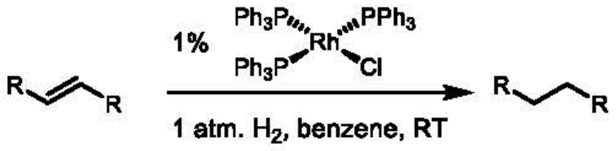
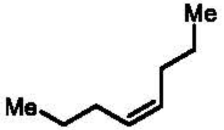
1. For the following hydrogenation reaction, rank the substrates in increasing rate of reaction.

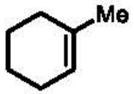


A



B

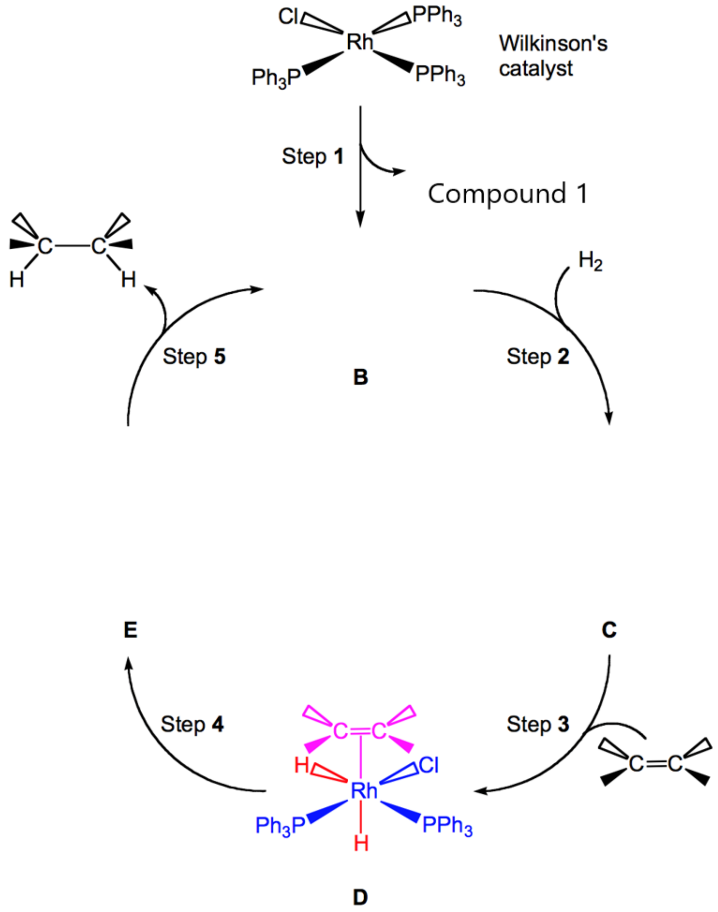
C



D

$D < A < B < C$ (or $C > B > A > D$)

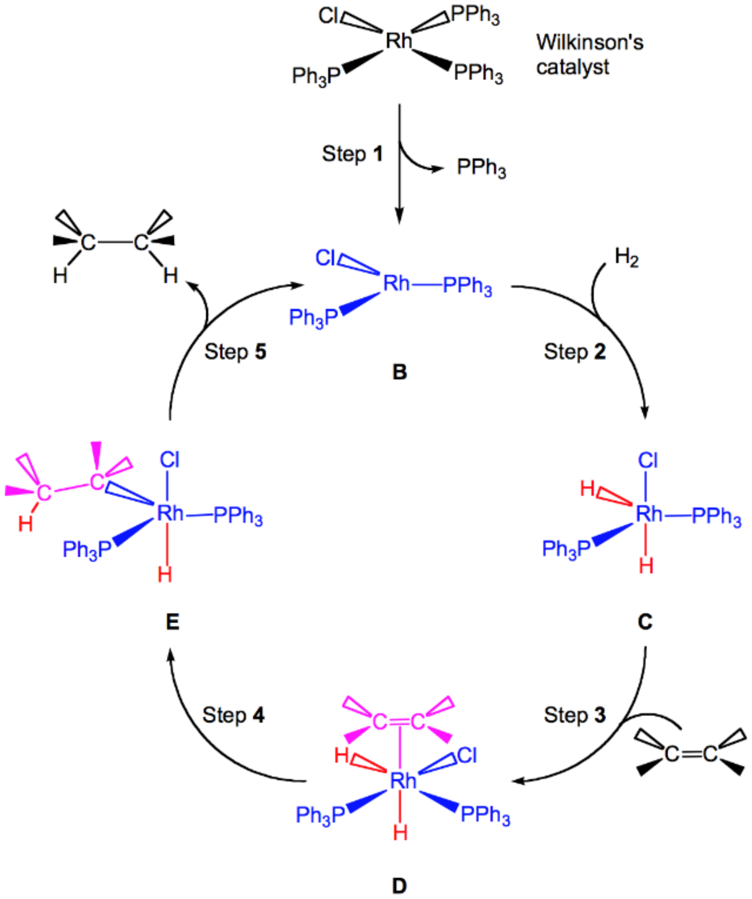
Please complete the following mechanistic cycle for Wilkinson’s catalyst. (1) What is compound 1. (2) Draw the structures of compounds B, C, and E.



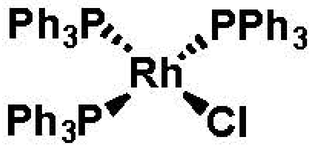
A:

1. Compound 1: PPh3

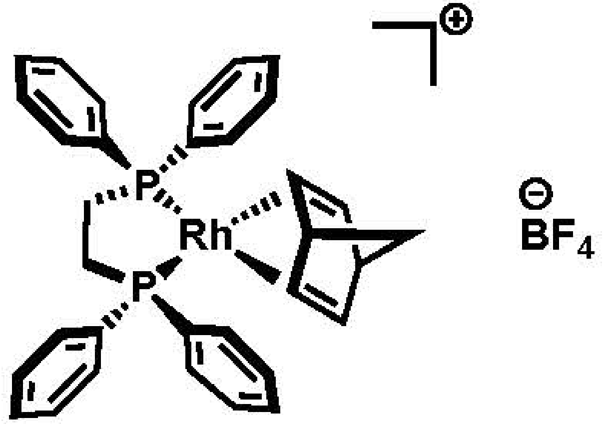
2: see this:



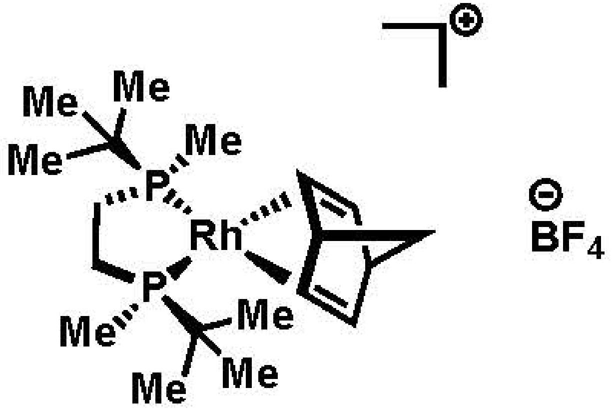
Extensive studies by Osborn and Halpern have elucidated the mechanistic differences between directed homogeneous hydrogenation of olefins between neutral Wilkinson's catalyst $Rh(PPh_3)_3Cl$, **1**, and cationic $[Rh(NBD)(DIPHOS)][BF_4]$, **2**.



Wilkinson's Catalyst
1



$[Rh(NBD)(DIPHOS)][BF_4]$
2



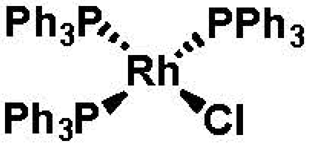
3

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

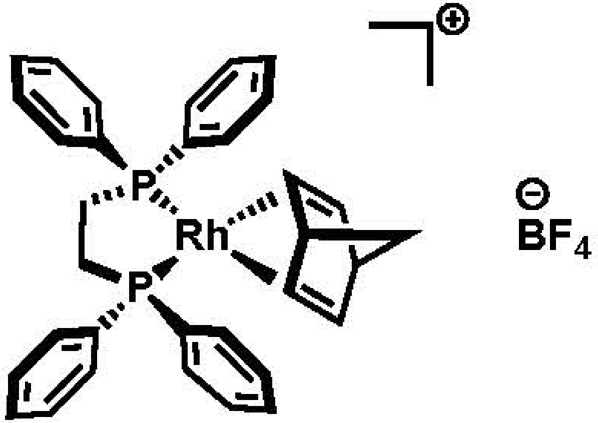
Answers for previous slide:

For catalyst 1, it is H_2 first, meaning H_2 oxidative addition first.
For catalyst 2, it is olefin first, meaning the binding of olefin at first.
See lecture notes.

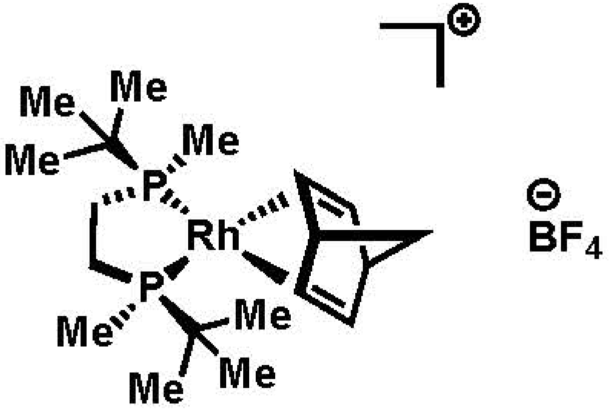
Extensive studies by Osborn and Halpern have elucidated the mechanistic differences between directed homogeneous hydrogenation of olefins between neutral Wilkinson's catalyst $Rh(PPh_3)_3Cl$, **1**, and cationic $[Rh(NBD)(DIPHOS)][BF_4]$, **2**.



Wilkinson's Catalyst
1



$[Rh(NBD)(DIPHOS)][BF_4]$
2



3

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

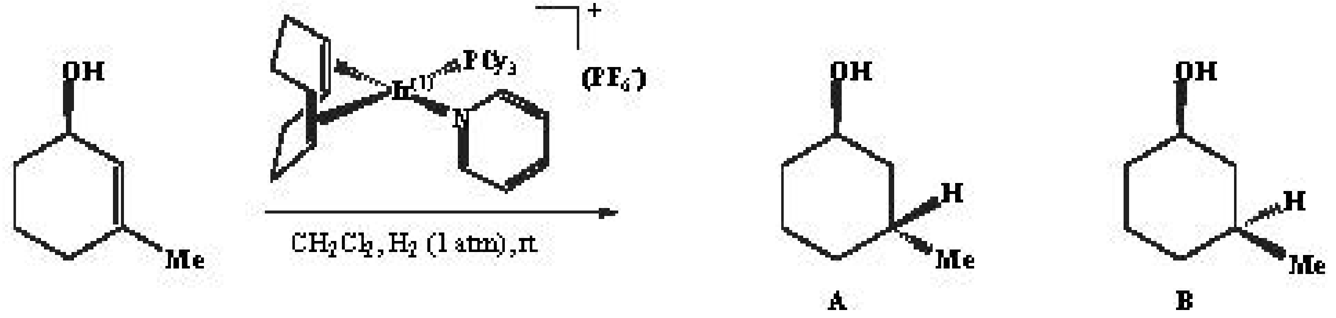
Answers for previous slide:

Catalyst 3 should follow a similar mechanism to catalyst 2.
So it is olefin first, meaning the binding of olefin at first.

Potential advantages:

1. Alkyl groups instead of ary groups. More electron rich, so good for oxidative addition.
2. The ligand in 3 is chiral. So potential application in asymmetric catalysis.

High catalyst loadings: diminished yields and selectivities



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

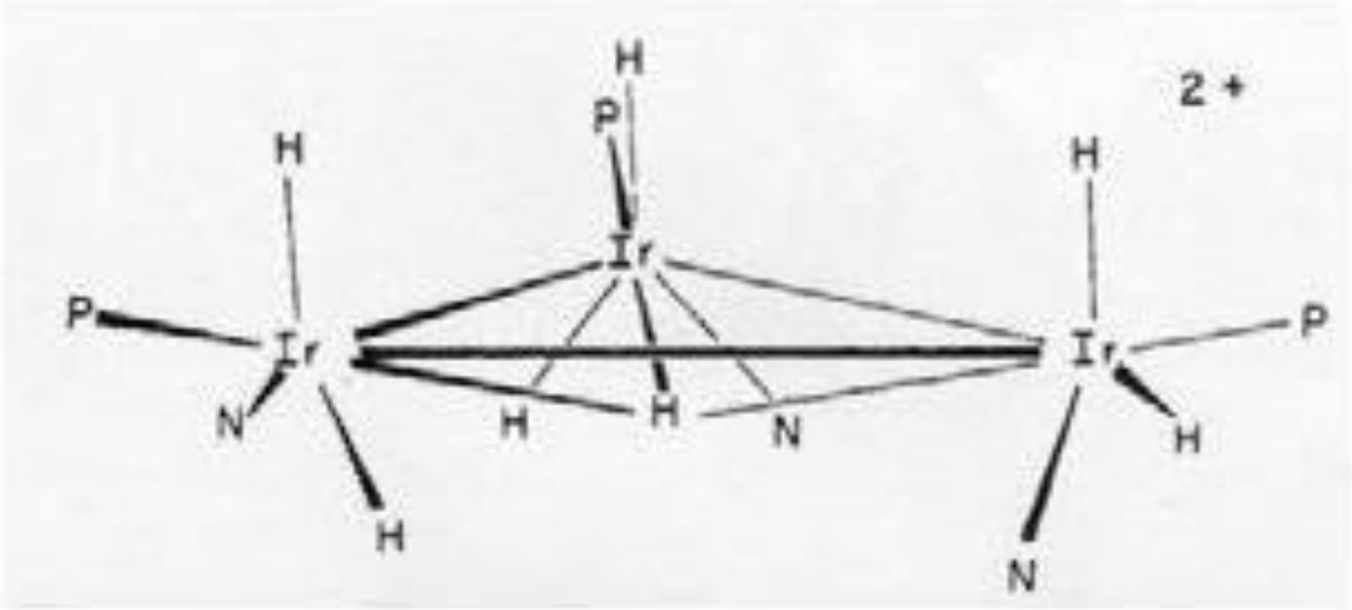
Stork *JACS* **1983** (105) 1072.
Crabtree *JOC* **1986** (51) 2655.

Why?

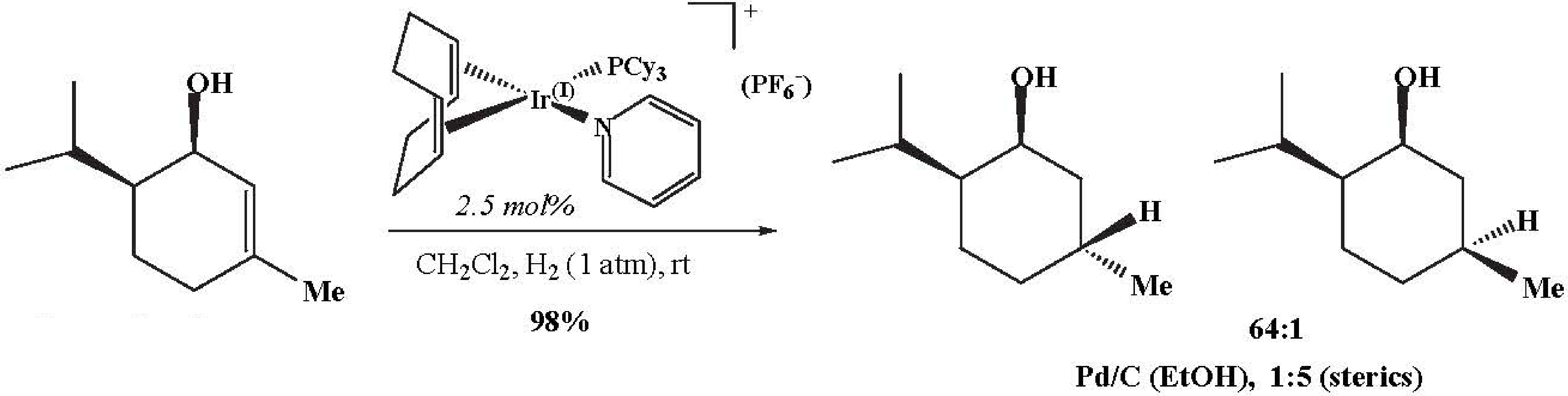
Answers for previous slide:

At higher catalyst concentrations, the catalyst aggregates to form less active compounds. See the next slide for the structure of one of the aggregates.

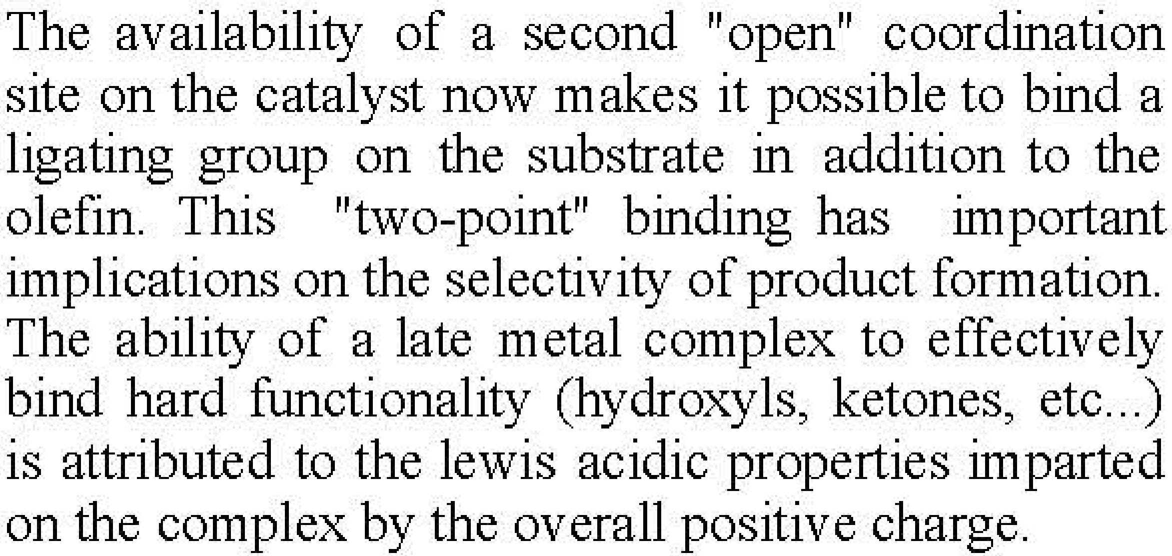
Dimished yields are observed with higher catalyst loadings. This can be rationalized on the basis that higher catalyst loadings promote the irreversible trimerization of the coordinatively unsaturated catalysts to yield inactive triiridium hydride bridged complexes. Such complexes have been isolated by Crabtree from reaction mixtures of more sterically hindered olefins that did not proceed to completion.



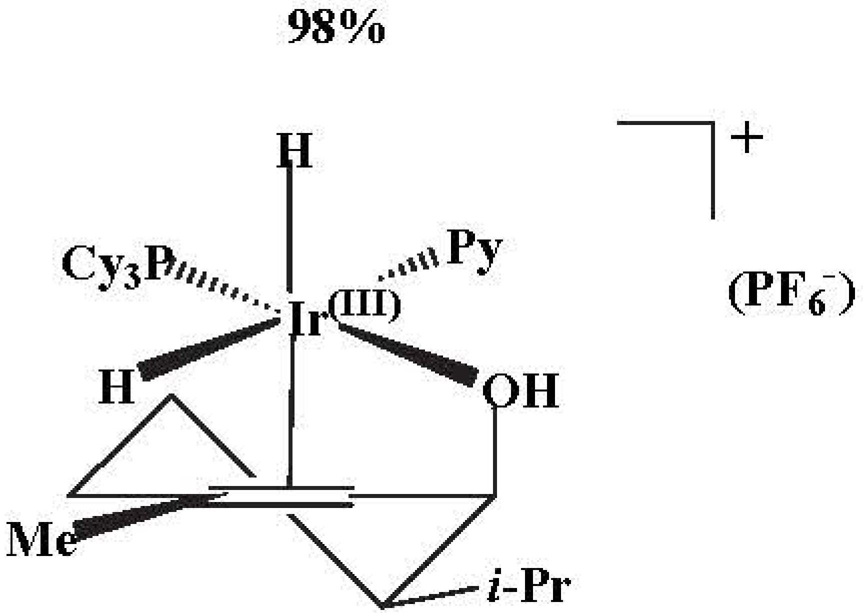
Propose a reason for the selectivity observed in this process.



Answer to the previous slide:

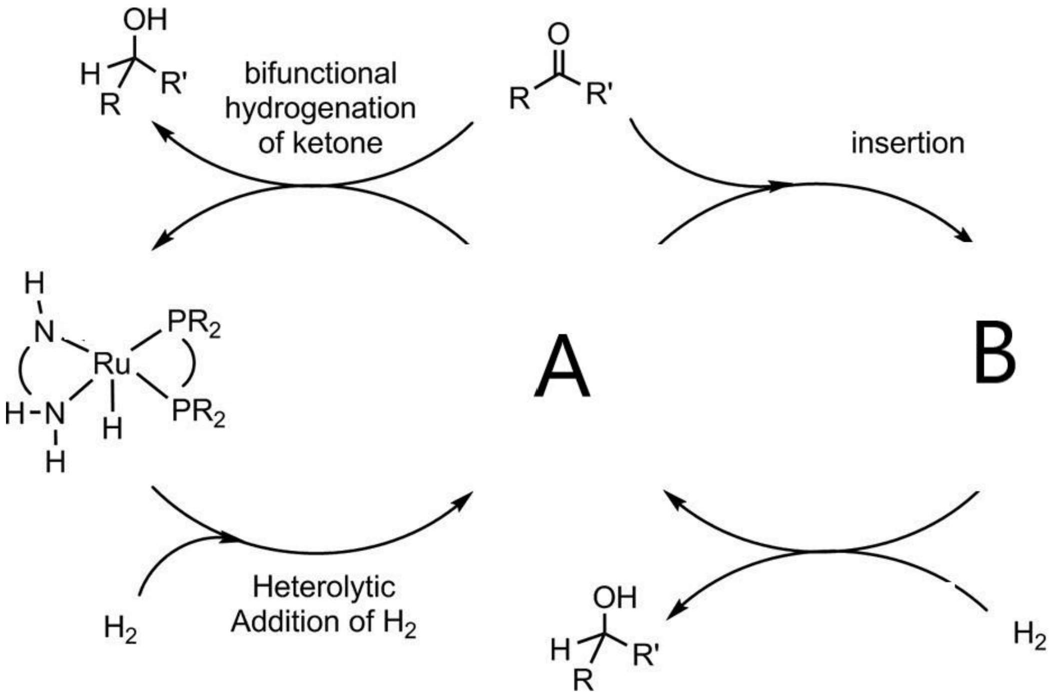


The availability of a second "open" coordination site on the catalyst now makes it possible to bind a ligating group on the substrate in addition to the olefin. This "two-point" binding has important implications on the selectivity of product formation. The ability of a late metal complex to effectively bind hard functionality (hydroxyls, ketones, etc...) is attributed to the lewis acidic properties imparted on the complex by the overall positive charge.



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

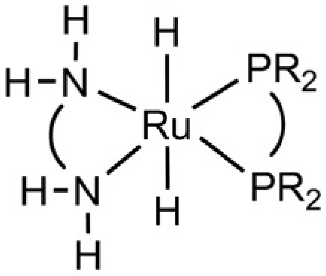
1. (1) What is the oxidation state of the Ru catalyst in the left.
2. (2) Draw the structure of intermediates A and B
3. (3) What is the oxidation state of Ru in A and B?



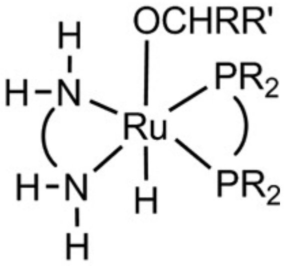
(1) What is the oxidation state of the Ru catalyst in the left.

+2

(2)



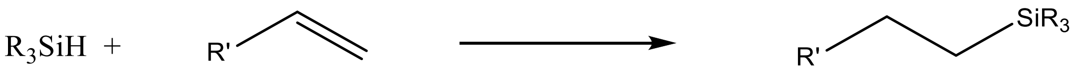
A



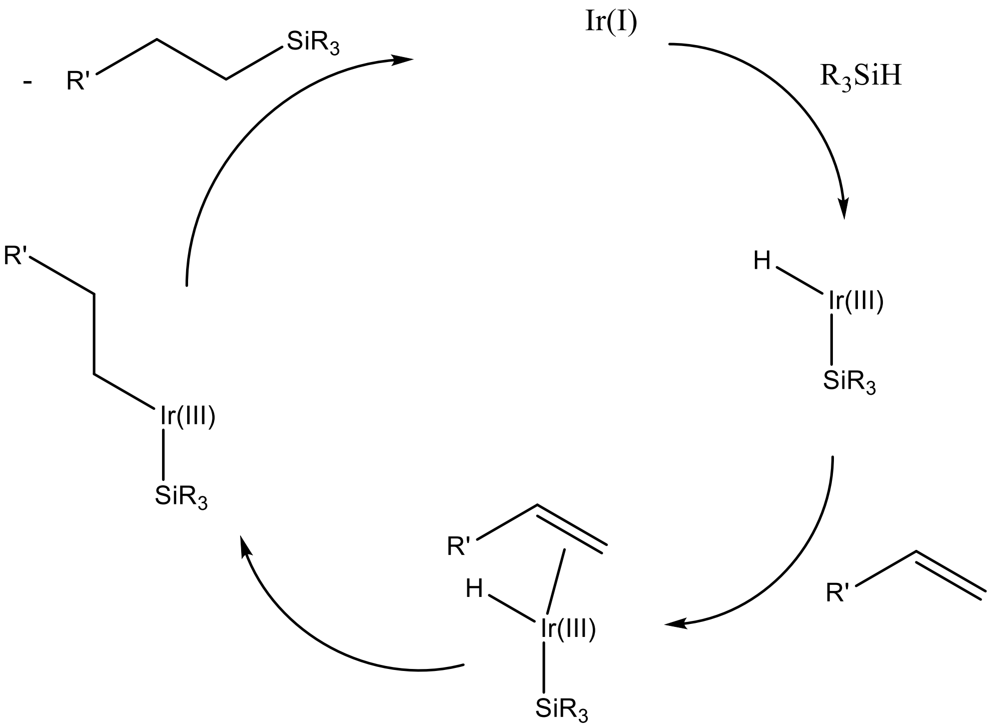
B

(3) +2

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.


Ir(I)
R$_3$SiH
H
Ir(III)
SiR$_3$
R'
- R' SiR$_3$