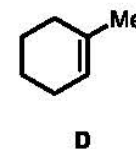
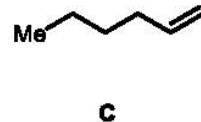
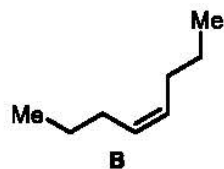
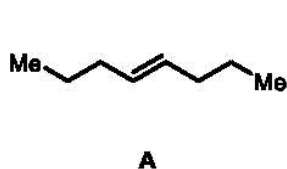
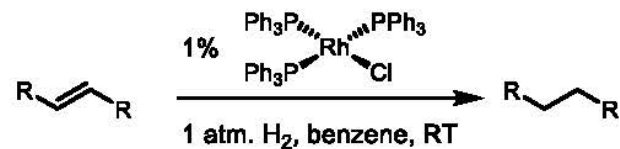
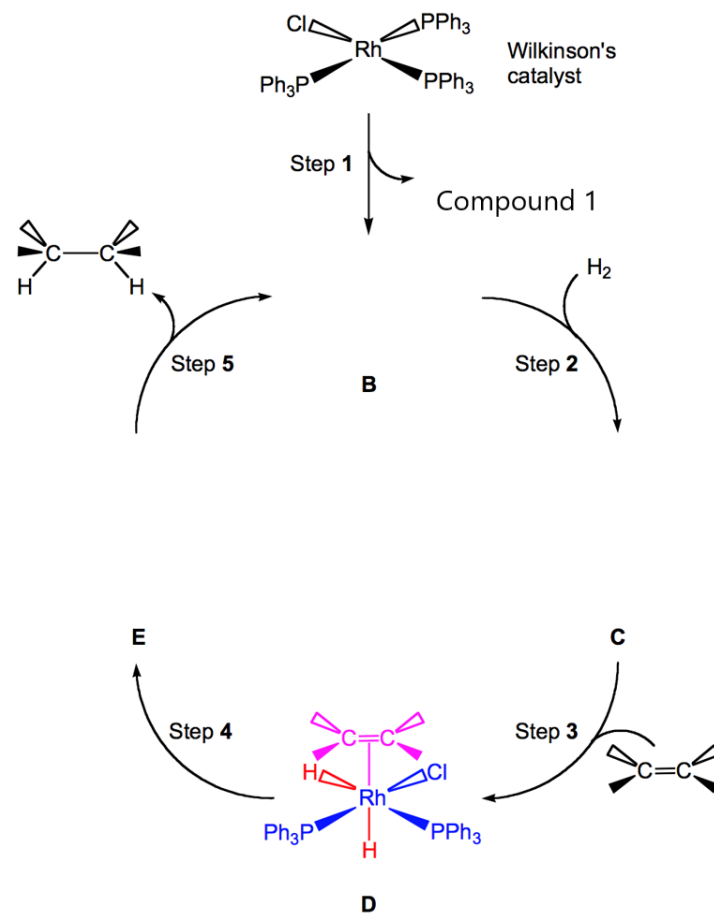


1. For the following hydrogenation reaction, rank the substrates in increasing rate of reaction.



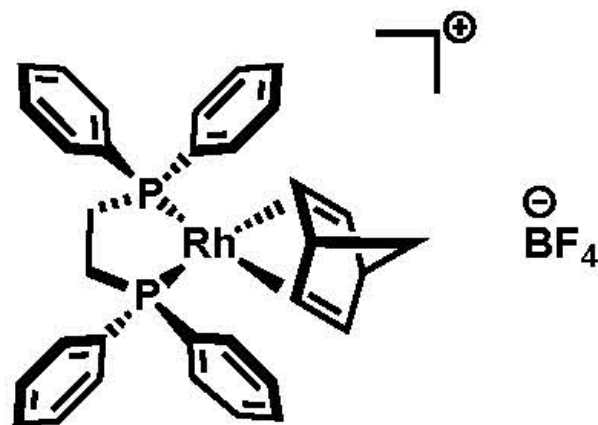
Please complete the following mechanistic cycle for Wilkinson's catalyst. (1) What is compound 1. (2) Draw the structures of compounds B, C, and E.



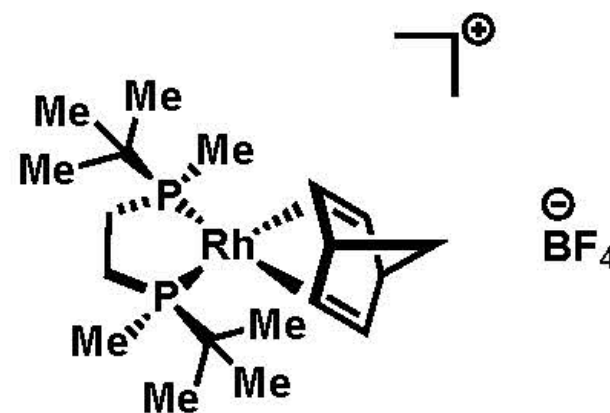
Extensive studies by Osborn and Halpern have elucidated the mechanistic differences between directed homogeneous hydrogenation of olefins between neutral Wilkinson's catalyst $\text{Rh}(\text{PPh}_3)_3\text{Cl}$, **1**, and cationic $[\text{Rh}(\text{NBD})(\text{DIPHOS})][\text{BF}_4]$, **2**.



Wilkinson's Catalyst
1



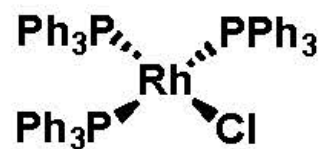
$[\text{Rh}(\text{NBD})(\text{DIPHOS})][\text{BF}_4]$
2



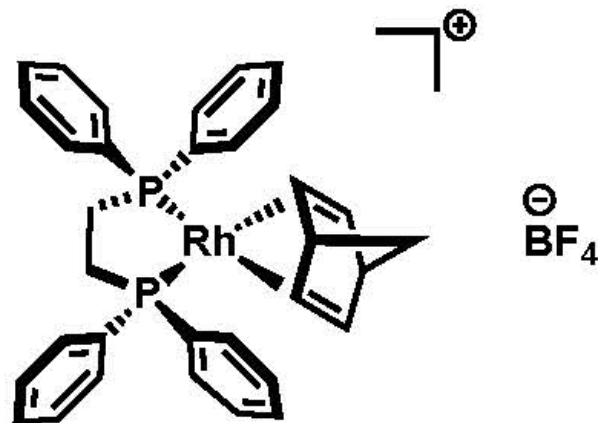
3

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?

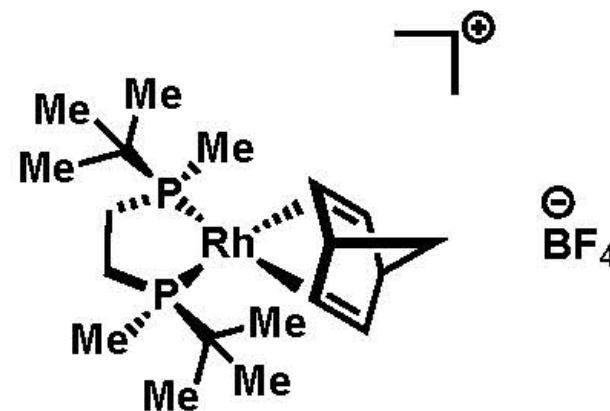
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Wilkinson's Catalyst
1



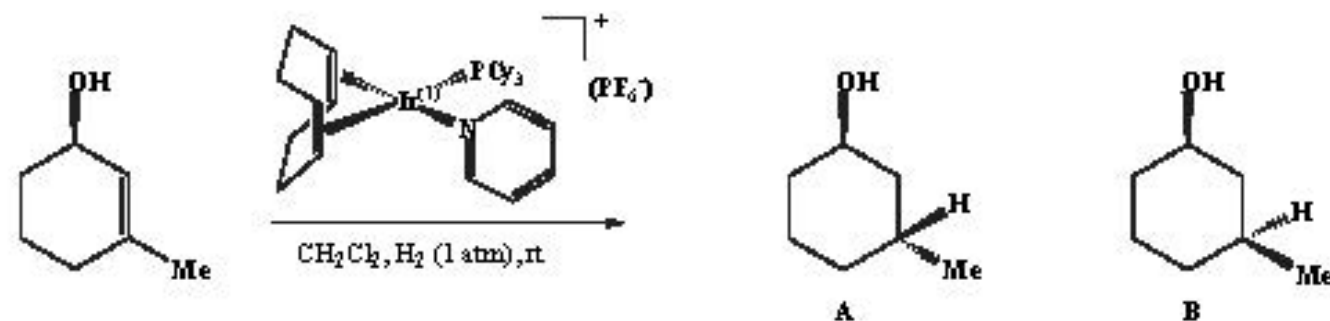
$[\text{Rh}(\text{NBD})(\text{DIPHOS})][\text{BF}_4]$
2



3

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



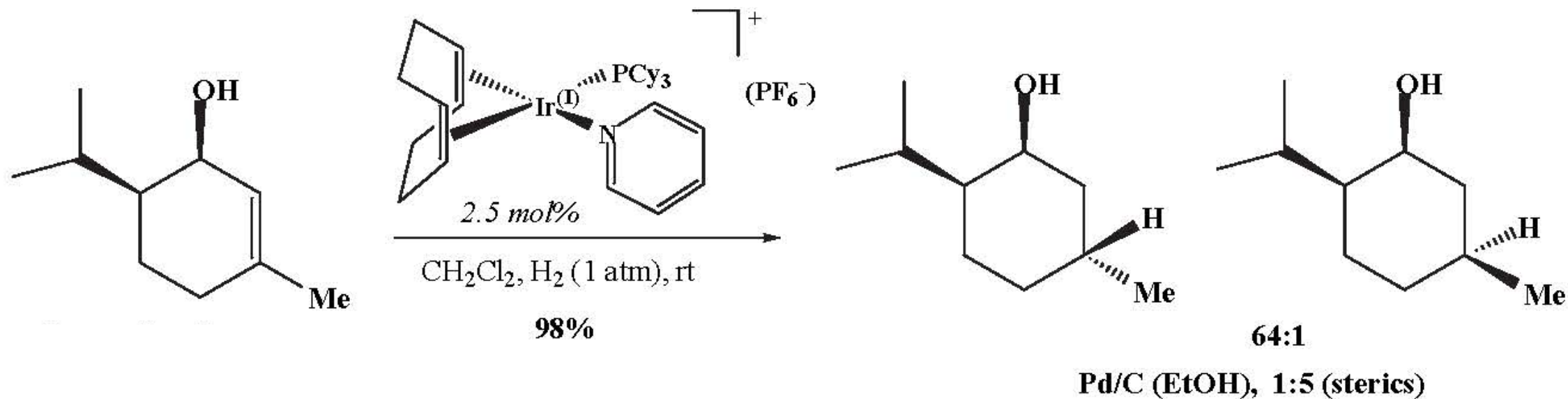
	yield	selectivity (ratio A:B)
2.5 mol%	99%	139:1
20 mol%	48%	74:1

Stork *JACS* 1983 (105) 1072.

Crabtree *JOC* 1986 (51) 2655.

Why?

Propose a reason for the selectivity observed in this process.

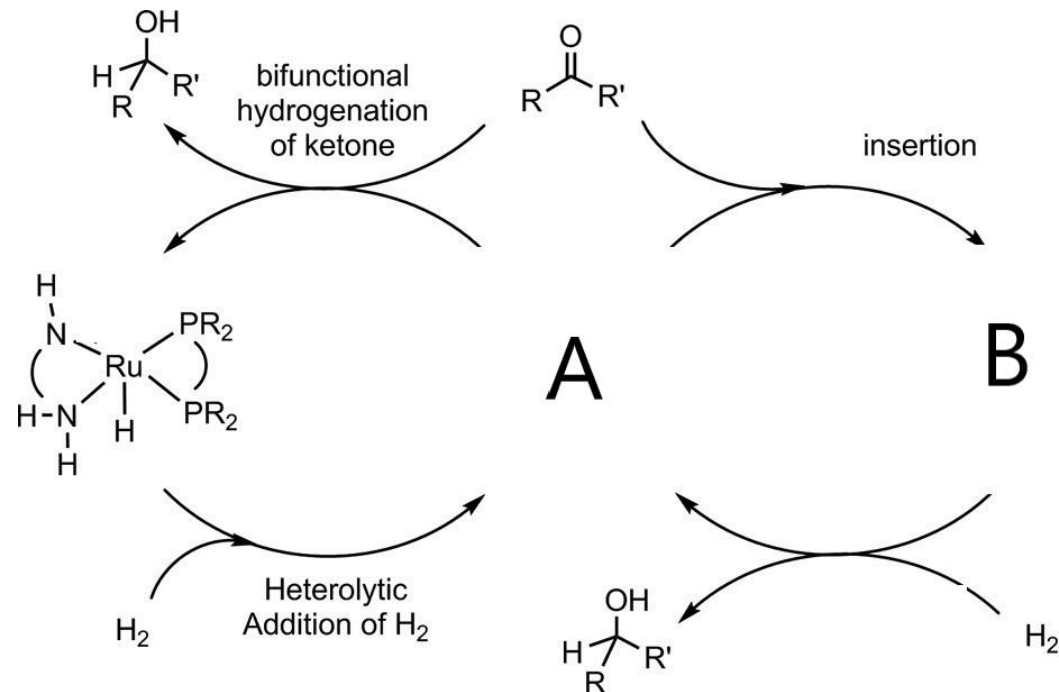


For the following Ru-catalyzed hydrogenation. Two possible mechanisms are known: a bifunctional mechanism and a step-wise mechanism. Please complete the following questions.

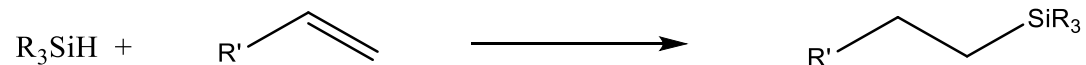
(1) What is the oxidation state of the Ru catalyst in the left.

(2) Draw the structure of intermediates A and B

(3) What is the oxidation state of Ru in A and B?



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.