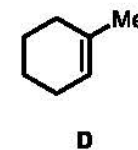
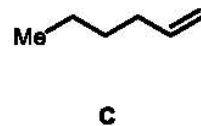
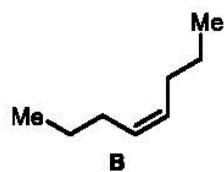
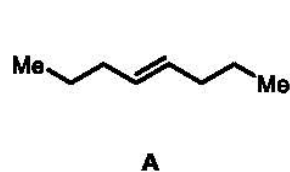
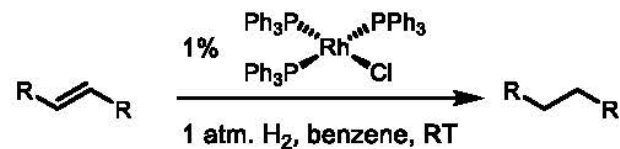
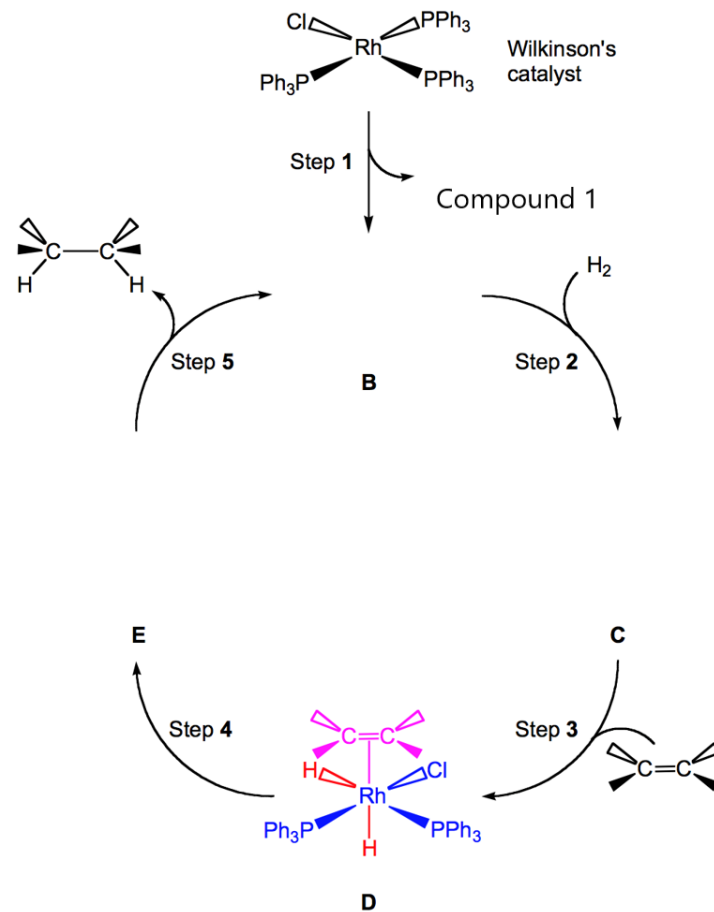


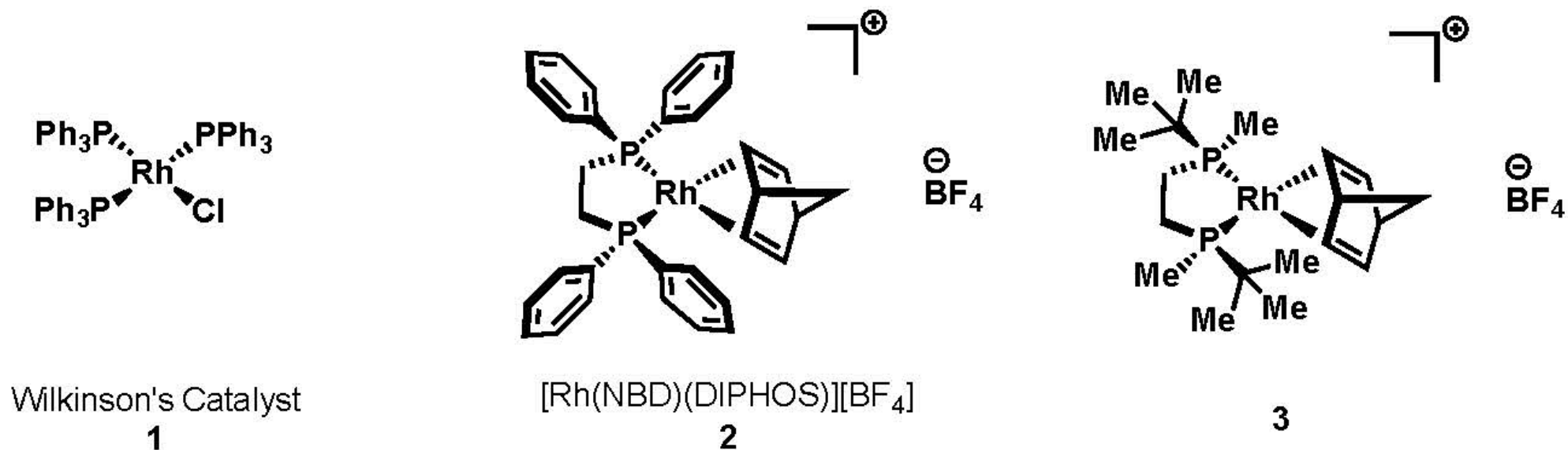
1. For the following hydrogenation reaction, rank the substrates in increasing rate of reaction.



Please complete the following mechanistic cycle for Wilkinson's catalyst. (1) What is compound 1. (2) Draw the structures of compounds B, C, and E.

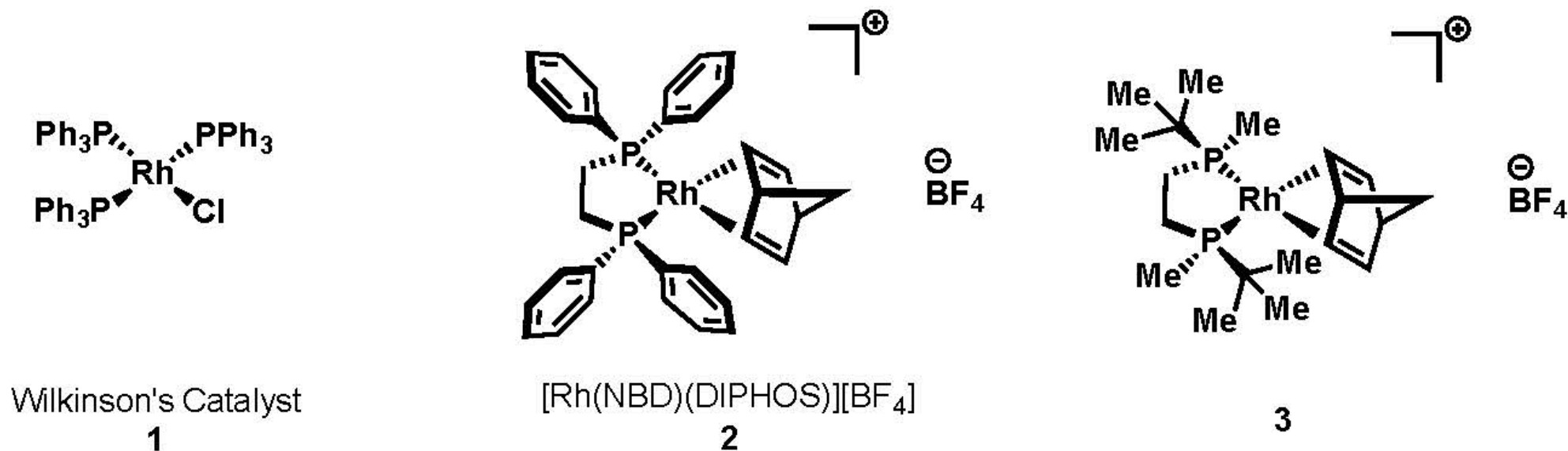


Extensive studies by Osborn and Halpern have elucidated the mechanistic differences between directed homogeneous hydrogenation of olefins between neutral Wilkinson's catalyst  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ , **1**, and cationic  $[\text{Rh}(\text{NBD})(\text{DIPHOS})][\text{BF}_4]$ , **2**.



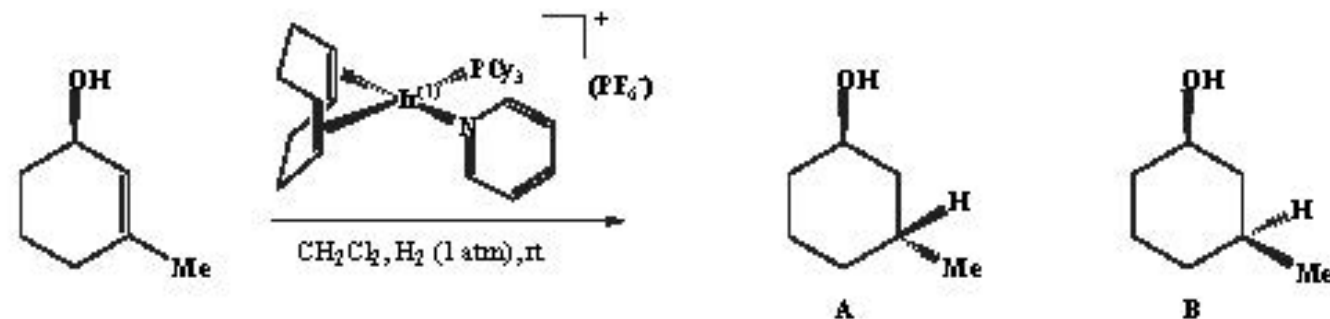
In lecture we discussed two major mechanistic regimes for homogeneous hydrogenation (*i.e.* "hydrogen first", "olefin-first"). What mechanisms do catalysts **1** and **2** follow?

Extensive studies by Osborn and Halpern have elucidated the mechanistic differences between directed homogeneous hydrogenation of olefins between neutral Wilkinson's catalyst  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ , **1**, and cationic  $[\text{Rh}(\text{NBD})(\text{DIPHOS})][\text{BF}_4]$ , **2**.



What mechanism do you expect catalyst 3 to follow? Compare to catalyst 2, which is the potential advantage?

*High catalyst loadings: diminished yields and selectivities*



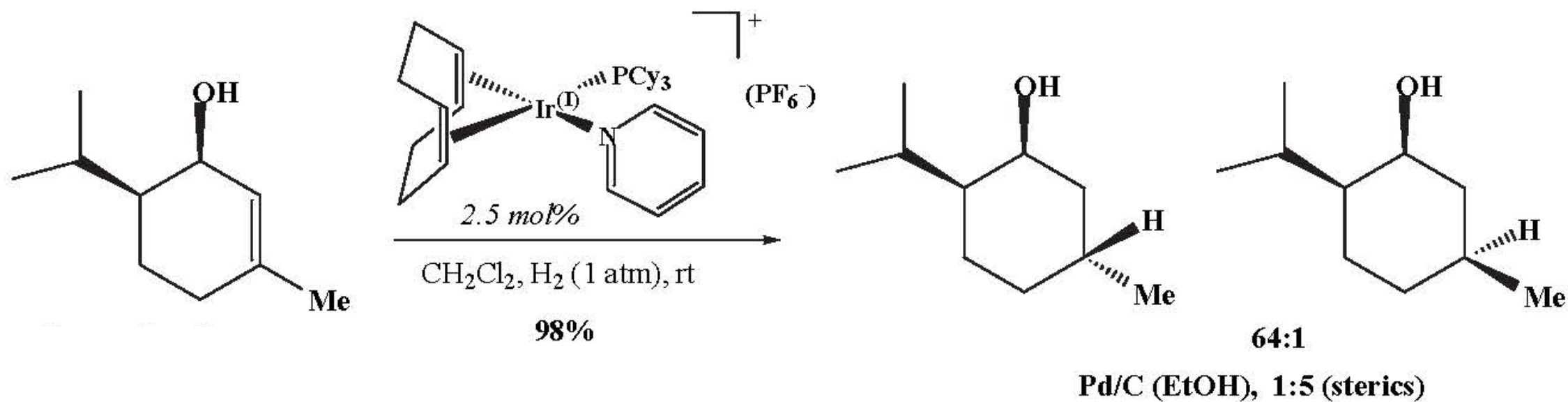
	yield	selectivity (ratio A:B)
2.5 mol%	99%	139:1
20 mol%	48%	74:1

Stork *JACS* 1983 (105) 1072.

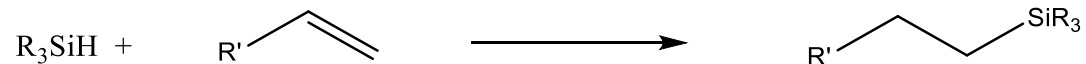
Crabtree *JOC* 1986 (51) 2655.

Why?

Propose a reason for the selectivity observed in this process.



Hydrosilylation of alkene is similar to hydrogenation of alkene. The reaction is shown below:



An Ir(I) complex is known to catalyze this reaction. In the catalytic cycle, the first step is oxidative addition of silane on the Ir(I) complex. The last step is the C-Si reductive elimination. Based on this information, draw the catalytic cycle of this Ir-catalyzed hydrosilylation. Label the oxidation state of Ir intermediates. You can use “Ir(I)” to present the initial catalyst.

1. Hydroformylation of alkenes is an extension of hydrogenation of alkenes.

(a) In the catalytic cycle below, please fill in the blanks with the name of the reaction (boxes adjacent to the arrows) and the structure of the specific intermediates with the correct geometry at the given step. (b) Name two possible side products of the reaction above.

