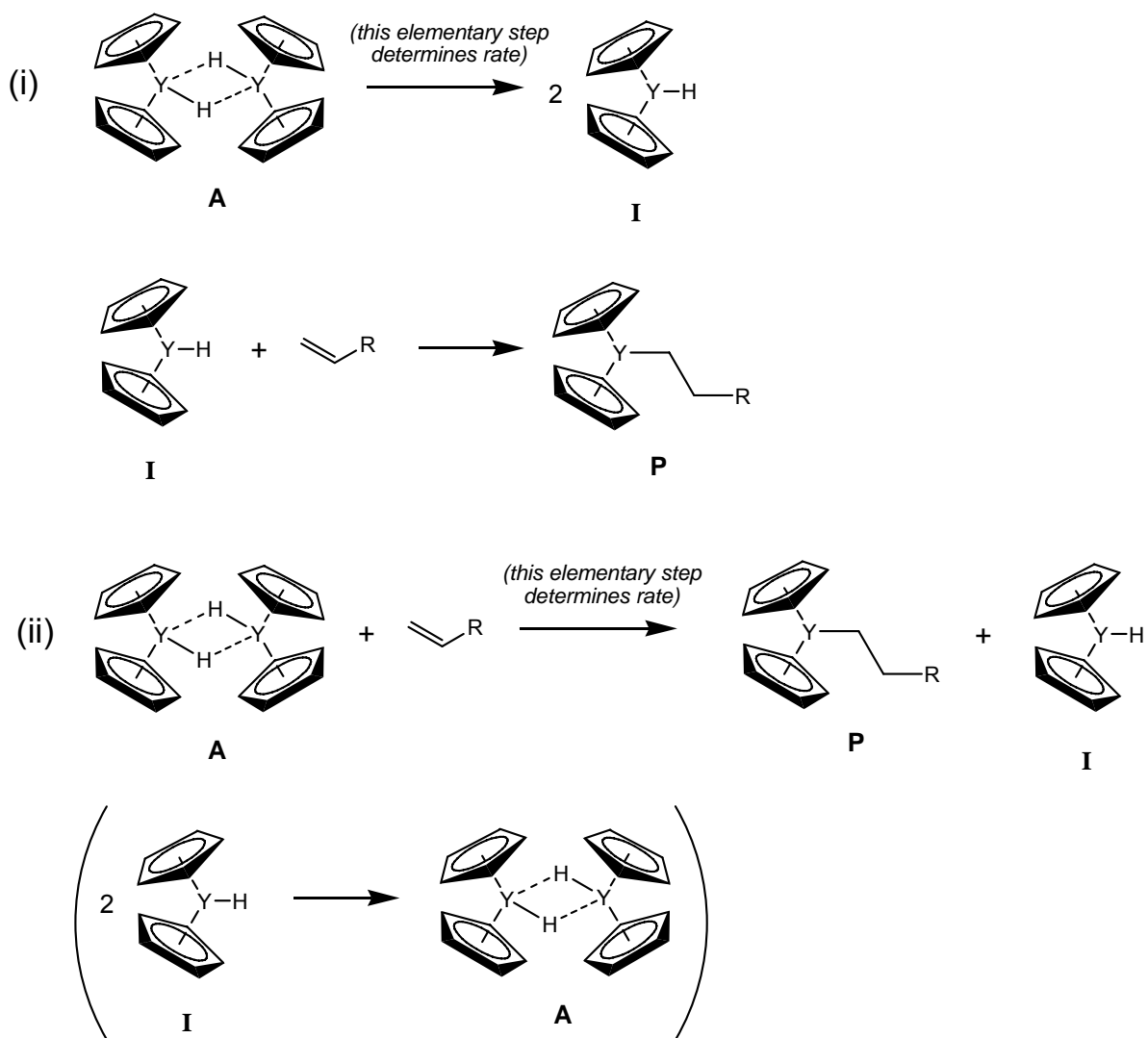


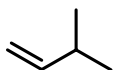
Workshop 4

1. Casey and coworkers have studied the mechanisms by which organometallic complexes accept alkene ligands, with the goal of developing new alkene polymerization catalysts. Recently, the Casey group has reported that dimeric yttrium complexes **A** can react with alkenes to form yttrium alkyl products **P** via two mechanisms: (i) a dissociative mechanism, in which the rate of the whole reaction is determined entirely by the rate at which **A** splits into two halves; or (ii) a direct reaction, in which the reaction rate is determined by interaction between the two reactants.¹

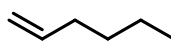


¹ Casey, C. P.; Tunge, J. A.; Lee, T.-Y.; Carpenetti, D. W. *Organometallics* **2002**, *21*, 389-396.

(It probably looks strange that two hydrogen atoms are divalent—bound to two other atoms—in **A**. This happens sometimes with low-valency metals; for the purpose of this problem, pretend that the pair of electrons in each dotted bond is really on the metal, with the understanding that they are shared a little with the hydrogen.) Casey and coworkers performed kinetic experiments to test which mechanism better described the reaction of **A** with 3-methyl-1-butene and 1-hexene. These experiments were run by mixing **A** (0.01 M) with a substantial (ten- to hundred-fold) molar excess of alkene and monitoring the concentration of product $[\mathbf{P}]_t$ with time. Data collected from these experiments are shown on the next page.



3-methyl-1-butene



1-hexene

- Write integrated rate laws for each of the mechanisms (i) and (ii) that relate the product concentration $[\mathbf{P}]_t$ to time, starting with an expression for $\partial[\mathbf{P}]/\partial t$. For mechanism (i), you can assume that every molecule of the monomeric yttrium intermediate is instantly converted into a molecule of **P**, and that as a result $\partial[\mathbf{P}]/\partial t = \partial[\mathbf{I}]/\partial t$ from the first step only. (Overall for both steps, $\partial[\mathbf{I}]/\partial t = 0$, because each molecule of the intermediate is consumed as soon as it's created. More on that in a couple of lectures.) Try not to use the term $[\mathbf{A}]_0$ in your answer; put everything in terms of product concentrations $[\mathbf{P}]$ by making the substitution $[\mathbf{A}]_0 = [\mathbf{P}]_\infty$, as Casey did.
- The investigators used a substantial excess of alkene in their experiments. Why? Why were the kinetics experiments structured the way they were? (And why do the y -axes represent such complicated quantities?)
- Based on the kinetic data, which mechanism (and which rate law) is most appropriate for which alkene?
- Evaluate any rate constants k that appear in your rate laws in part (a). Make sure these are fundamental constants k and not k_{obs} values.
- Draw electron-pushing diagrams to describe the alkene addition step for each of the two mechanisms. Make sure you account for where the bridging H atoms go.
- Casey argued that the mechanistic difference between the two alkene reactants was caused by the different steric environment of each alkene. What did he mean by this?

