

Transition metal Chemistry:

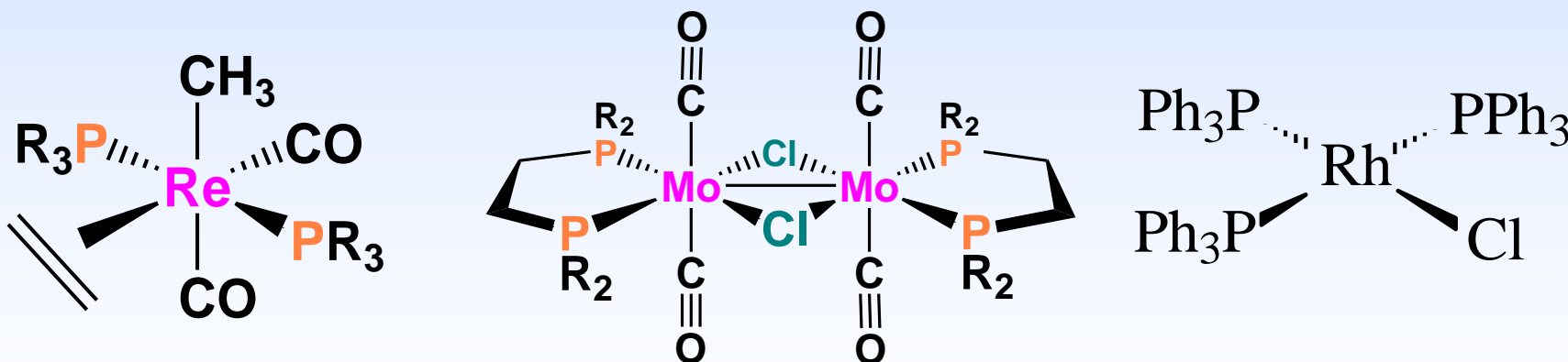
Organometallic compounds
&
Catalysis

Transition metal organometallic compounds & Catalysis

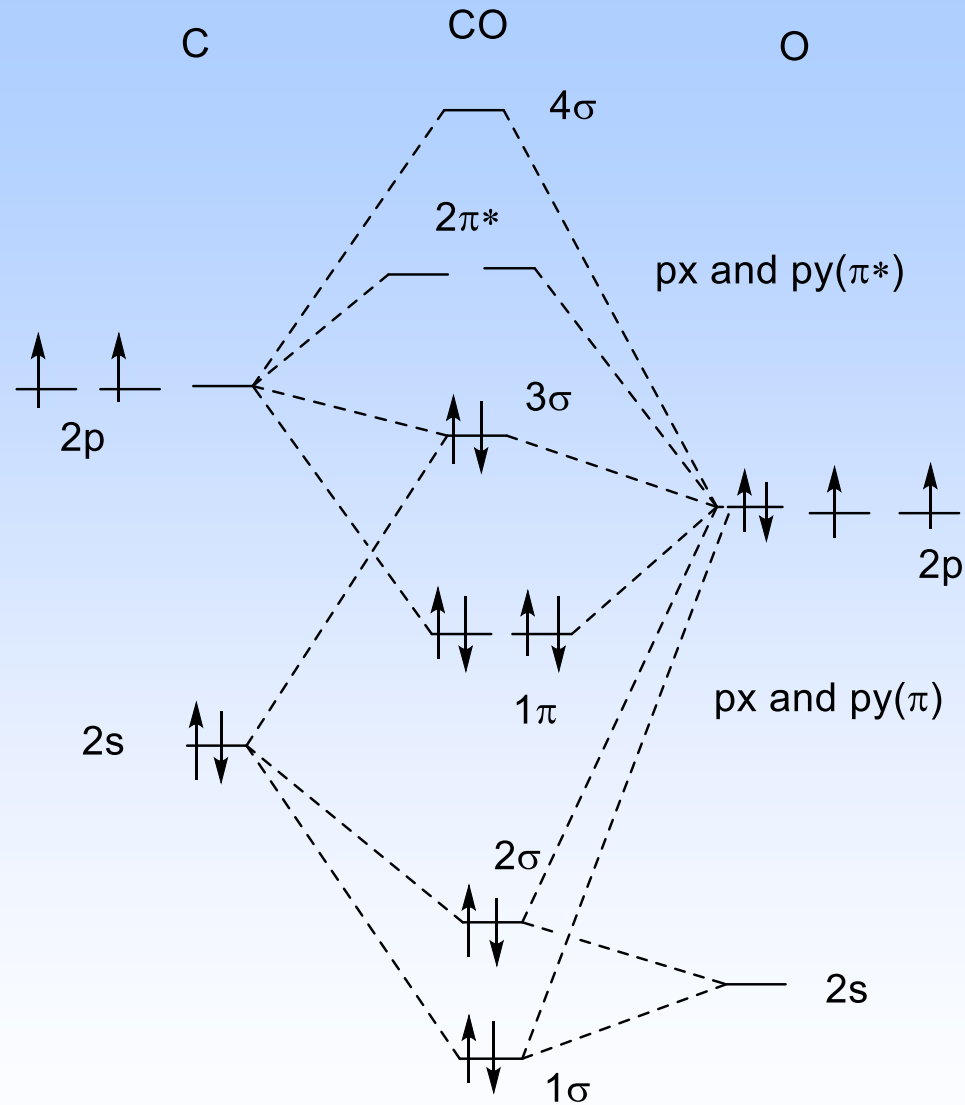
Which one is organometallic?

$\text{Ni}(\text{CO})_4$ or NaCN ?

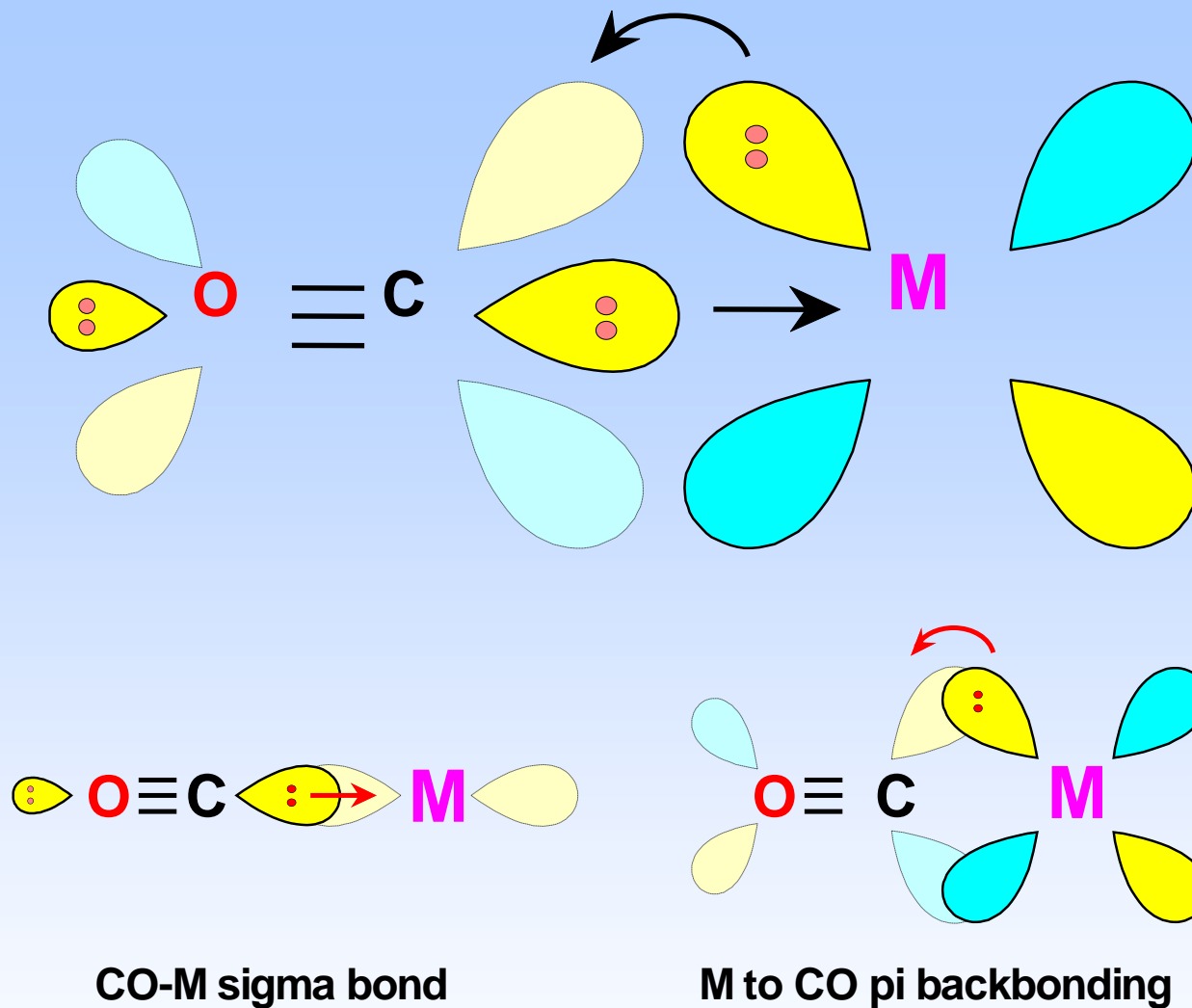
Metal-carbon bond should be present.



Stabilizing Low Oxidation State: CO Can Do the Job

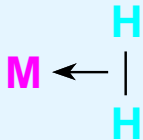
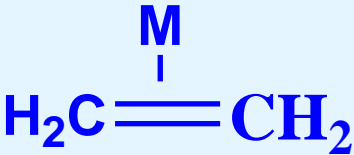


1σ and 3σ are essentially nonbonding and bond order is 3.



Ni(CO)_4 , $[\text{Fe(CO)}_5]$, $[\text{Cr(CO)}_6]$, $[\text{Mn}_2(\text{CO})_{10}]$,
 $[\text{Co}_2(\text{CO})_8]$, $\text{Na}_2[\text{Fe(CO)}_4]$, $\text{Na}[\text{Mn(CO)}_5]$

Organometallic Compound: Looking closer

Ligand Name	Bonding Type
Molecular Hydrogen: H_2	
Hydride H^-	$\text{M}-\text{H}$
Phosphine: PR_3	$\text{M}-\text{PR}_3$
Carbonyl: $\text{C}\equiv\text{O}$	$\text{M}-\text{C}\equiv\text{O}$
Alkyl , Aryl	$\text{M}-\text{CR}$ $\text{M}-\text{Ph}$
Alkene	

18 electron rule

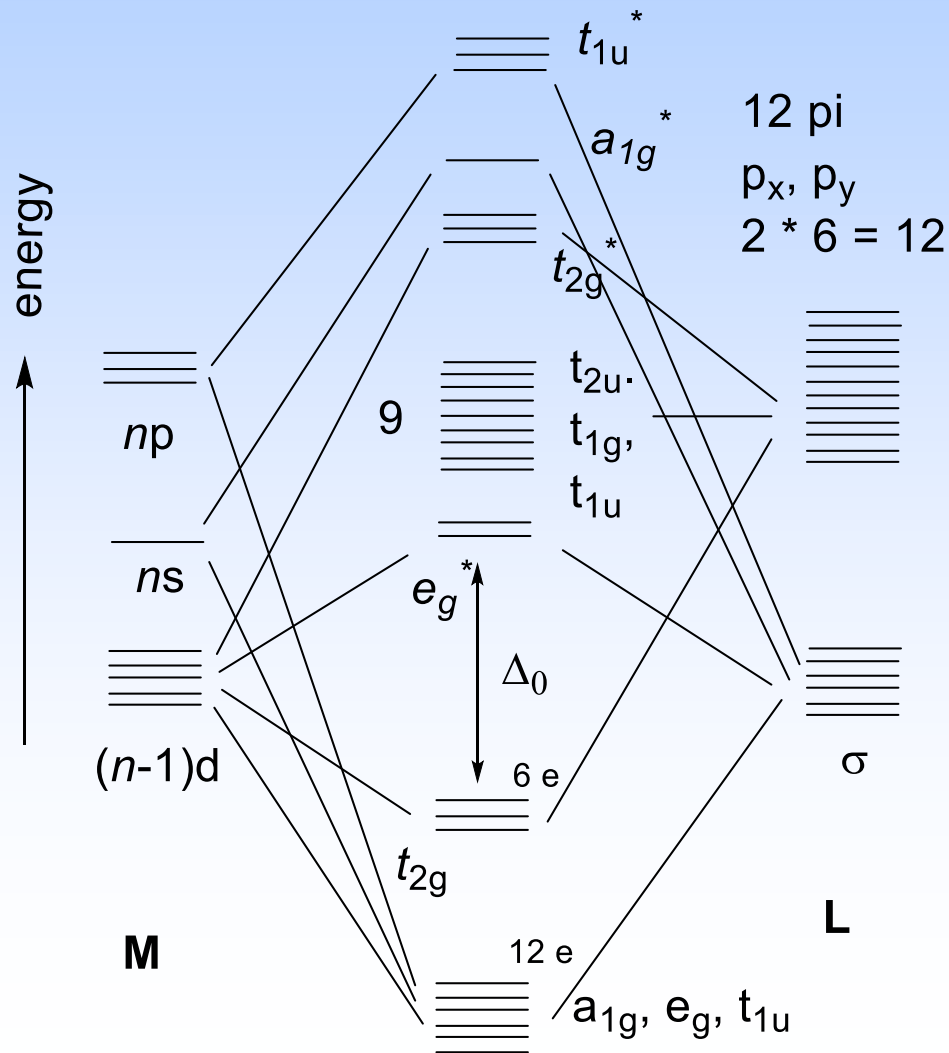
1920

British Chemist

Sidgwick

Organic compounds – Octet rule Organometallic – 18 electron rule

• 18 valence electron –
inert gas configuration



18 electron rule

- Stable low oxidation state complexes are found to have a total of 18 bonding electrons
 - metal electrons plus lone pairs from ligands
- Ni(CO)_4 - $4s^2 3d^8$ and 4 lone pairs
- Fe(CO)_5 - $4s^2 3d^6$ and 5 lone pairs
- Cr(CO)_6 - $4s^2 3d^4$ and 6 lone pairs
- The stability of these 18 electron species can be explained using MO theory
 - Corresponds to filling all the molecular bonding orbitals and none of the antibonding orbitals
- However, the 18 electron rule only works for species with metals in a low oxidation state NOT FOR MOST COMPLEXES

**To determine the 18 VE count for a metal complex:
Neutral Atom method**

Find out the total number of valence electrons (s and d only) – the group number plus the number of electrons donated by ligands as per the table.

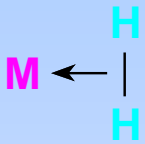
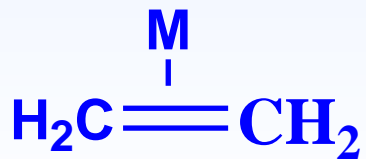
For anionic complex, add that many number of electrons equal to the negative charge.

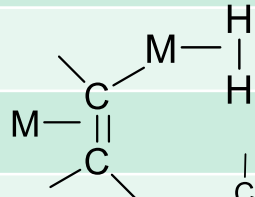
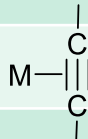
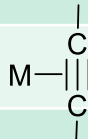
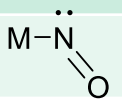
For cationic complex, subtract that many number of electrons equal to the positive charge.

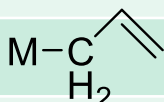
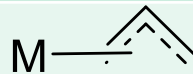
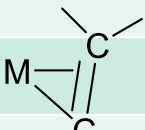
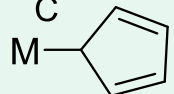
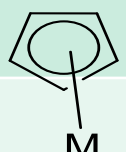
For every M-M single bond, add one electron to the count of each metal atom.


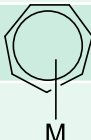
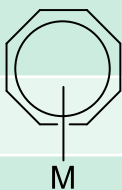
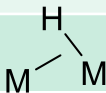
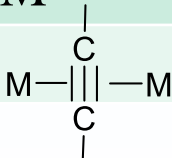
Neutral Atom method versus oxidation method (not following)

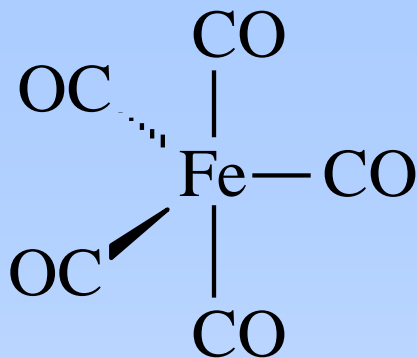
Counting the number of electrons

Ligand Name	Bonding Type	Formal Charge	Electrons donated
Molecular Hydrogen: H ₂		0	2
Hydride H ⁻	M-H	-1	1
Halide X ⁻	M-X	-1	1
Amine, phosphine, arsine: NR ₃ , PR ₃ , AsR ₃	M-NR ₃ M-PR ₃	0	2
Carbonyl: C≡O	M-C≡O	0	2
Alkyl , Aryl	M-CR ₃ M-Ph	-1	1
Alkene		0	2

	Neutral atom electron count	Oxidation state electron count
M-CO	2	2
M-CS	2	2
M-PR3	2	2
M-NR3	2	2
M-N≡N	2	2
dihydrogen		2
alkene		2
Alkyne*		2
Isocyanide M-CNR		2
Nitrosyl, bent,		2
Nitrosyl, linear,	M-N≡O	2
M-X (halogen)	1	2
M-H	1	2
M-R	1	2

	Neutral atom electron count	Oxidation state electron count
M-COR	1	2
M-Ph	1	2
M-NR ₂	1	2
M-PR ₂	1	2
M-OR	1	2
M-SR	1	2
Carbene =alkylidene M=CR ₂	2	4
Carbyne =alkylidyne M≡CR	3	6
η ¹ -allyl, 	1	2
η ³ -allyl, 	3	4
η ² -enyl, 	3	4
η ¹ -cyclopentadienyl, 	1	2
η ⁵ -cyclopentadienyl, 	5	6

		Neutral atom electron count	Oxidation state electron count
η^6 -benzene		6	6
		1	2
η^7 -cycloheptatrienyl		7	6
		1	2
η^7 -cyclooctatetraenyl		8	10
		1	2
M-CO-M		2	2
M-X-M		3	4
M-H-M		2	2
M-(CR ₃)-M		2	2
M-(NR ₂)-M		3	4
M-(PR ₂)-M		3	4
M-(OR)-M		3	4
		4	4



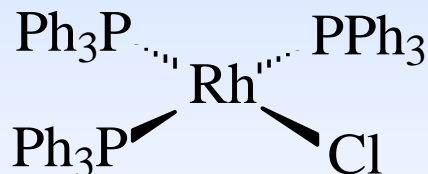
Fe is $4s^2 3d^6 = 8e$



each CO donates 2 e = $10e$

$$8e + 10e = 18e$$

coordinely saturated



Rh is $s^1 d^8 = 9e$

since Cl is -1, Rh is $+1$ (the complex is neutral)

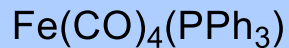
$$9e - 1e + 8e = 16e$$

4 ligands x 2e each = $8e$

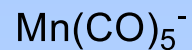
therefore coordinely **unsaturated**



$$\begin{array}{rcl} \text{Cr} & = & 6 \text{ e} \\ 6\text{CO} & = & 12 \text{ e} \\ \hline & & 18 \text{ VE} \end{array}$$



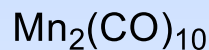
$$\begin{array}{rcl} \text{Fe} & = & 8 \text{ e} \\ 4\text{CO} & = & 8 \text{ e} \\ \text{Ph}_3\text{P} & = & 2 \text{ e} \\ \hline & & 18 \text{ VE} \end{array}$$



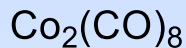
$$\begin{array}{rcl} \text{Mn} & = & 7 \text{ e} \\ 5\text{CO} & = & 10 \text{ e} \\ \text{charge} & = & 1 \text{ e} \\ \hline & & 18 \text{ VE} \end{array}$$



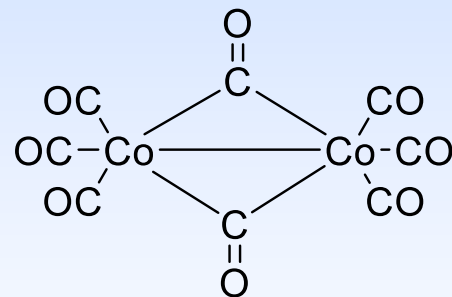
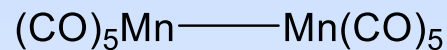
$$\begin{array}{rcl} \text{Co} & = & 9 \text{ e} \\ 4\text{CO} & = & 8 \text{ e} \\ \text{charge} & = & 1 \text{ e} \\ \hline & & 18 \text{ VE} \end{array}$$



$$\begin{array}{rcl} 2\text{Mn} & = & 14 \text{ e} \\ 10\text{CO} & = & 20 \text{ e} \\ \text{Mn-Mn} & = & 2 \text{ e} \\ \hline & & 36 \text{ VE} \\ 36/2 & = & 18 \text{ VE/Mn} \end{array}$$



$$\begin{array}{rcl} 2\text{Co} & = & 18 \text{ e} \\ 8\text{CO} & = & 16 \text{ e} \\ \text{Co-Co} & = & 2 \text{ e} \\ \hline & & 36 \text{ VE} \\ 36/2 & = & 18 \text{ VE/Co} \end{array}$$



terminal or bridging CO
2 e donor only

Neutral atom Oxidation state

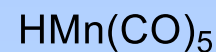


$$\begin{array}{r} \text{Pt} = 10 \text{ e} \\ 4\text{Cl} = 4 \text{ e} \\ \text{charge} = 2 \text{ e} \\ \hline 16 \text{ VE} \end{array}$$

$$\begin{array}{r} \text{Pt}^{2+} = 8 \text{ e} \\ 4\text{Cl}^- = 8 \text{ e} \\ \hline 16 \text{ VE} \end{array}$$

Neutral atom

Oxidation state



$$\begin{array}{r} \text{Mn} = 7 \text{ e} \\ 5\text{CO} = 10 \text{ e} \\ \text{H} = 1 \text{ e} \\ \hline 18 \text{ VE} \end{array}$$

$$\begin{array}{r} \text{Mn}^+ = 6 \text{ e} \\ 5\text{CO} = 10 \text{ e} \\ \text{H}^- = 2 \text{ e} \\ \hline 18 \text{ VE} \end{array}$$

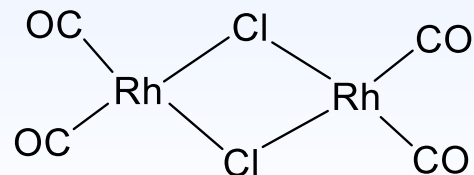
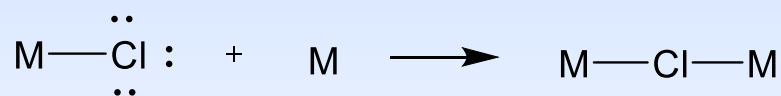
Neutral atom

Oxidation state

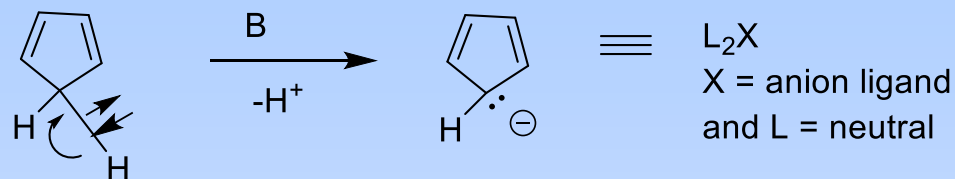


$$\begin{array}{r} 2\text{Rh} = 18 \text{ e} \\ 4\text{CO} = 8 \text{ e} \\ 2\text{Cl(bridging)} = 6 \text{ e} \\ \hline 32 \text{ VE} \\ \text{or } 16 \text{ VE/Rh} \end{array}$$

$$\begin{array}{r} 2\text{Rh}^+ = 16 \text{ e} \\ 4\text{CO} = 8 \text{ e} \\ 2\text{Cl(bridging)} = 8 \text{ e} \\ \hline 32 \text{ VE} \\ \text{or } 16 \text{ VE/Rh} \end{array}$$

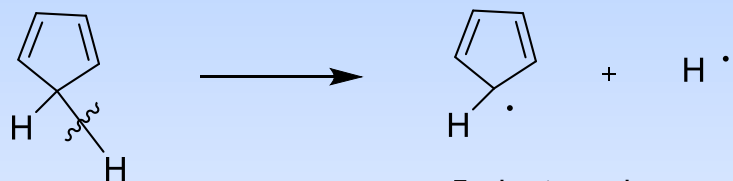


$C_5H_5^-$ cyclopentadienyl anion

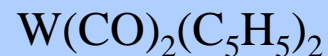


$\equiv L_2X$
 $X = \text{anion ligand}$
 and $L = \text{neutral}$

6 electron donor



5 electron donor



$$W = 6$$

$$2Cp = 10$$

$$2CO = 4$$

$$20 \text{ VE}$$

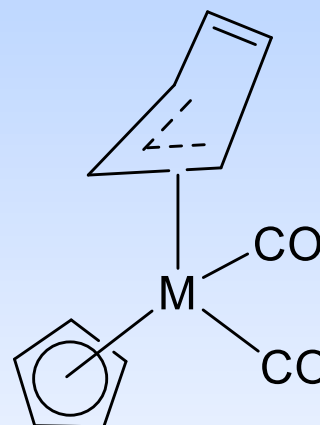
$$W = 6$$

$$1Cp = 5$$

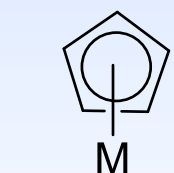
$$1Cp = 3$$

$$2CO = 4$$

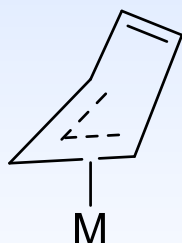
$$18 \text{ VE}$$



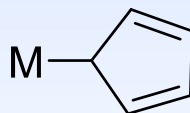
The predicted structure was observed!!!!



$\eta^5-C_5H_5$



$\eta^3-C_5H_5$



$\eta^1-C_5H_5$

Hapticity as η^x – as the number of contiguous ligand atoms simultaneously bound to a metal center

21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper
39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver
57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold

Early Transition Metals

16e and sub-16e configurations are common

Coordination geometries higher than 6

Middle Transition Metals

18e configurations are common

Coordination geometries of 6 are common

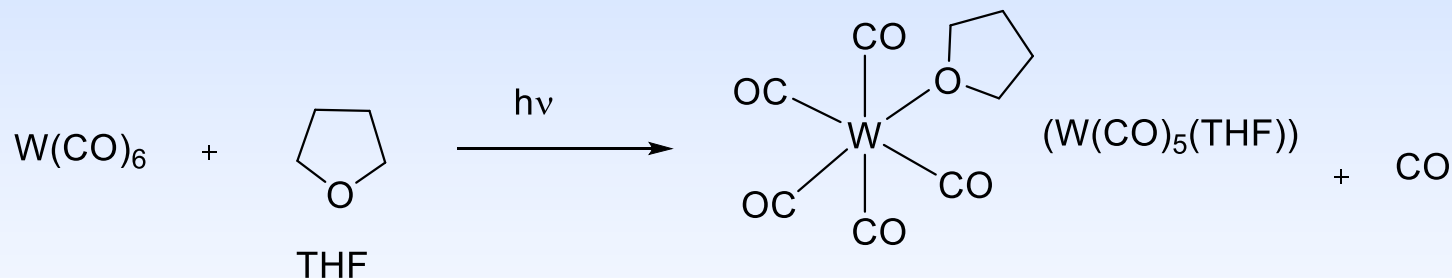
Late Transition Metals

16e and sub-16e configurations are common

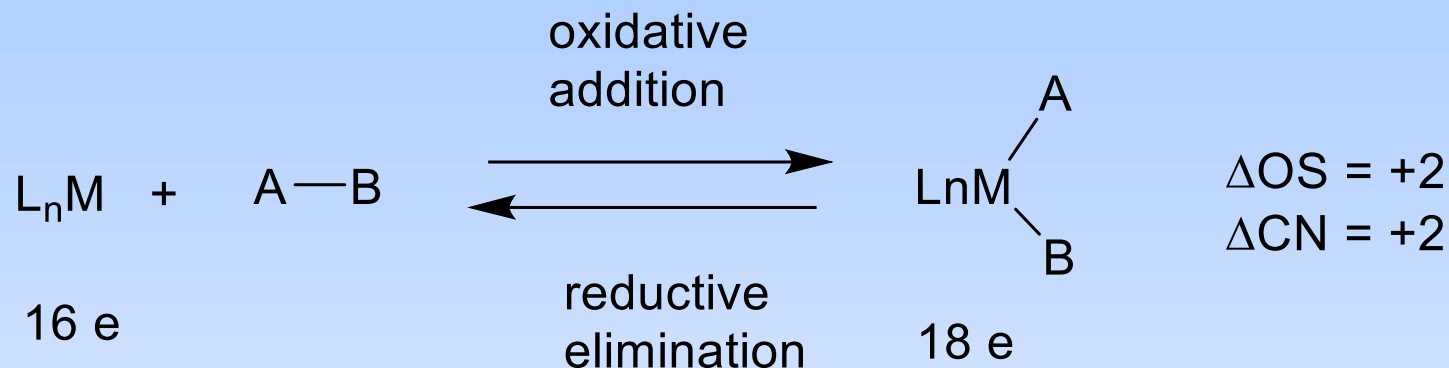
Coordination geometries of 5 or lower

Basic reactions in Organometallics

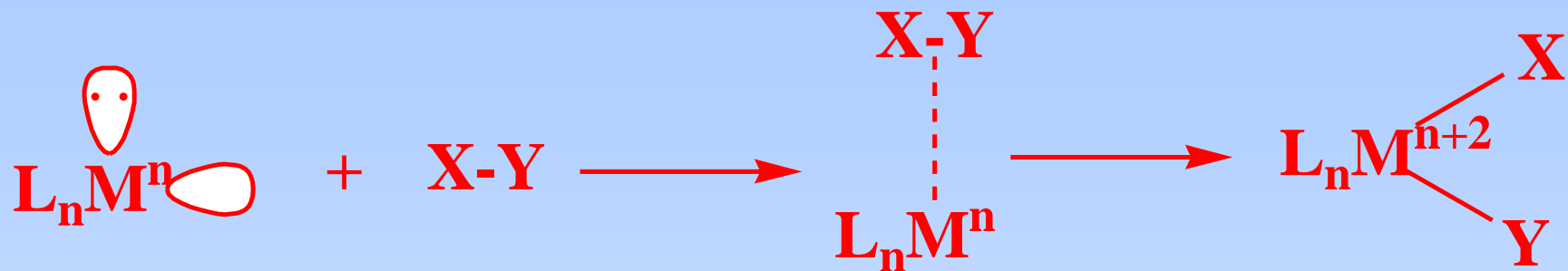
(1) Ligand substitution reactions



2. Oxidative addition and Reductive elimination

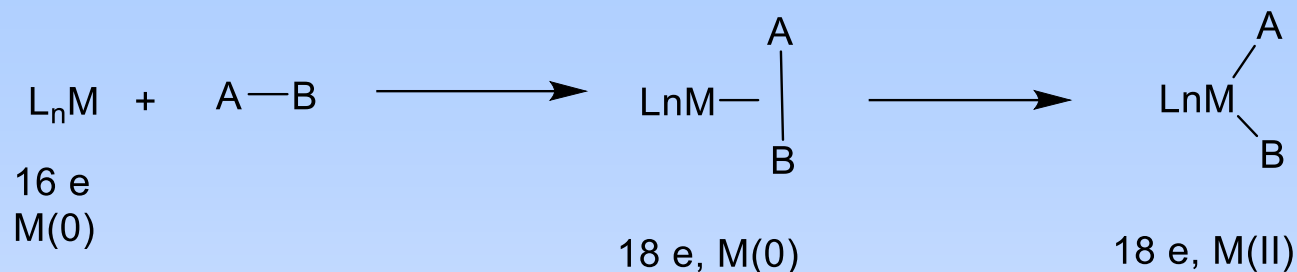


1. Two vacant coordination sites – 16 VE, coordinatively unsaturated
2. Suitable orbitals containing nonbonding electrons.
3. Electron rich low valent metal with stable oxidation states separated by two units.
4. governed by the overall thermodynamics: relative stability of 4 CN versus 5 or 6 CN and by the strength of new bonds (M-X and M-Y) formed versus the bond broken (X-Y)

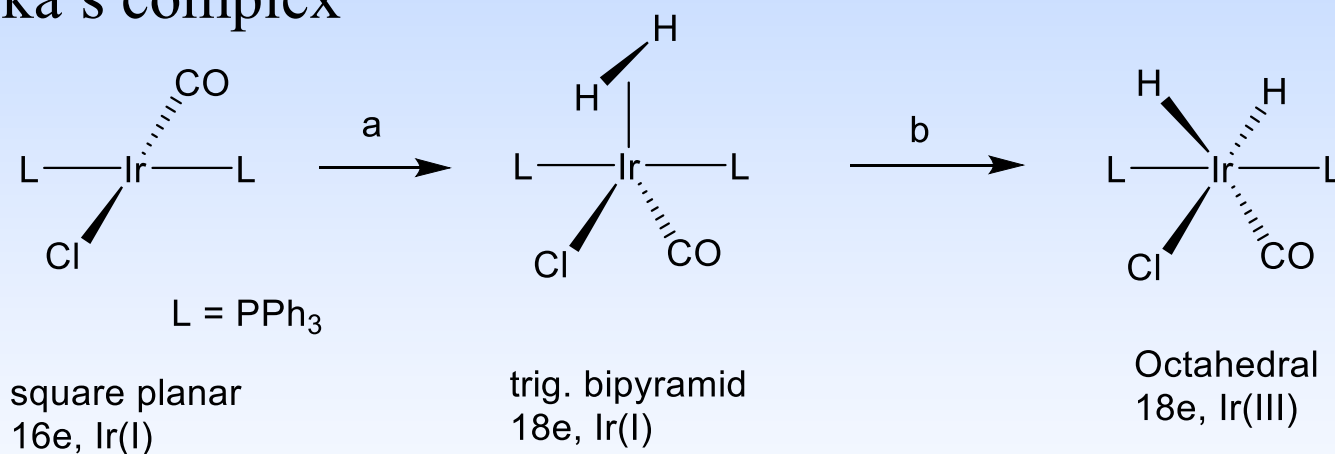


-occurs when a complex behaves simultaneously as a Lewis base and a Lewis acid

Concerted Additions

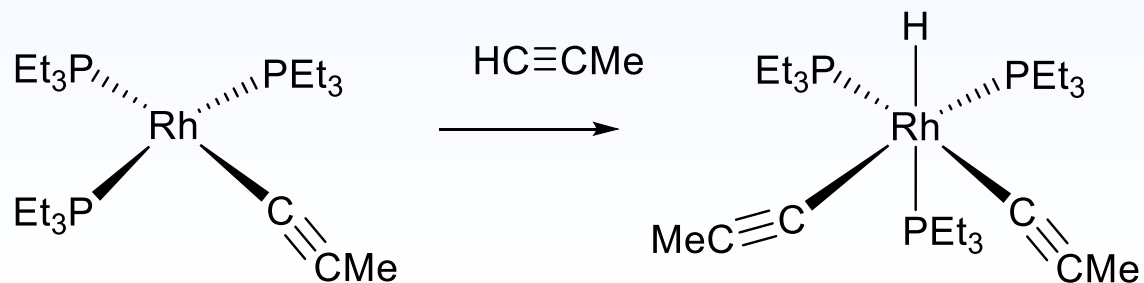
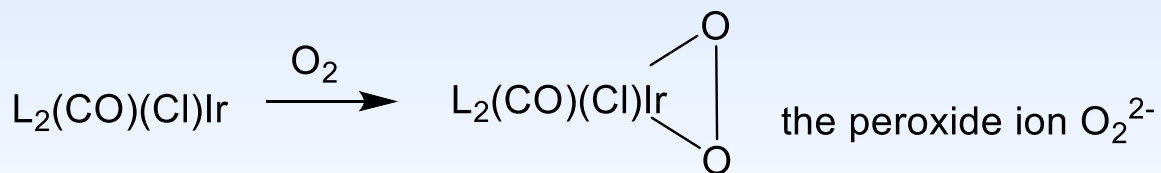
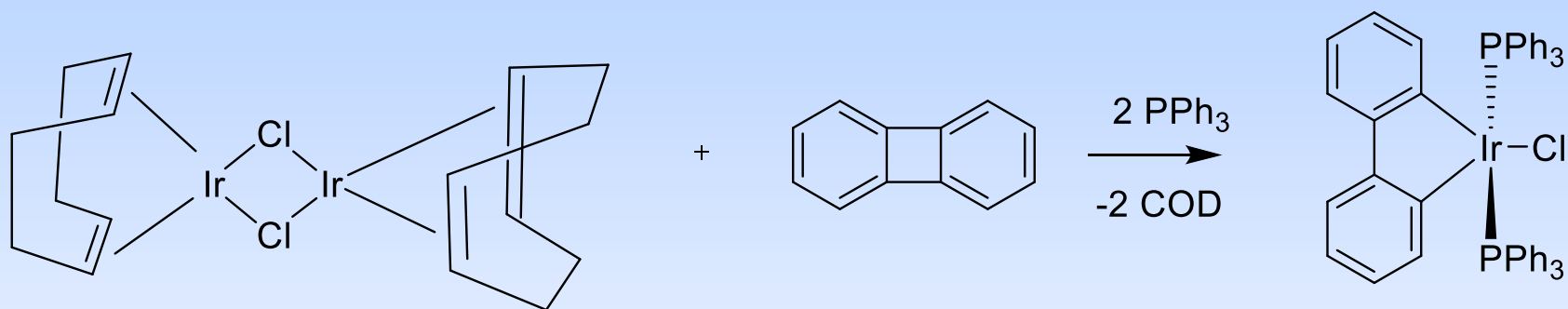
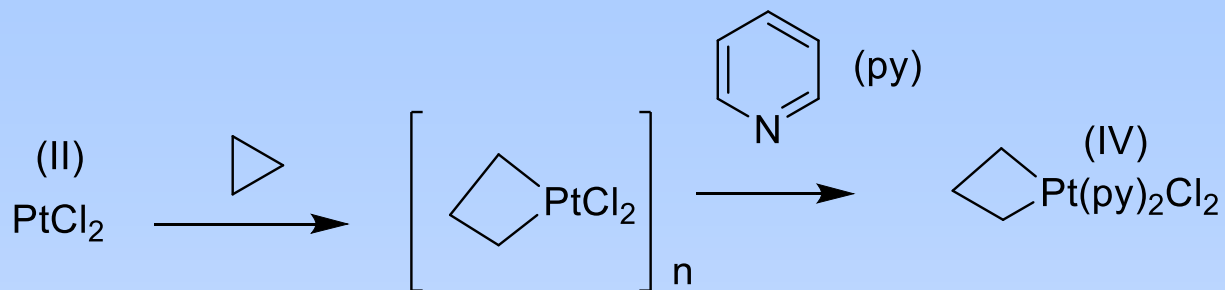


Vaska's complex

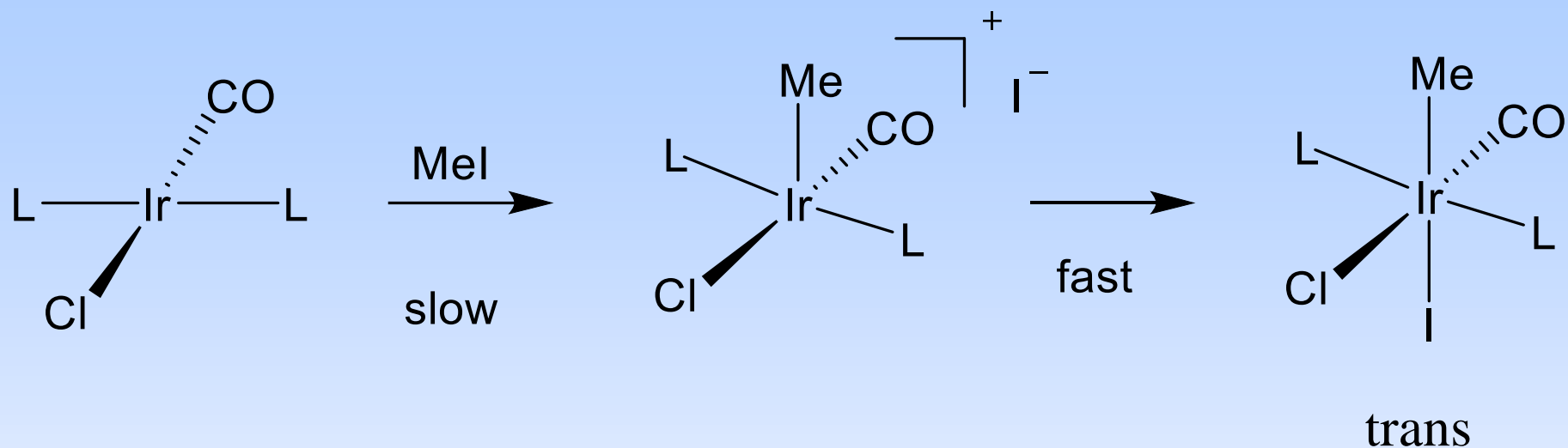


Nonpolar reagents such as H_2 , O_2 , C-H, Si-H bonds

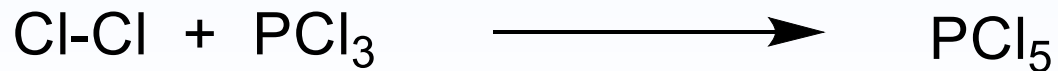
Step a the associative step, sigma complex; Step b, transfer of electron to σ^* of A-B bond cis product



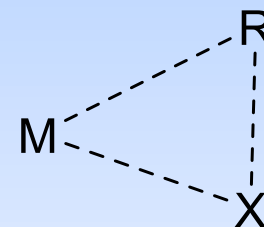
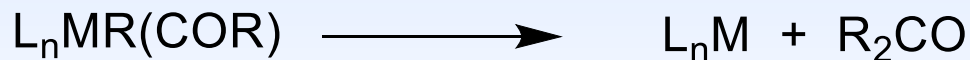
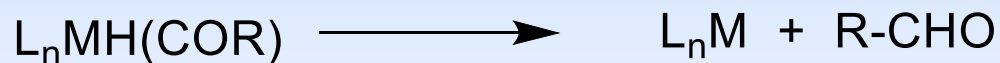
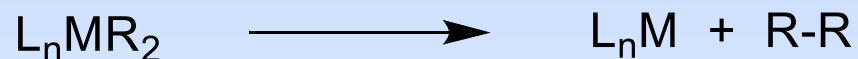
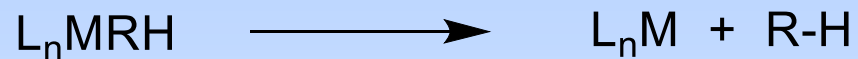
S_N2 Reactions



With a polar substrate, both cis and trans isomers possible.

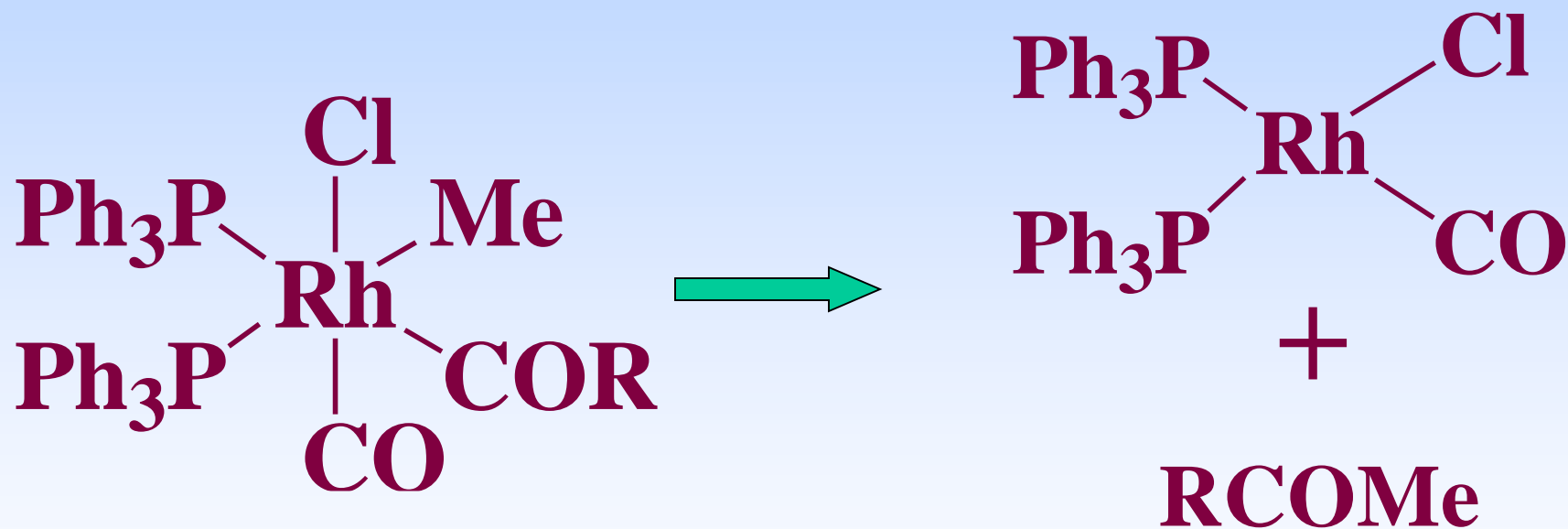


Reductive Elimination



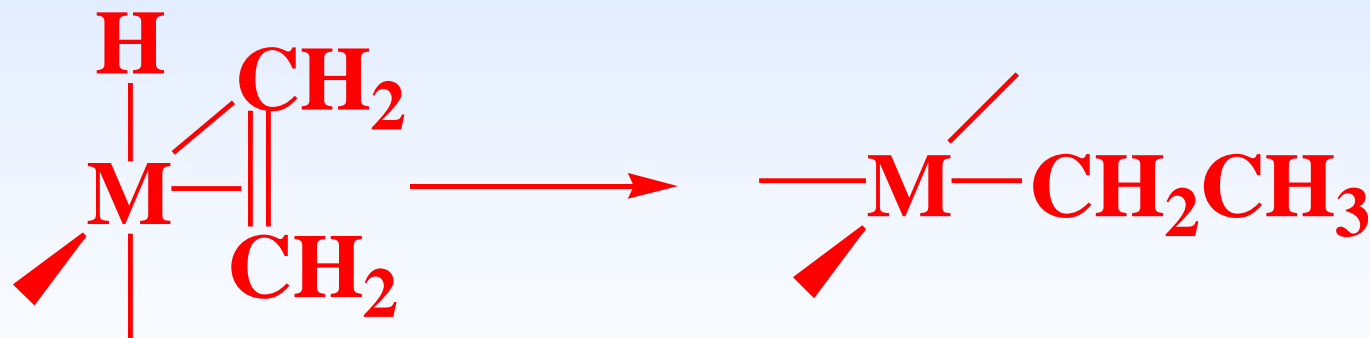
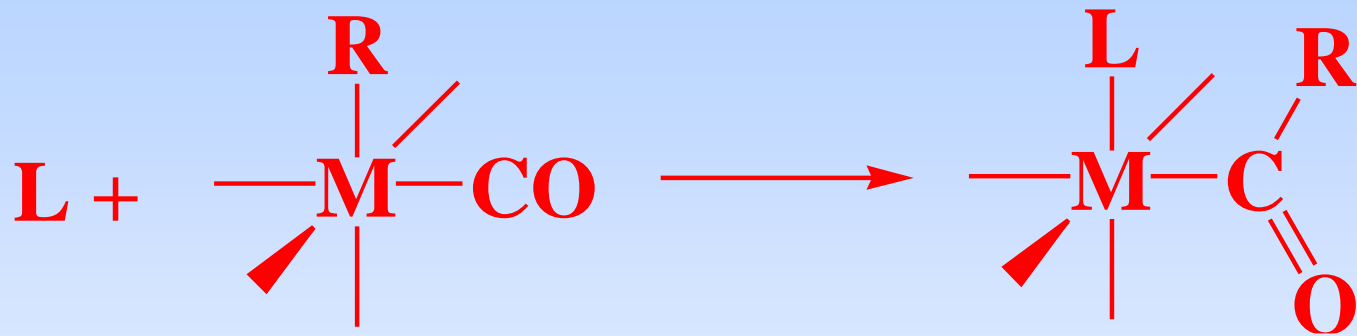
three center T.S.

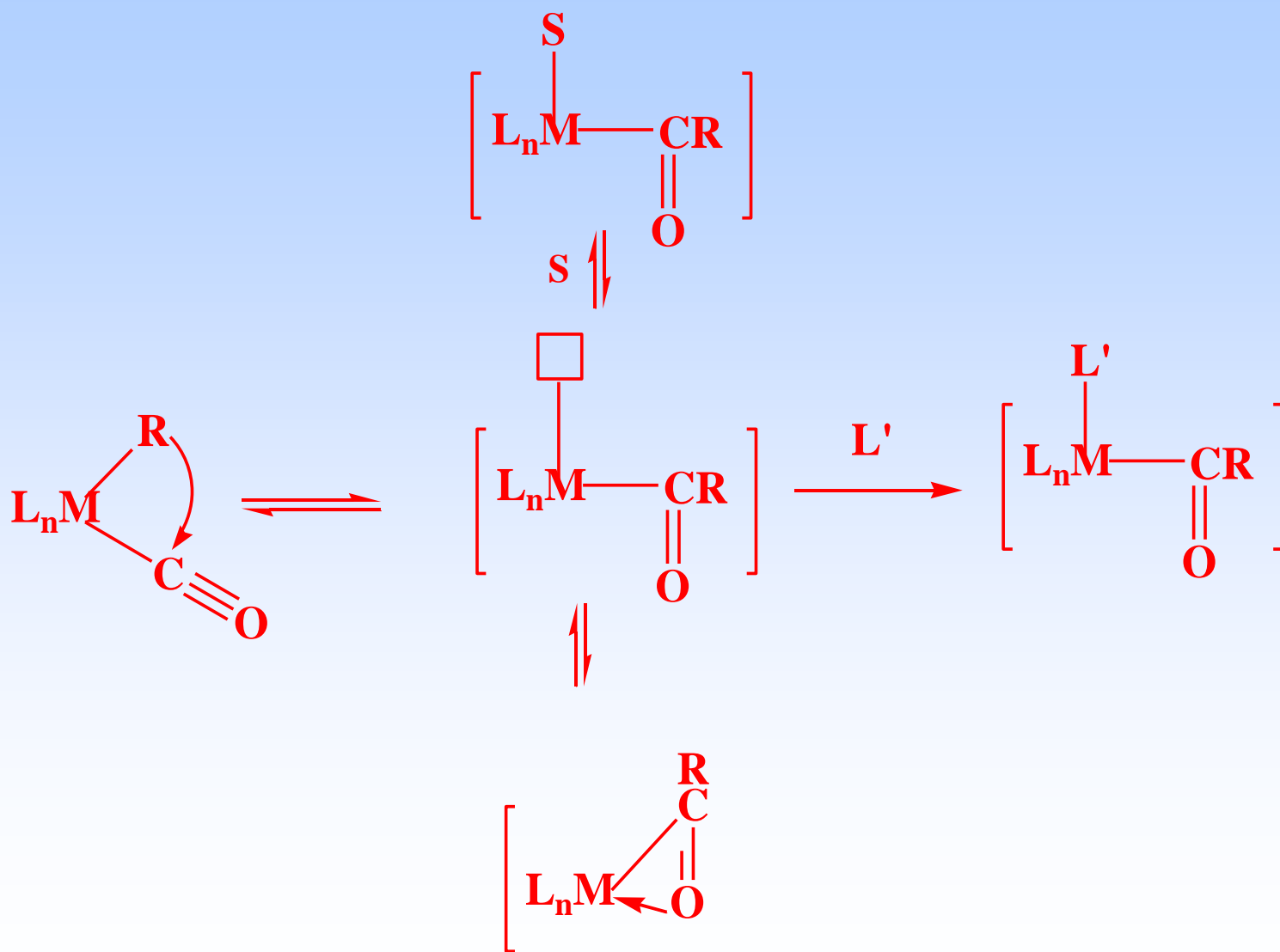
Reductive elimination



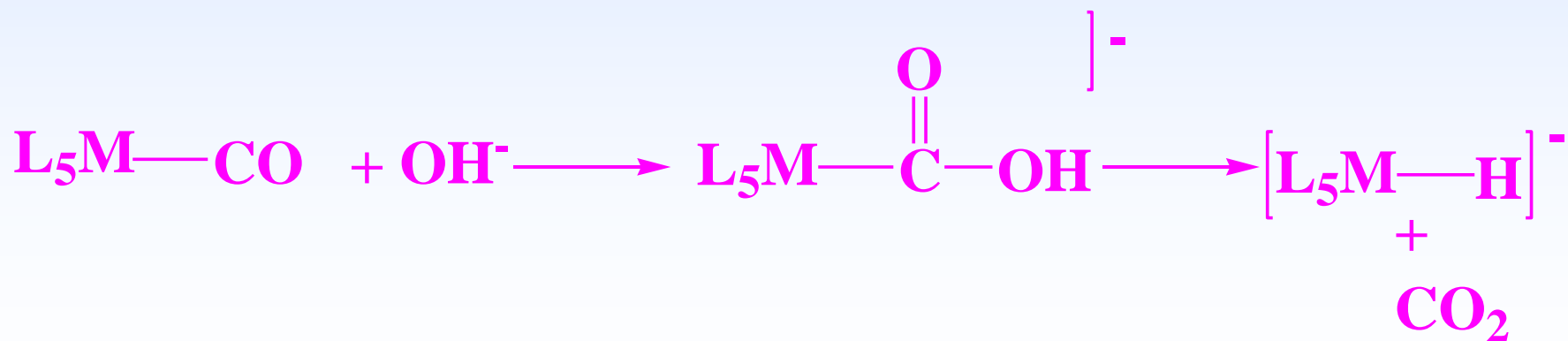
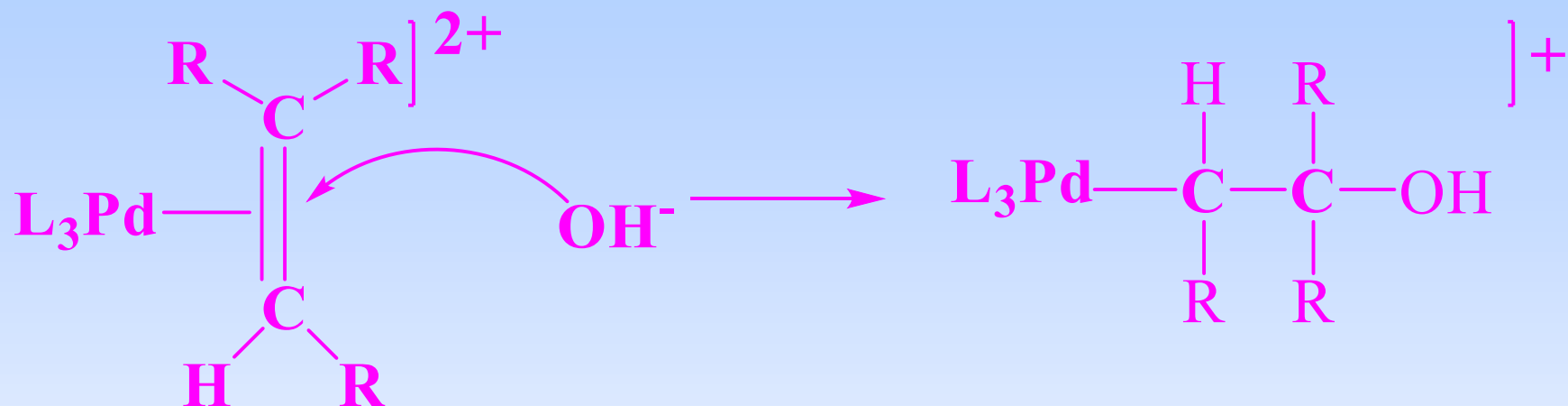
(c) Insertion or migration

Migration of alkyl and hydride ligands





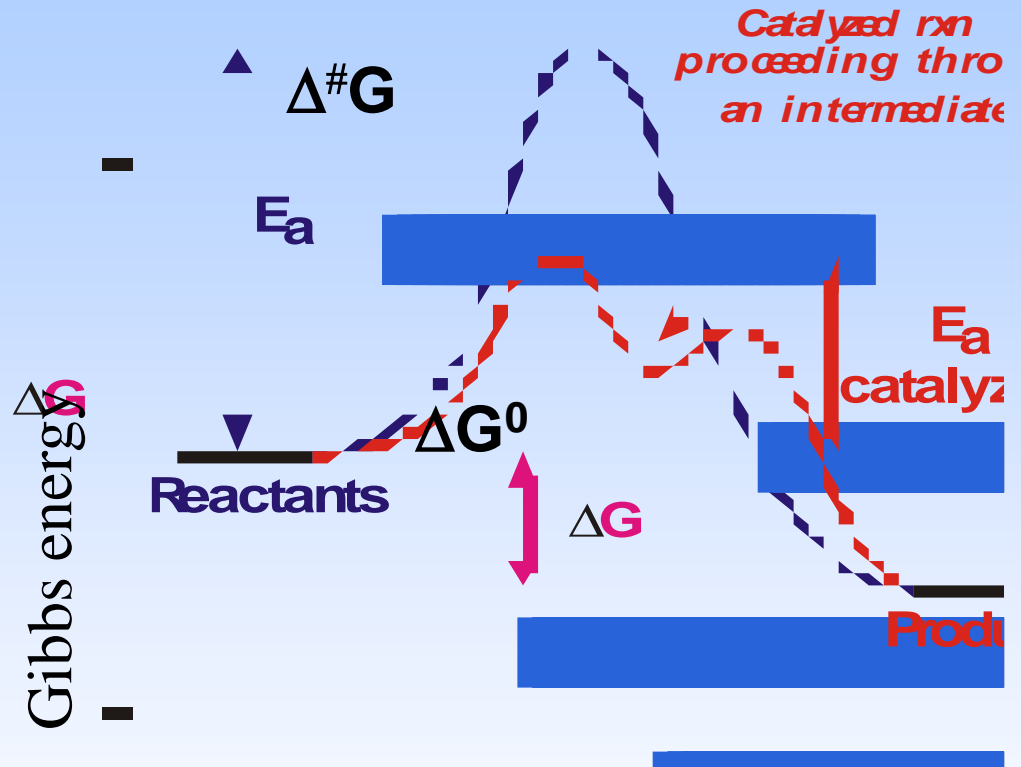
(d) Nucleophilic attack



Catalysis



A catalyst is a substance that increases the rate of the reaction but is not itself consumed.



Introduces new pathways with lower Gibbs energies of activation, $\Delta^\#G$.

It does not change the thermodynamics

Catalysis : Why?

Heterogeneous

Homogeneous

Synthesis of chemicals... pharmaceutical, agricultural

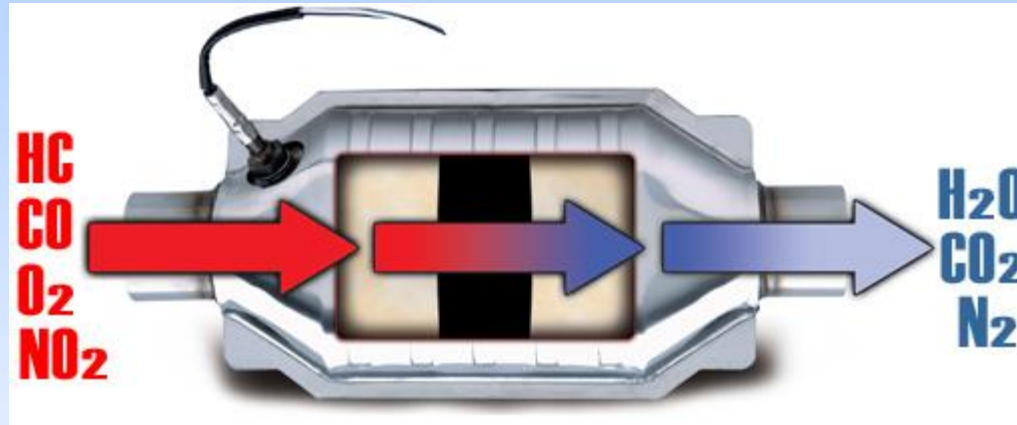
Catalytic converter ... environmental

Biology: Enzymes

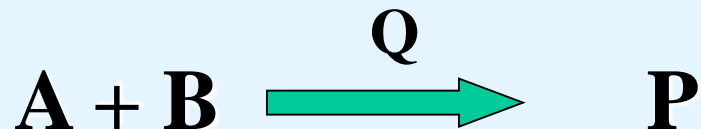
Biological system – efficient catalyst

Organometallic compounds, metals etc.

Catalytic Converter



How to select an efficient catalyst?



Activity: related to rate of reaction $v = d[\text{P}]/dt$

efficient catalyst: good activity

Turnover frequency $N = v/[Q]$

Large turnover frequency – efficient catalyst

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

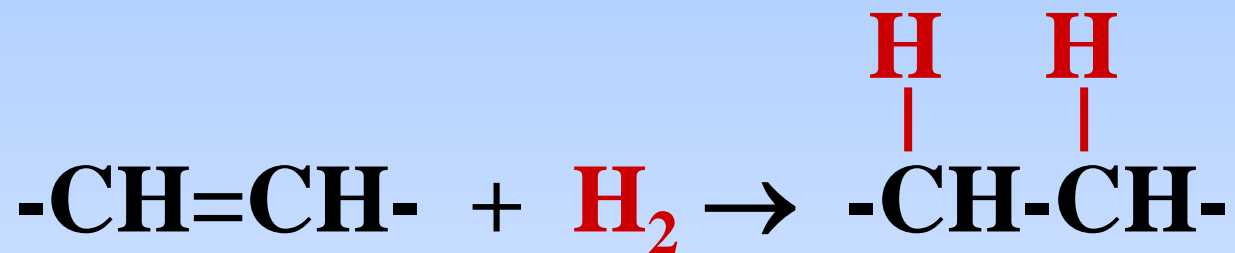
Poisoning: decomposition of catalyst, adsorption of reactant/product

Coordination compounds in catalysis

Nobel Prizes

2005	<i>Yves Chauvin, Robert H. Grubbs and Richard R. Schrock.</i>
2001	KNOWLES, NOYORI, SHARPLESS
1973	WILKINSON
1963	ZIEGLER, NATTA
1918	HABER
1909	OSTWALD

Hydrogenation of Unsaturated Hydrocarbons



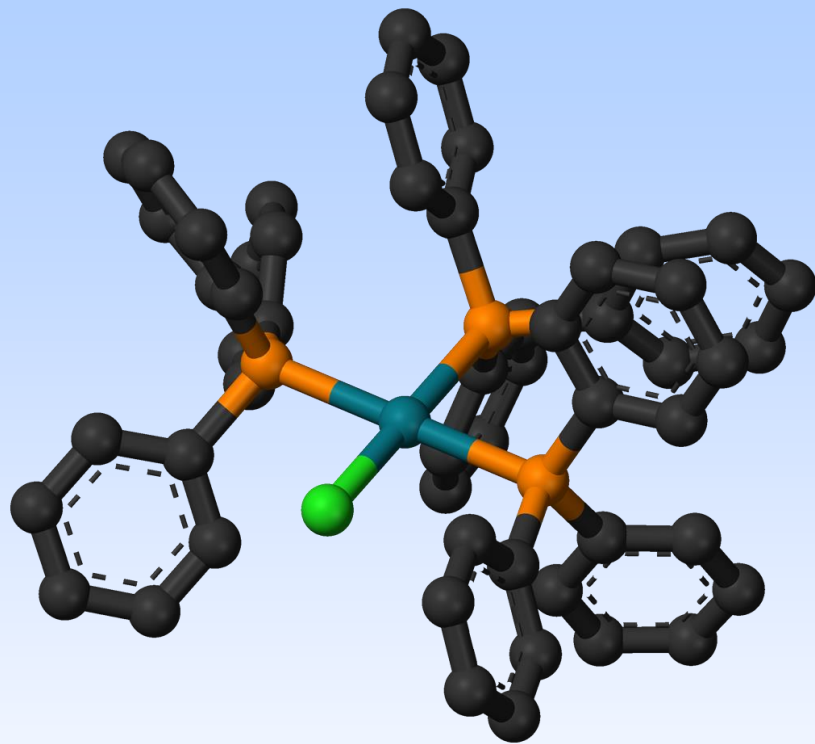
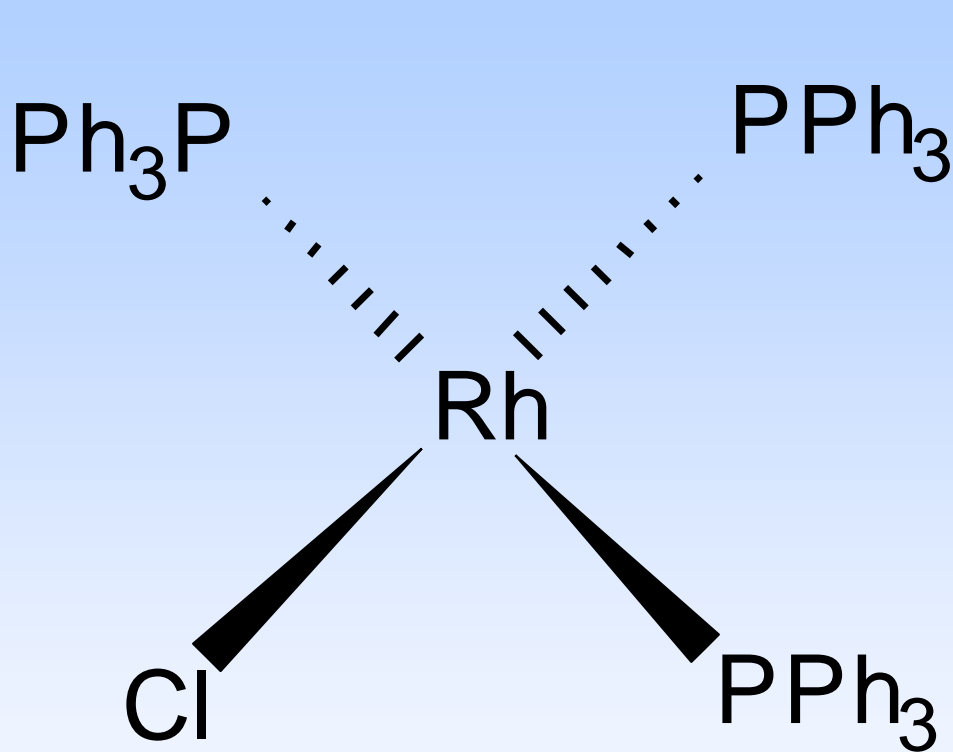
NOBEL : 1973

The most common catalyst



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

Wilkinson's Catalyst (WC)



Chlorotris(triphenylphosphine)rhodium(I)

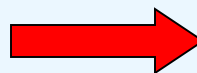
square planar d⁸ configuration

Geoffrey Wilkinson

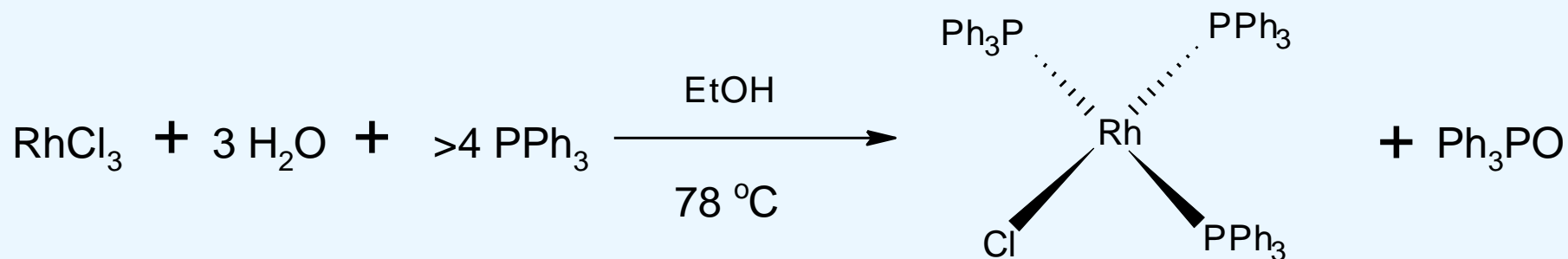
- Born July 14, 1921, Yorkshire, England
- Ph.D from Cal Berkeley studying with Glenn Seaborg
- First published compound in 1965 in Journal of the Chemical Society - *Chemical Communications*
- Nobel Prize in Chemistry 1973 (shared with Ernst Otto Fischer) for their pioneering work, performed independently,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



Organometallic compounds prepared by
Wilkinson in display at Harvard Univ.

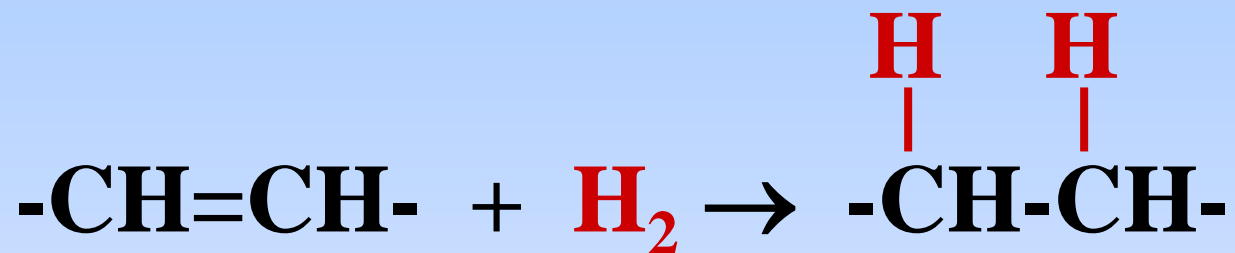


Synthesis of WC



Commercially available

Hydrogenation of Unsaturated Hydrocarbons



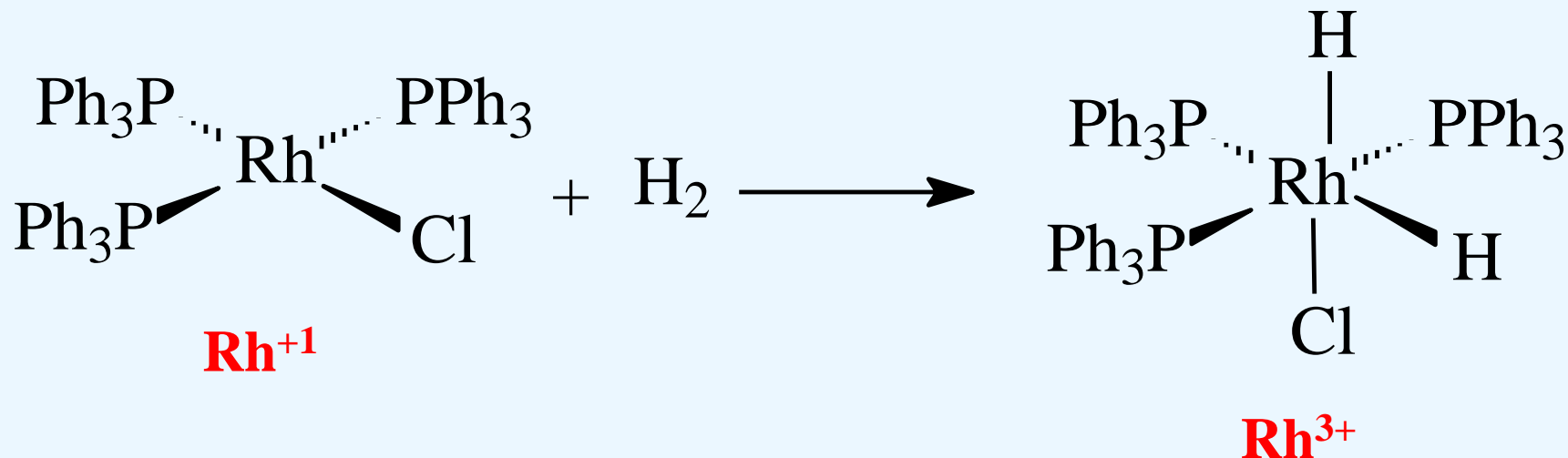
$$\Delta H^0 = -136 \text{ kJ /mol}; \Delta G^0 = -101 \text{ kJ/mol}$$

Though thermodynamically favorable,
at r.t. and pressure, does not take place.

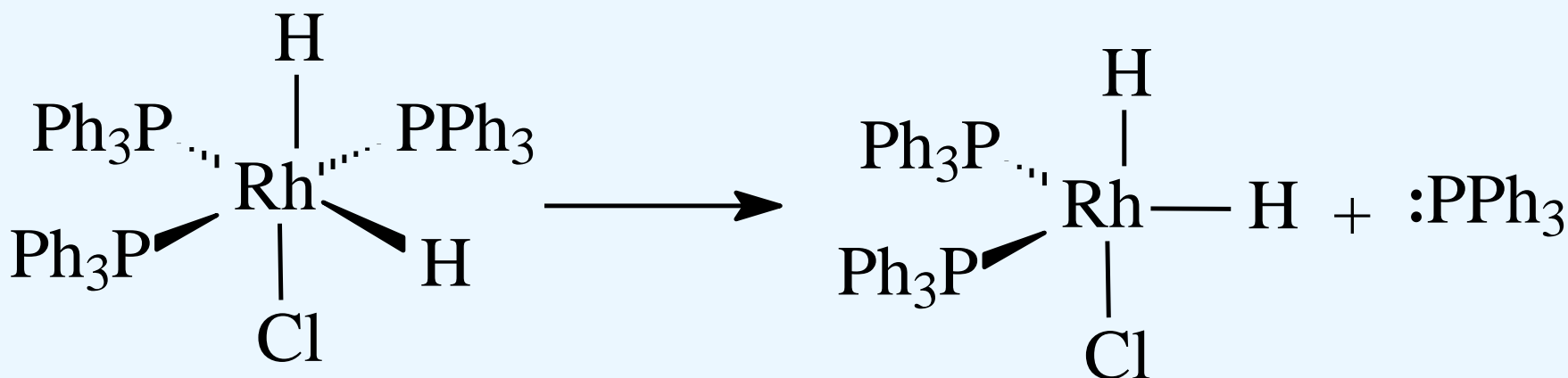
In the presence of metals such as Ni, Cu, Pd or Pt,
The reaction is fast –heterogeneous.

WC in alkene Hydrogenation: Catalytic Steps

(1) Oxidative addition

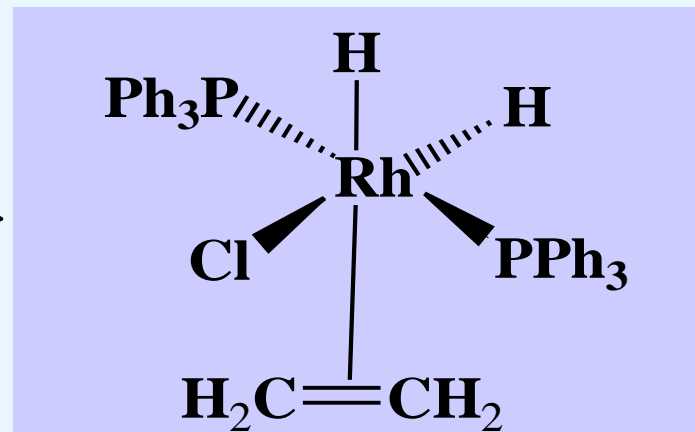
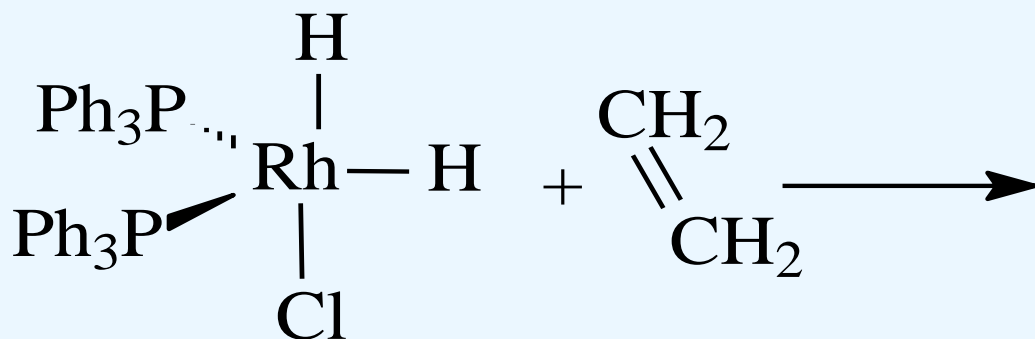


(2) Ligand Dissociation

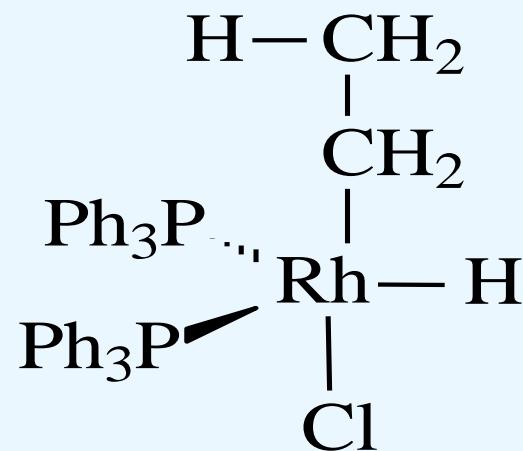
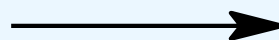
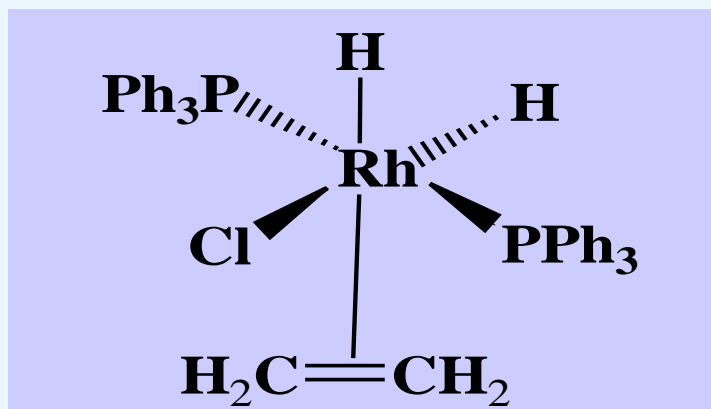


WC in alkene Hydrogenation: Catalytic Steps

(3) Ligand Association

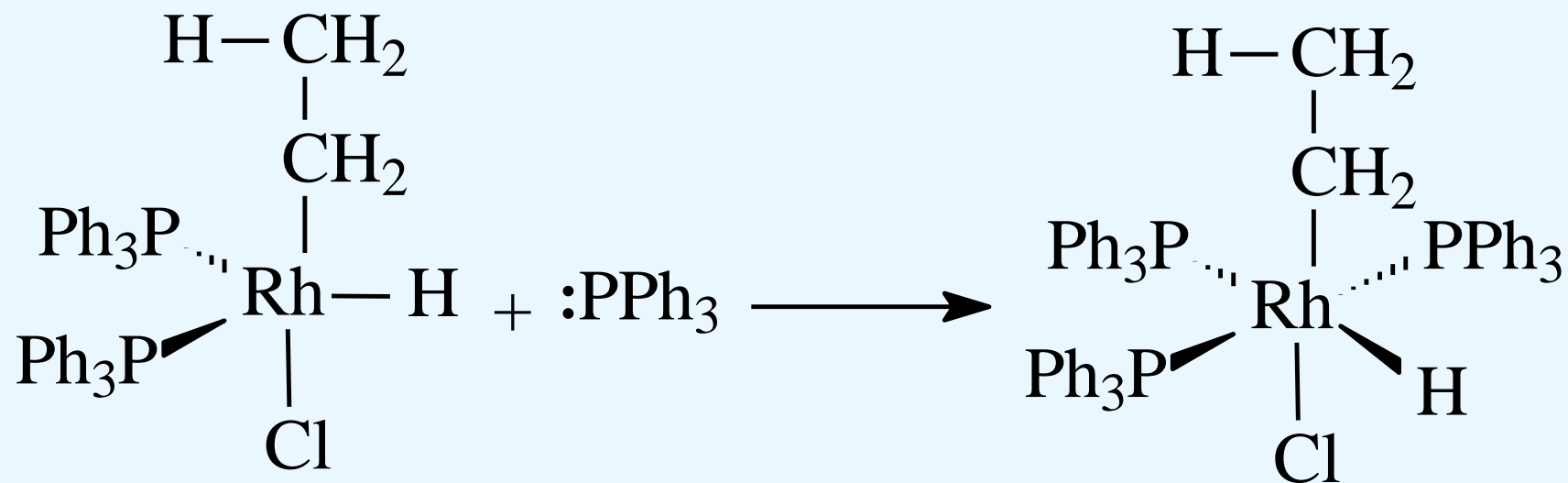


(4) Migration/Insertion



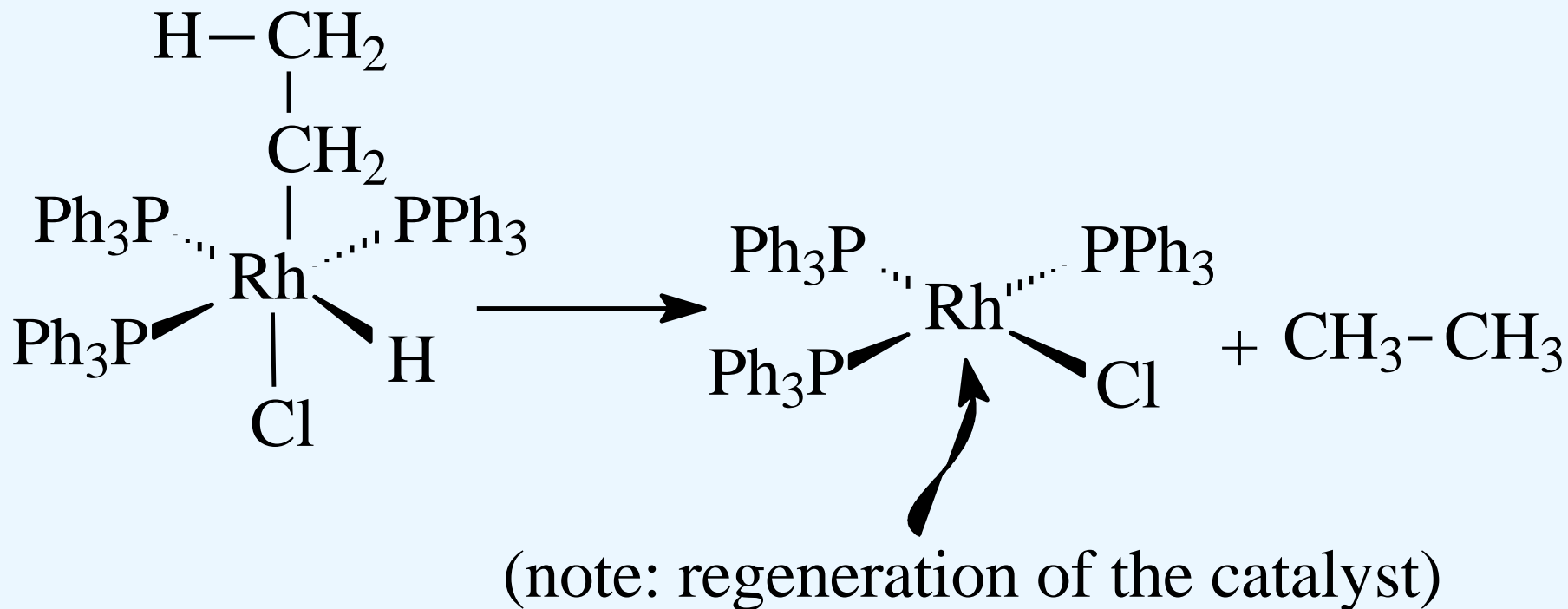
WC in alkene Hydrogenation: Catalytic Steps

(5) Ligand association



WC in alkene Hydrogenation: Catalytic Steps

(6) Reductive elimination



Oxidative addition

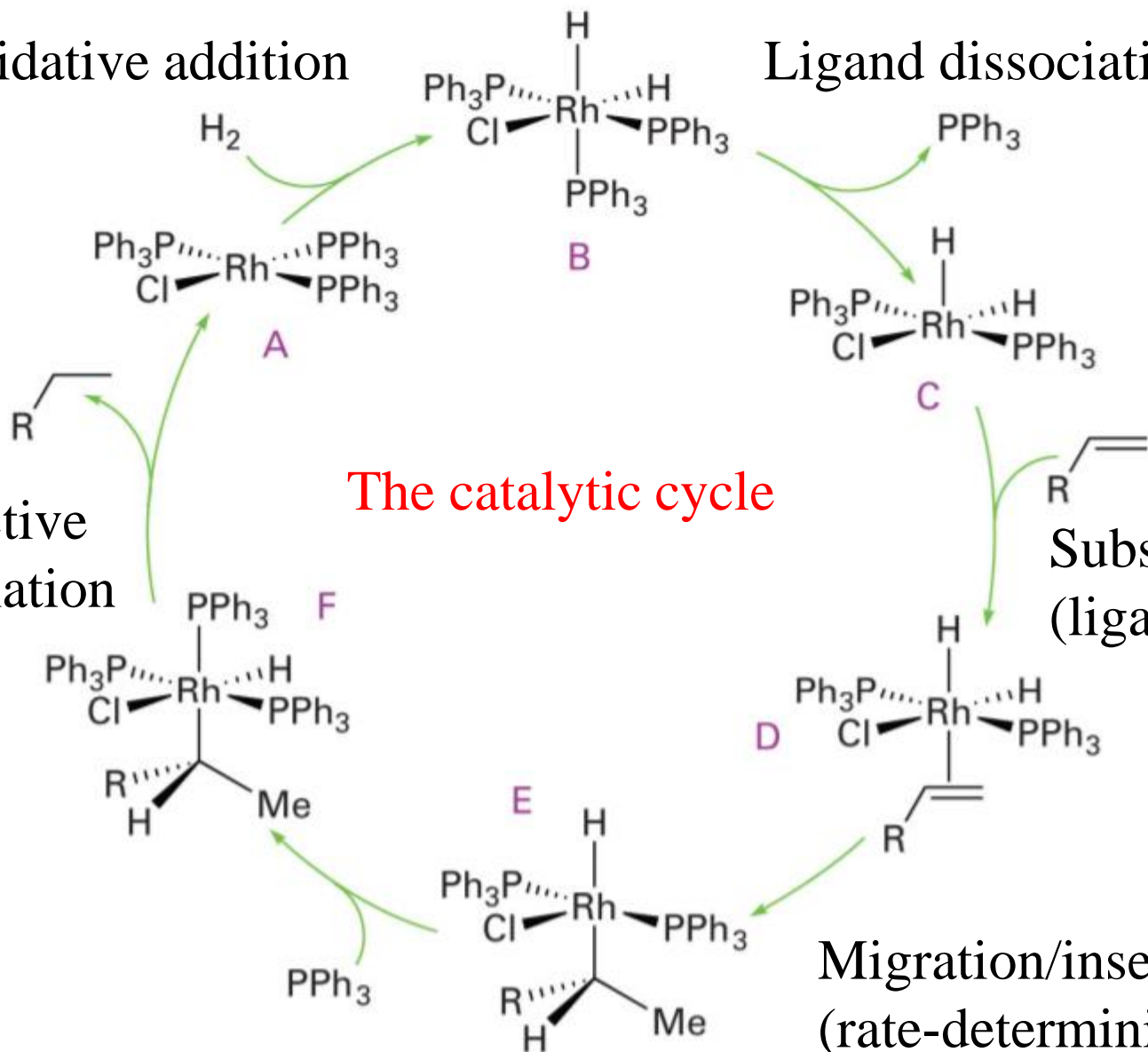
Ligand dissociation

The catalytic cycle

Substrate binding
(ligand association)

Migration/insertion
(rate-determining step)

Reductive
elimination



Turnover number is the number of cycles for which a catalyst survives.

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**

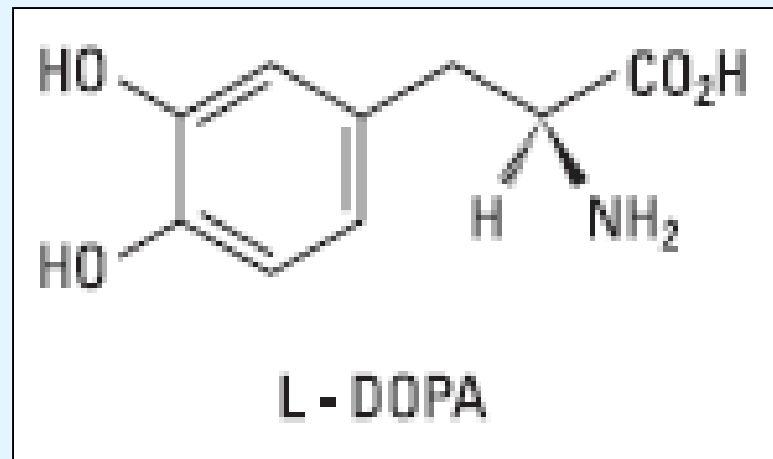
- * Production of fine chemicals**

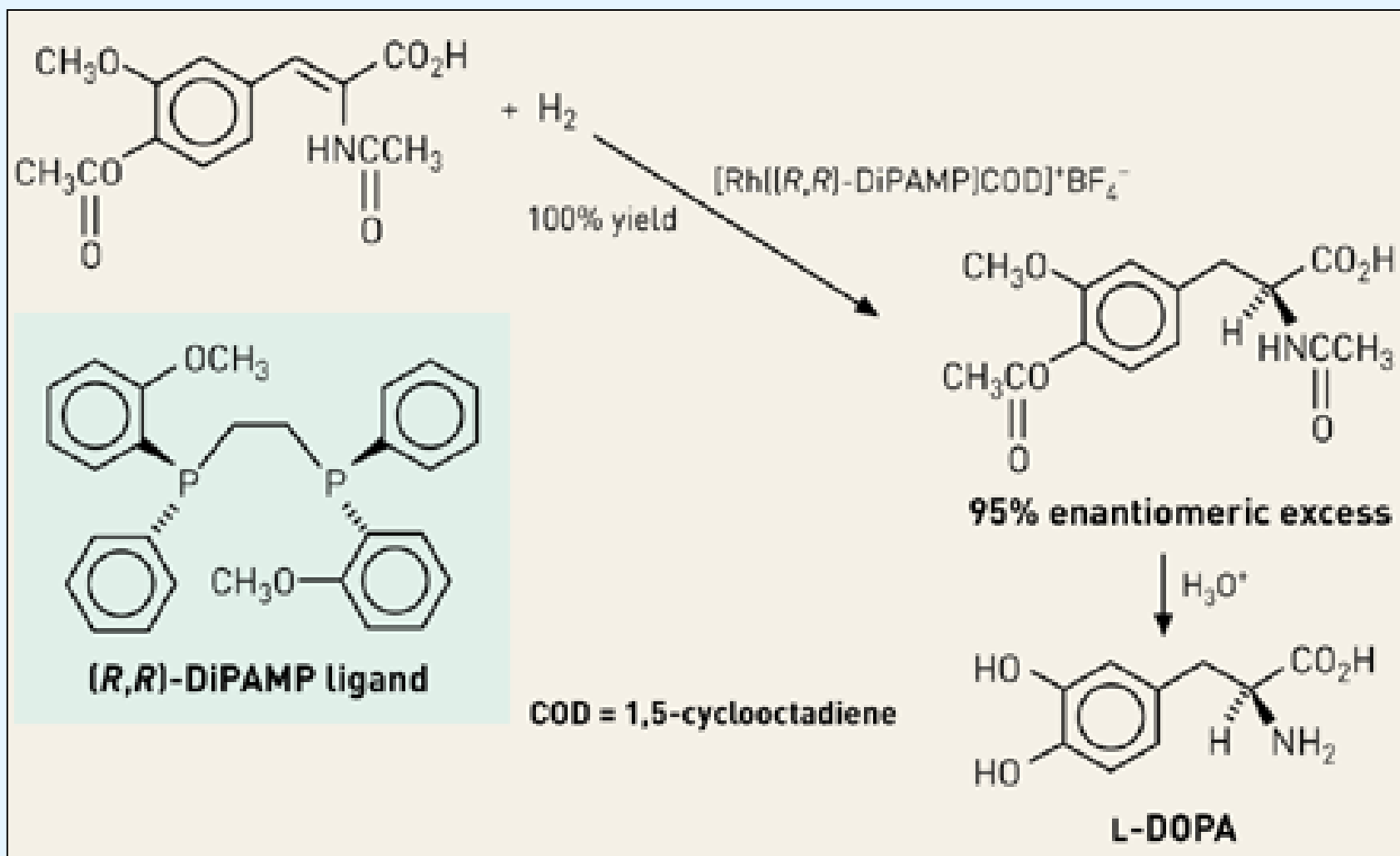
Alkene Hydrogenation & Chirality

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.

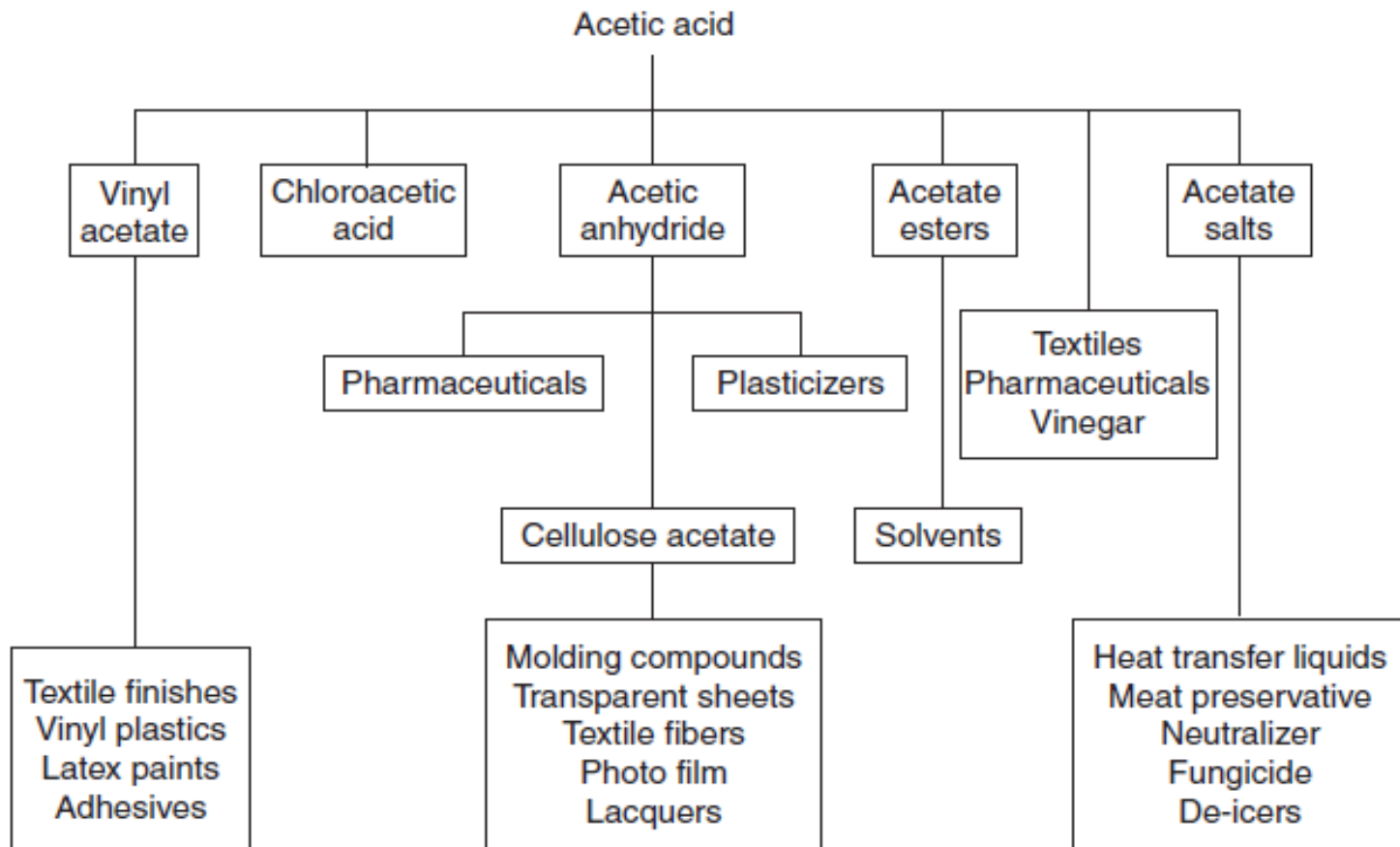




This reaction, developed by Knowles, Vineyard, and Sabacky, was used at Monsanto as a commercial route to the Parkinson's drug L-DOPA.

Acetic Acid

- Acetic acid is an important industrial chemical
- Over 8 million tonnes is produced all over the world annually



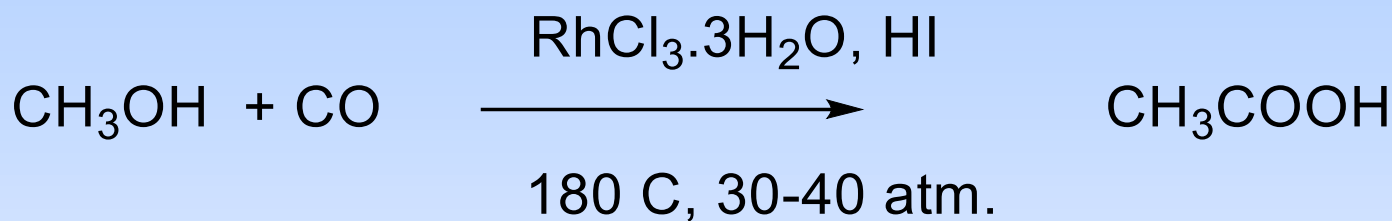
Synthesis of Acetic Acid

The traditional synthesis involves aerobic bacterial action on dilute aqueous ethanol to give vinegar, acetic acid.



This is uneconomical and not supplying concentrated ethanoic acid for industry.

Industrial acetic acid synthesis involves carbonylation of methanol in the presence of metal catalyst.

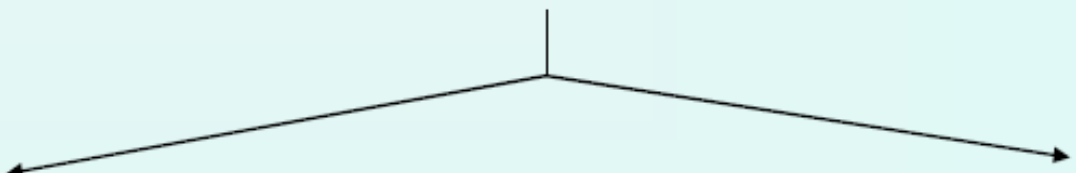


catalyzed by all three members of Group 9 (Co, Rh and Ir) complexes.

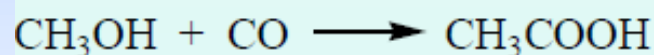
Relatively low pressure with Rh complex developed at Monsanto - called Monsanto process. Rh(III) is reduced to the active Rh(I) catalyst $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ by CO –homogeneous catalysis

Methanol carbonylation (Monsanto Process)

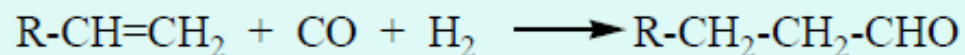
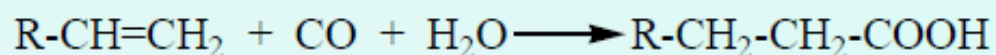
Carbonylation reactions



Carbonylation of alcohols:

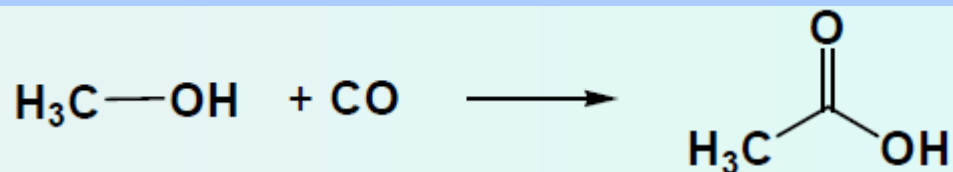


Carbonylation of alkenes and alkynes:



Prior to 1970, acetic acid was made using cobalt catalysts (BASF process)

In 1970 Monsanto commercialized a rhodium carbonyl iodide catalyst that is commonly called the Monsanto Acetic Acid Process

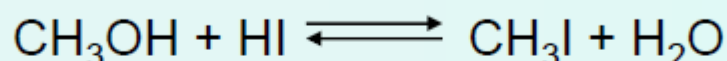


Precatalyst: $[\text{Rh}(\text{CO})_2\text{I}_2]\text{-AsPh}_4^+$

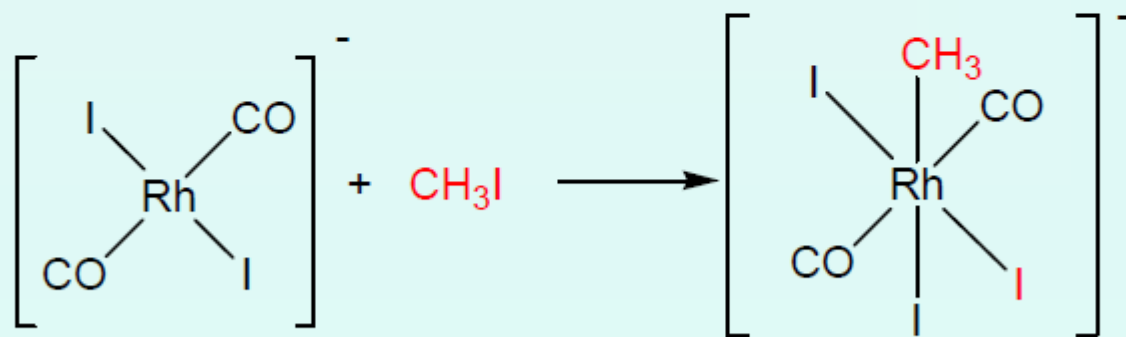
For the reaction to be possible the source of I_- should exist (usually HI)

Mechanism of “Monsanto” carbonylation:

1. CH_3I generation:

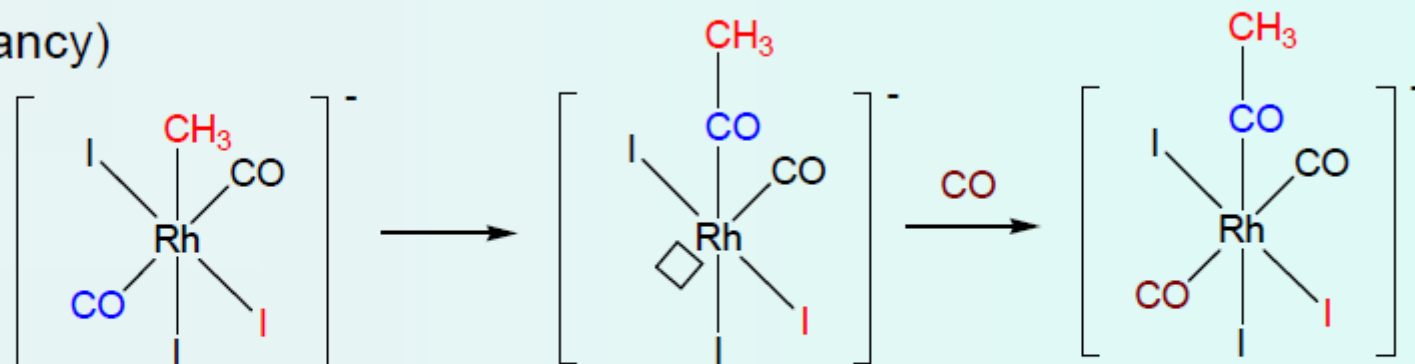


2. Oxidative addition of CH_3I to the Rh^{I} -complex

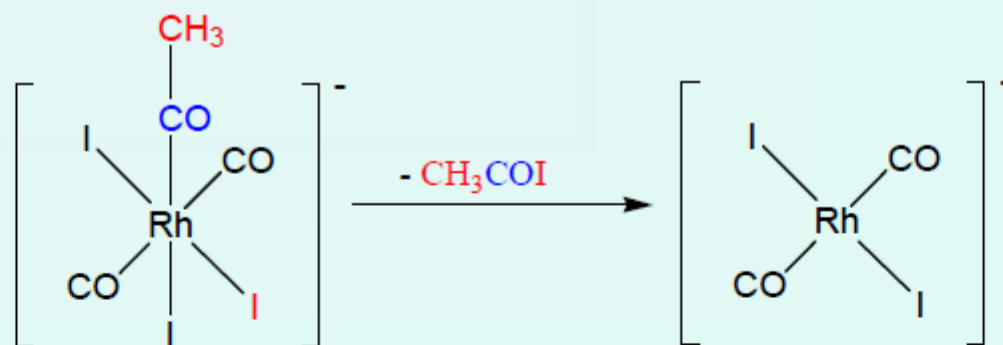


This is the slowest stage of the process

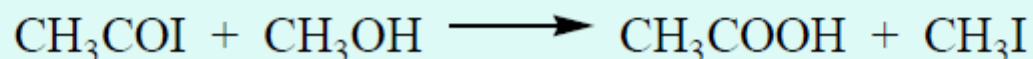
3. Migration insertion of CO (plus new CO addition to the coordination vacancy)



4. Reductive elimination of CH_3COI



5. Formation of acetic acid through the following processes:



The catalytic cycle

