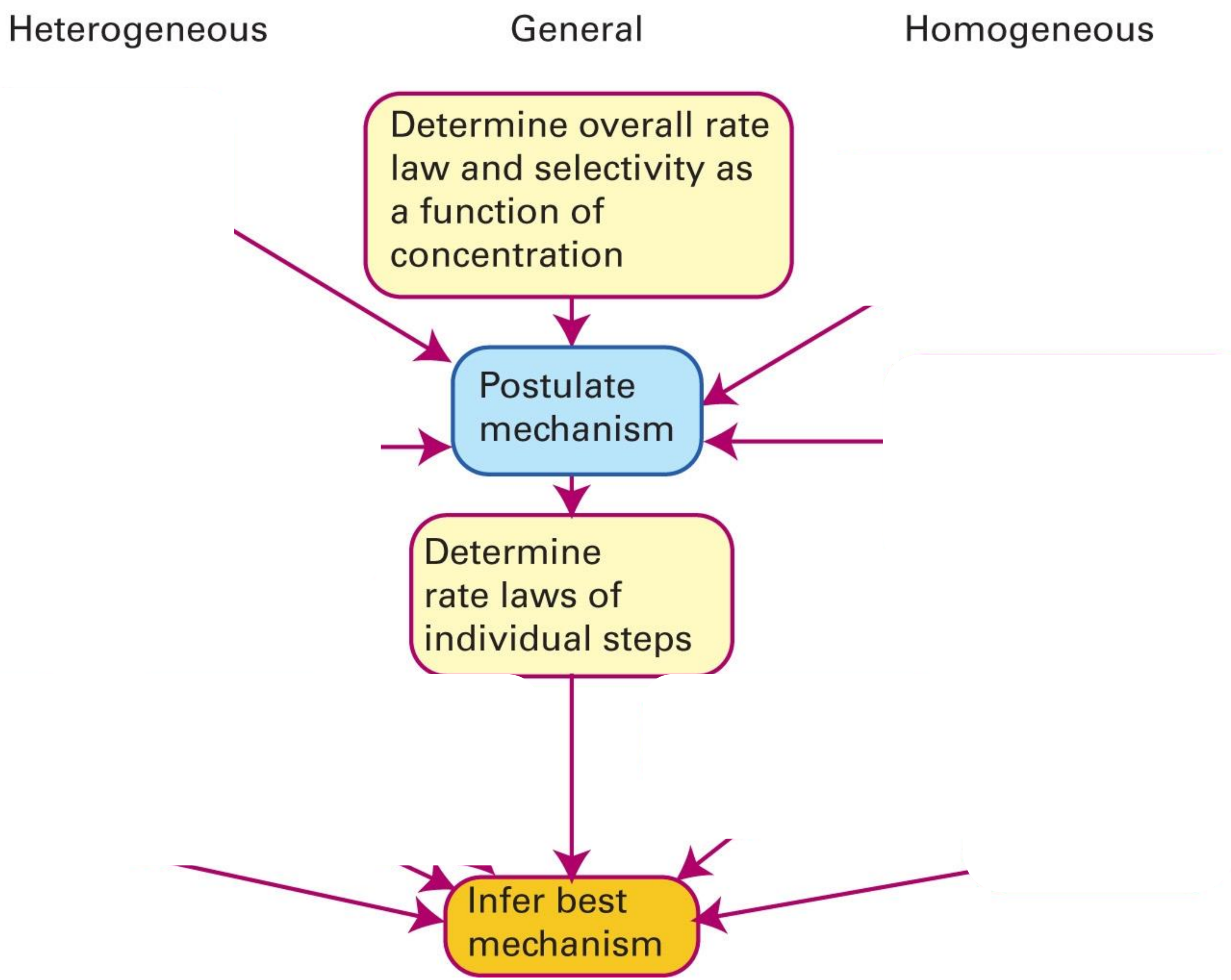
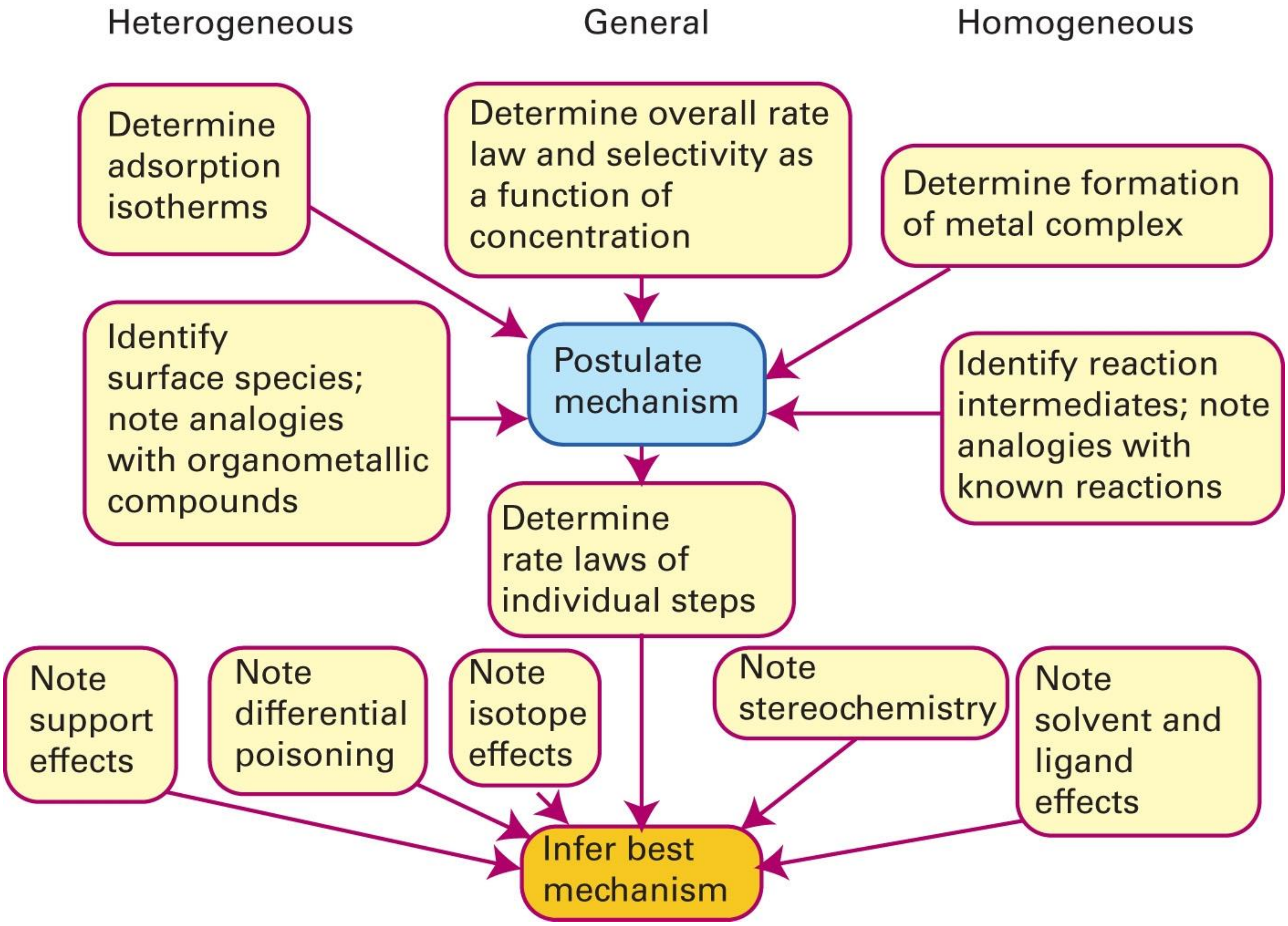
Catalysis

Catalyst Development

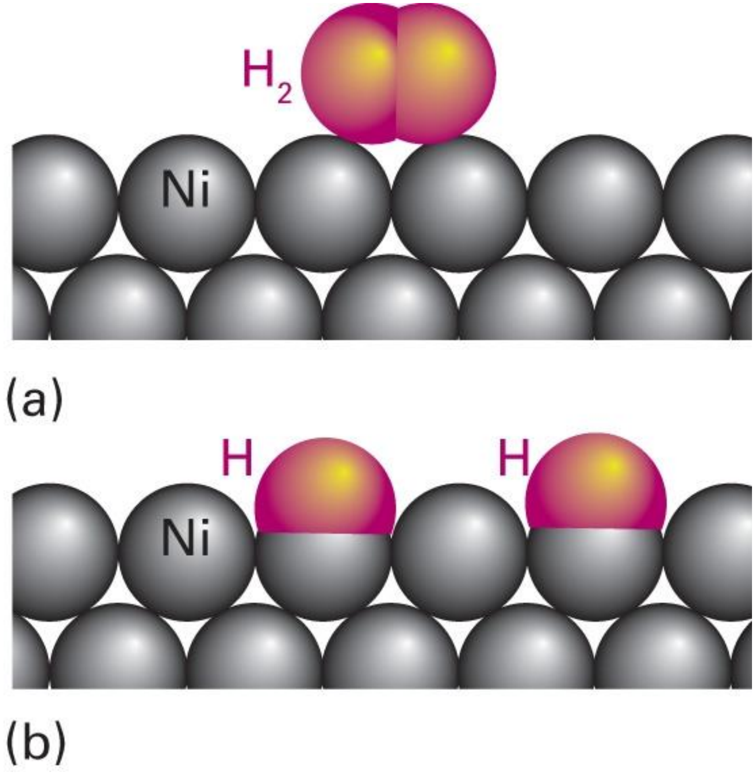


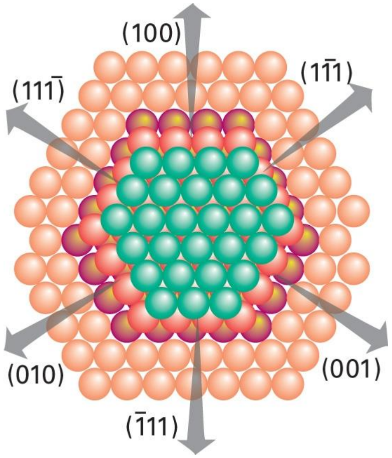
Catalyst Development

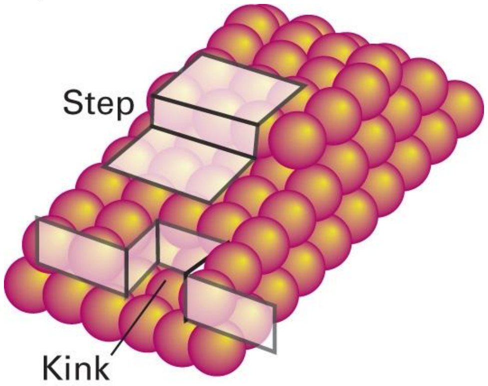


Schematic representation of physisorption and chemisorption of Hydrogen on a nickel metal surface

Schematic representation of Diverse sites exposed on a Metal surface—a) different Exposed planes, edges; b) steps And kinks from irregularities



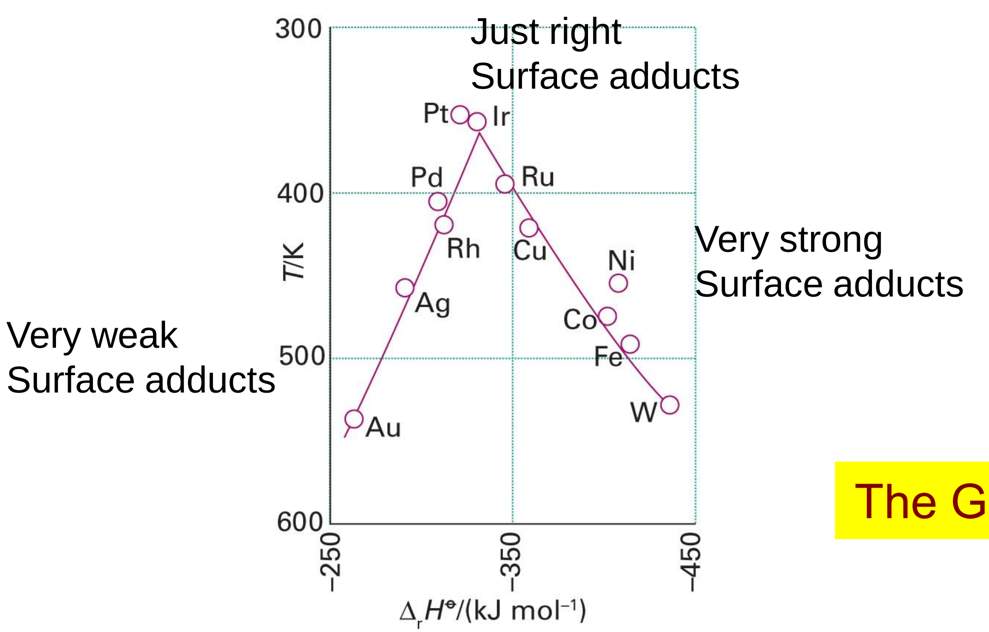


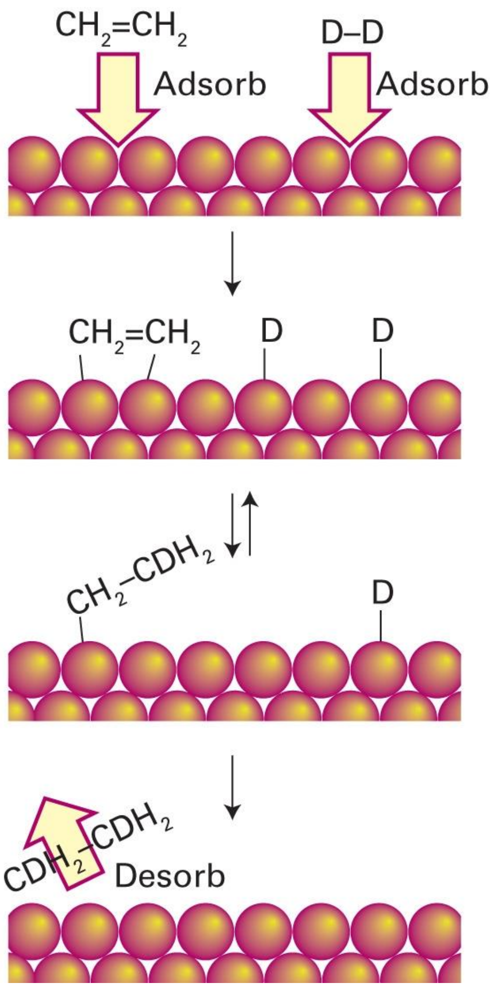


Hydrogenation of alkenes on supported metal Involves H_2 dissociation and migration of H-atoms to an adsorbed ethene molecule. (Paul Sabatier, 1890)

Mechanism: All isotopomers are seen, therefore highly Reversible prior to loss of the ethane.

Volcano diagrams relate stability of products on Surface: Temp. for a set rate of release vs. the Enthalpy. *Intermediate values of ΔH_f, with the rate being a combination of the rate of adsorption and the rate of desorption gives best catalyst.*

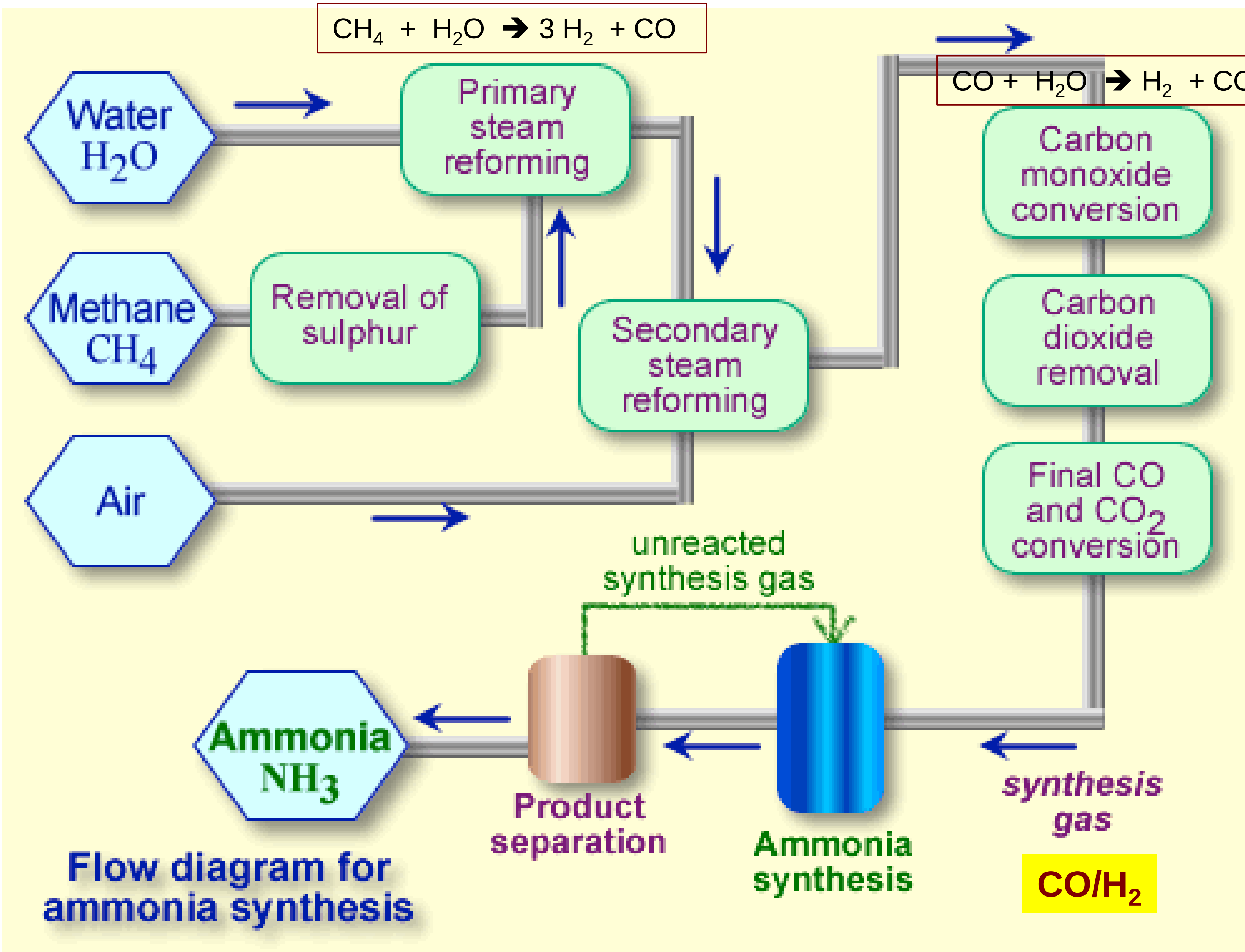




The Goldilocks' Effect

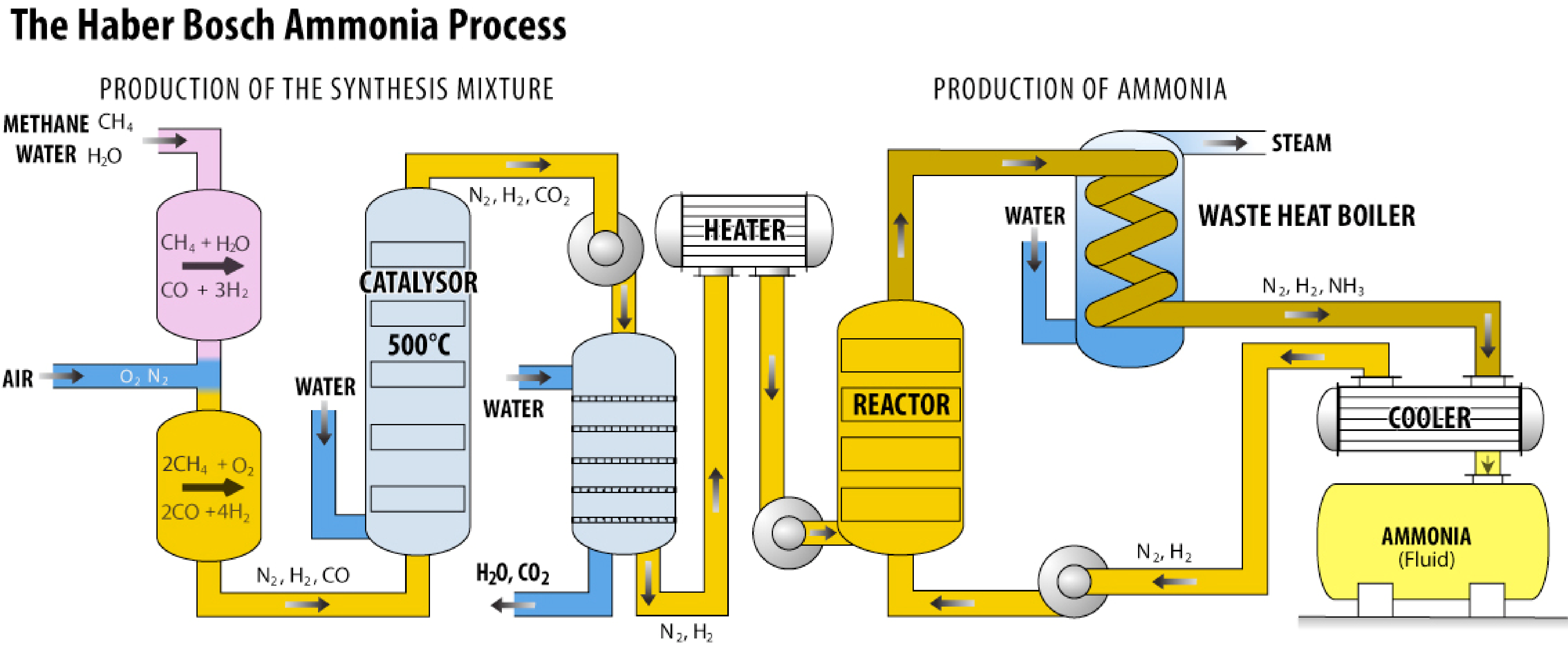
A Prominent Example of Heterogeneous Hydrogenation Catalysis: Ammonia Synthesis

http://www.greener-industry.org.uk/pages/ammonia/6AmmoniaPMHaber.htm



$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \ (\Delta H = -46 kJ\ mol^{-1})$$

500 x 10^6 tons/year; Known as “population detonator”



http://www.greener-industry.org.uk/pages/ammonia/6AmmoniaPMHaber.htm

Ammonia Synthesis

The synthesis gas is compressed to 100 - 250 atmospheres, heated to 350 - 550ºC and passed over an iron oxide catalyst with potassium hydroxide and alumina promoters.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \; (\Delta H = -46 kJ\ mol^{-1})$$

Under the reactor conditions, the iron oxide (Fe_3O_4) is reduced to give iron particles with many small pores (8 nm in diameter). The alumina prevents the pores in the iron collapsing, which would reduce the surface area. Potassium hydroxide increases the activity of the iron catalyst by donating its outer electron to the iron, increasing its electron density and its ability to bond to the nitrogen.

Further details of this catalysed reaction can be found on the **catalysis site**

The synthesis reactor normally contains 2 - 4 catalyst beds, with heat exchangers or injections of cold process gas to remove heat between catalyst beds. This helps to ensure maximum conversion to ammonia. The ammonia produced is cooled and condensed, with un-reacted gases added back into the synthesis gas and recycled. By continuous recycling of un-reacted gas, yields of up to 98% ammonia are produced.

http://www.greener-industry.org.uk/pages/ammonia/6AmmoniaPMHaber.htm

Conditions

According to the equation, the equilibrium mixture will contain more ammonia:

- When the temperature is lower (the reaction is exothermic in the ammonia direction)
- When pressure is higher (4 moles of reactant gas make 2 moles of product gas)

In practice, the equilibrium is run under conditions of moderate temperatures and pressure.

Low temperatures affect the equilibrium favorably, but the reaction would be too slow. Very high pressures, though favoring product creation, increase the costs of plant construction, and present a greater risk to plant workers.

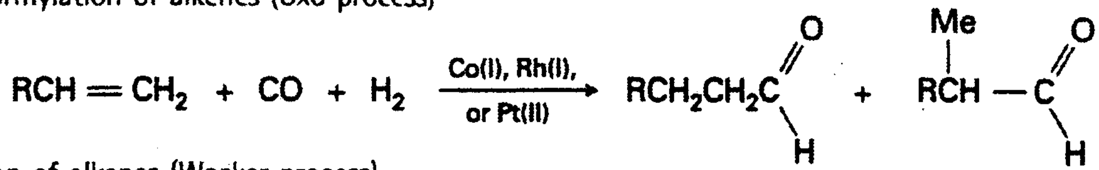
With the conditions used, a yield of approximately 20 - 30 % is achieved from each pass over the catalyst.

http://www.greener-industry.org.uk/pages/ammonia/6AmmoniaPMHaber.htm

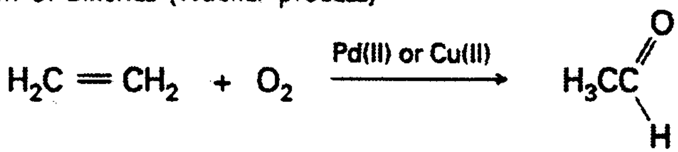
Some homogeneous catalytic processes

(Adapted from J. Halpern, *Inorg. Chim. Acta* 1981, *50*, 11)

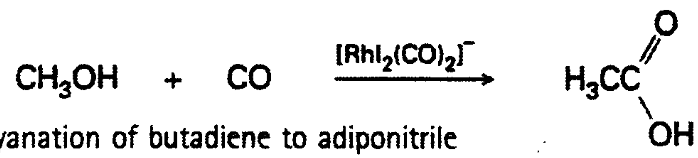
Hydroformylation of alkenes (Oxo process)



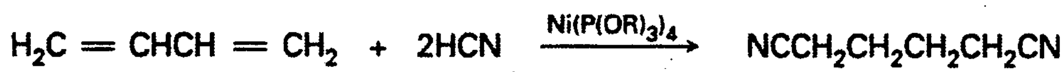
Oxidation of alkenes (Wacker process)



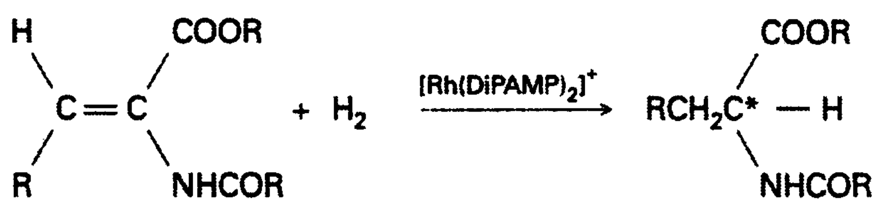
Carbonylation of methanol to acetic acid (Monsanto process)



Hydrocyanation of butadiene to adiponitrile



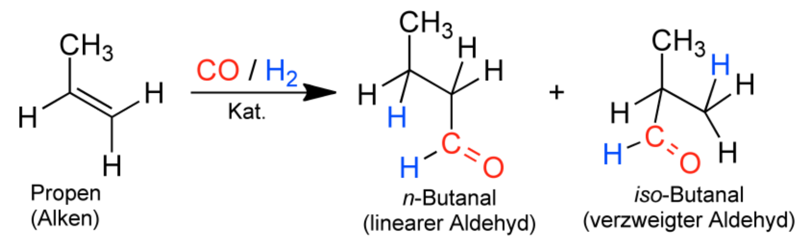
Asymmetric hydrogenation of prochiral alkenes

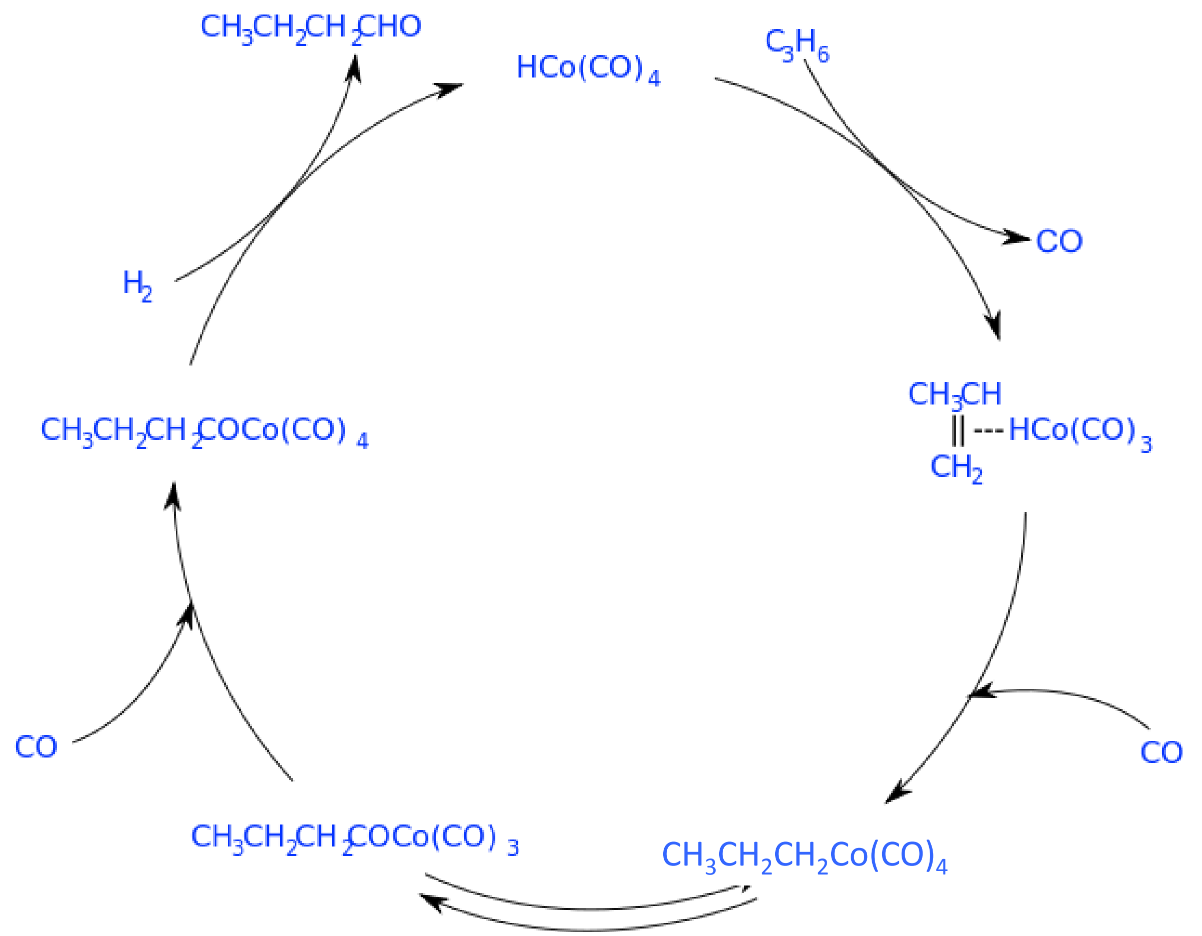


90 per cent L

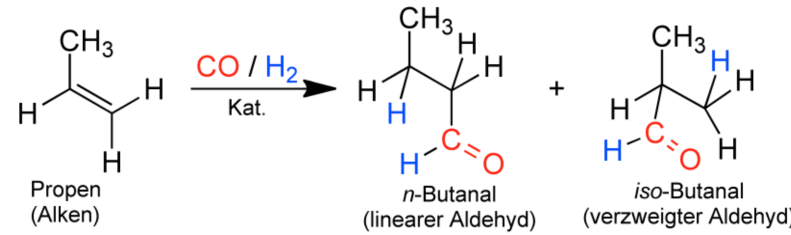
Cyclotrimerization of acetylene

Hydroformylation:

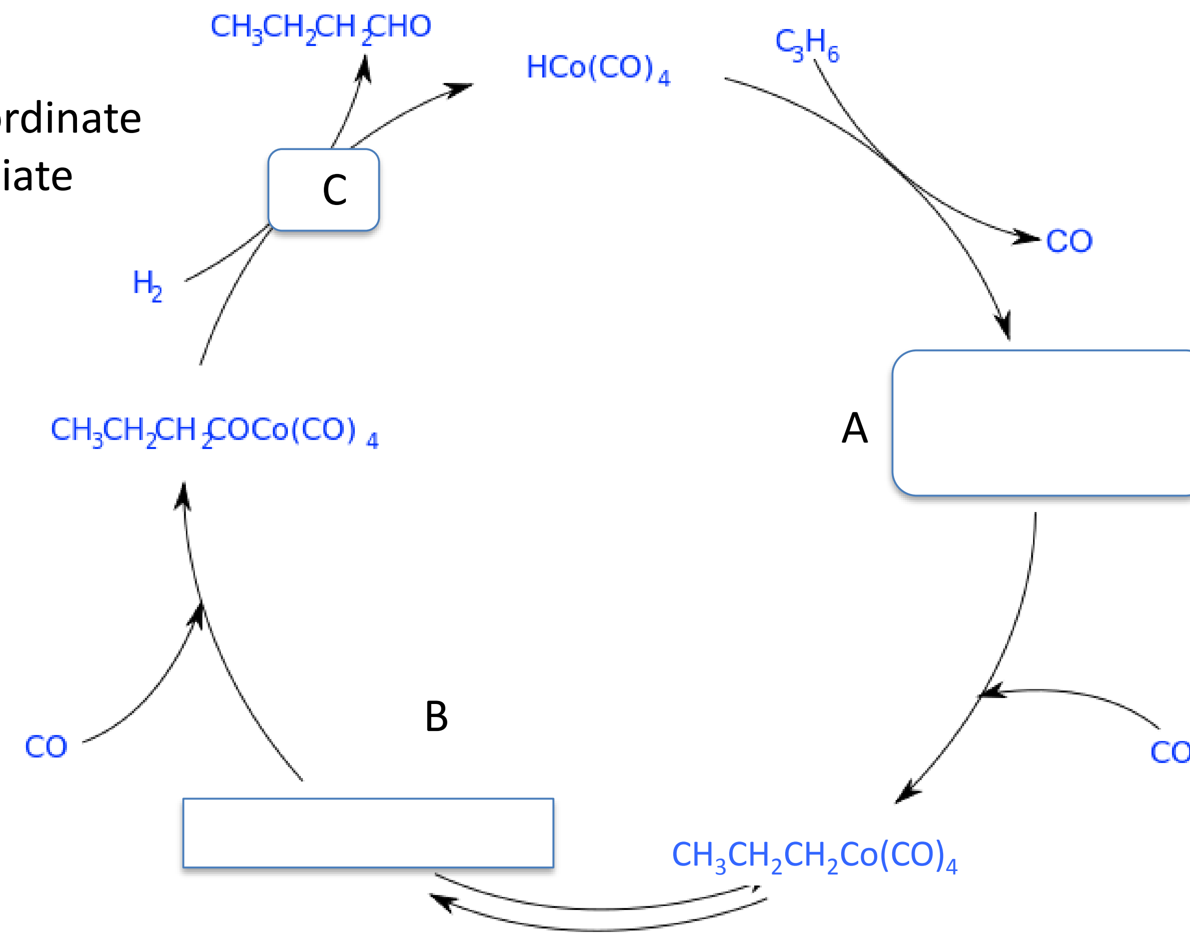




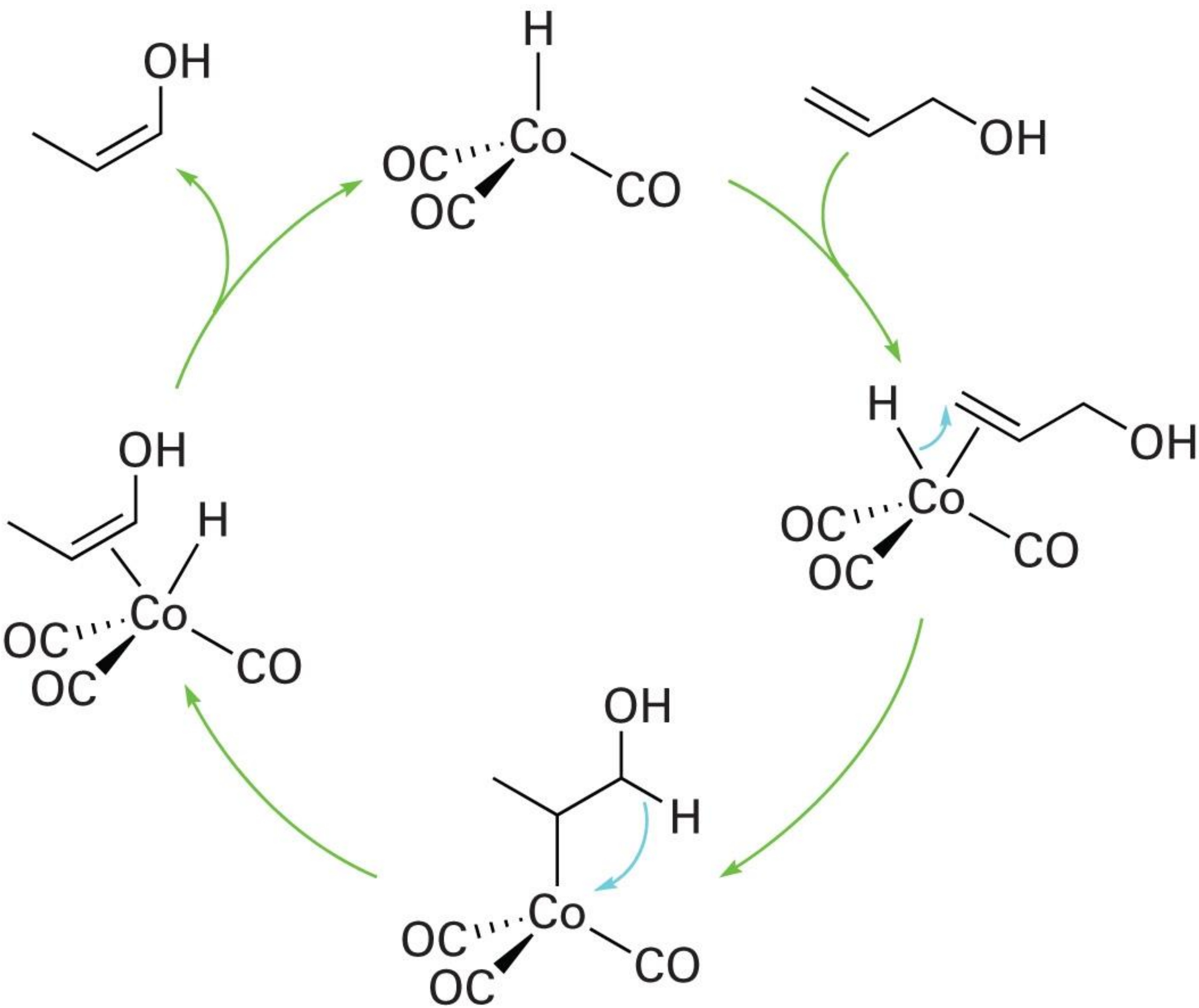
Hydroformylation:



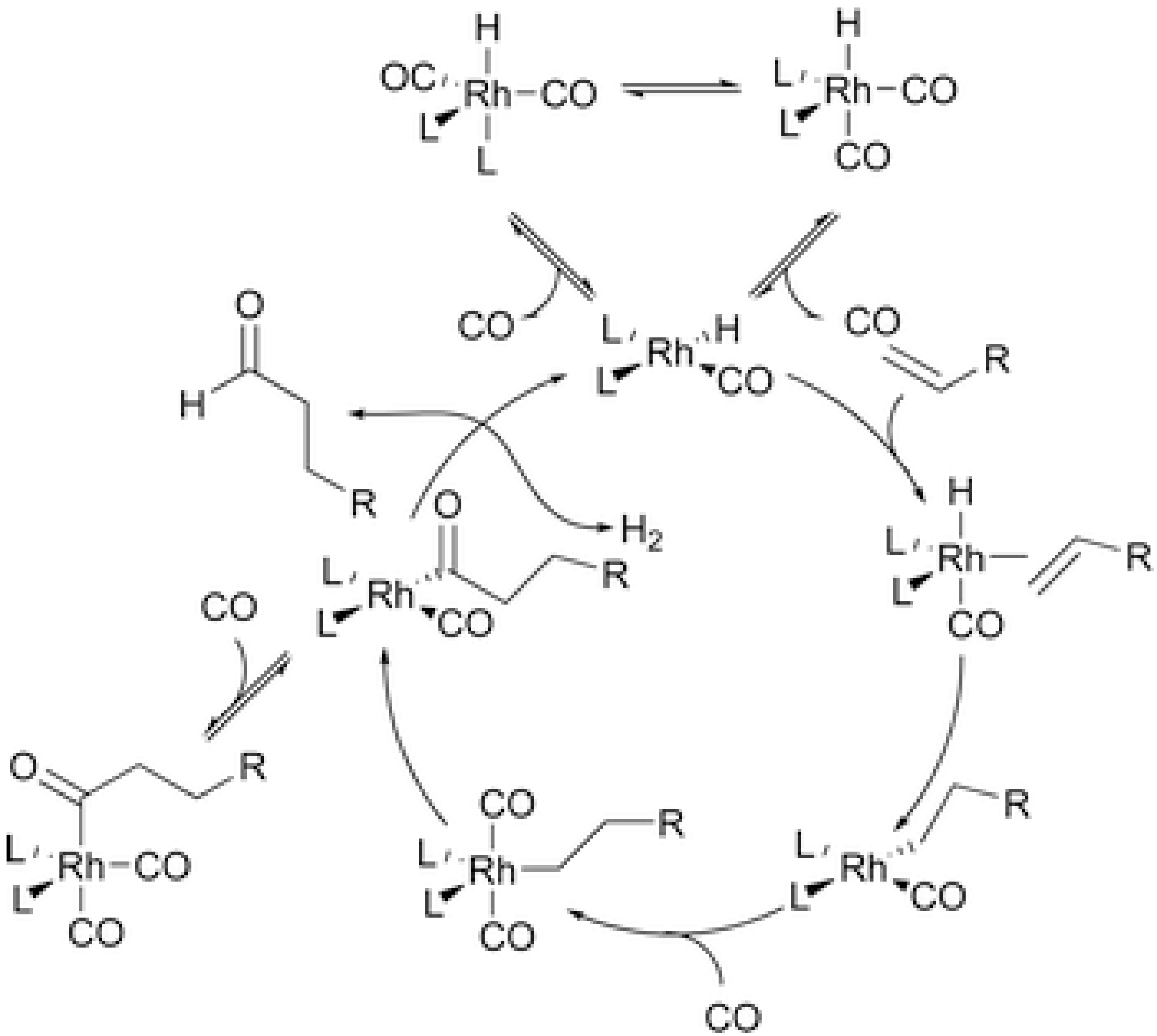
C = 6-coordinate intermediate



Olefin Isomerization

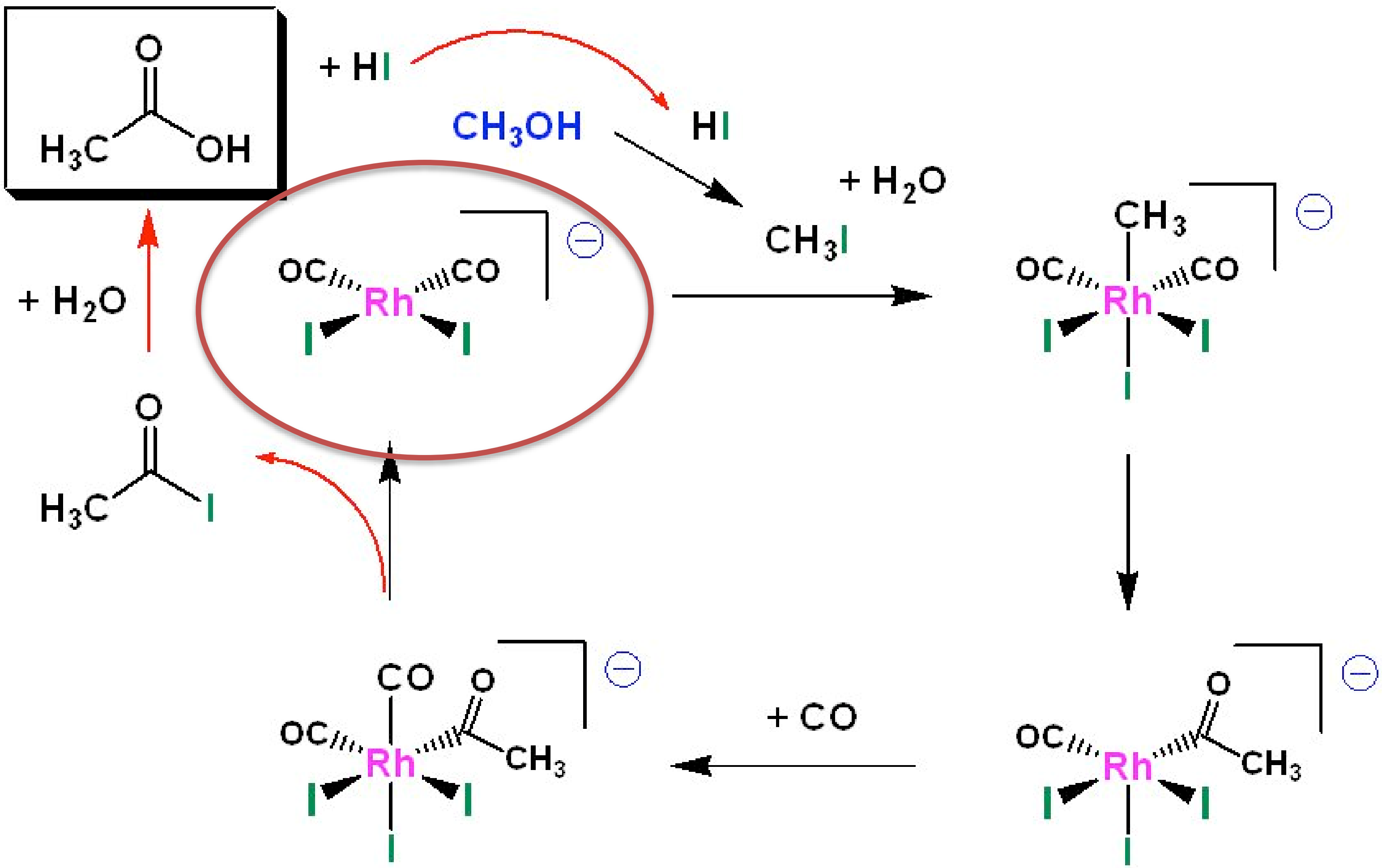


Hydroformylation : Union Carbide process



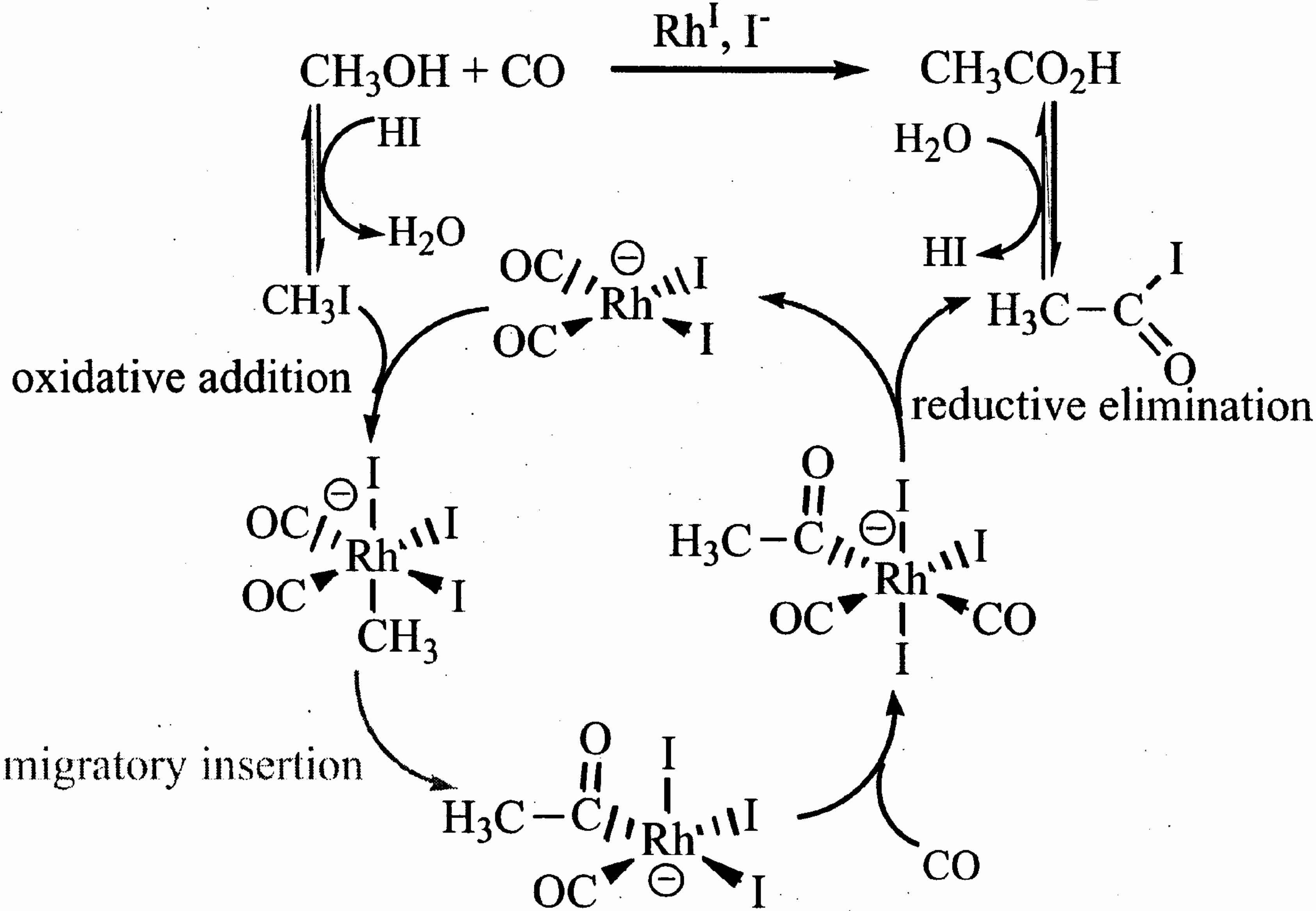
Monsanto Acetic Acid Synthesis

MeOH + CO → MeC(=O)OH



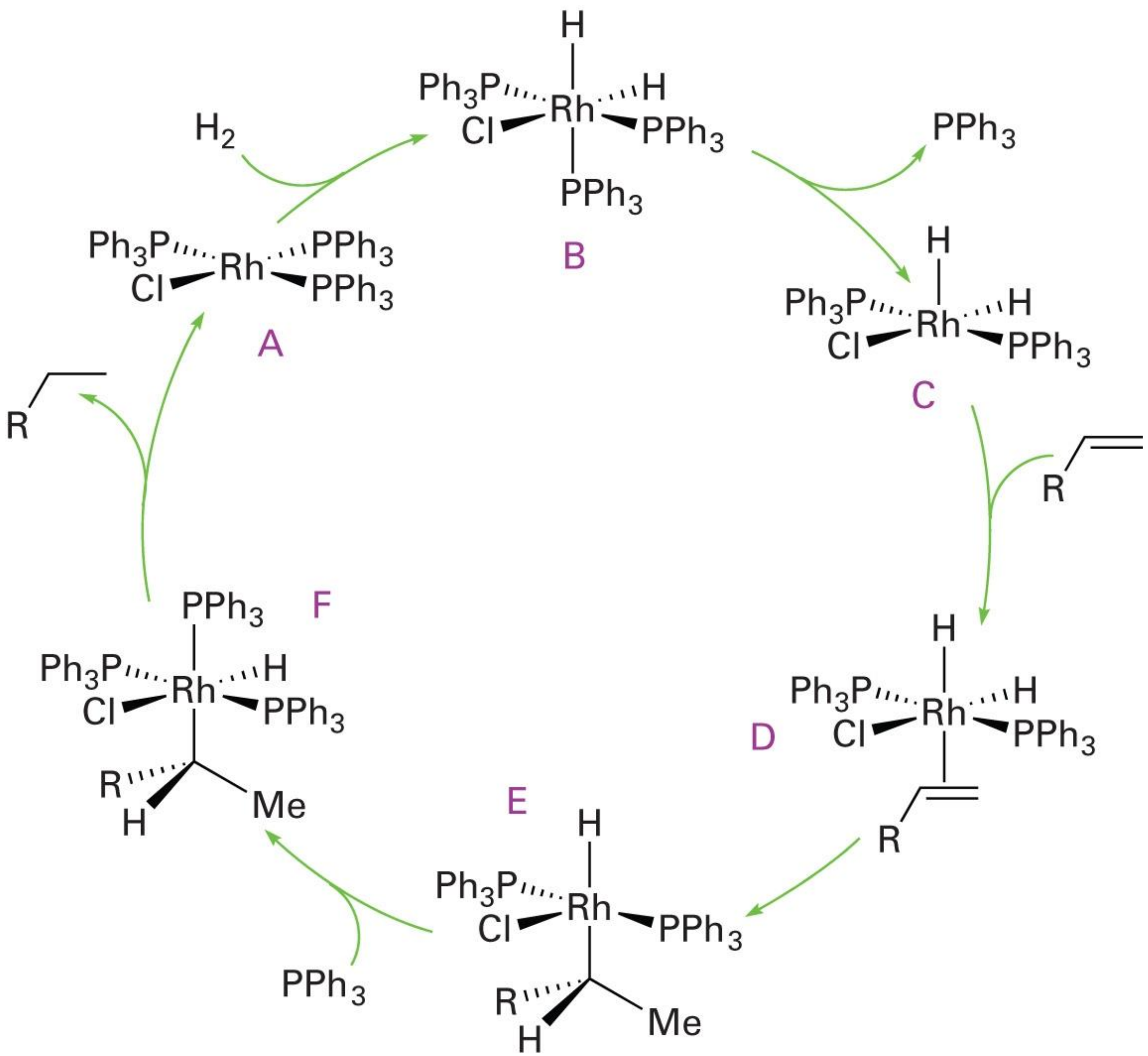
- The reaction is independent of CO pressure
- First order in both rhodium and MeI.
- Rate determining step is the oxidative addition of MeI to the $[Rh(CO)_2I_2]^-$ catalyst.

Catalytic processes - Monsanto's acetic acid process.



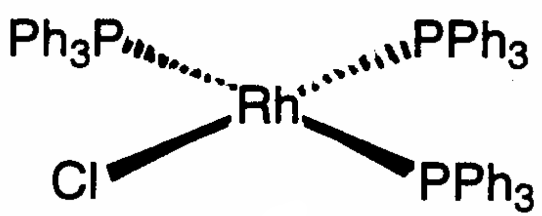
from Collman, Stanford

Hydrogenation of Alkenes: Wilkinson's catalyst and (one of several versions of) the mechanism

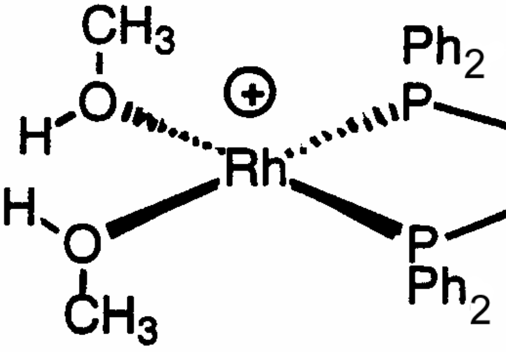


Catalytic homogeneous hydrogenation.

Typical catalysts (achiral):



Wilkinson's catalyst

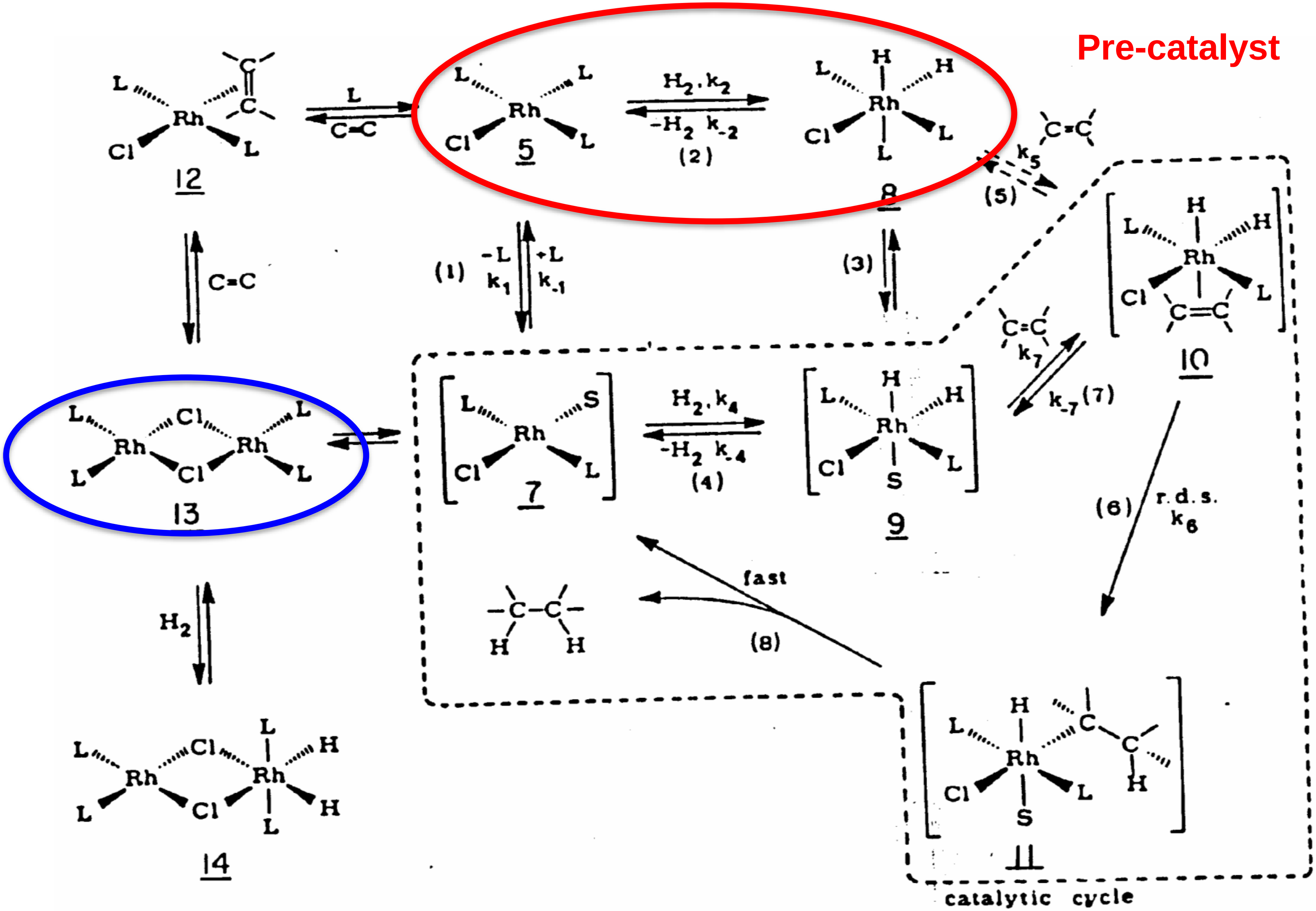


Mechanism:
H_2 activation prior to olefin addition

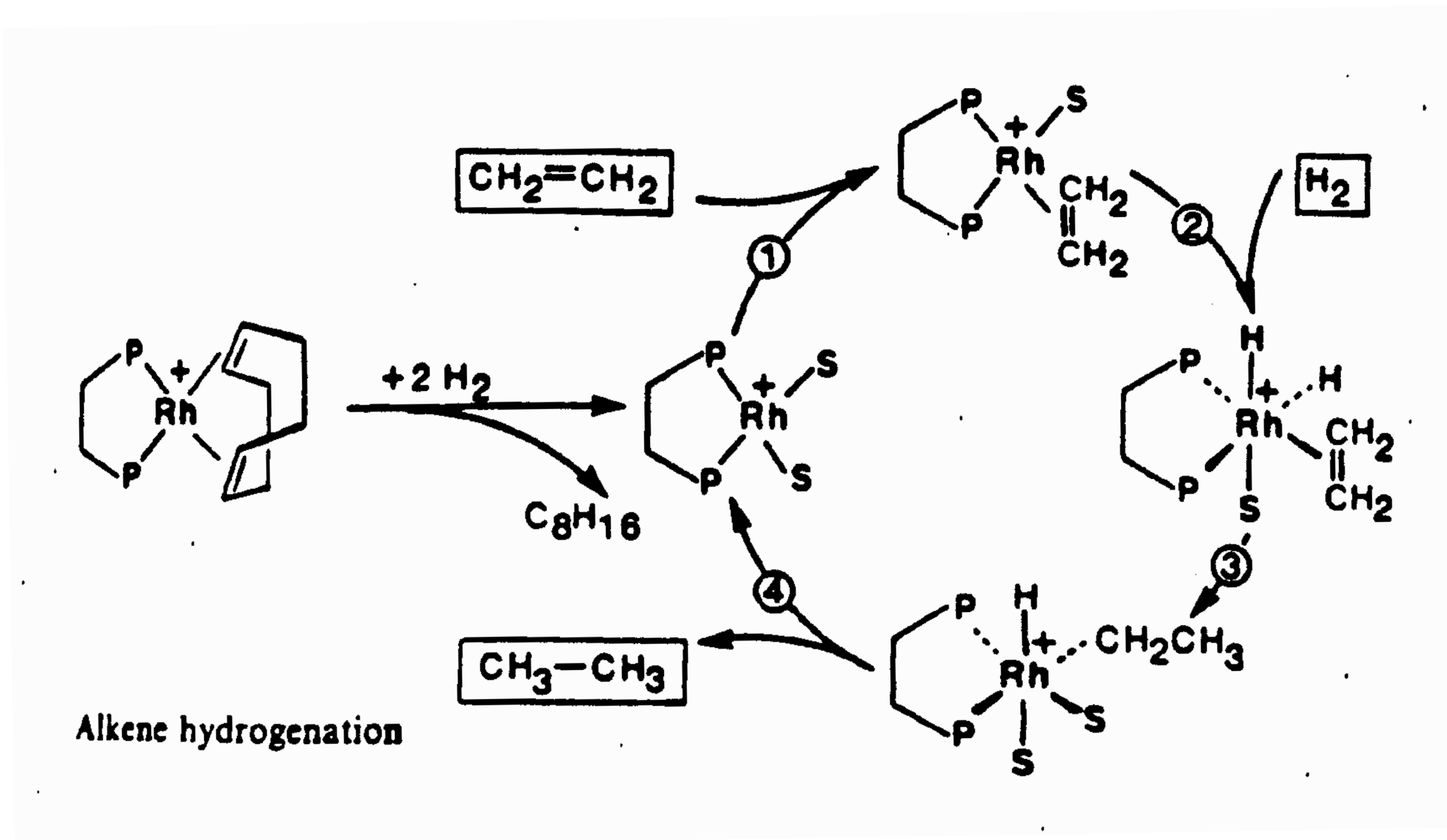
Mechanism:
Olefins add first to cationic catalyst

Wilkinson's Catalyst: Mechanism for Olefin Hydrogenation

Pre-catalyst



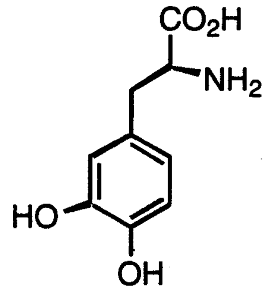
With the Rh(I) cationic precursor: Olefin adds prior to H_2 oxidative addition.*



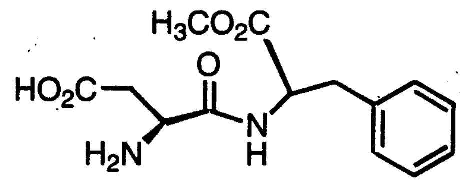
This mechanistic route followed by asymmetric Hydrogenation process

Asymmetric catalytic hydrogenation.

Products of asymmetric catalytic hydrogenation:

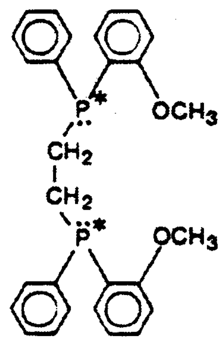


L-dopa (S)

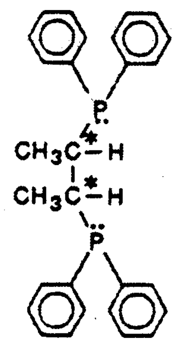


aspartame (Nutrasweet), (S,S)

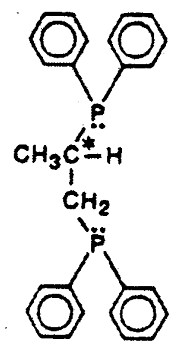
Ligands for asymmetric hydrogenation:



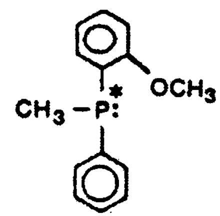
(DIPAMP)



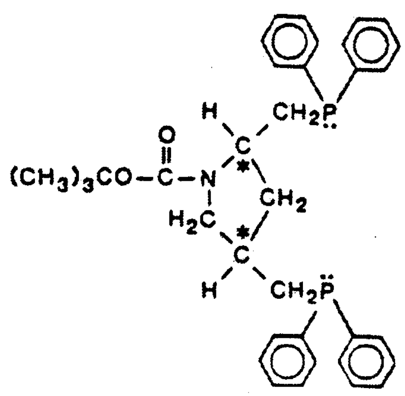
(CHIRAPHOS)



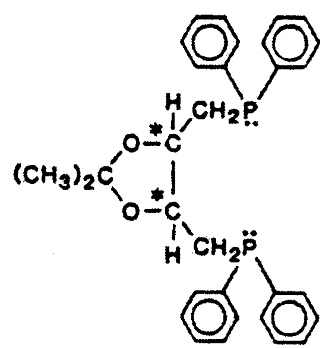
(PROPHOS)



(PAMP)



(BPPM)

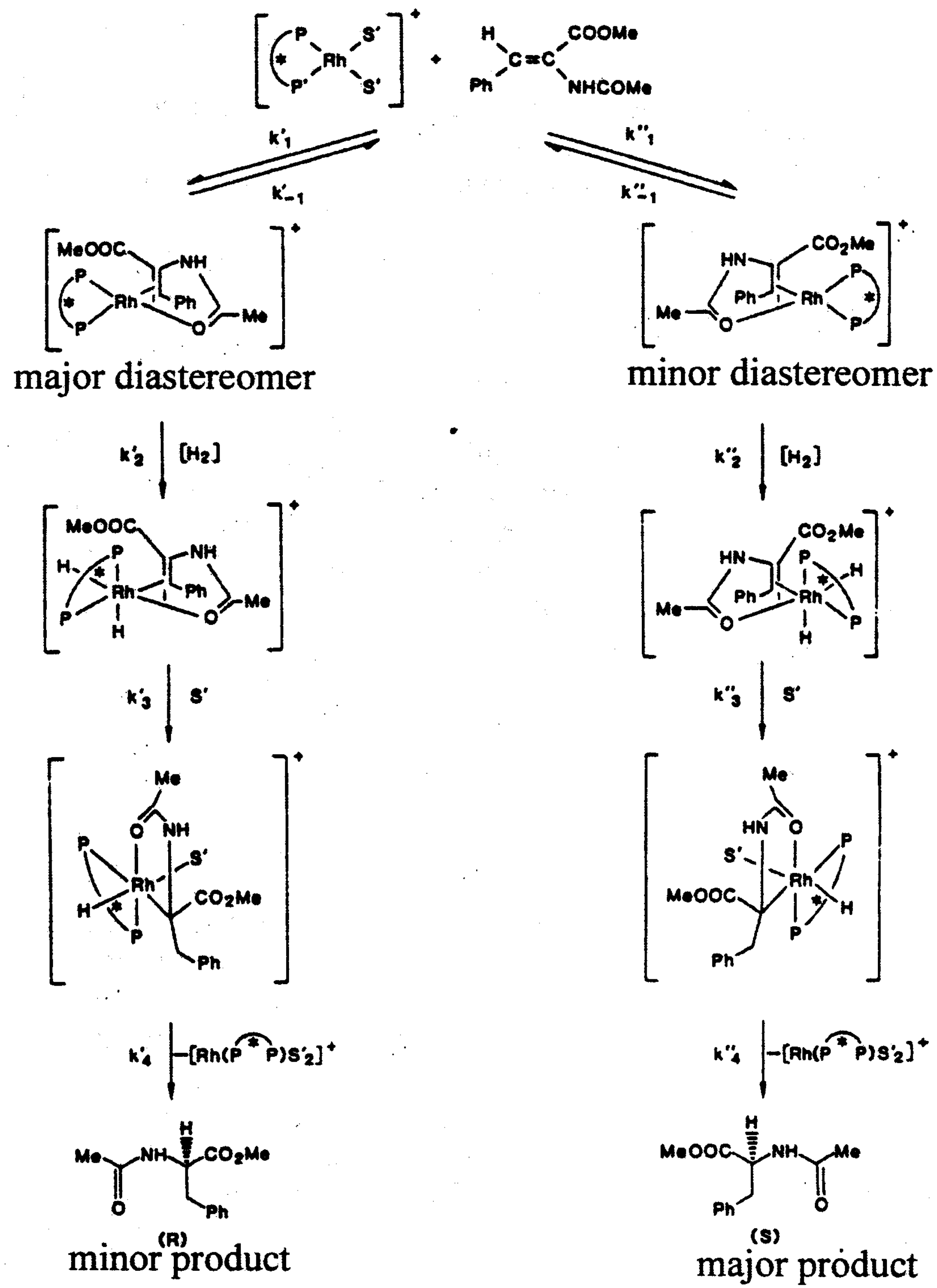


(DIOP)

Halpern, *Science*, **1982**

Halpern
(*Science*, **1982**, p. 401)

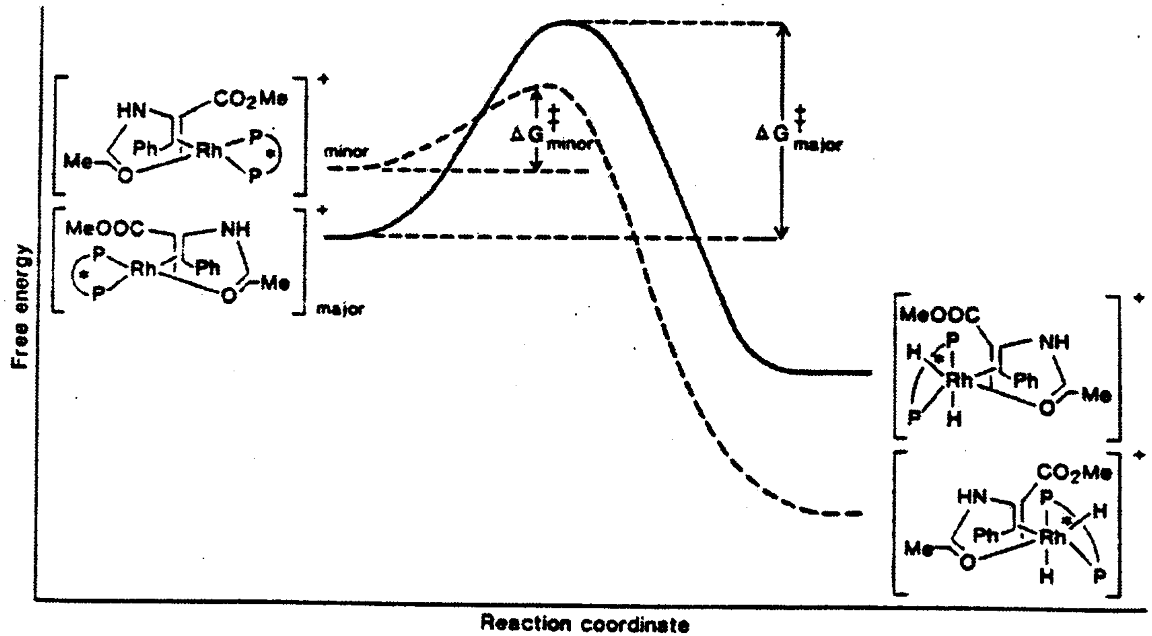
Synthesis of L-dopa: mechanism.



Halpern
(*Science*, **1982**, p. 401)

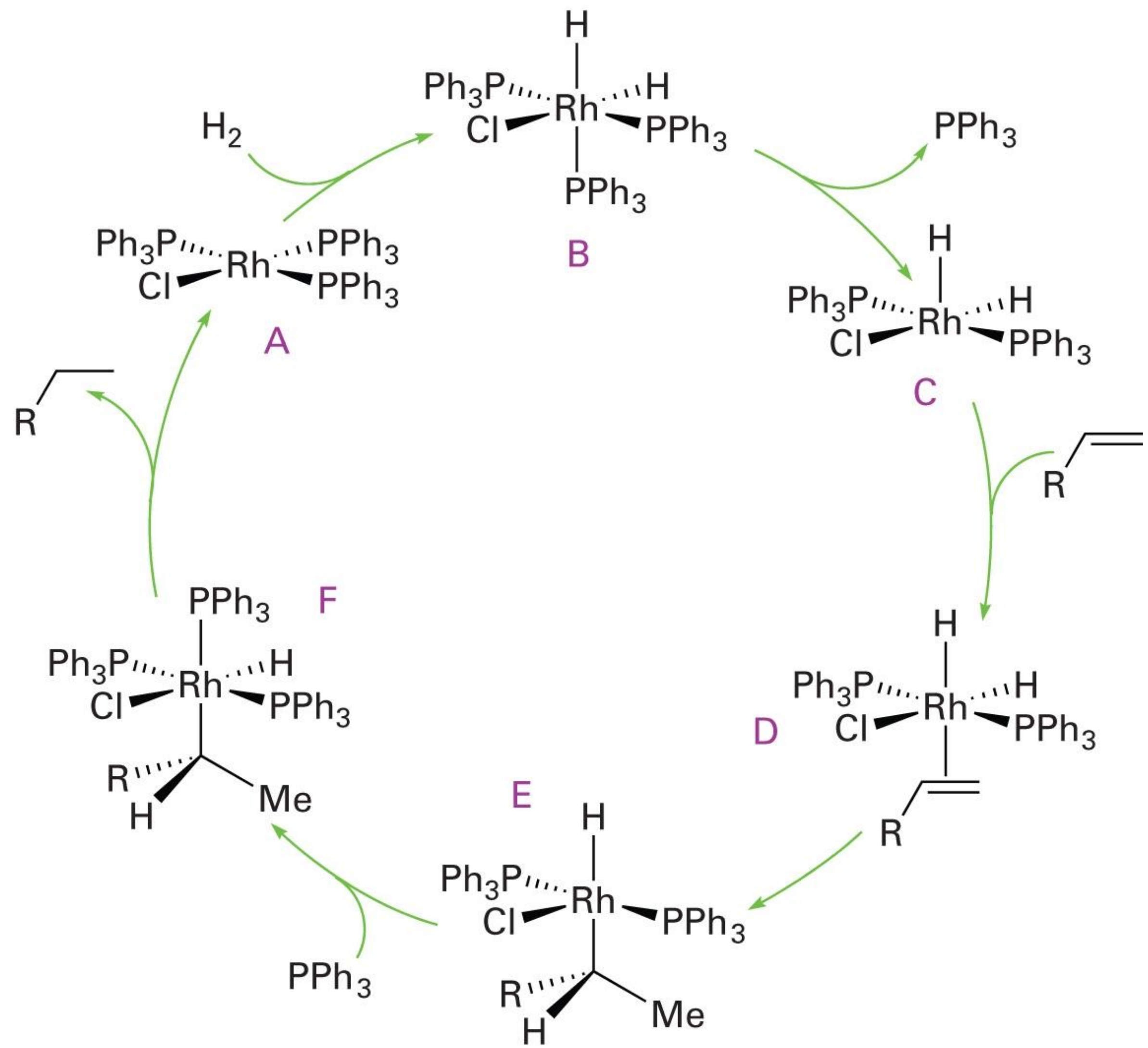
Mechanism of chiral induction in L-dopa synthesis.

1. The ee increases at higher temperature.
2. At higher pressures of H_2, the dominant enantiomer changes from S to R.



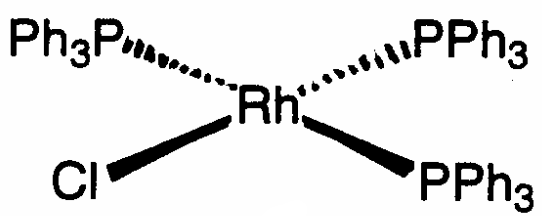
	major diastereomer	minor diastereomer
relative steady-state concentrations	580	1
reactivity toward H_2	10^{-3}	1
absolute reactivity	0.02	1

Hydrogenation of Alkenes: Wilkinson's catalyst and (one of several versions of) the mechanism

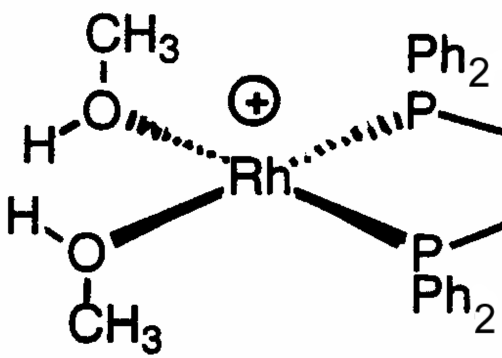


Catalytic homogeneous hydrogenation.

Typical catalysts (achiral):



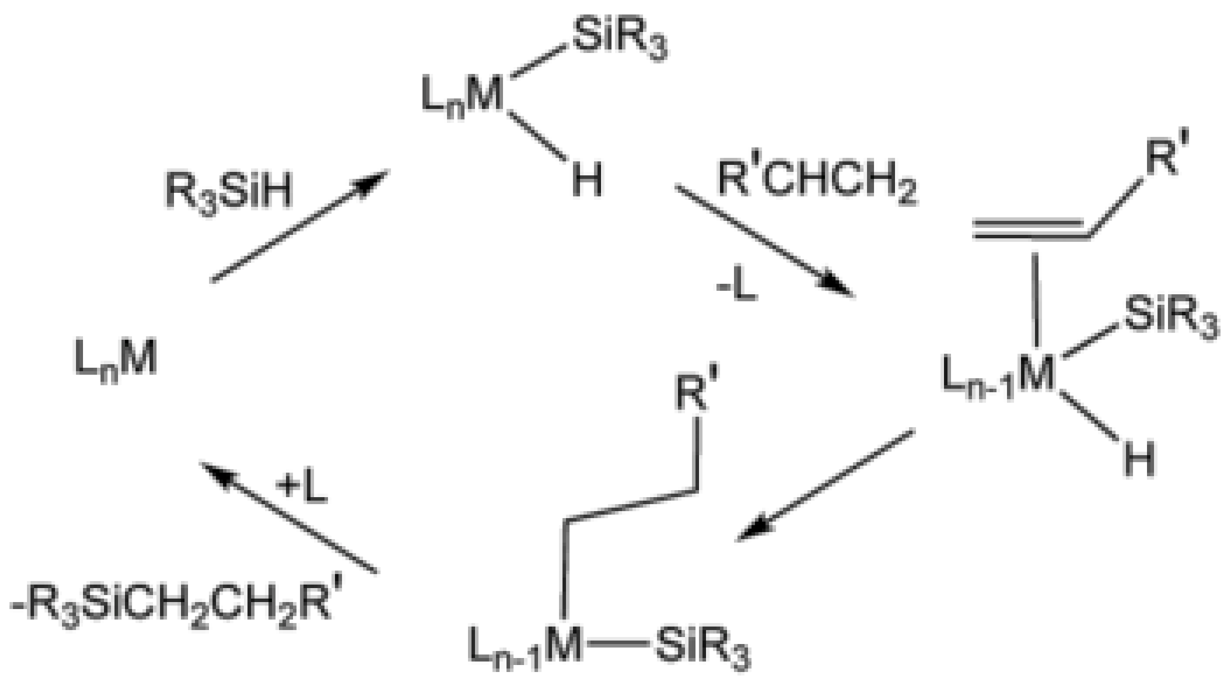
Wilkinson's catalyst



Mechanism:
H_2 **activation prior to olefin addition**

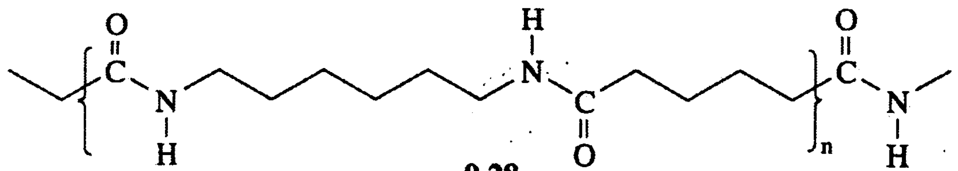
Mechanism:
Olefins add first to cationic catalyst

Hydrosilation of Terminal Alkenes



Industrial catalytic processes - hydrocyanation.

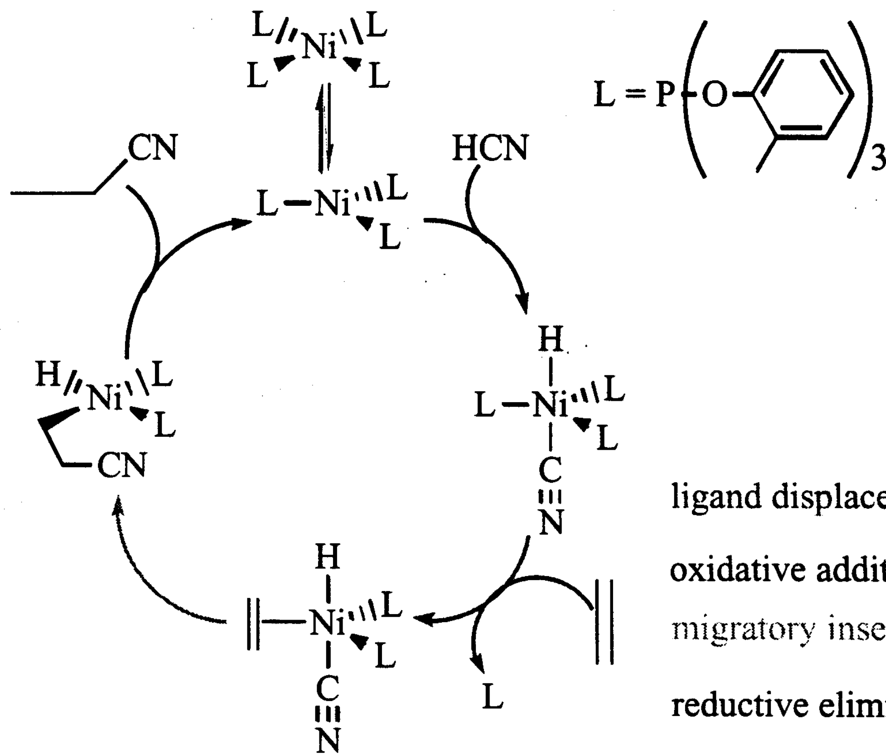
Invented by duPont to produce both precursors for 6,6-nylon:



9.28

Nylon-6, 6

Mechanism (C_2H_4 instead of butadiene, for simplicity):



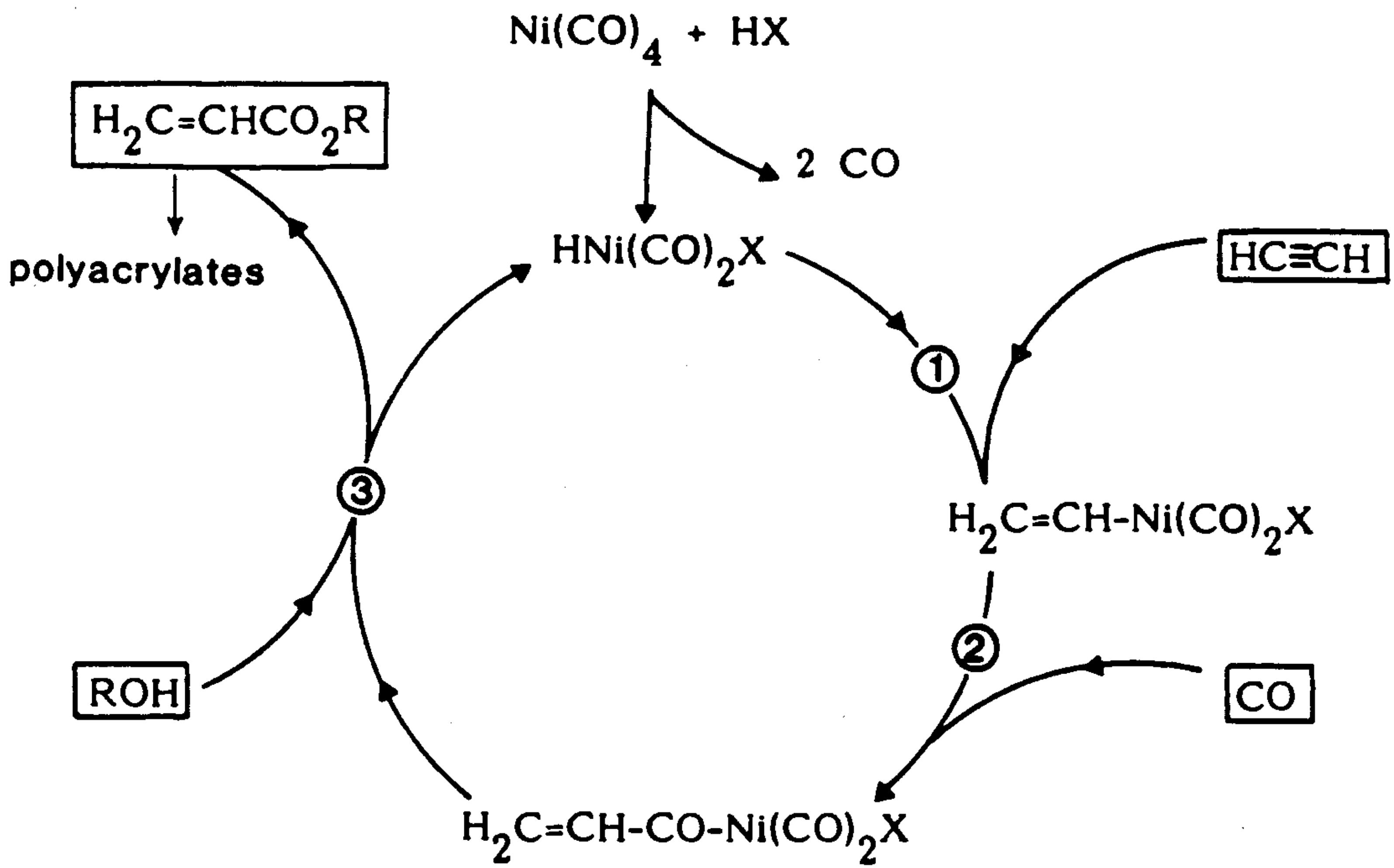
ligand displacement

oxidative addition

migratory insertion

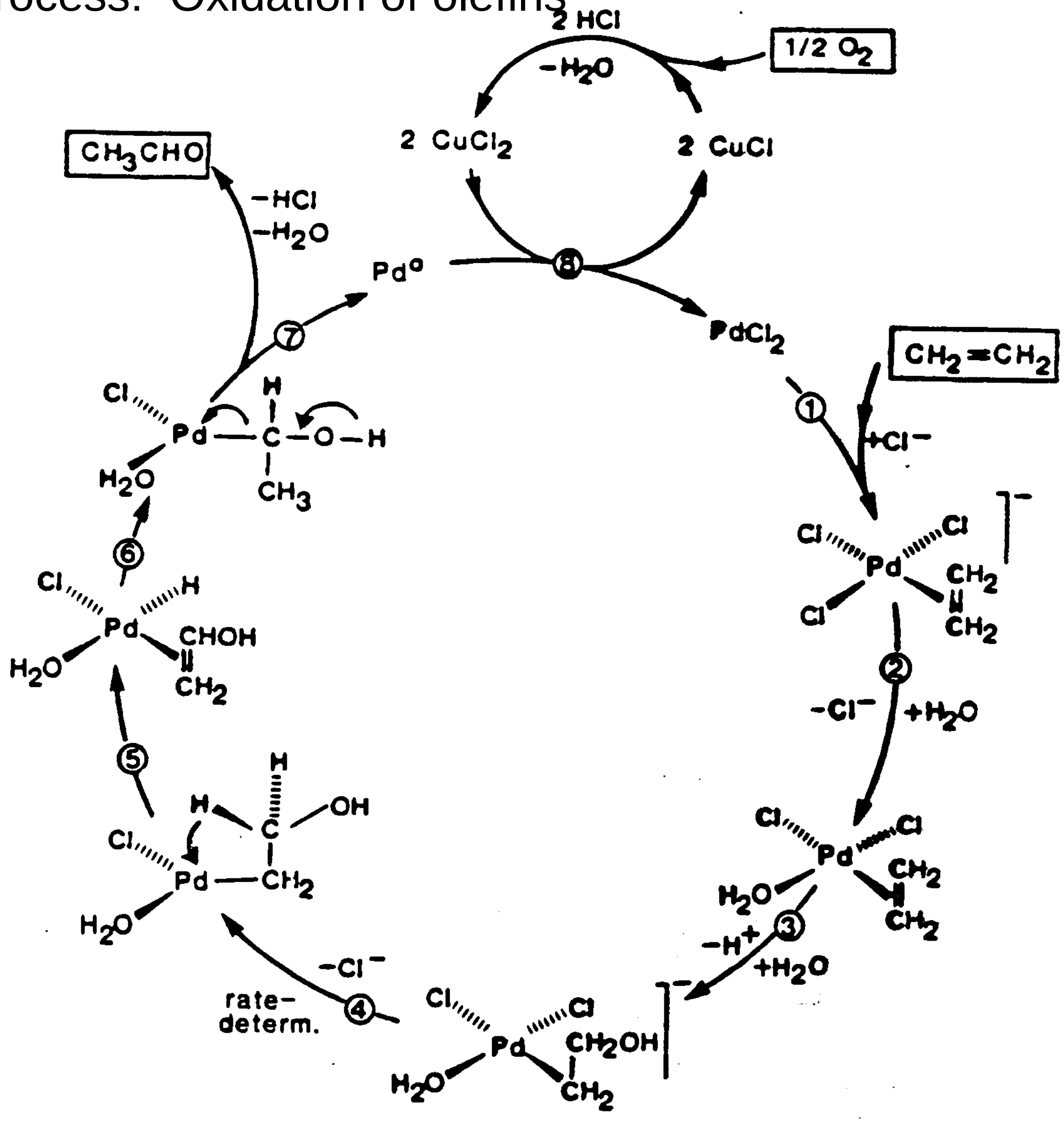
reductive elimination

from Collman, Stanford

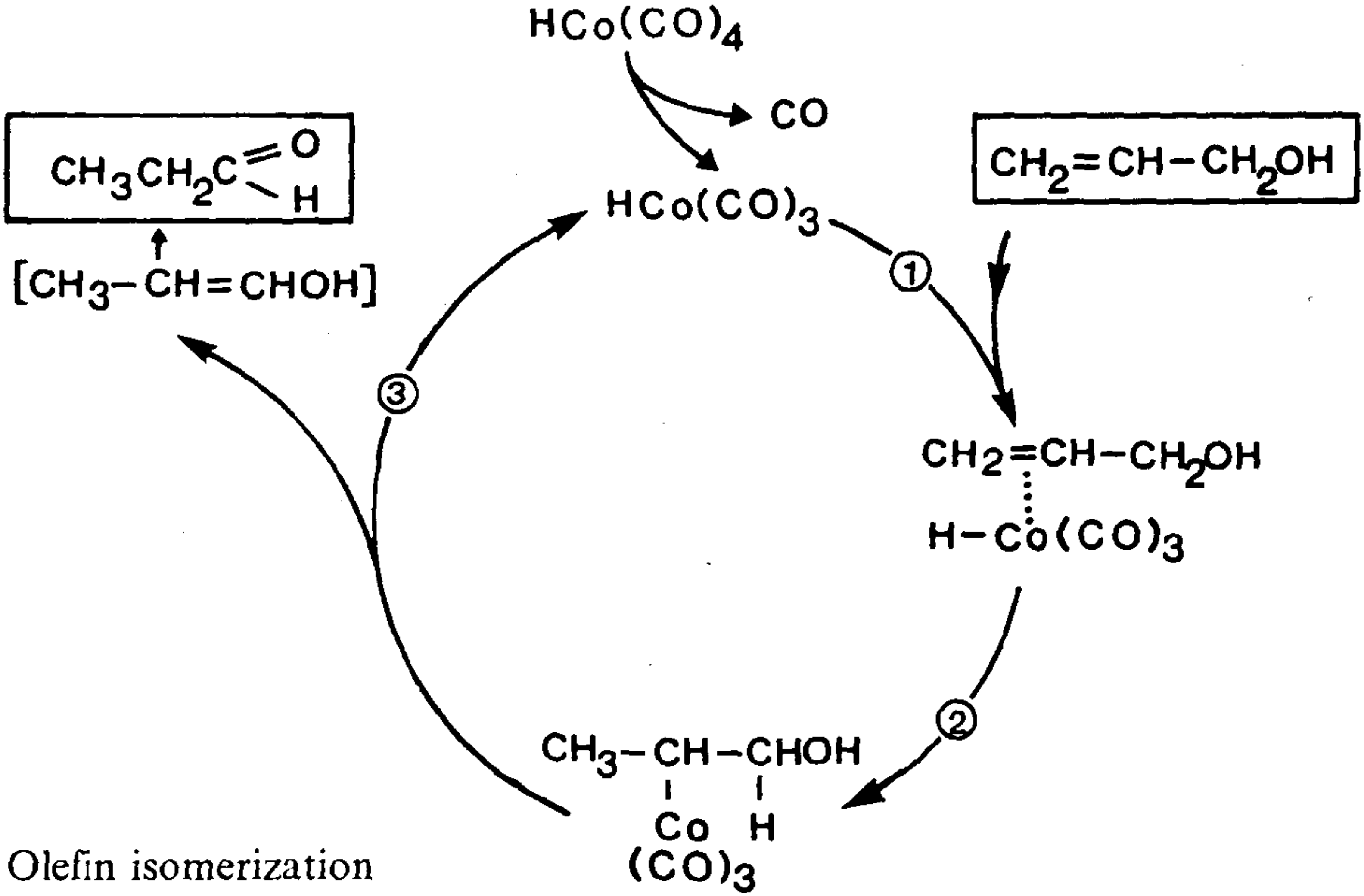


Reppe carbonylation

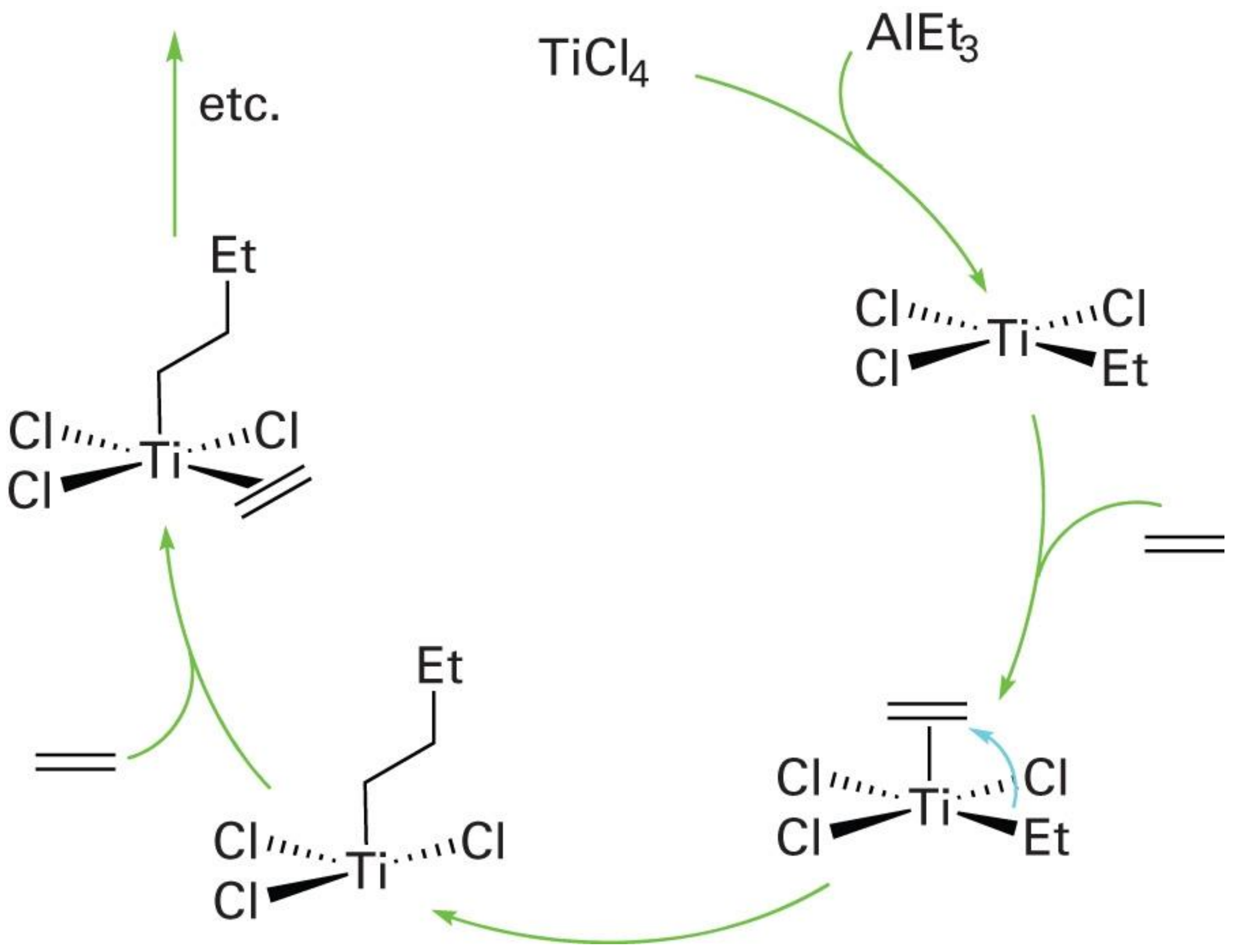
Wacker process: Oxidation of olefins

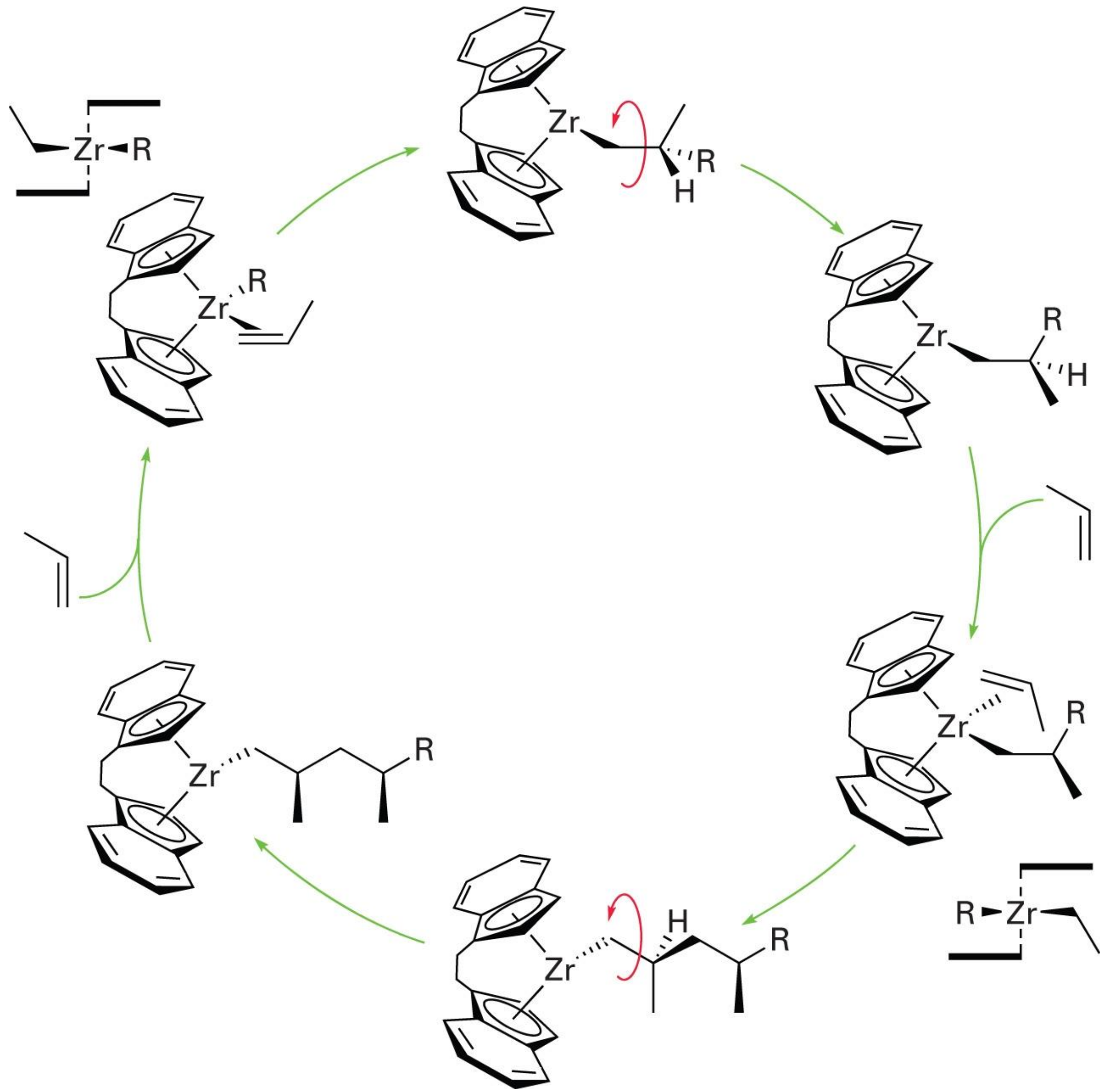


Wacker process



Olefin isomerization


TiCl4
AlEt3
etc.
Et
Cl
Cl
Ti
Cl
Cl
Ti
Cl
Cl
Et
Cl
Cl
Ti
Cl
Et
Et
Cl
Cl
Ti
Cl


Zr
R
H
Zr
R
H
Zr
R
R
Zr
R
Zr
H
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Zr
R
Zr
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Zr
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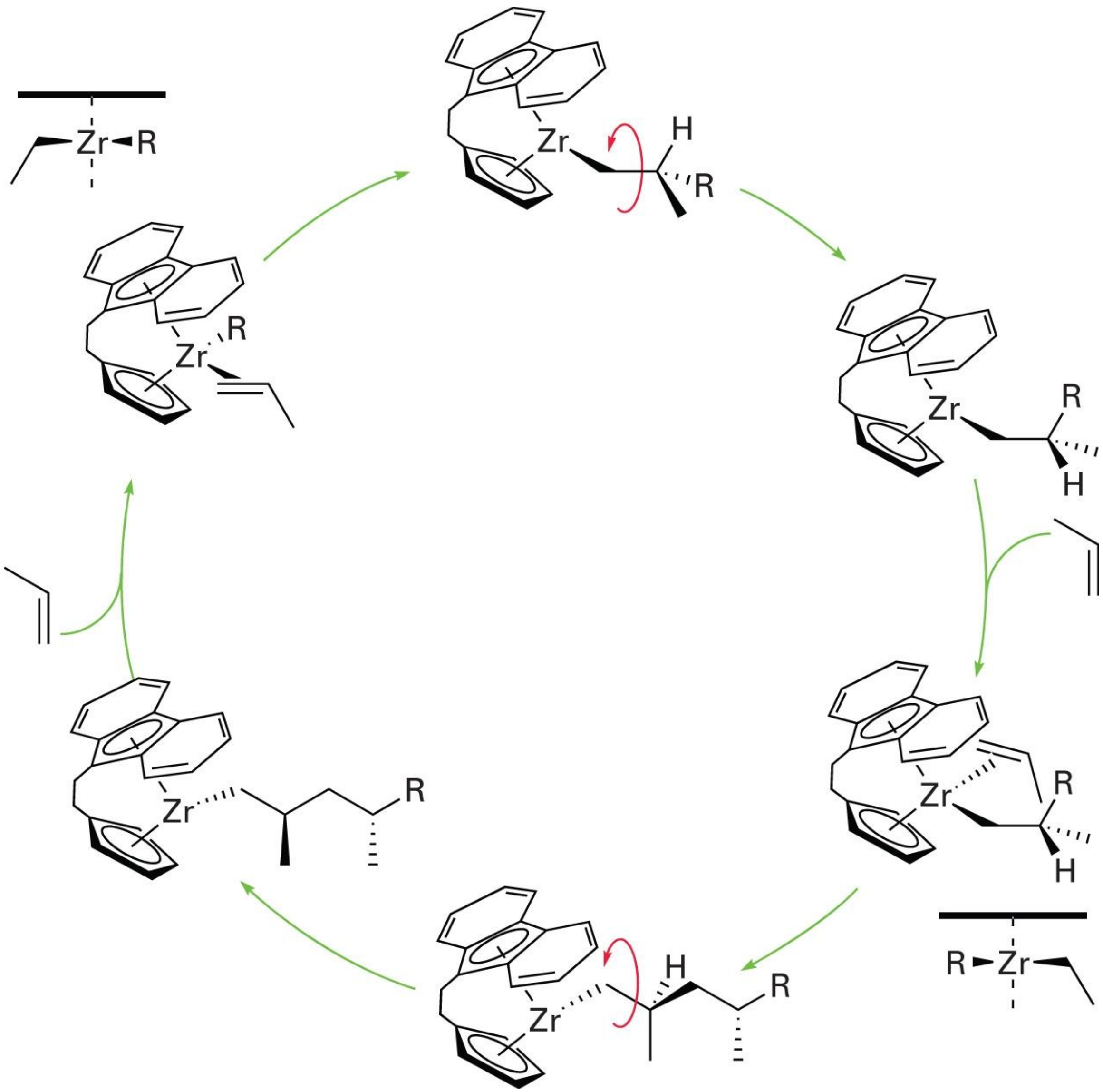
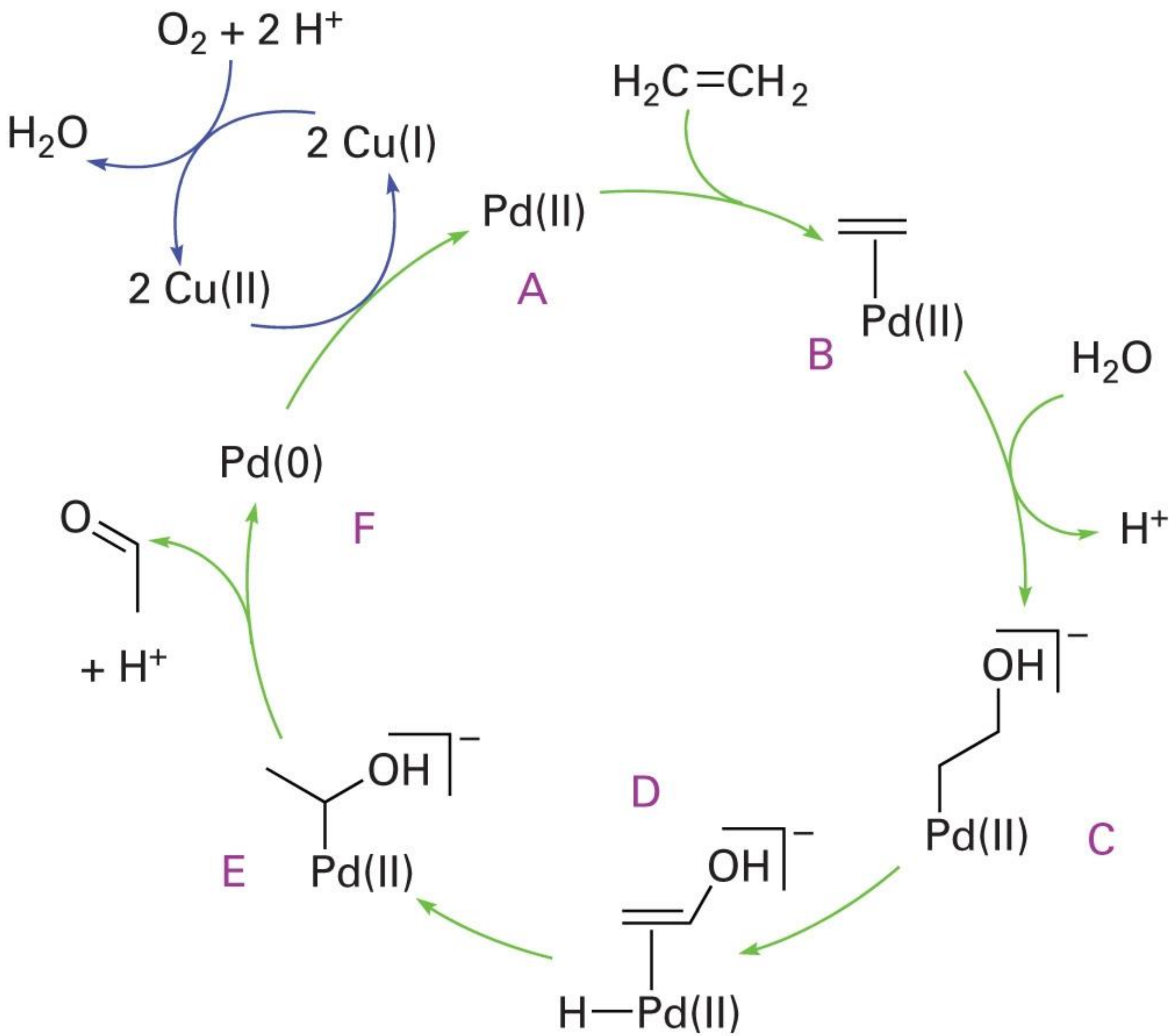
R
Zr
R

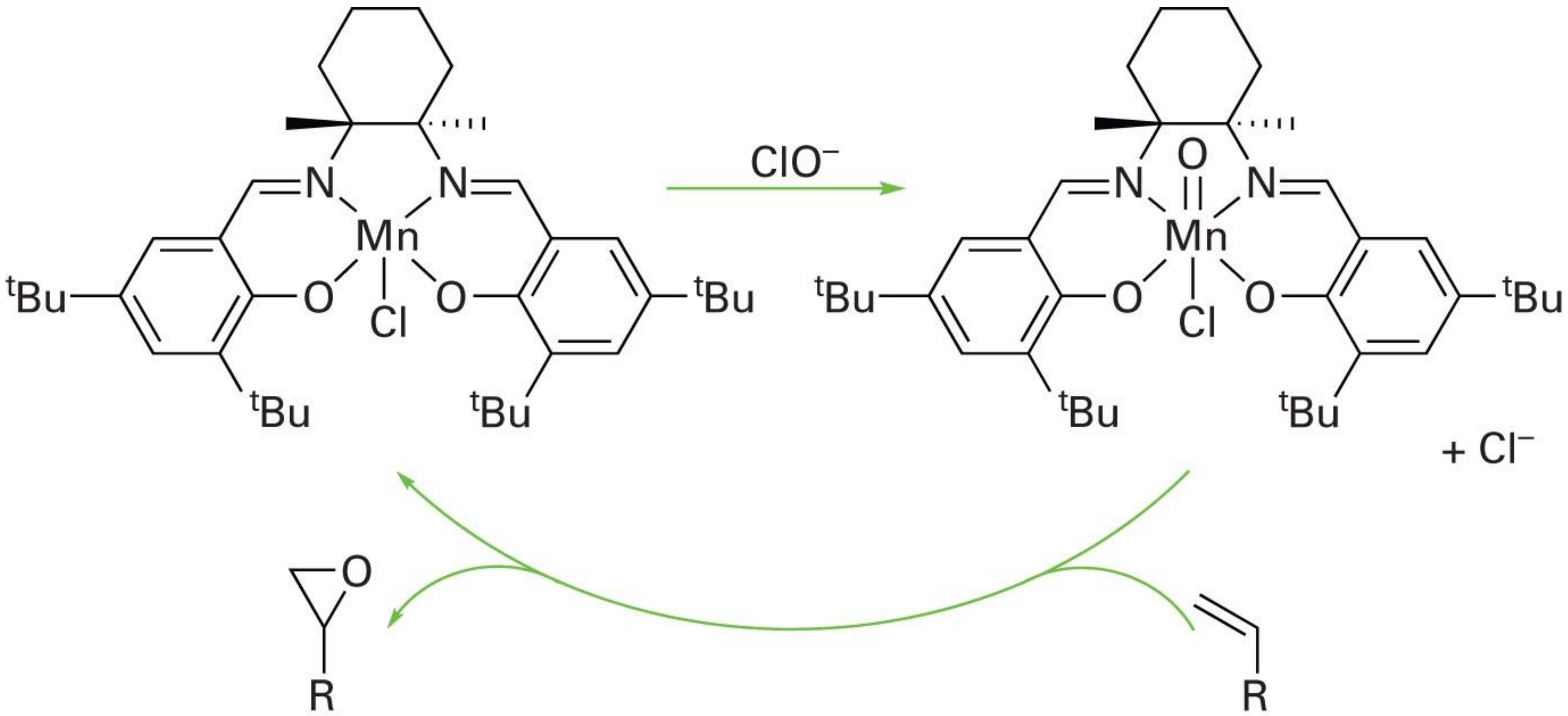
W. H. FREEMAN



Wacker Oxidation of Olefins: Two parts



Olefin Oxidation making epoxides: Not organometallic but ???

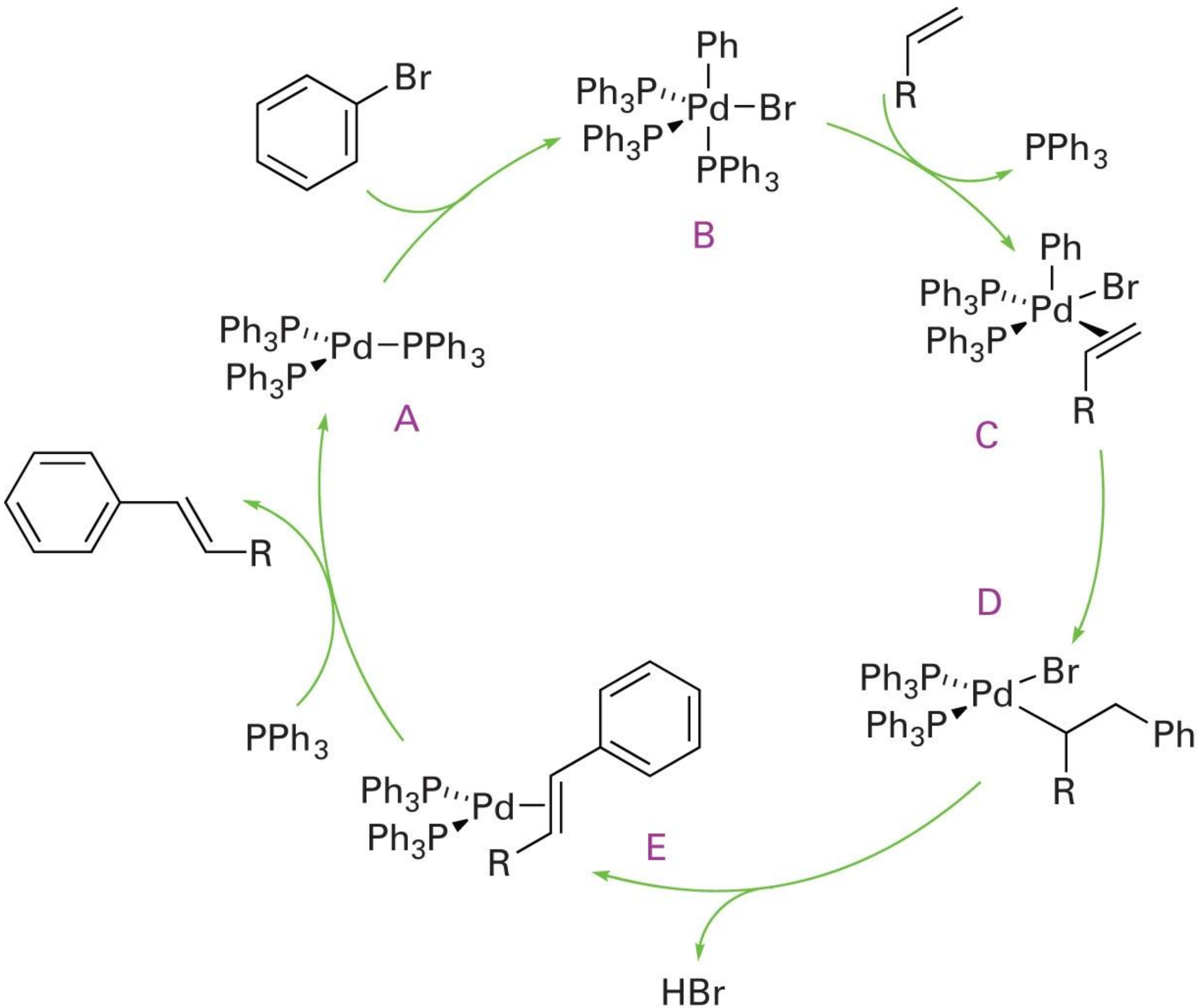


Carbon-carbon bond formation:

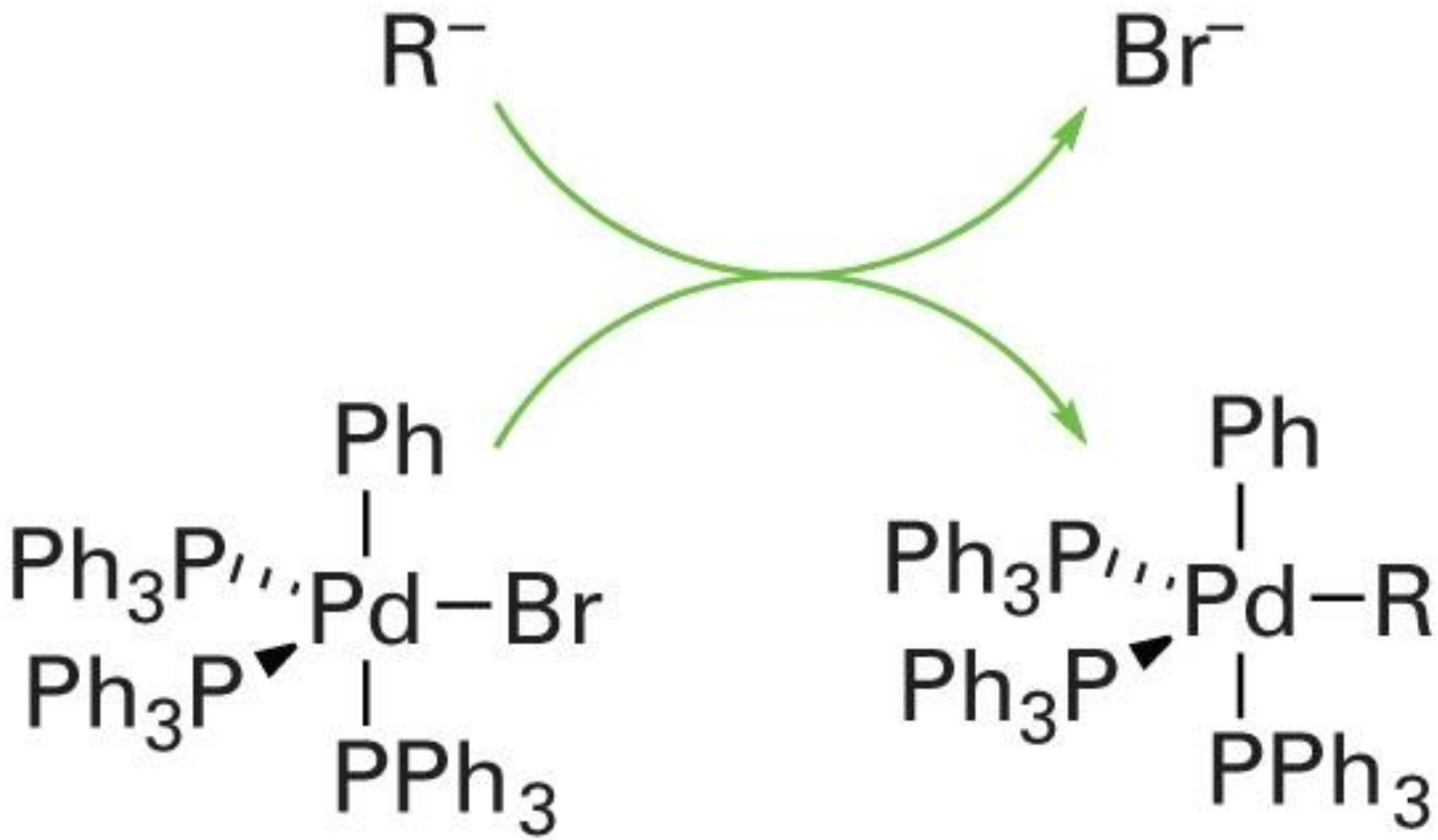
Cross Coupling

- Cross-coupling reactions:

A. Negishi* Reaction
B. Heck* Reaction
C. Stille Reaction
D. Suzuki* Reaction
E. Sonogashira Reaction
F. Buchwald-Hartwig Reaction

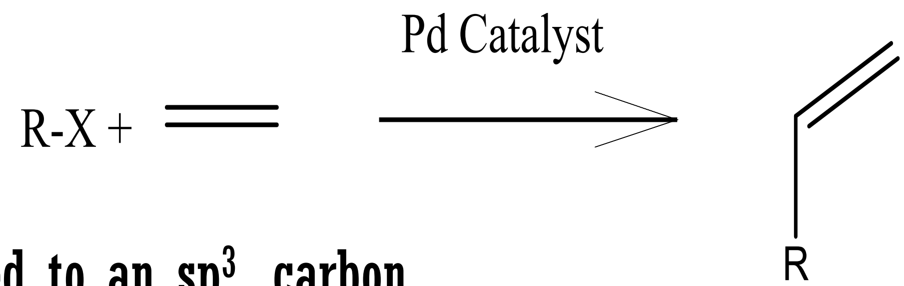


Br
Ph
Ph3P
Pd
Br
Ph3P
PPh3
B
R
PPh3
Ph
Ph3P
Pd
Br
Ph3P
R
C
Ph3P
Pd
PPh3
Ph3P
A
R
D
Ph3P
Pd
Br
Ph3P
Ph
R
PPh3
Ph3P
Pd
Ph3P
R
E
HBr


R⁻
Br⁻
Ph
Ph3P
Pd–Br
Ph3P
PPh3
Ph
Ph3P
Pd–R
Ph3P
PPh3

Heck reaction (olefination)

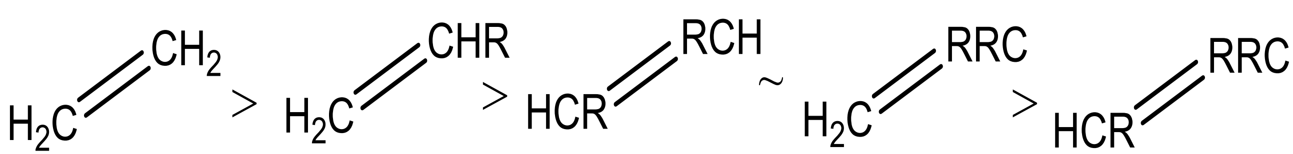
- General reaction scheme:



- R: Lacks a β **hydrogen attached to an sp^3 carbon. (Aryl/Benzyl/Vinyl/Allyl)**

- X: Typically Cl, Br, I, Otf

- Regioselectivity and rates are determined by steric hindrance at the alkene



The Heck Cross coupling Reaction

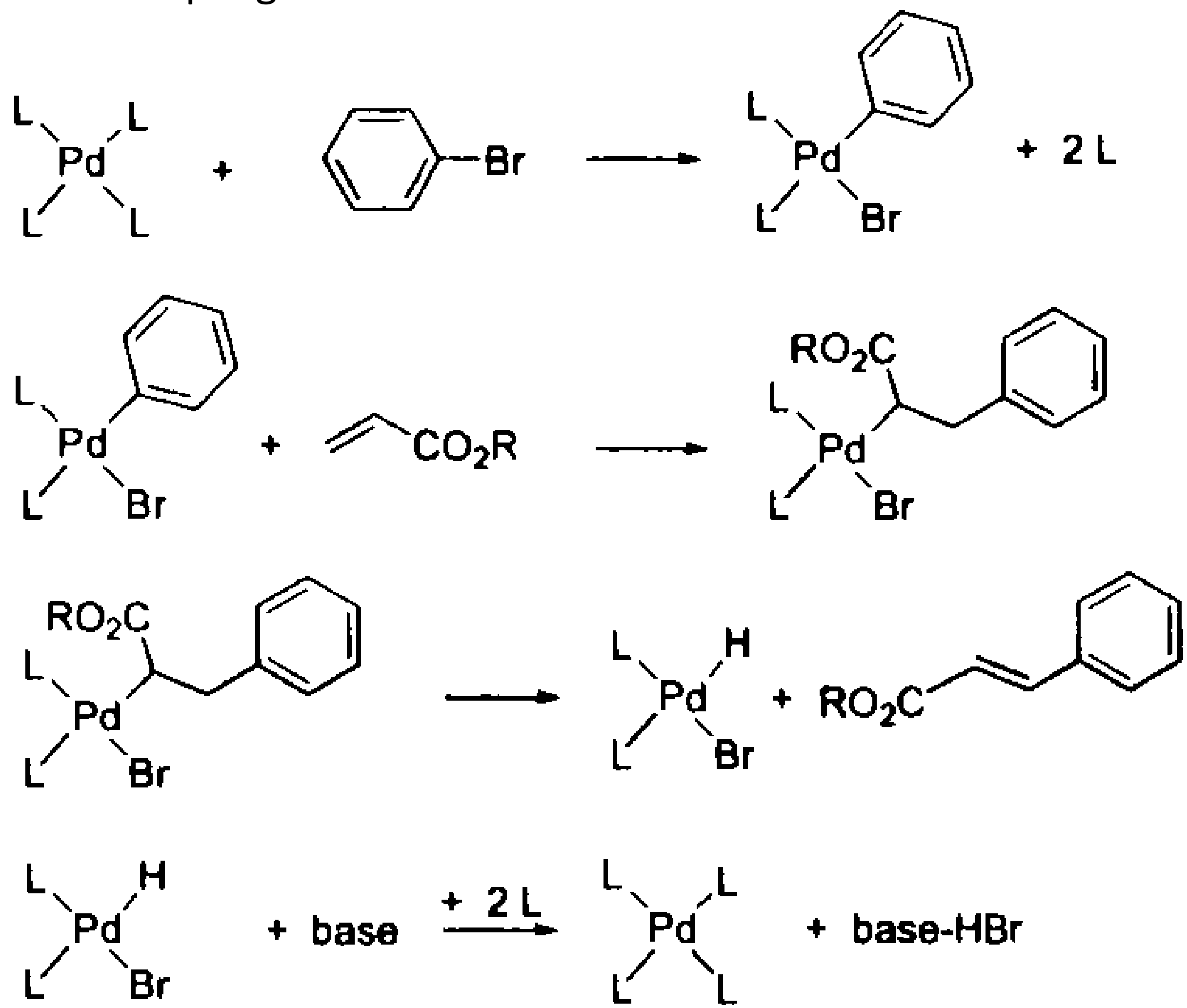
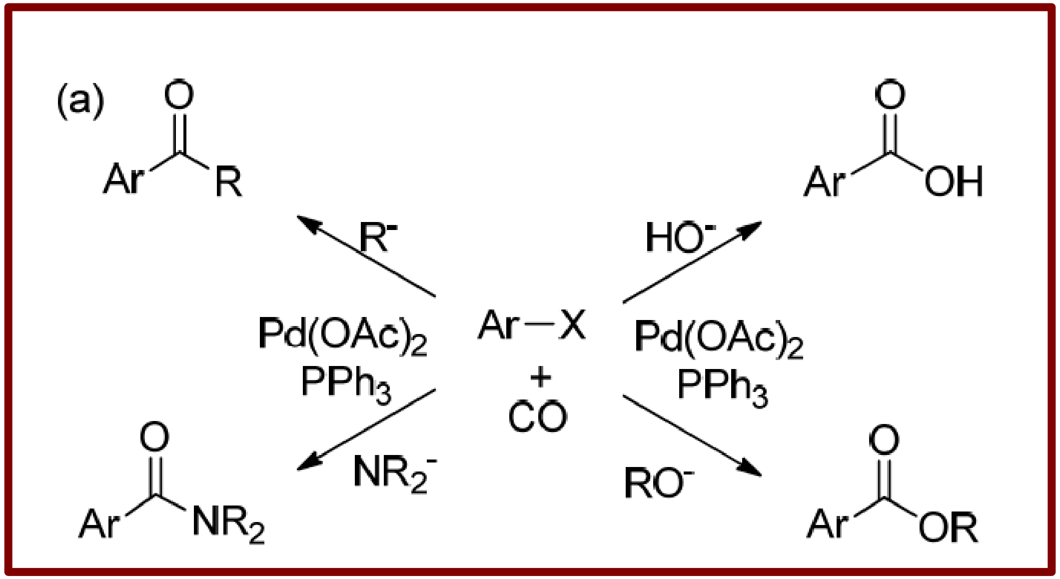
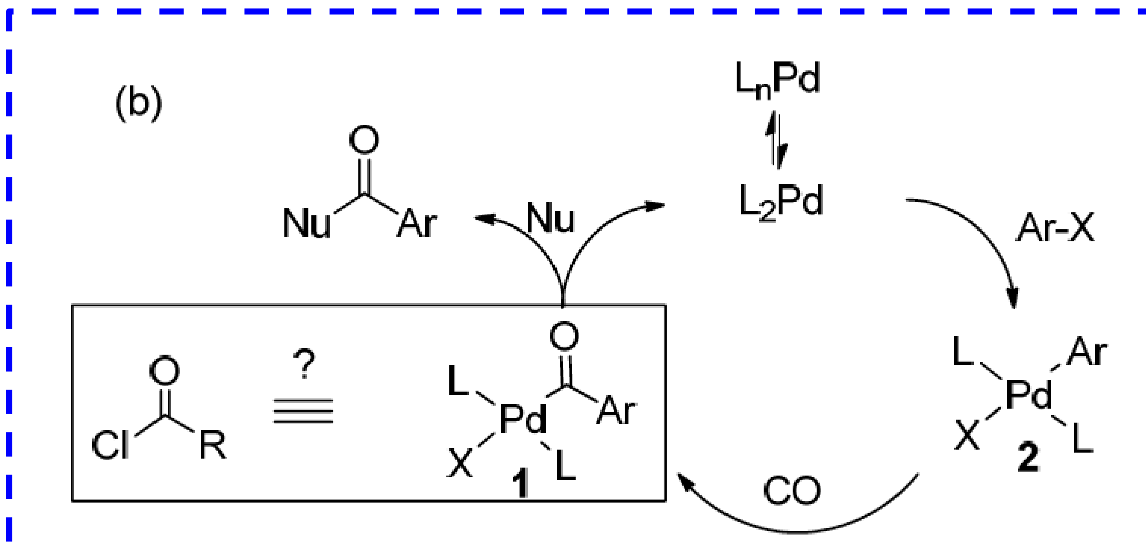


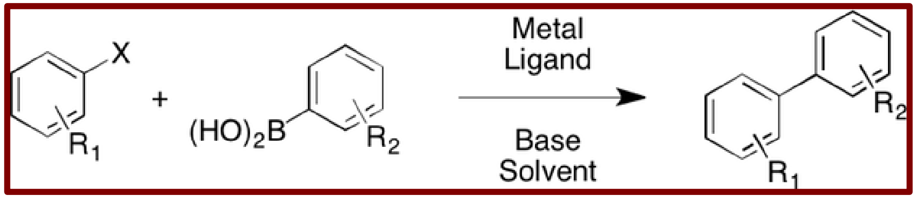
Figure 13.15. Mechanism of the Heck reaction

Heck Reaction and Mechanism

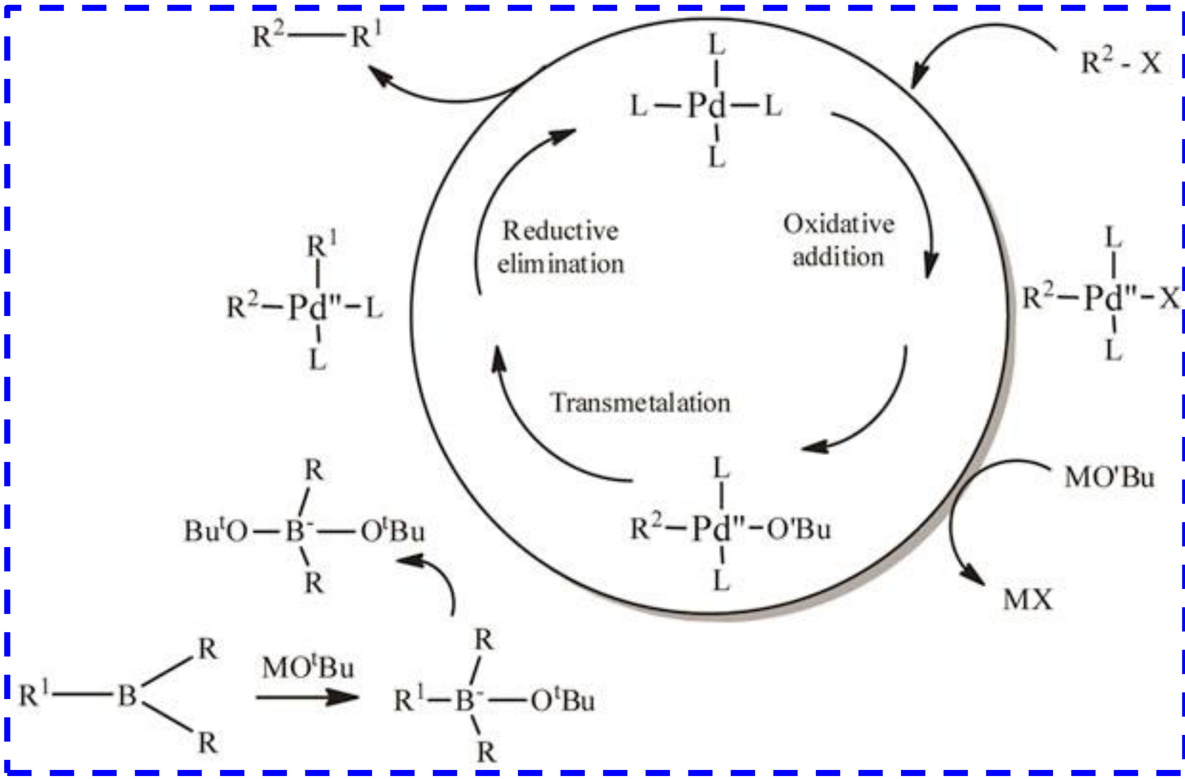




Susuki Coupling : the overall reaction



Susuki Coupling : the mechanism



Negishi Coupling: Uses Zn