Chemistry 462 Fall 2017
MYD

Organometallic Chemistry and Applications

Note: Organometallic Compounds and Complexes Contain a M-C Bond.

Organometallic chemistry timeline

1760 Louis Claude Cadet de Gassicourt investigates inks based on cobalt salts and isolates Cacodyl from cobalt mineral containing arsenic

1827 William Christopher Zeise produces Zeise's salt; the first platinum / olefin complex

1848 Edward Frankland discovers diethylzinc

1863 Charles Friedel and James Crafts prepare organochlorosilanes

1890 Ludwig Mond discovers nickel carbonyl

1899 Introduction of Grignard reaction

1899 John Ulric Nef discovers alkylation using sodium acetylides.

1900 Paul Sabatier works on hydrogenation of organic compounds with metal catalysts. Hydrogenation of fats kicks off advances in food industry; see margarine!

1909 Paul Ehrlich introduces Salvarsan for the treatment of syphilis, an early arsenic based organometallic compound

1912 Nobel Prize Victor Grignard and Paul Sabatier

1930 Henry Gilman works on lithium cuprates, see Gilman reagent

1951 Walter Hieber was awarded the Alfred Stock prize for his work with metal carbonyl chemistry—(*but not the Nobel Prize)*.

1951 Ferrocene is discovered

1963 Nobel prize for Karl Ziegler and Giulio Natta on Ziegler-Natta catalyst: Polymerization of olefins

1965 Discovery of cyclobutadieneiron tricarbonyl

1968 Heck reaction

1973 Nobel prize Geoffrey Wilkinson and Ernst Otto Fischer on sandwich compounds

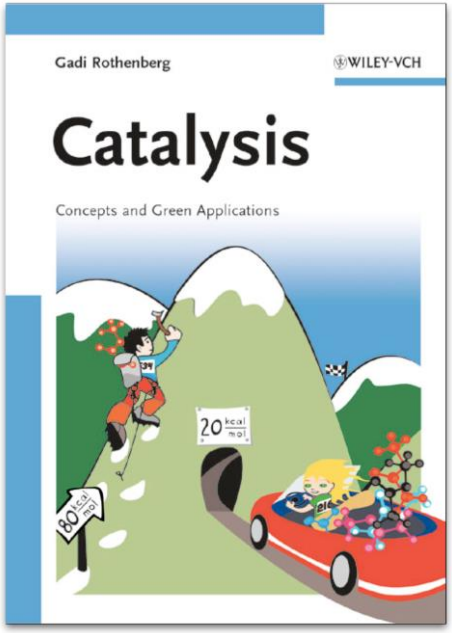
1981 Nobel prize Roald Hoffmann and Kenichi Fukui for expression of the Woodward-Hoffman Rules

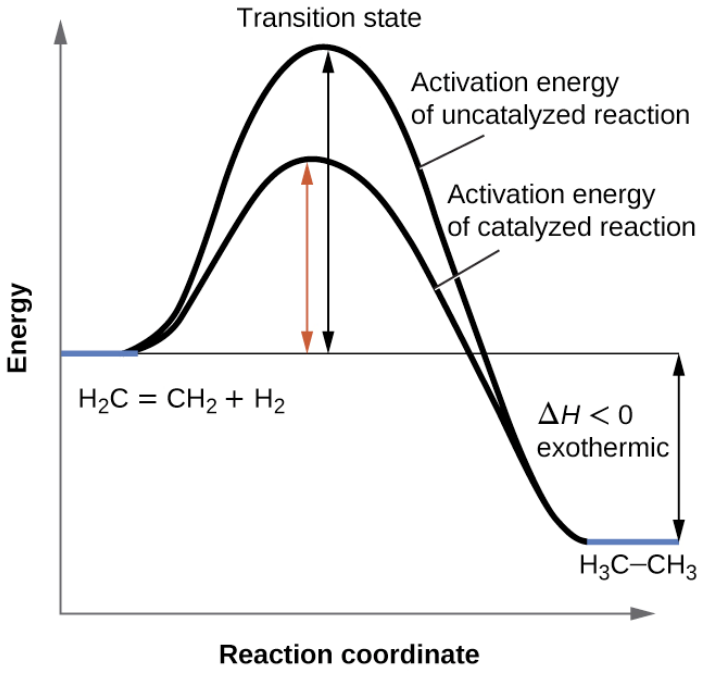
2001 Nobel prize W. S. Knowles, R. Noyori and Karl Barry Sharpless for asymmetric hydrogenation

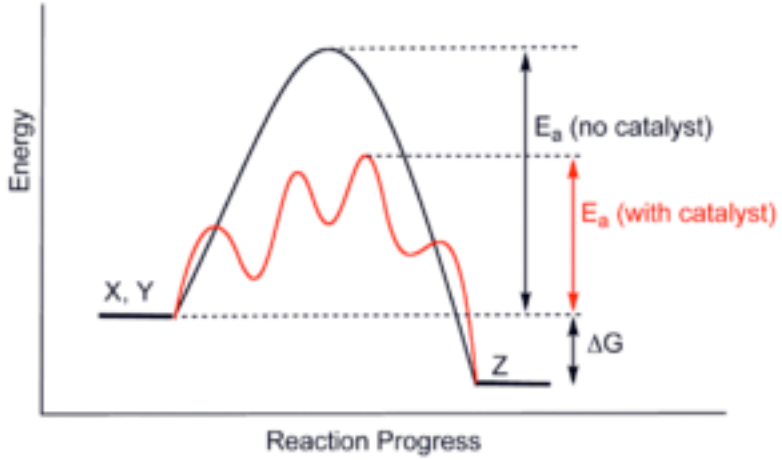
2005 Nobel prize Yves Chauvin, Robert Grubbs, and Richard Schrock on metal-catalyzed alkene metathesis

2010 Nobel prize Richard F. Heck, Ei-ichi Negishi, Akira Suzuki for palladium catalyzed cross coupling reactions

The following slides are meant merely as examples of the catalytic processes we will explore later this semester. Please don't get disturbed that threre is too much new information at this point.
Believe me, you will see them again.

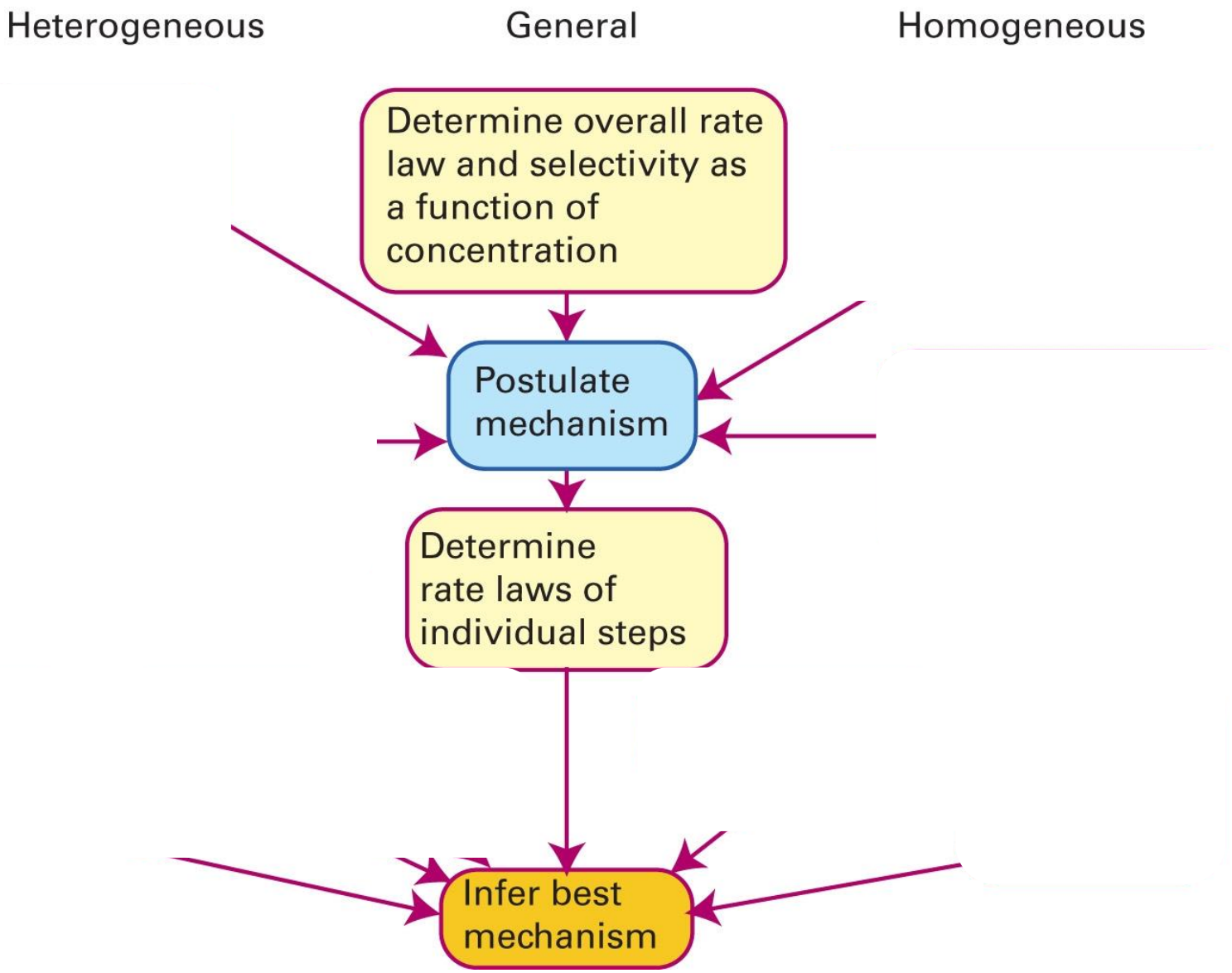




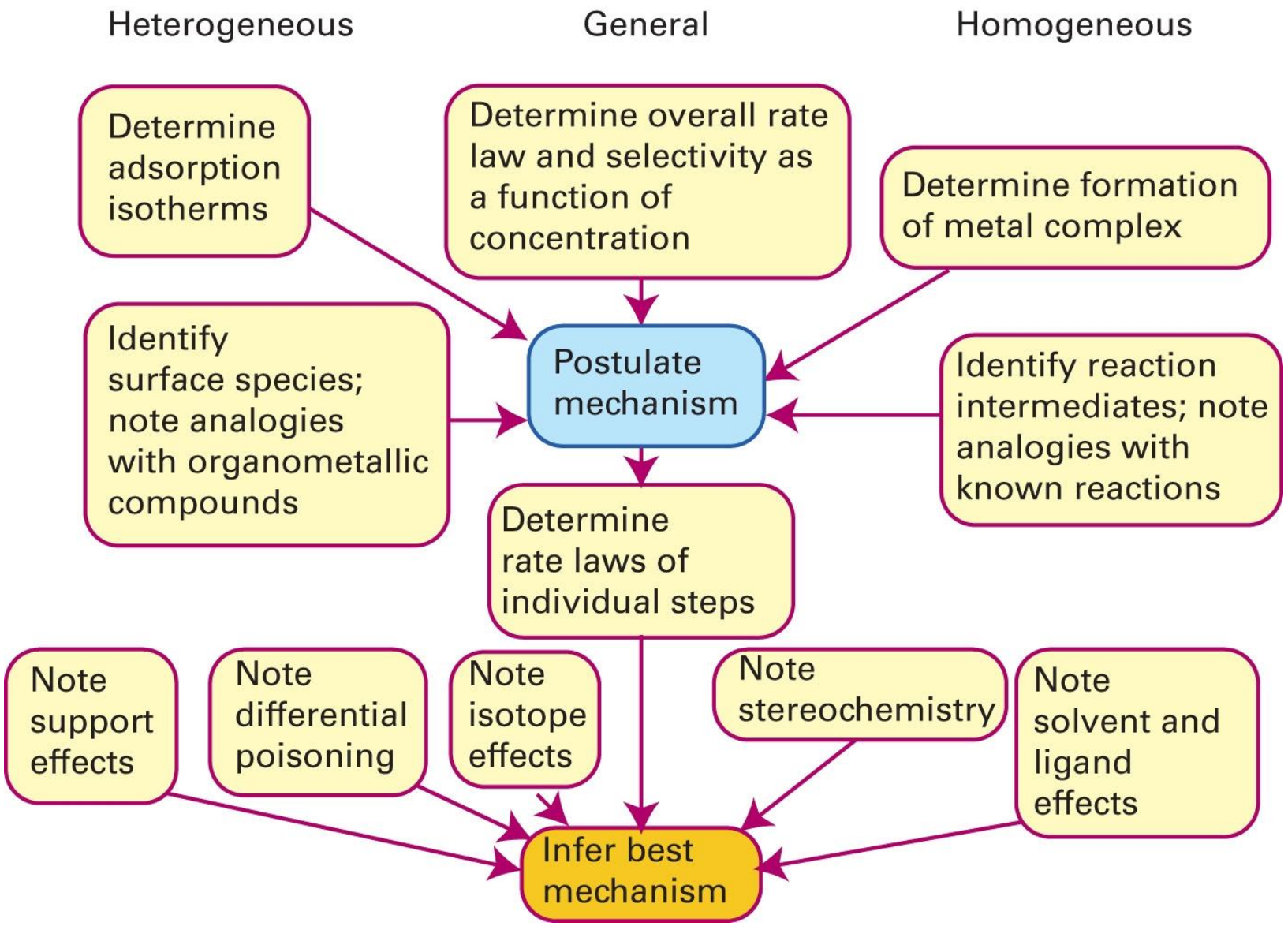


Catalysis (ca. 25% of US GNP)

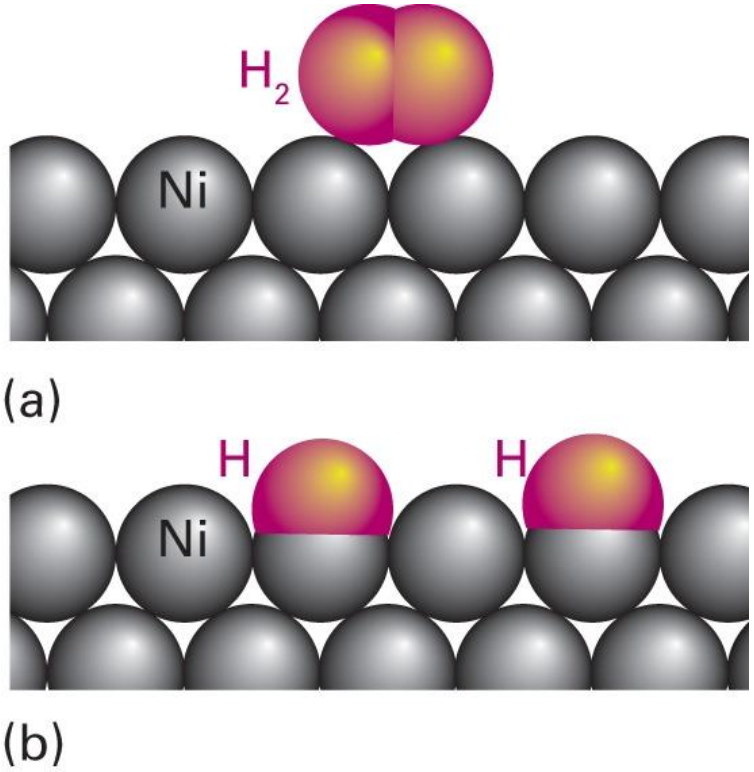
Catalyst Development



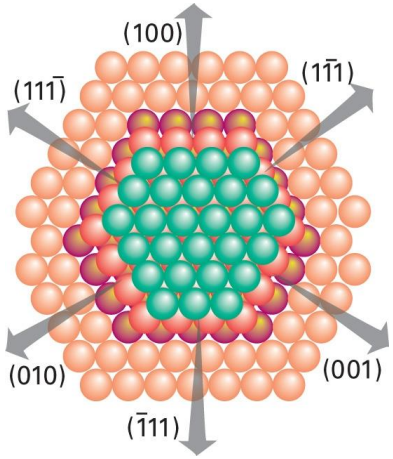
Catalyst Development

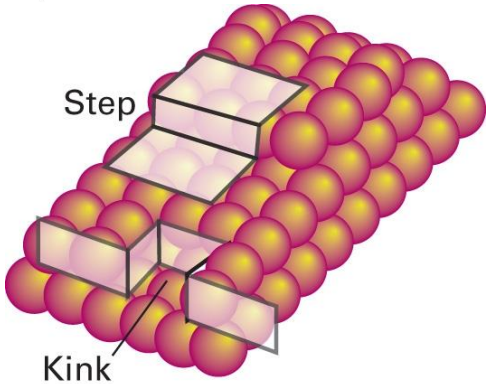


Schematic representation of physisorption and chemisorption of Hydrogen on a nickel metal surface



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

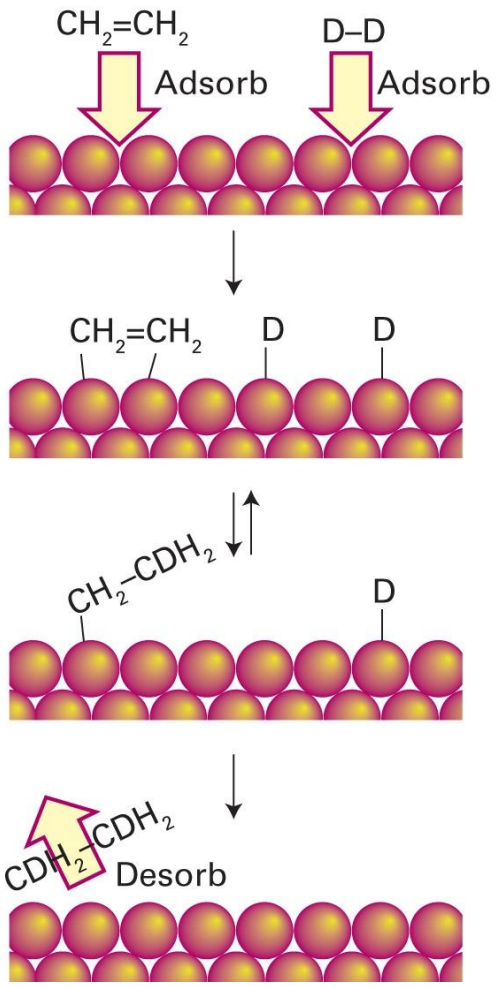


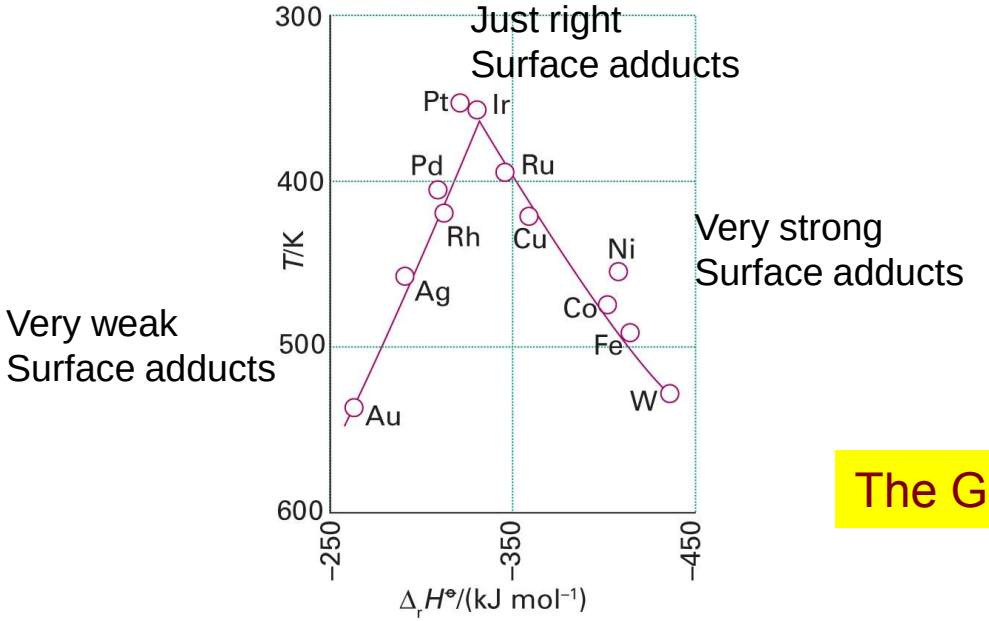


Hydrogenation of alkenes on supported metal
Involves H_2 dissociation and migration of H-atoms
to an adsorbed ethene molecule. (Paul Sabatier, 1890)

Mechanism: All isotopomers are seen, therefore highly Reversible processes precede loss of the ethane.

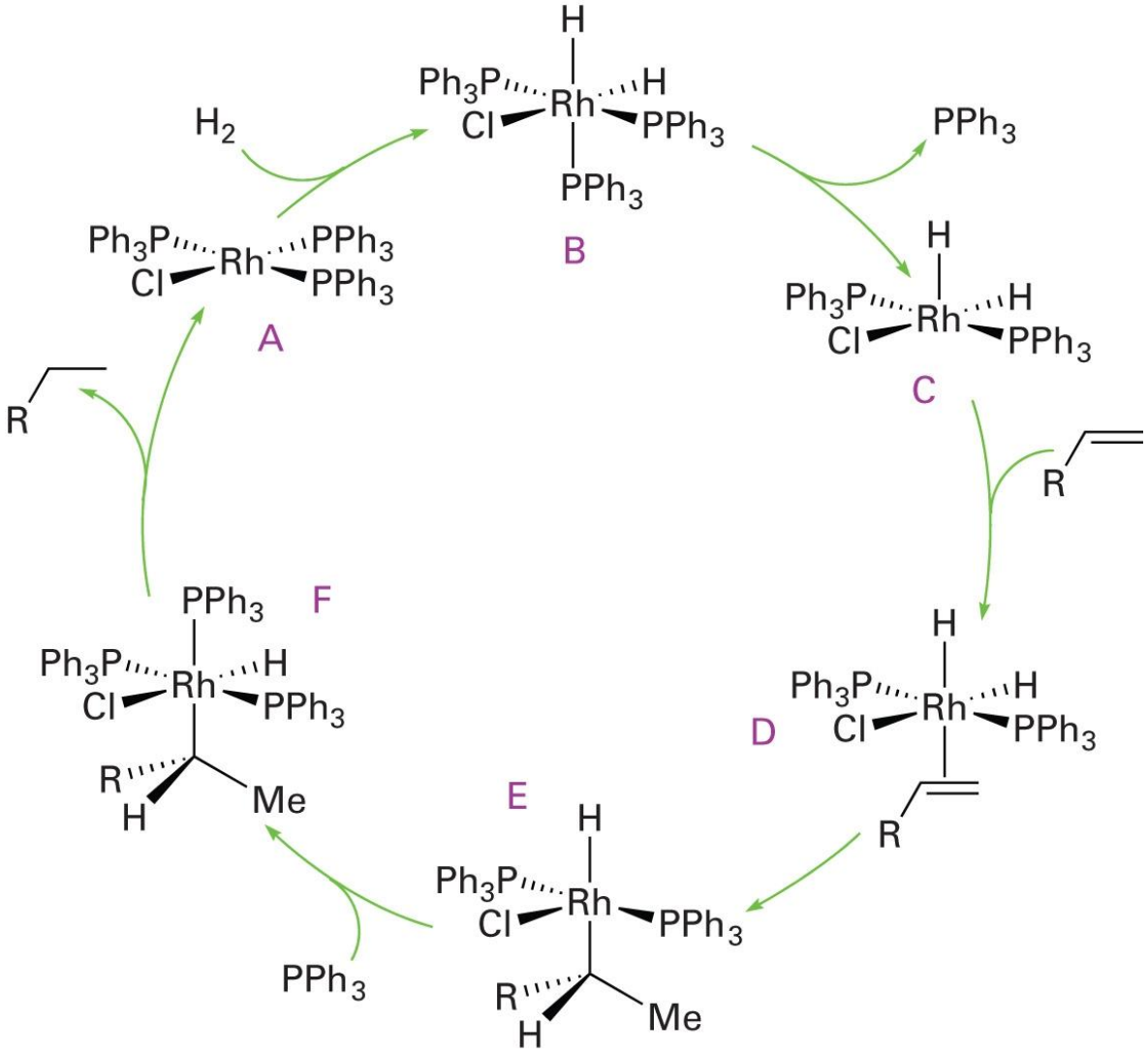
Volcano diagrams relate stability of products on Surface: Temp. for a set rate of release vs. the Enthalpy. *Intermediate values of ΔH_f, with the rate being a combination of the rate of adsorption and the rate of desorption gives best catalyst.*





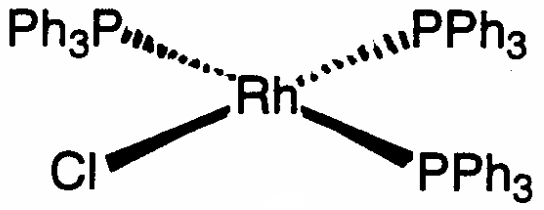
The Goldilocks' Effect

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

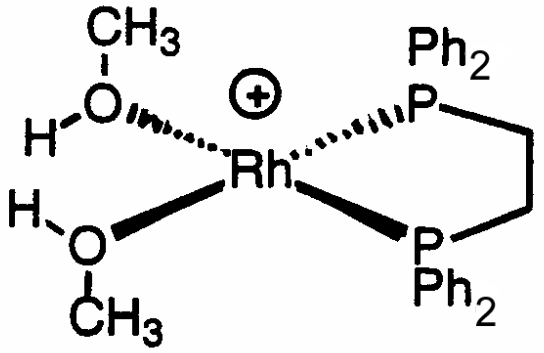


Catalytic homogeneous hydrogenation.

Typical catalysts (achiral):



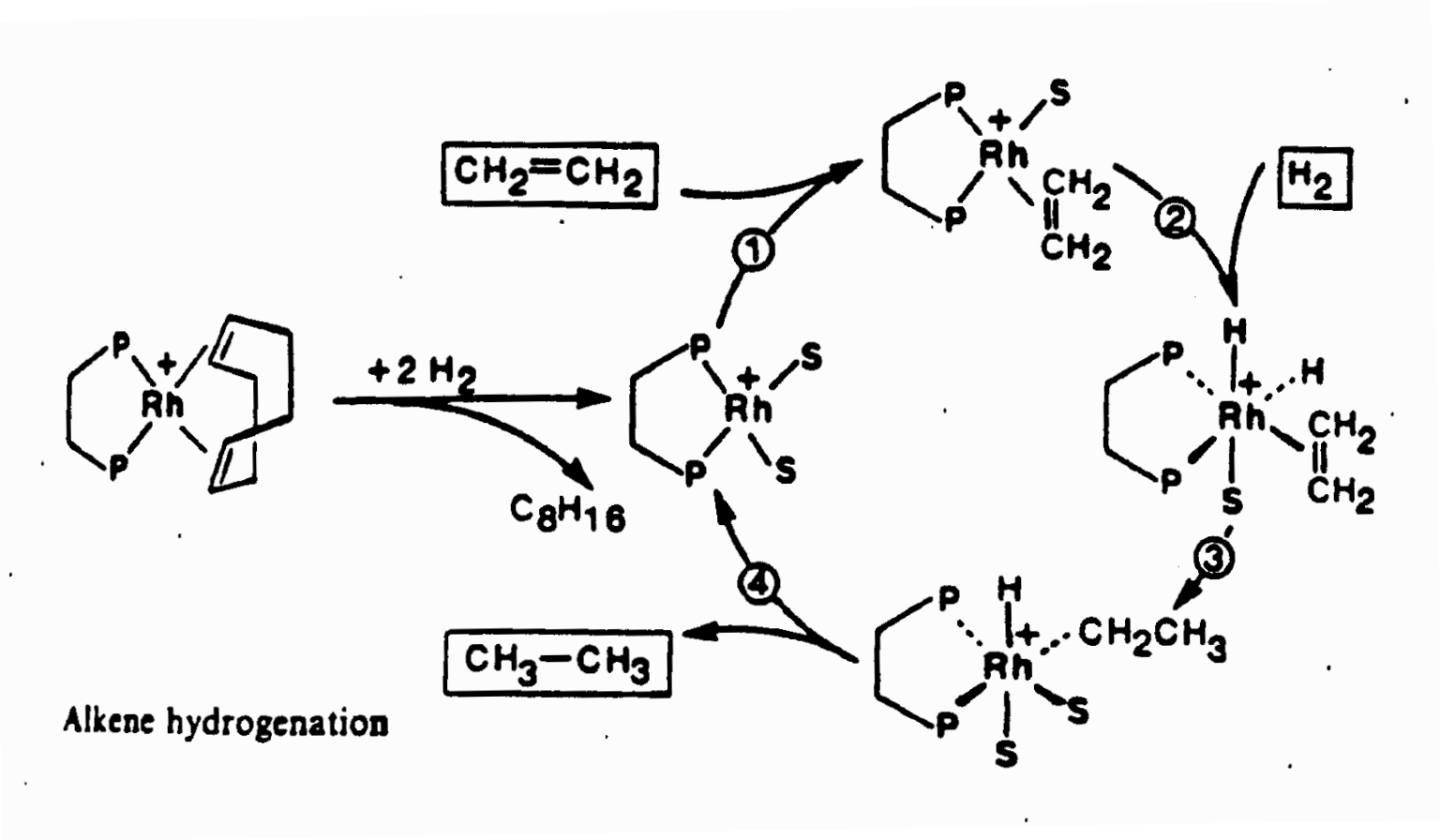
Wilkinson's catalyst



Mechanism:
H_2 activation prior to olefin addition

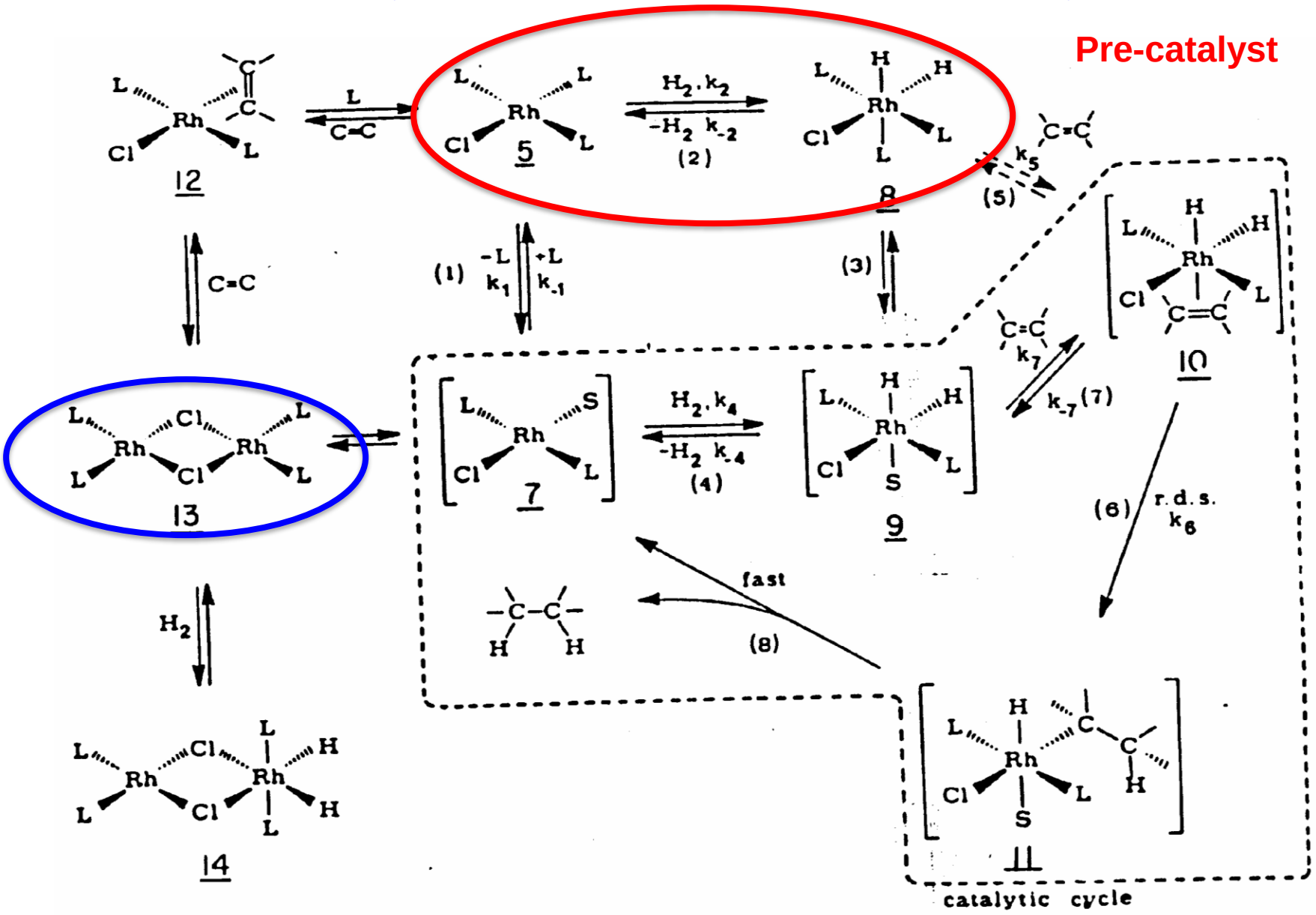
Mechanism:
Olefins add first to cationic catalyst

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



*This mechanistic route followed by asymmetric Hydrogenation process

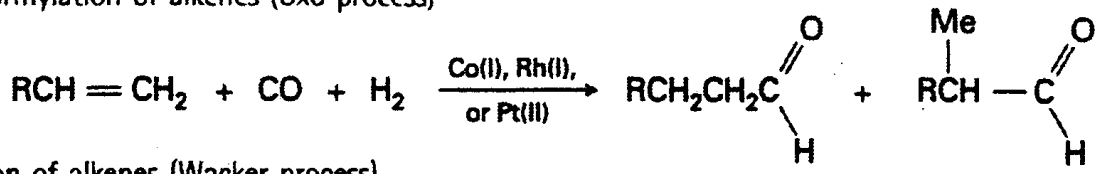
Wilkinson's Catalyst: Mechanism for Olefin Hydrogenation



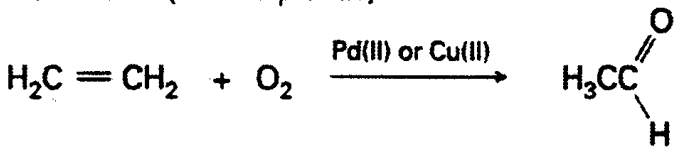
Some homogeneous catalytic processes

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

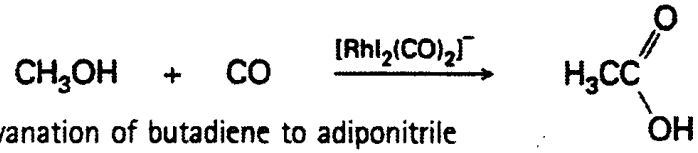
Hydroformylation of alkenes (Oxo process)



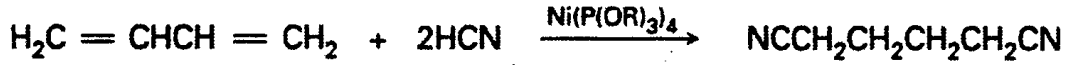
Oxidation of alkenes (Wacker process)



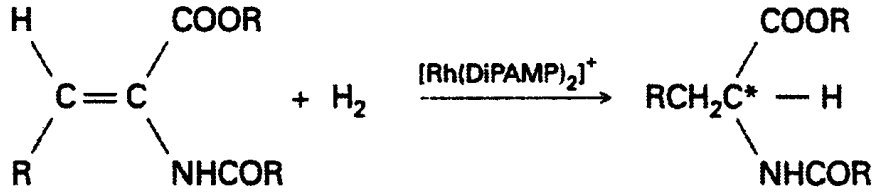
Carbonylation of methanol to acetic acid (Monsanto process)



Hydrocyanation of butadiene to adiponitrile



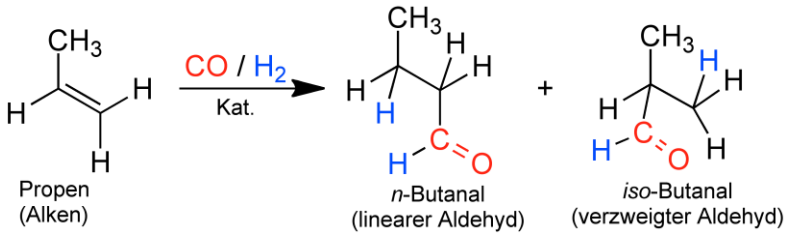
Asymmetric hydrogenation of prochiral alkenes

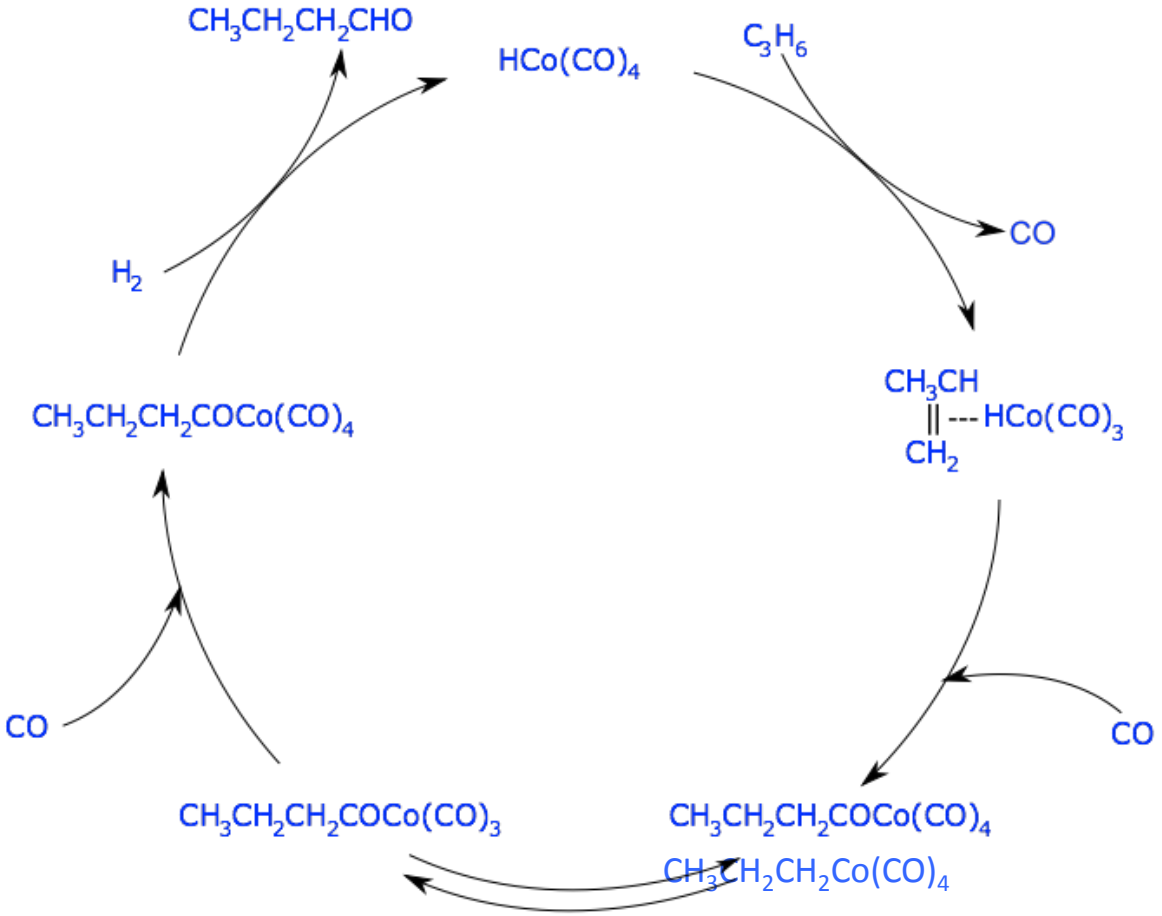


90 per cent L

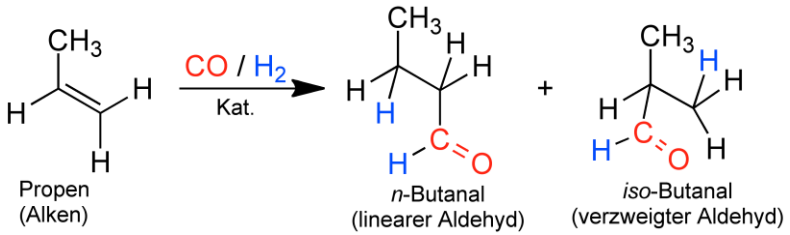
Cyclotrimerization of acetylene

Hydroformylation:

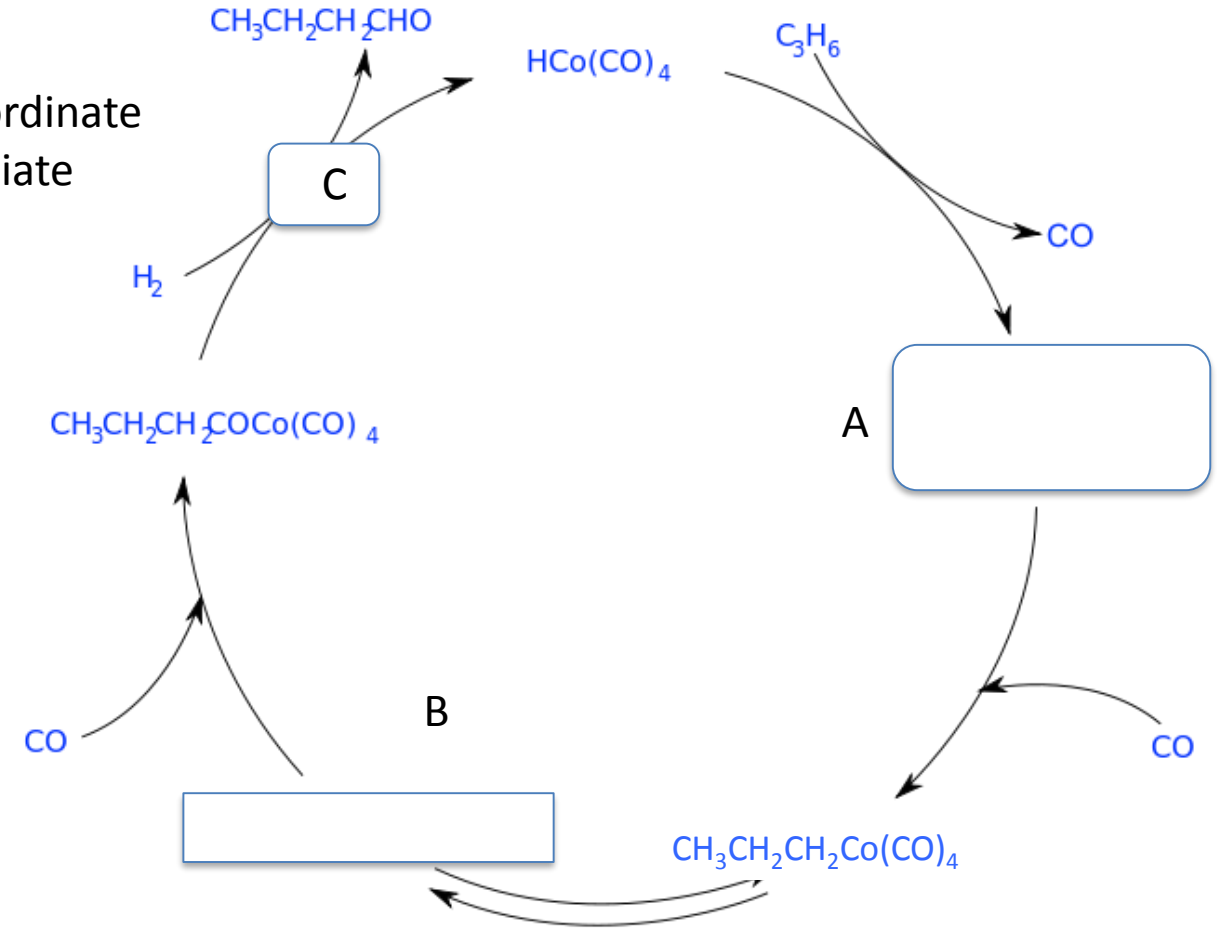




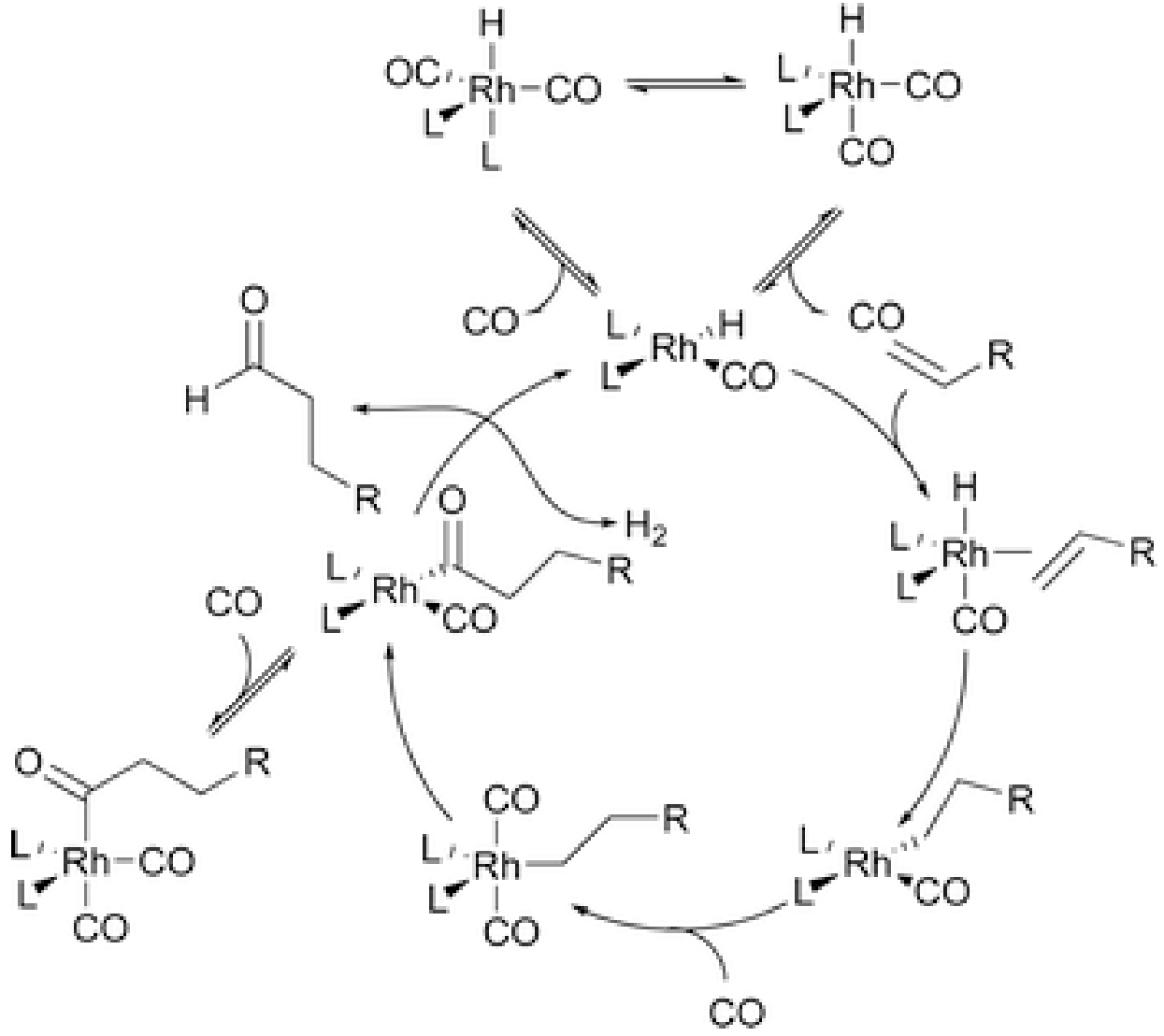
Hydroformylation:



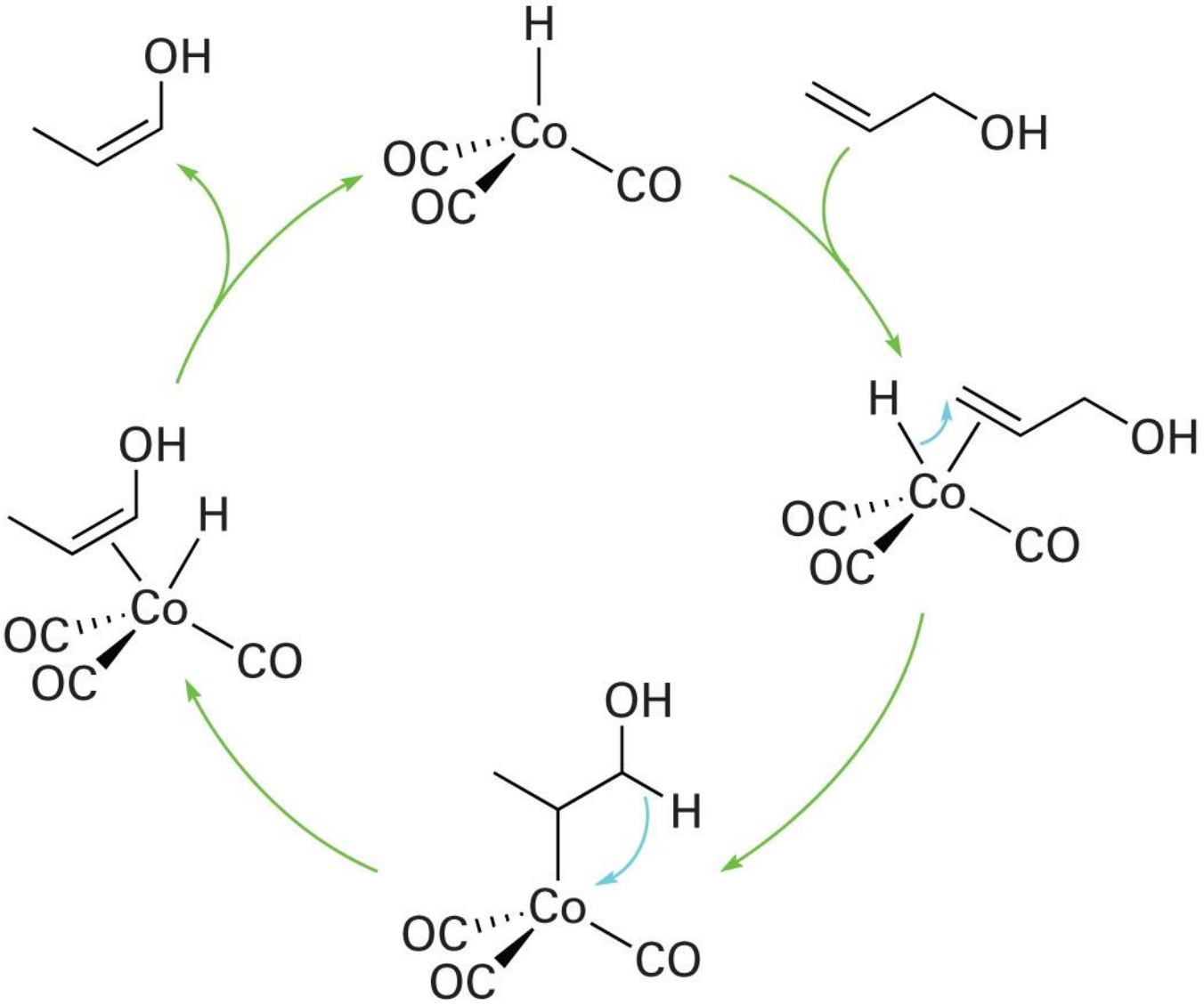
C = 6-coordinate intermediate



Hydroformylation : Union Carbide process

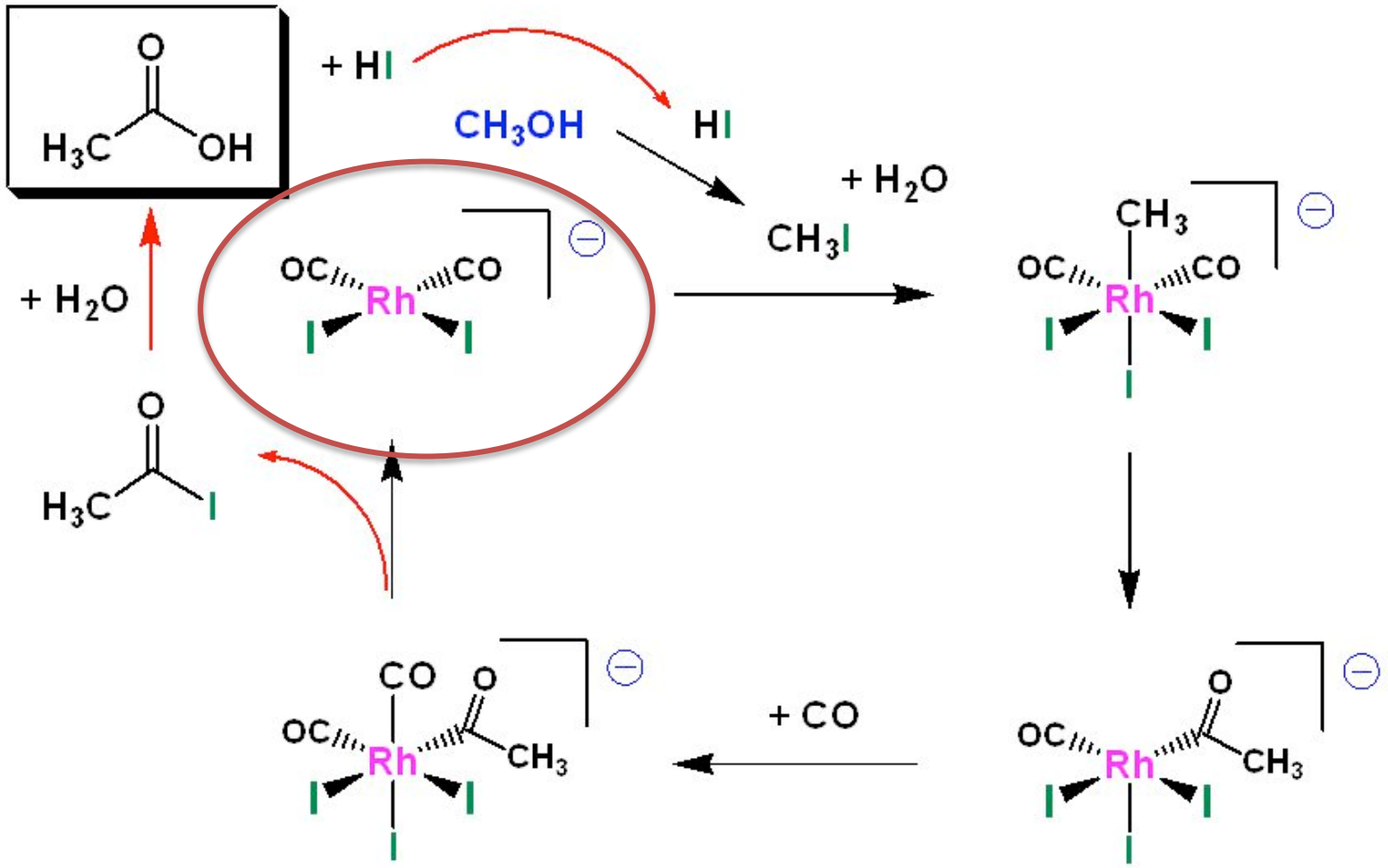


Olefin Isomerization



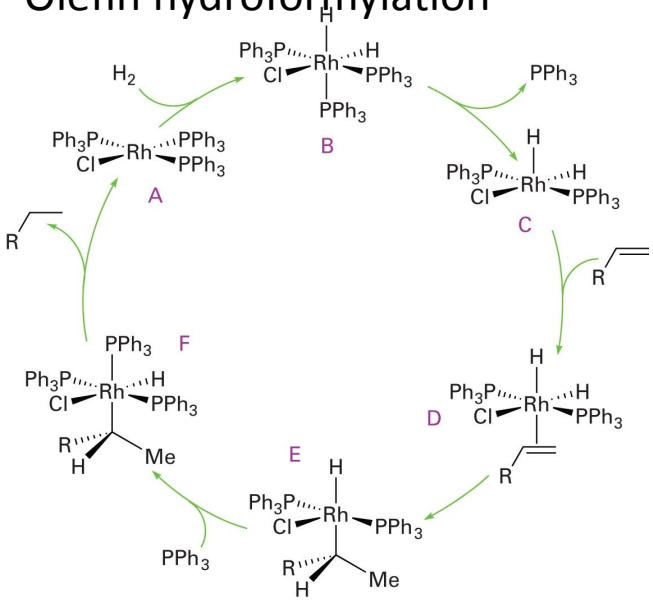
Monsanto Acetic Acid Synthesis

MeOH + CO → MeC(=O)OH

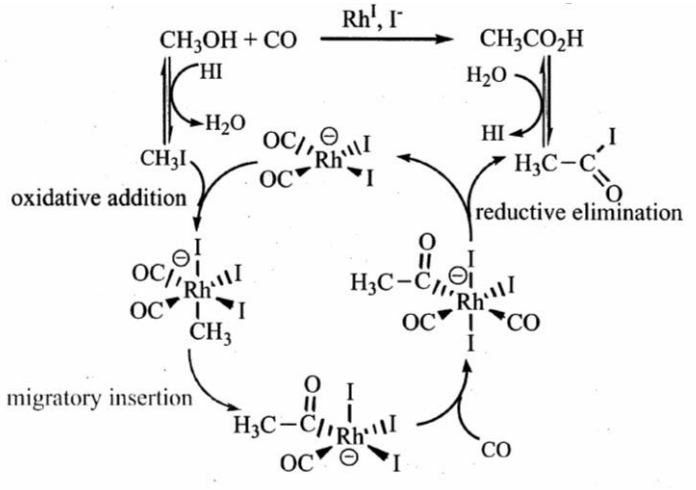


- The reaction is independent of CO pressure
- First order in both rhodium and MeI.
- Rate determining step is the oxidative addition of MeI to the $[Rh(CO)_2I_2]^-$ catalyst.

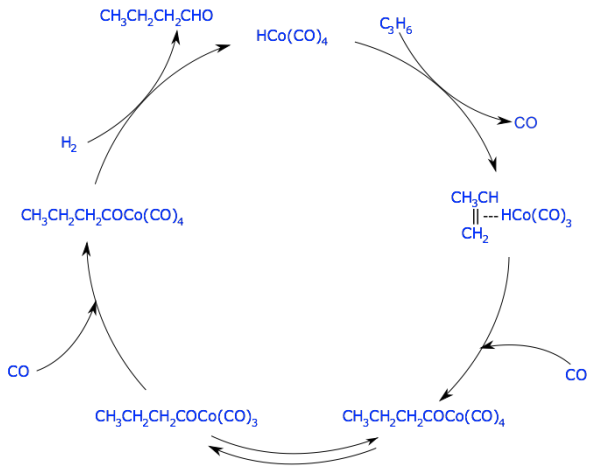
Olefin hydroformylation



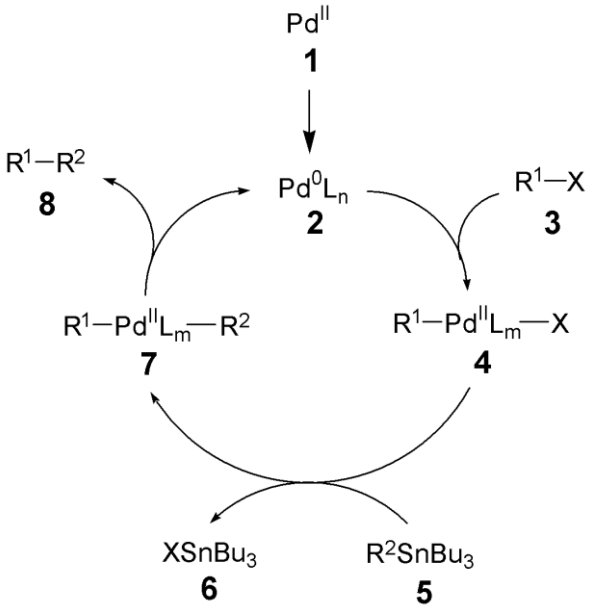
Monsanto Acetic Acid Process



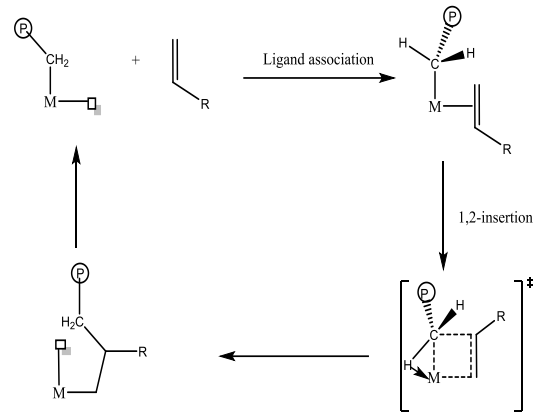
hydroformylation



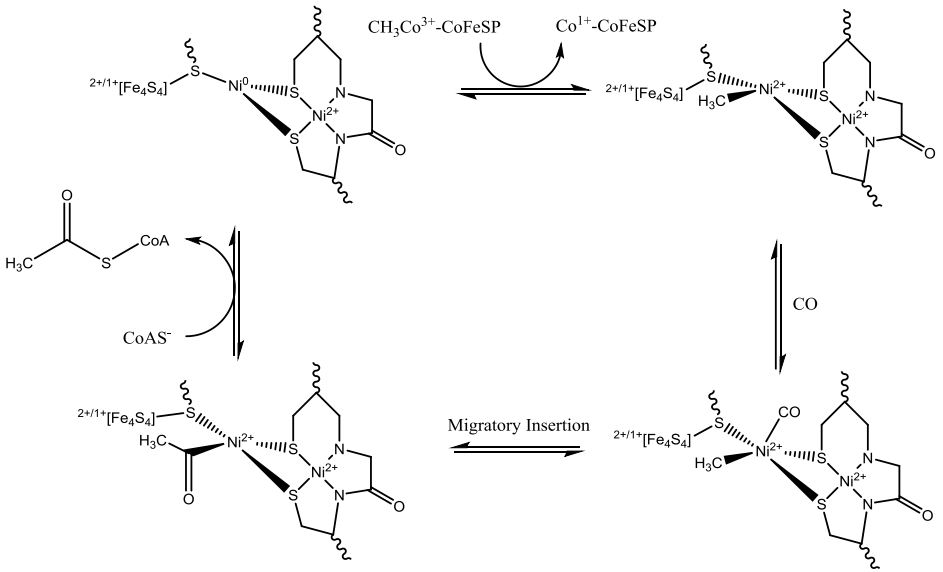
cross-coupling



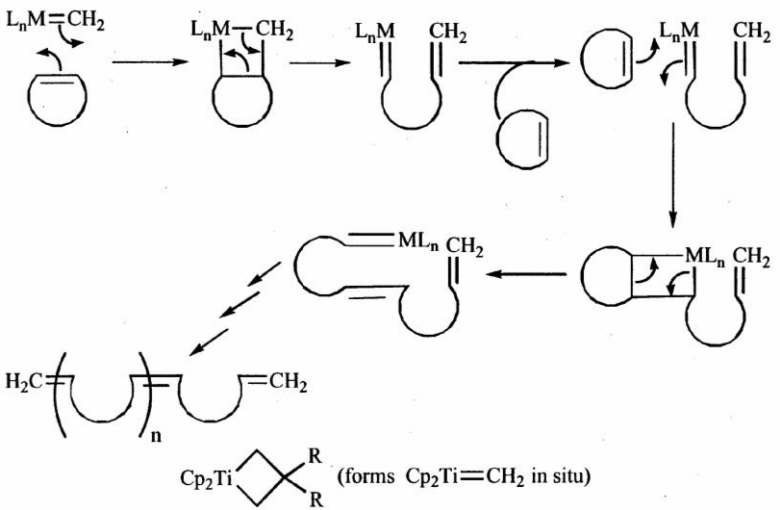
Cossee mechanism for olefin polymerization



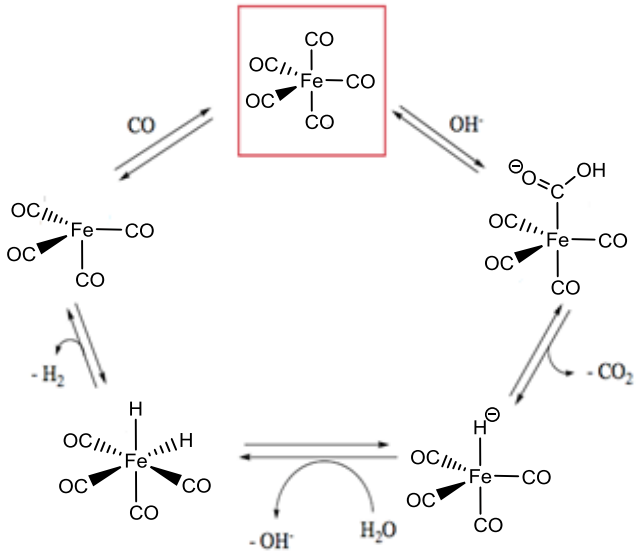
Acetyl co-A synthase



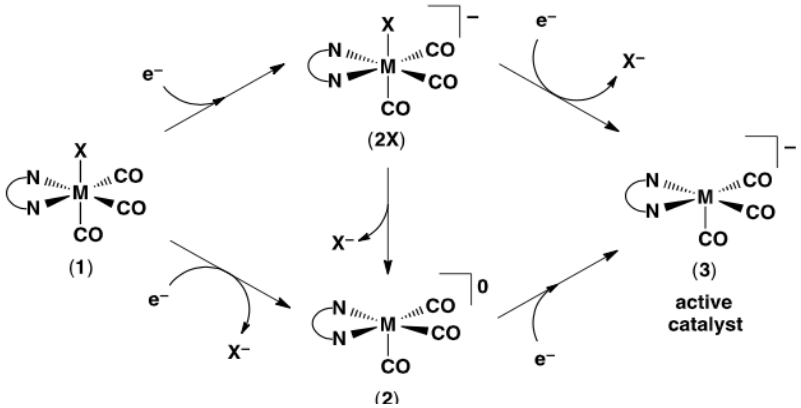
ring-opening metathesis polymerization



water-gas shift



CO_2 reduction catalyst



Chauvin mechanism for olefin metathesis