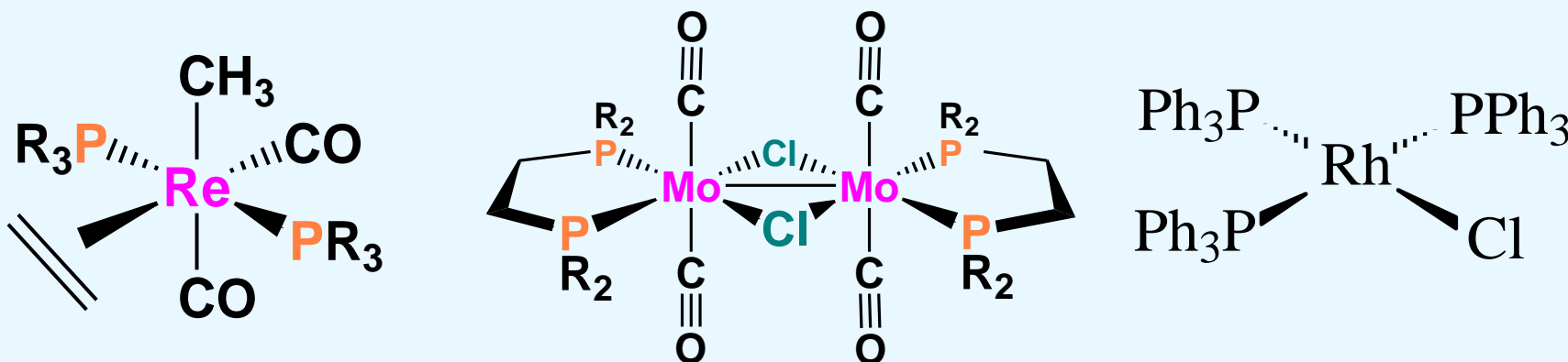


Transition metal organometallic compounds & Catalysis

French Chemist L. C. Cadet 1760 As_2Me_4 dicacodyl

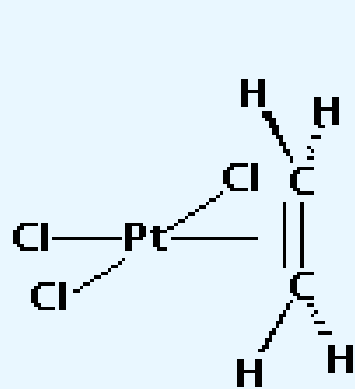
Which one is organometallic? $\text{Ni}(\text{CO})_4$ or NaCN ?

Metal-carbon bond: a few from many?

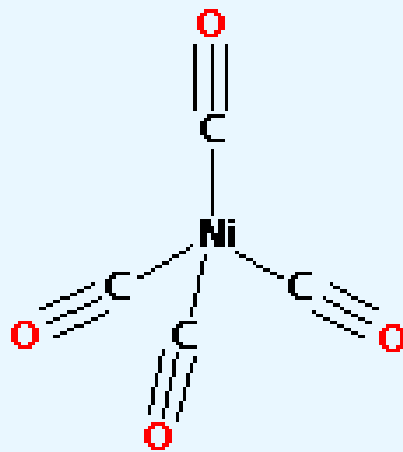


Organometallic Compound: Looking closer

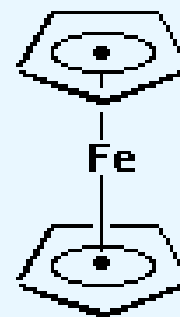
Ligand Name	Bonding Type
Molecular Hydrogen: H ₂	$\text{M} \leftarrow \begin{array}{c} \text{H} \\ \\ \text{H} \end{array}$
Hydride H ⁻	M-H
Phosphine: PR ₃	M-PR ₃
Carbonyl: C≡O	M-C≡O
Alkyl , Aryl	M-CR M-Ph
Alkene	$\begin{array}{c} \text{M} \\ \\ \text{H}_2\text{C}=\text{CH}_2 \end{array}$



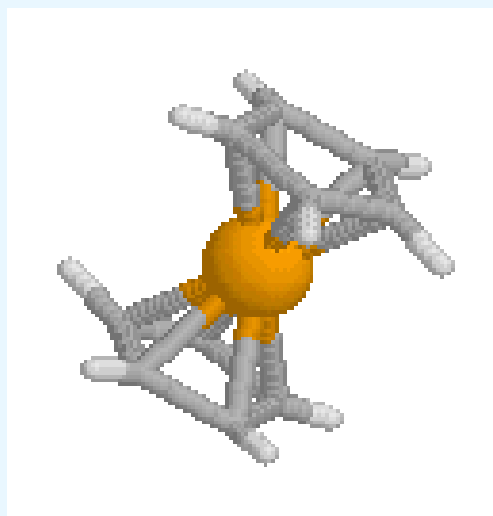
(1)



(2)



(3)



Catalysis : Basics

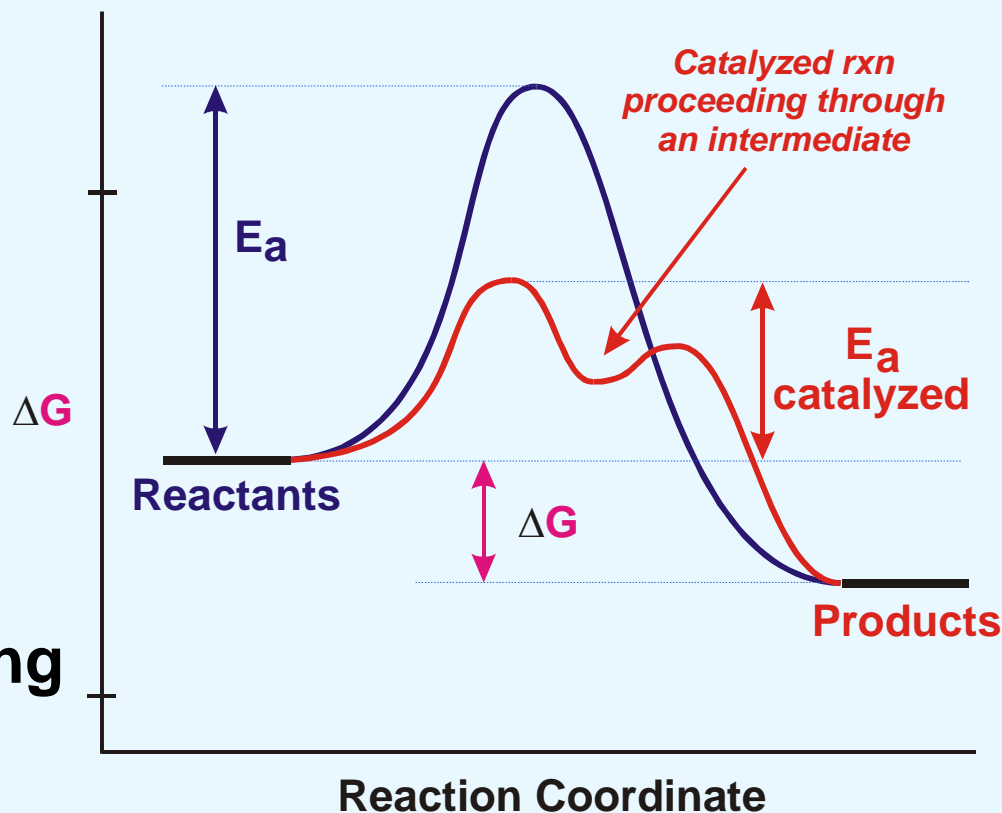


Heterogeneous

Homogeneous

A catalyst lowers the activation barrier for a transformation, by introducing a new reaction pathway.

It does not change the thermodynamics!!



Catalysis : Why

Synthesis of chemicals... pharmaceutical, agricultural

Catalytic converter ... environmental

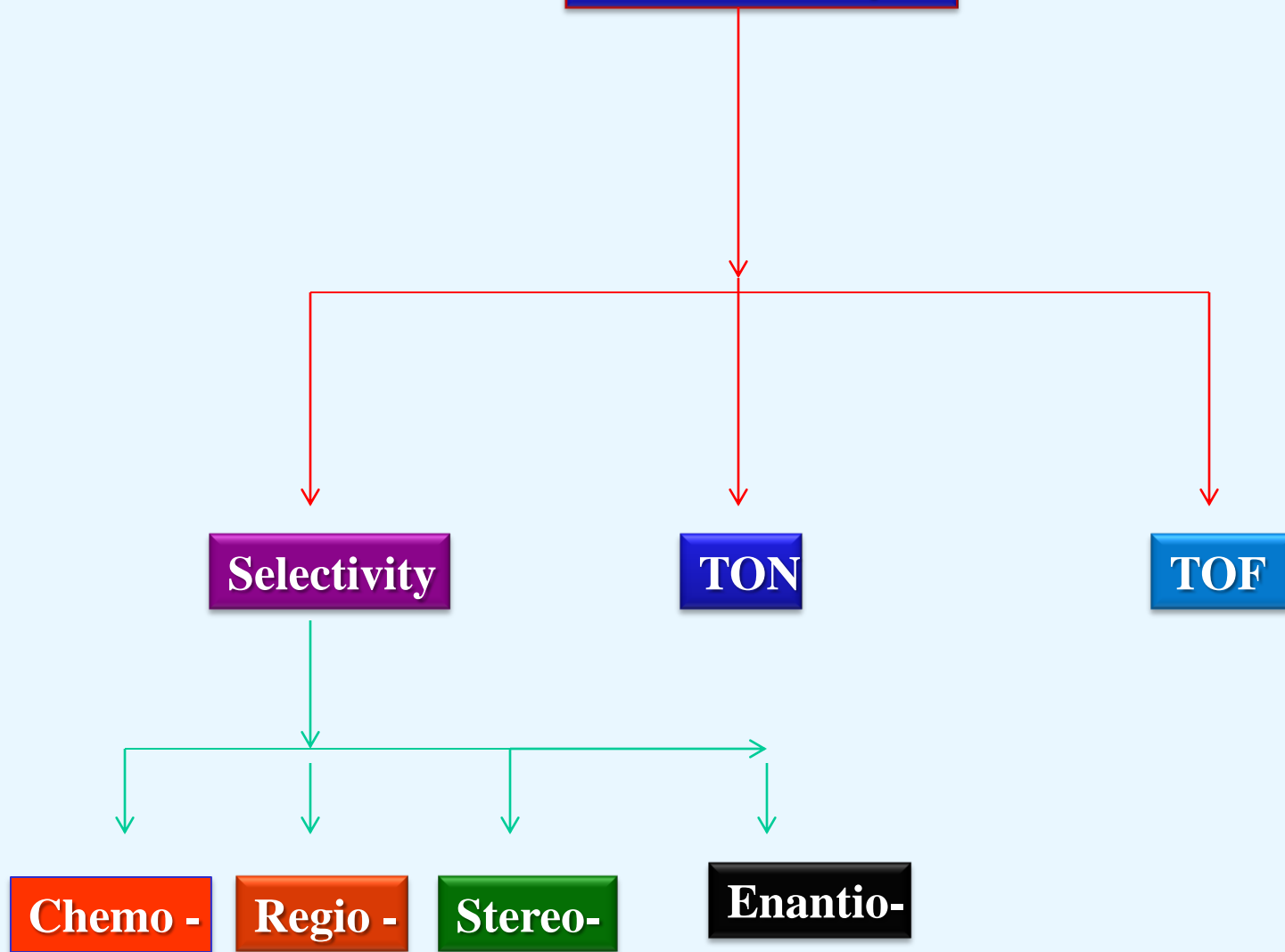
Biological system – efficient catalyst

Homogeneous and heterogeneous

How to select a good catalyst?

- Activity:** related to rate of reaction (also called turnover)
efficient catalyst: good activity
- Selectivity:** Byproducts should be minimized
- Lifetime:** It is costly to replace the catalyst frequently
- Cost:** The acceptable cost depends upon the catalyst lifetime, product value lifetime and product value
- Poisoning:** decomposition of catalyst

Good Catalysts



Structure of the Catalyst: Selectivity

Coordination compounds in catalysis

Nobel Prizes

2005 **Chauvin, Grubbs, Schrock**

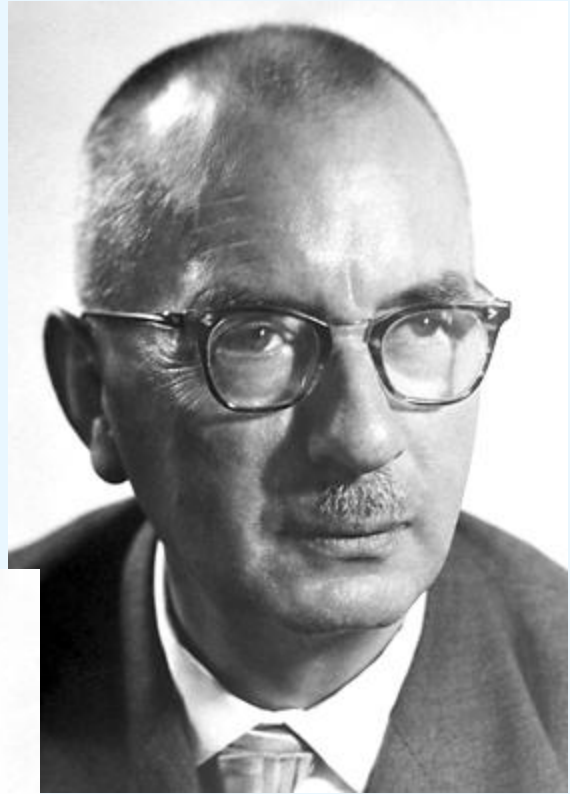
2001 **Knowles, Noyori, Sharpless**

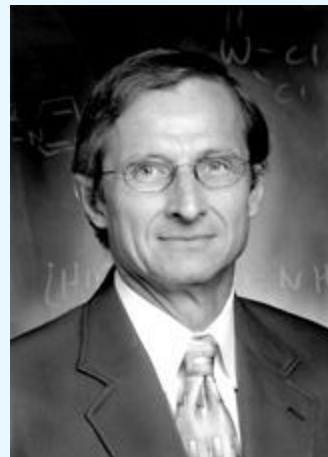
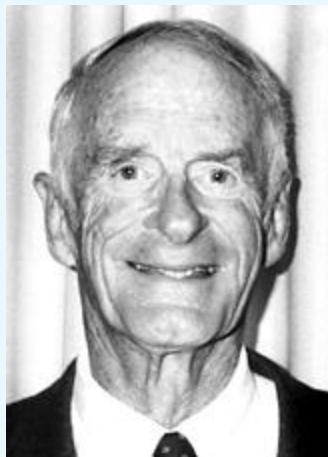
1973 **Wilkinson**

1963 **Ziegler, Natta**

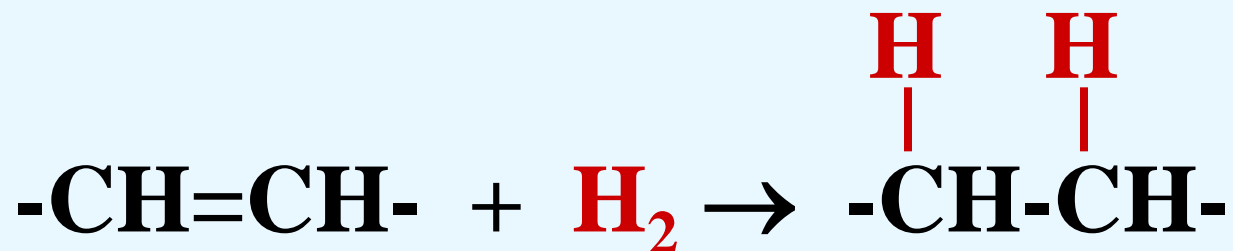
1918 **Haber**

1909 **Ostwald**





Hydrogenation of Unsaturated Hydrocarbons



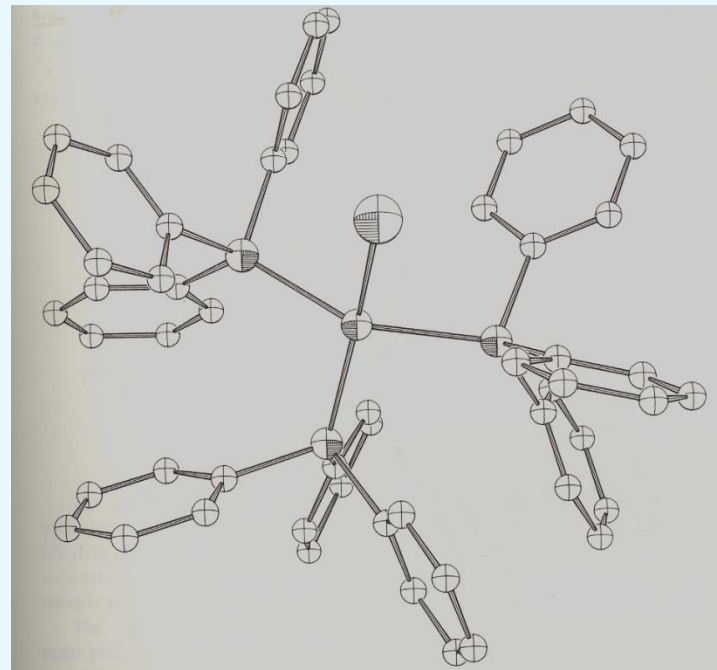
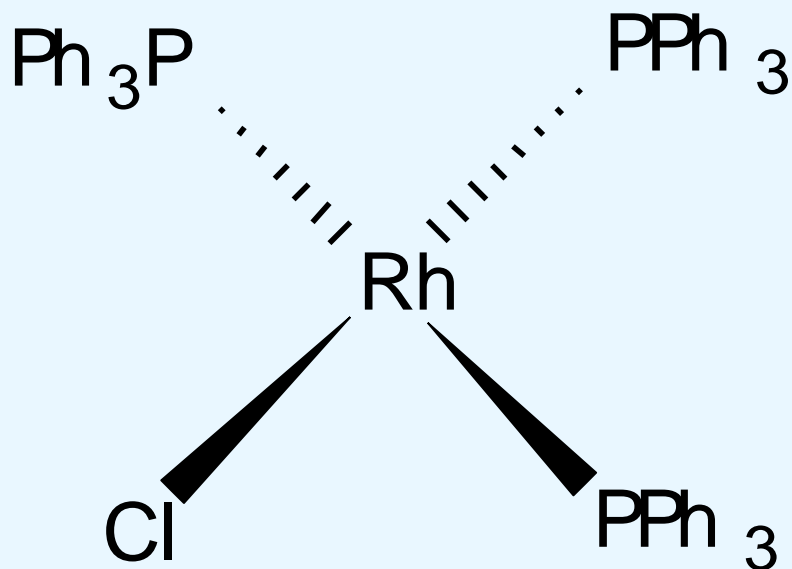
NOBEL : 2001

The most common catalyst



Wilkinson's Catalyst, $[\text{RhCl}(\text{PPh}_3)_3]$

Wilkinson's Catalyst (WC)



Chlorotris(triphenylphosphine)rhodium(I)

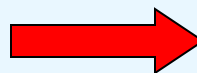
square planar d⁸ configuration

Geoffrey Wilkinson

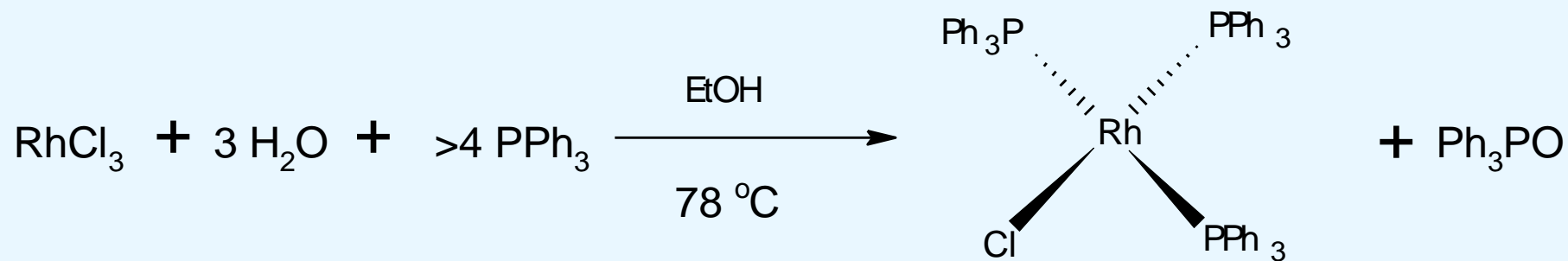
- Born July 14, 1921, Yorkshire, England
- Ph.D from Cal Berkeley studying with Glenn Seaborg
- First published compound in 1965 in Journal of the Chemical Society - *Chemical Communications*
- Nobel Prize in Chemistry 1973 (shared with Ernst Otto Fischer) for their pioneering work, performed independently, on the chemistry of the organometallic, so called sandwich compounds.



Organometallic compounds prepared by
Wilkinson in display at Harvard Univ.



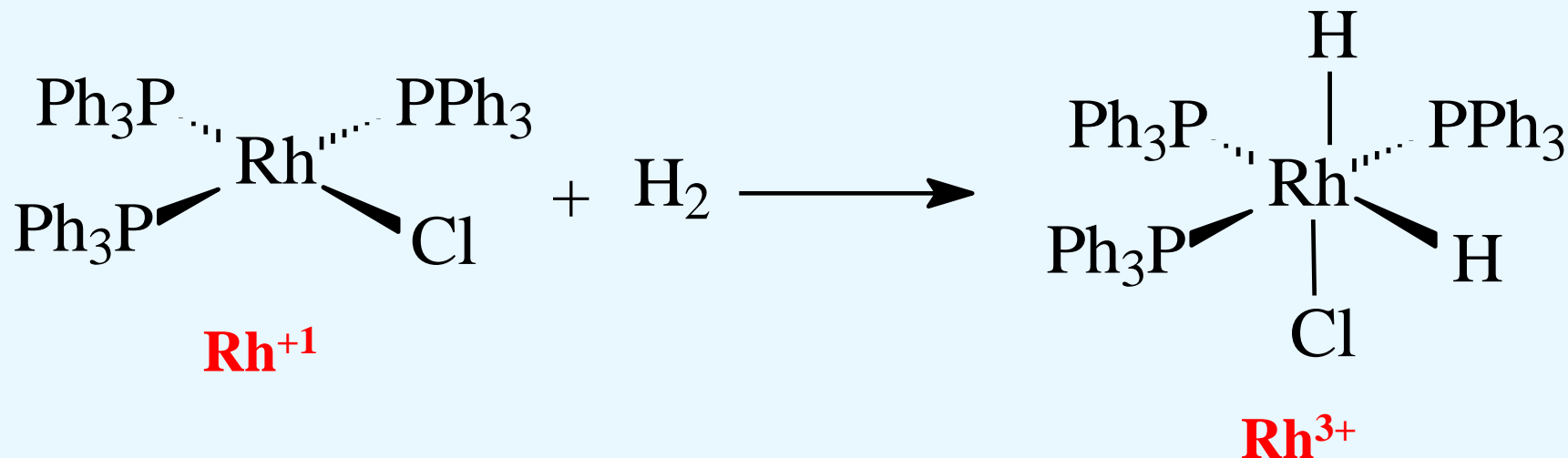
Synthesis of WC



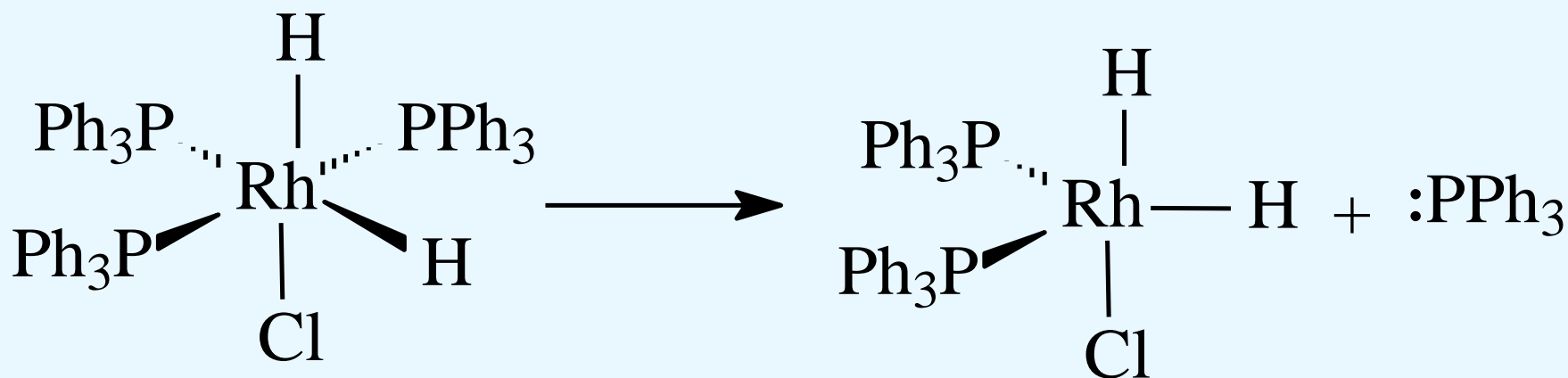
Commercially available

WC in alkene Hydrogenation: Catalytic Steps

(1) Oxidative addition

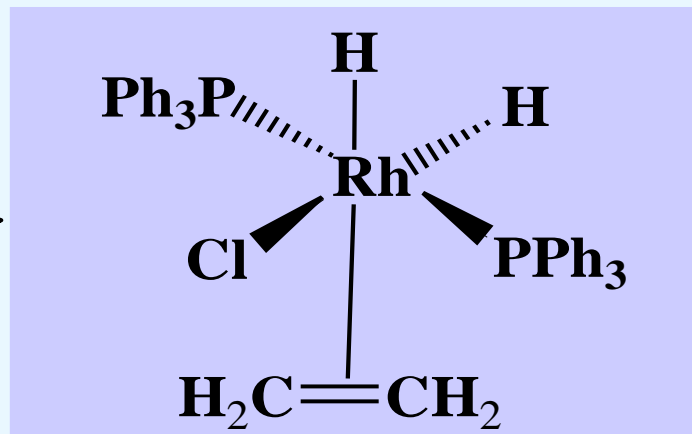
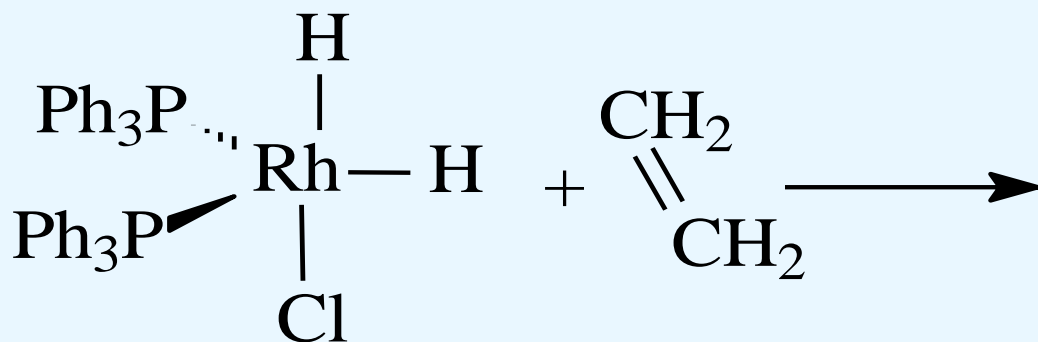


(2) Ligand Dissociation

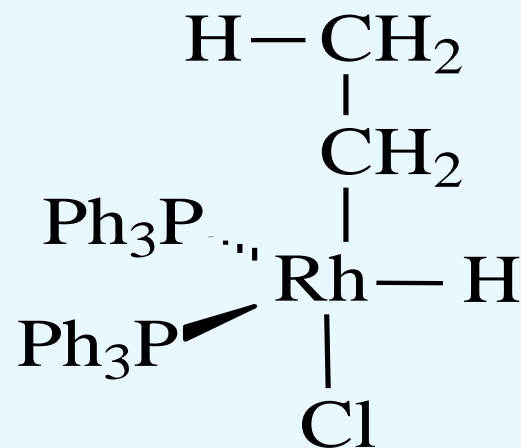
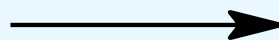
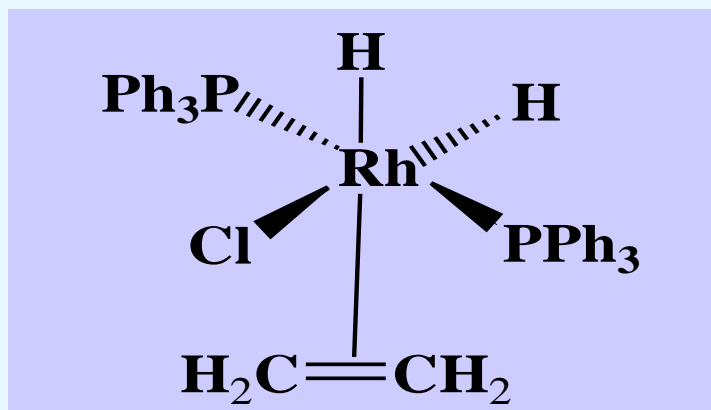


WC in alkene Hydrogenation: Catalytic Steps

(3) Ligand Association

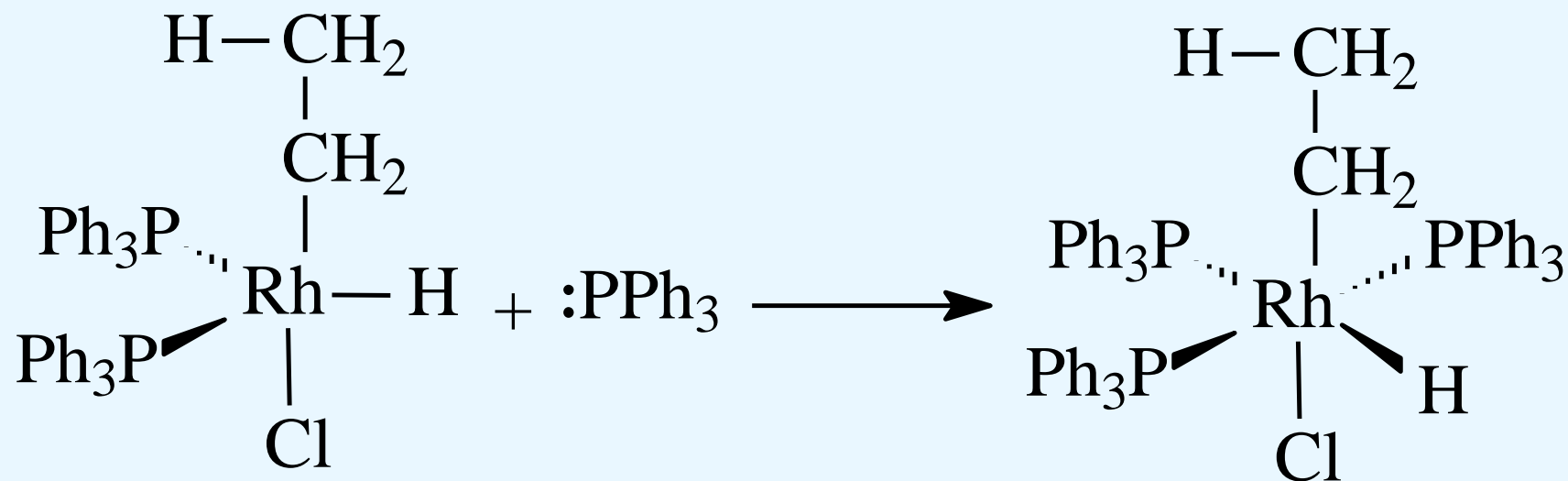


(4) Migration/Insertion



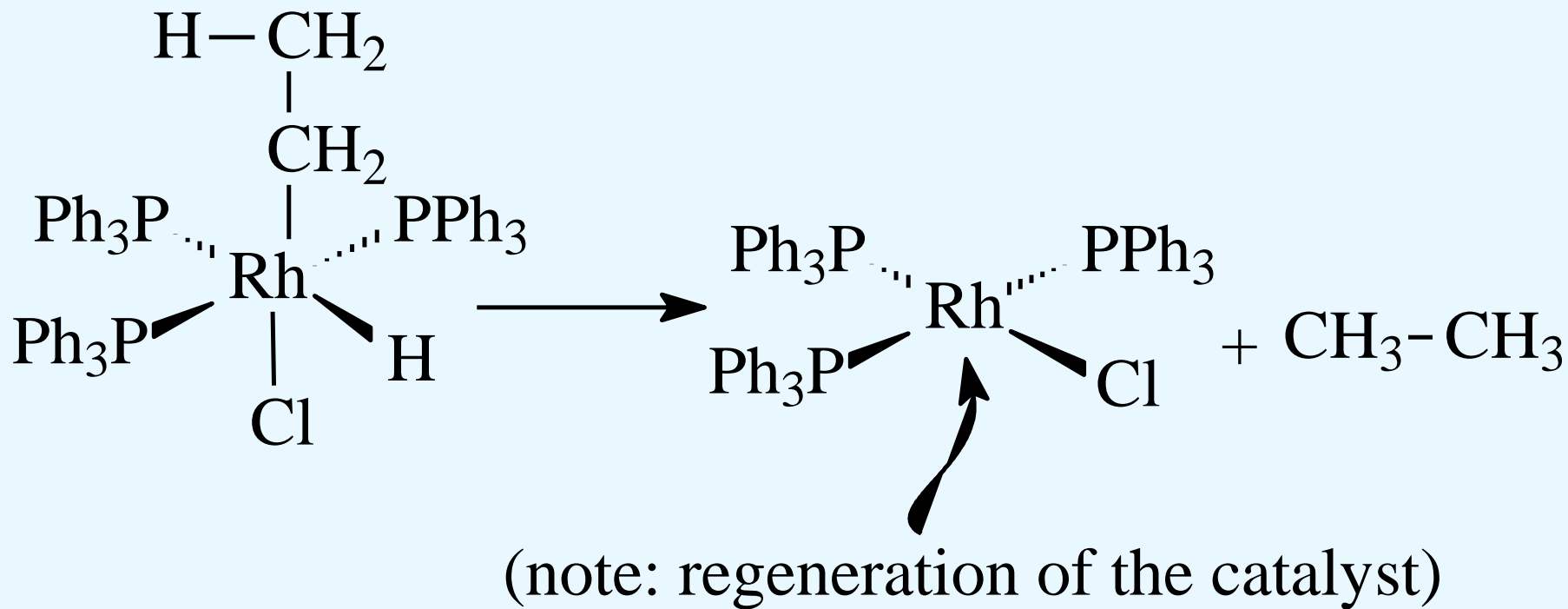
WC in alkene Hydrogenation: Catalytic Steps

(5) Ligand association

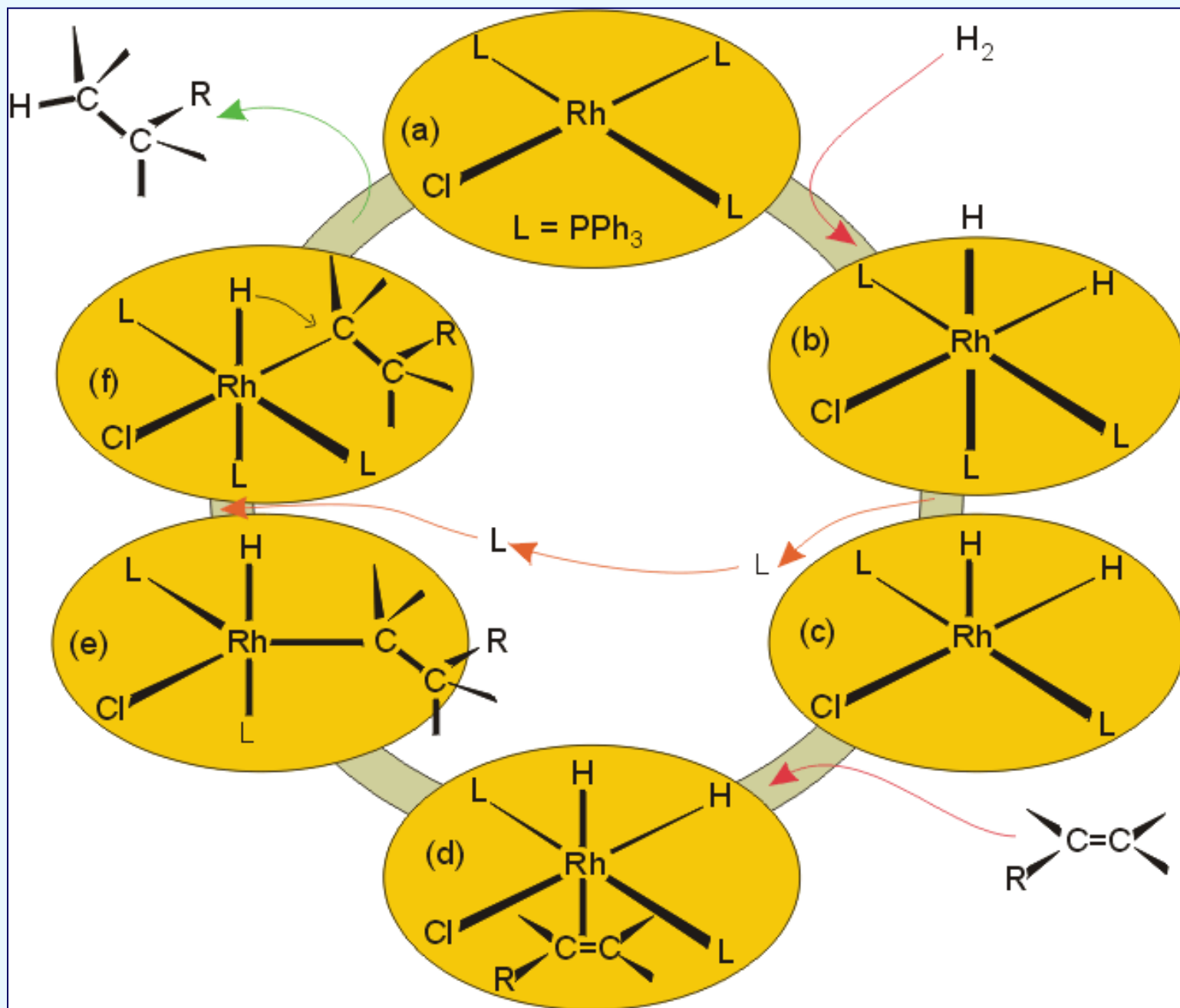


WC in alkene Hydrogenation: Catalytic Steps

(6) Reductive elimination



WC IN A C T I O N



WC in alkene Hydrogenation: Additional Notes

Rate of the reaction decreases as the alkyl substitution increases

Highly sensitive to the nature of the phosphine ligand

Analogous complexes with alkylphosphine ligands are inactive

Highly selective for $C=C$ over $C=O$

Applications

*** Laboratory scale organic synthesis**

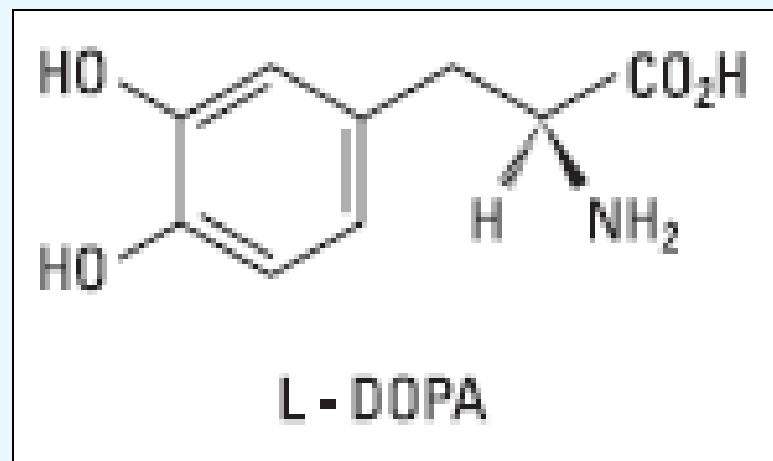
*** Production of fine chemicals**

Alkene Hydrogenation & Chirality & Nobel

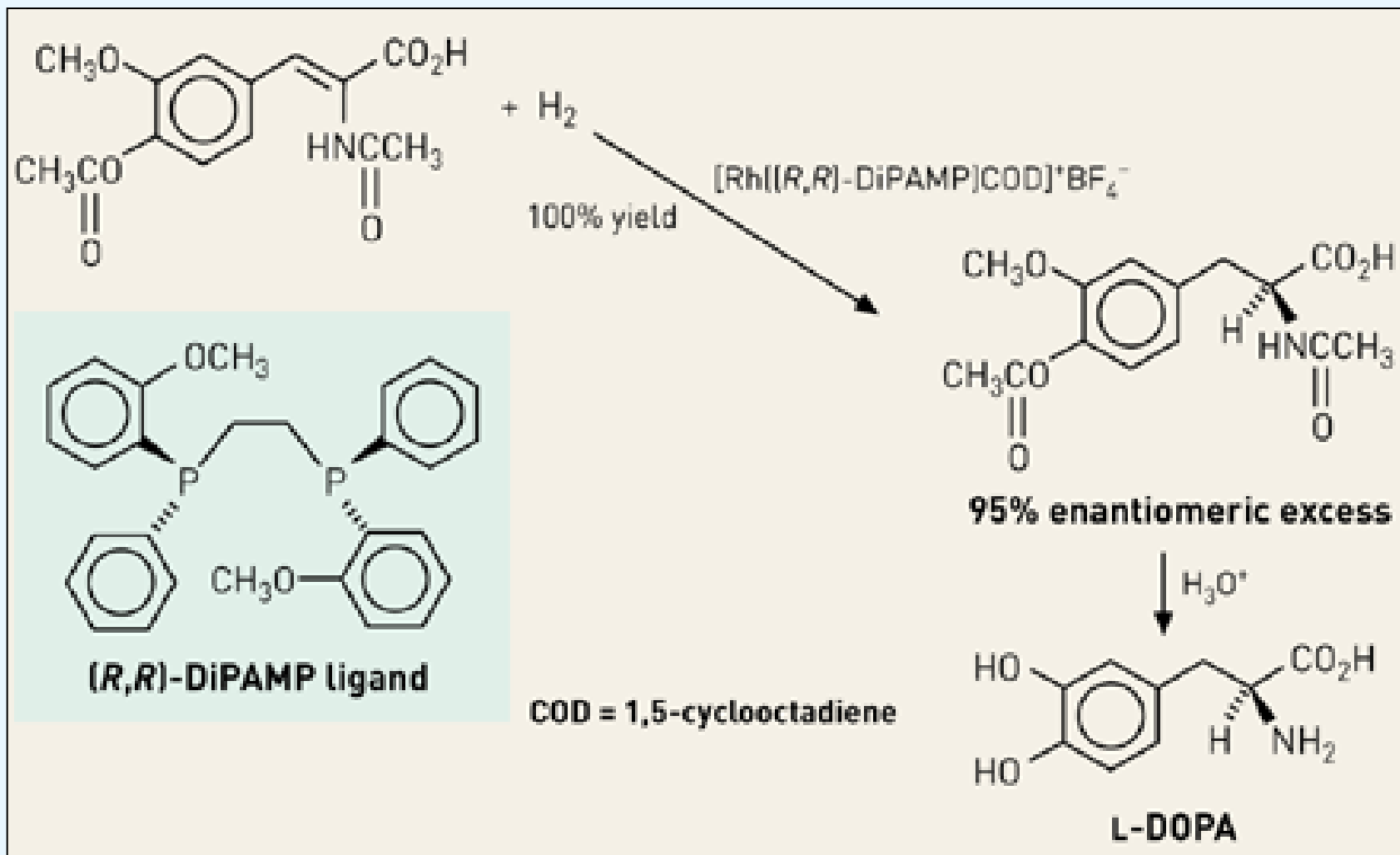
Chiral phosphine ligands have been developed to synthesize optically active products.

Synthesis of L-DOPA (Used in the treatment of Parkinson's diseases)
Synthetic route was developed by **Knowles & co-workers** at Monsanto

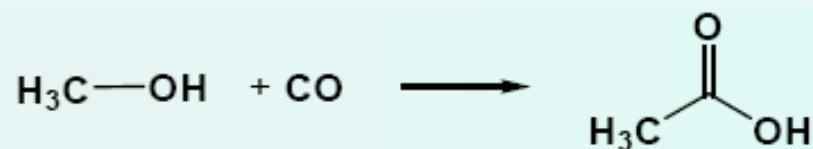
Dr. William S. Knowles received Nobel prize in chemistry 2001 along with other two scientists.



Alkene Hydrogenation, Chirality & Nobel



This reaction, developed by Knowles, Vineyard, and Sabacky, was used at Monsanto as a commercial route to the Parkinson's drug L-DOPA.



Precatalyst: $[\text{Rh}(\text{CO})_2\text{I}_2]\text{AsPh}_4^+$

Other possible precatalysts: $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, Rh_2O_3

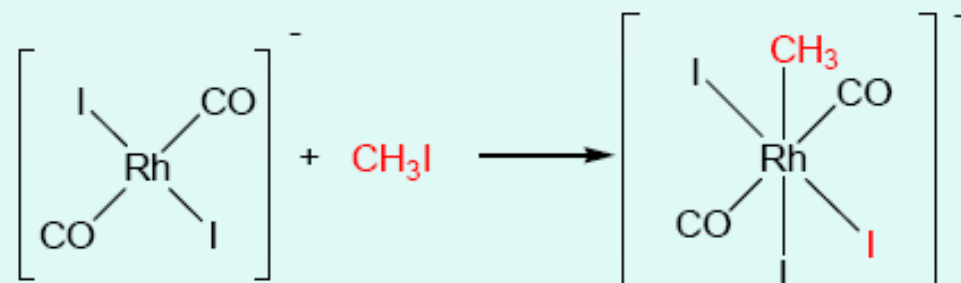
For the reaction to be possible the source of **I** should exist (usually **HI**)

Mechanism of “Monsanto” carbonylation:

1. CH_3I generation:

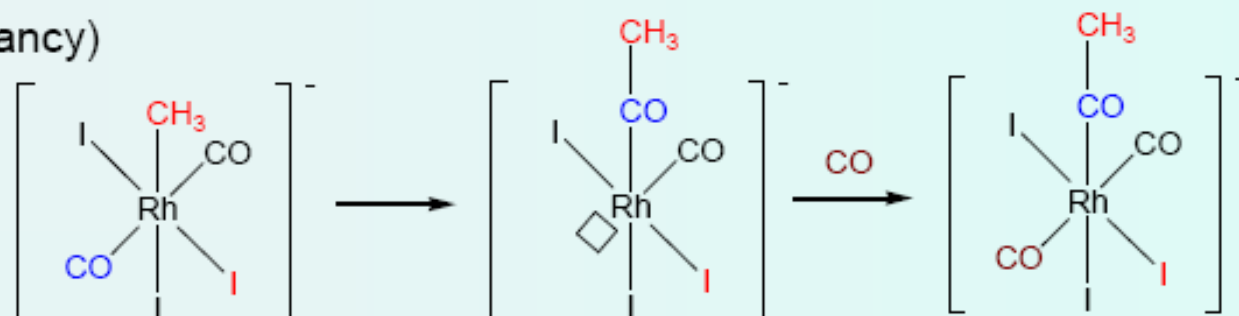


2. Oxidative addition of CH_3I to the Rh^{I} -complex

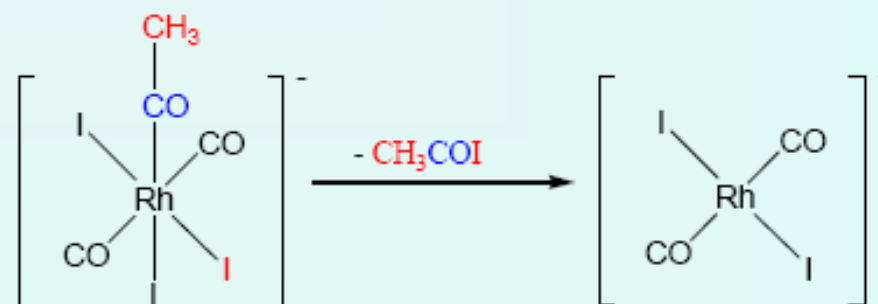


This is the slowest stage of the process

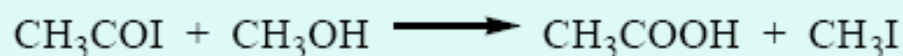
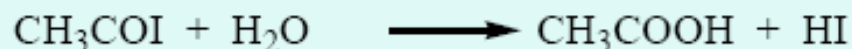
3. Migration insertion of CO (plus new CO addition to the coordination vacancy)

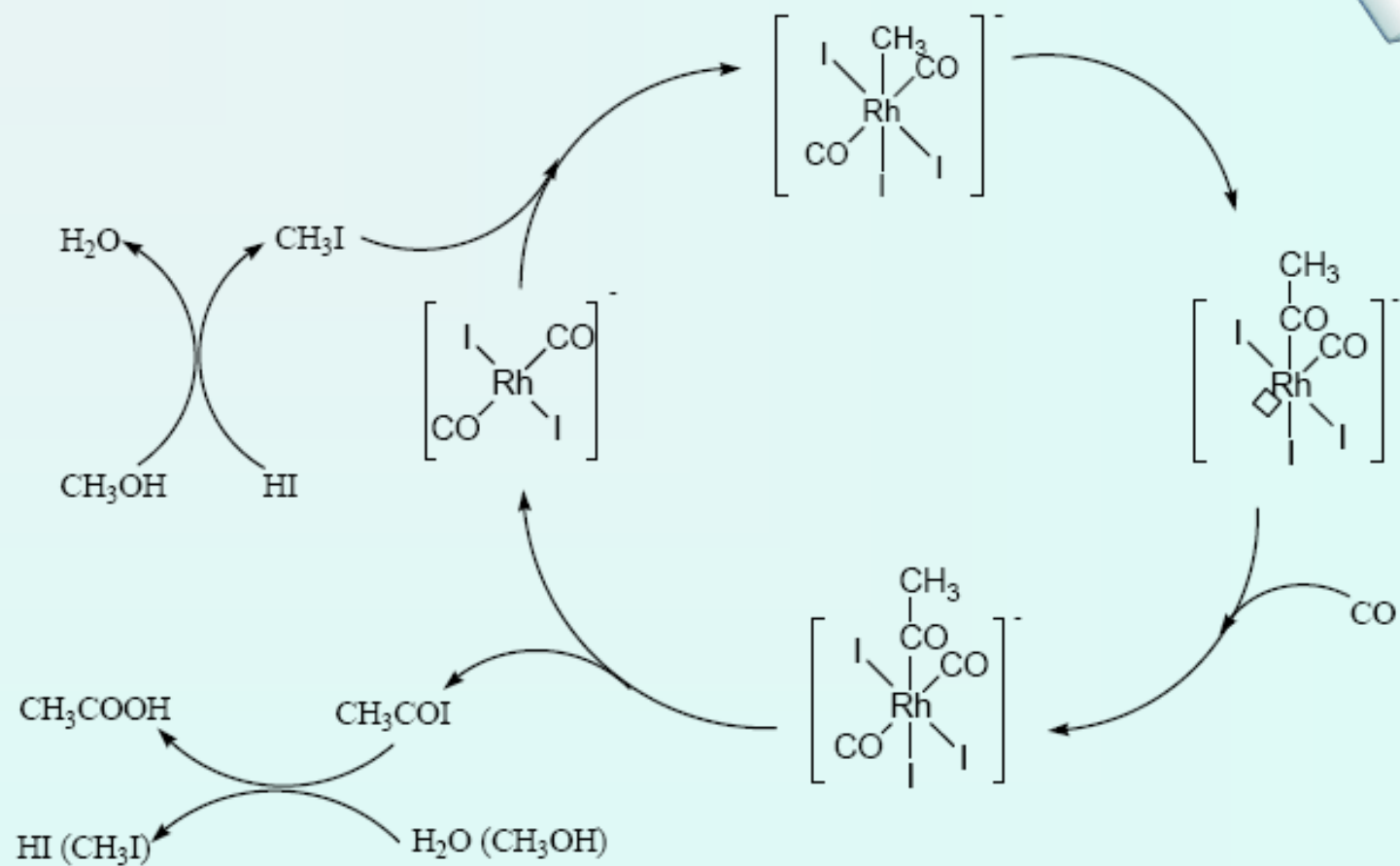


4. Reductive elimination of CH₃COI



5. Formation of acetic acid through the following processes:





Additional notes For interested students

(a) Ligand coordination and dissociation

Facile coordination of the reactant and facile loss of products.

Coordinationally unsaturated - 16-electron complexes

(b) Oxidative addition

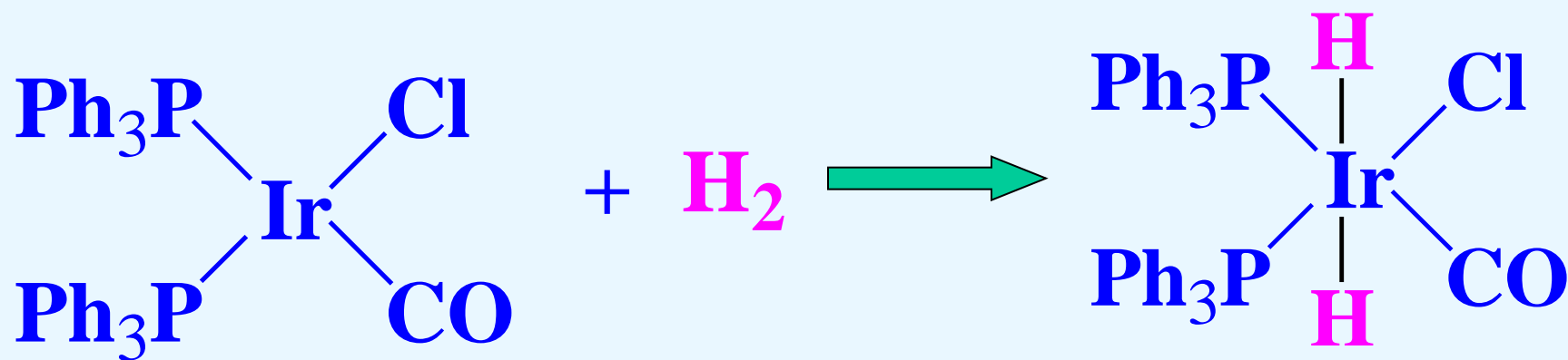
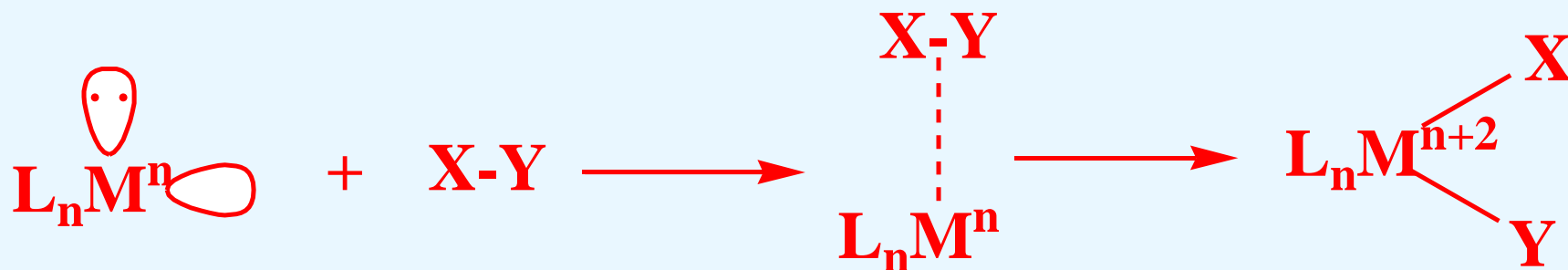
-occurs when a complex behaves simultaneously as a Lewis base and a Lewis acid

Metal must possess a non-bonding electron pair

Coordinationally unsaturated

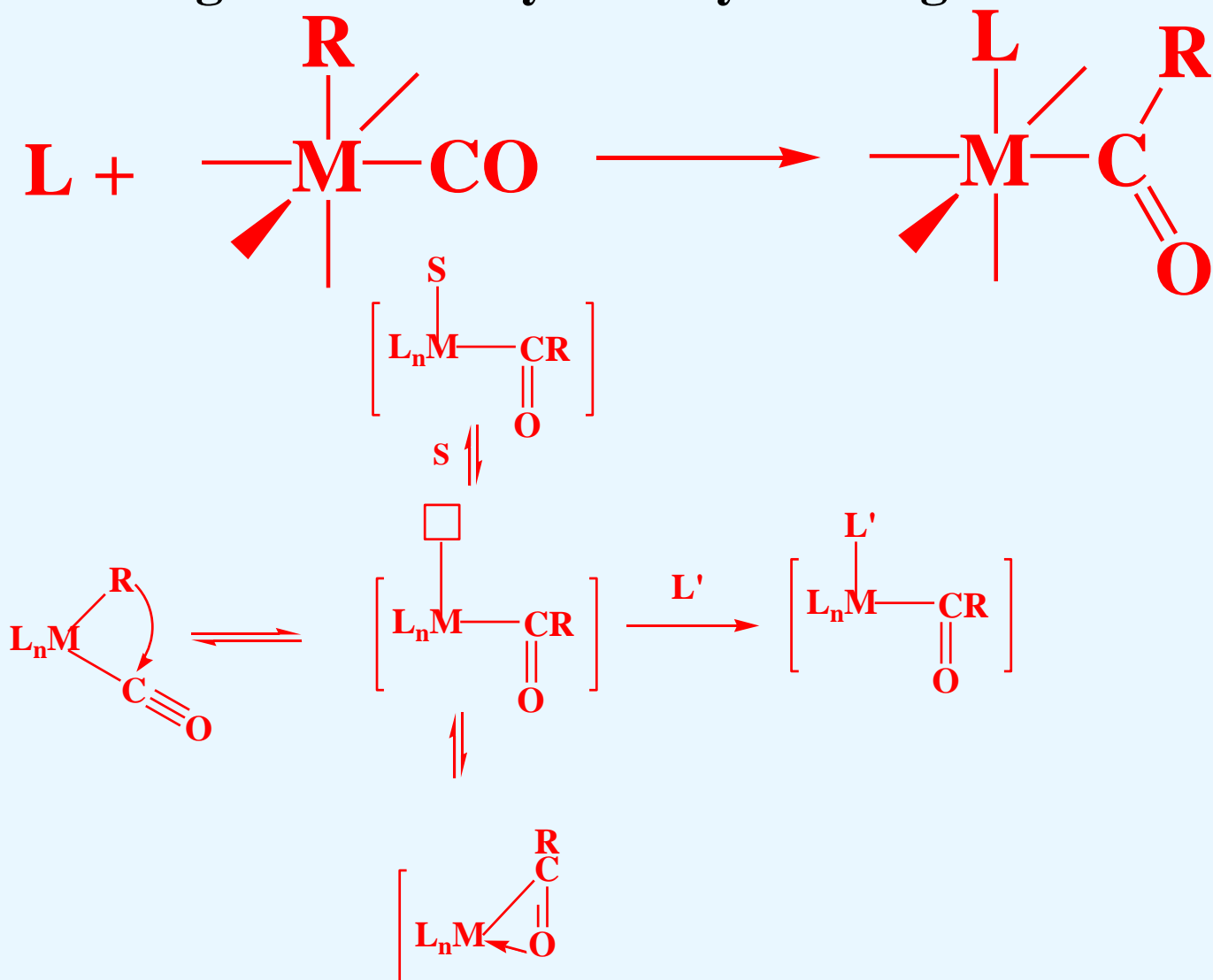
Oxidation of metal by two units – M^n to M^{n+2}

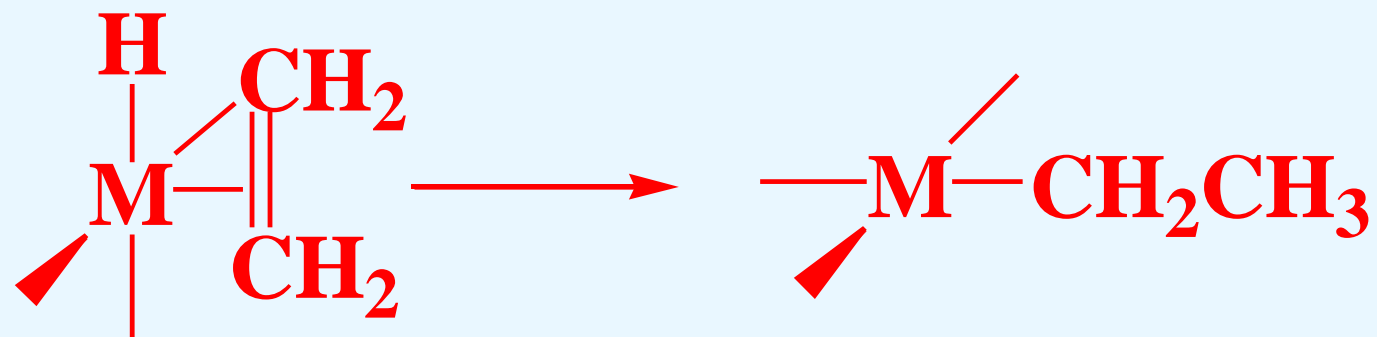
Oxidative addition...



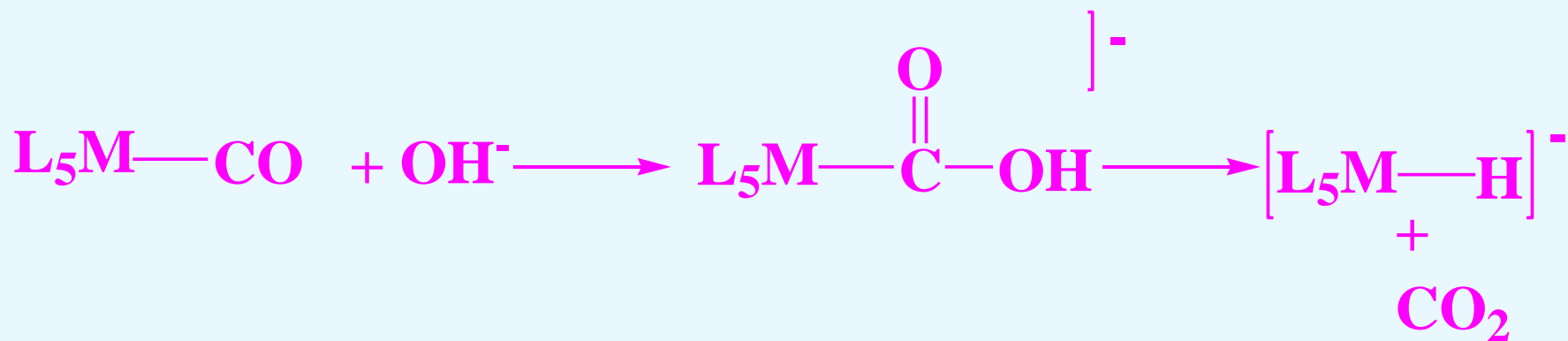
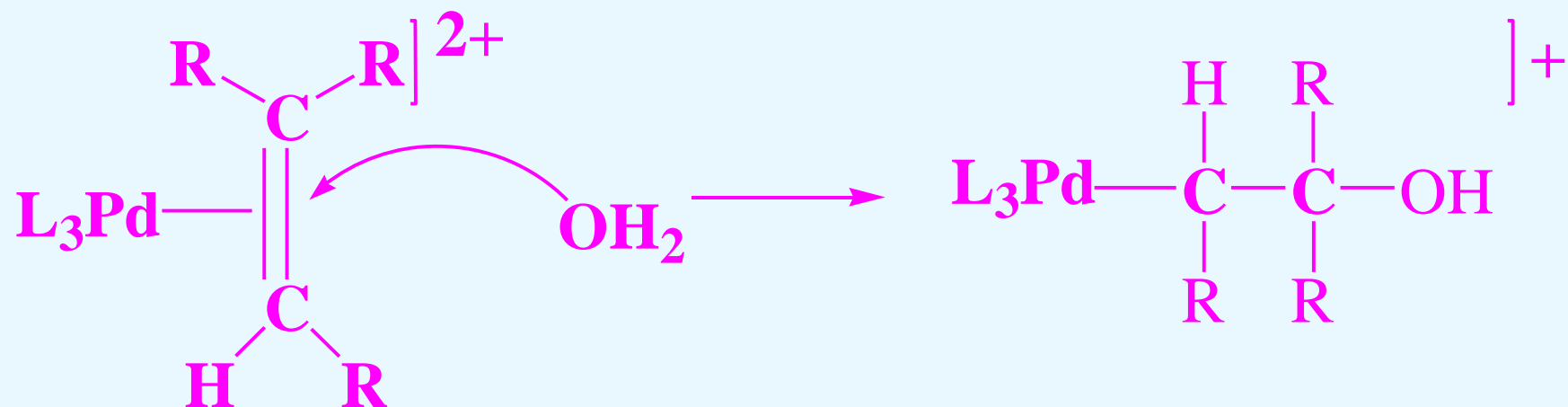
(c) Insertion or migration

Migration of alkyl and hydride ligands





(d) Nucleophilic attack



(e) Reductive elimination

Involves decrease in the oxidation and coordination number

