

Organometallic compounds & Catalysis

Books to Refer:

Inorganic Chemistry by James E. Huheey

Advanced Inorganic Chemistry: Cotton and Wilkinson

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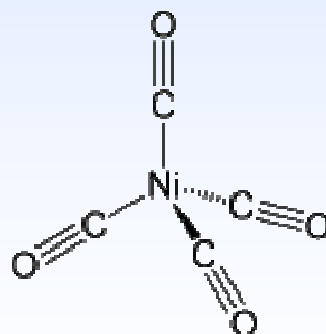
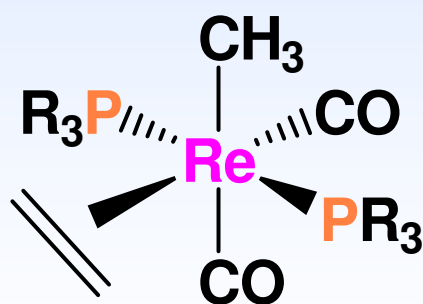
Email: mcdas@chem.iitkgp.ernet.in

~2000 billion dollars industry

Transition metal organometallic compounds & Catalysis

Which one is organometallic? Ni(CO)_4 or NaCN ?

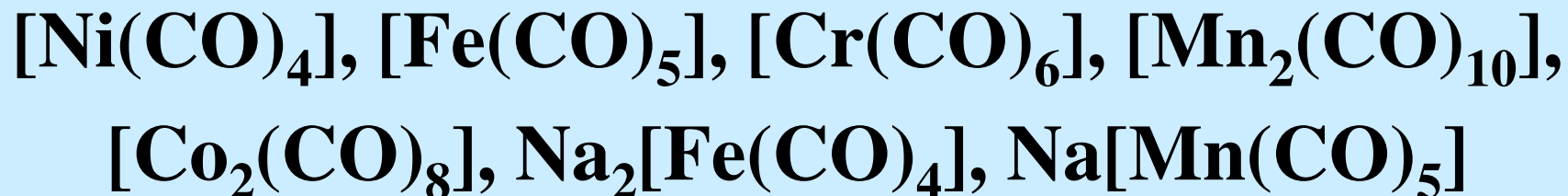
One metal-carbon bond should be present
(C: part of org gr or attached to H).



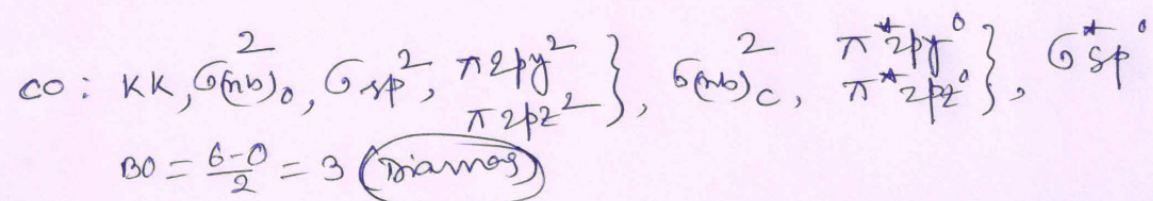
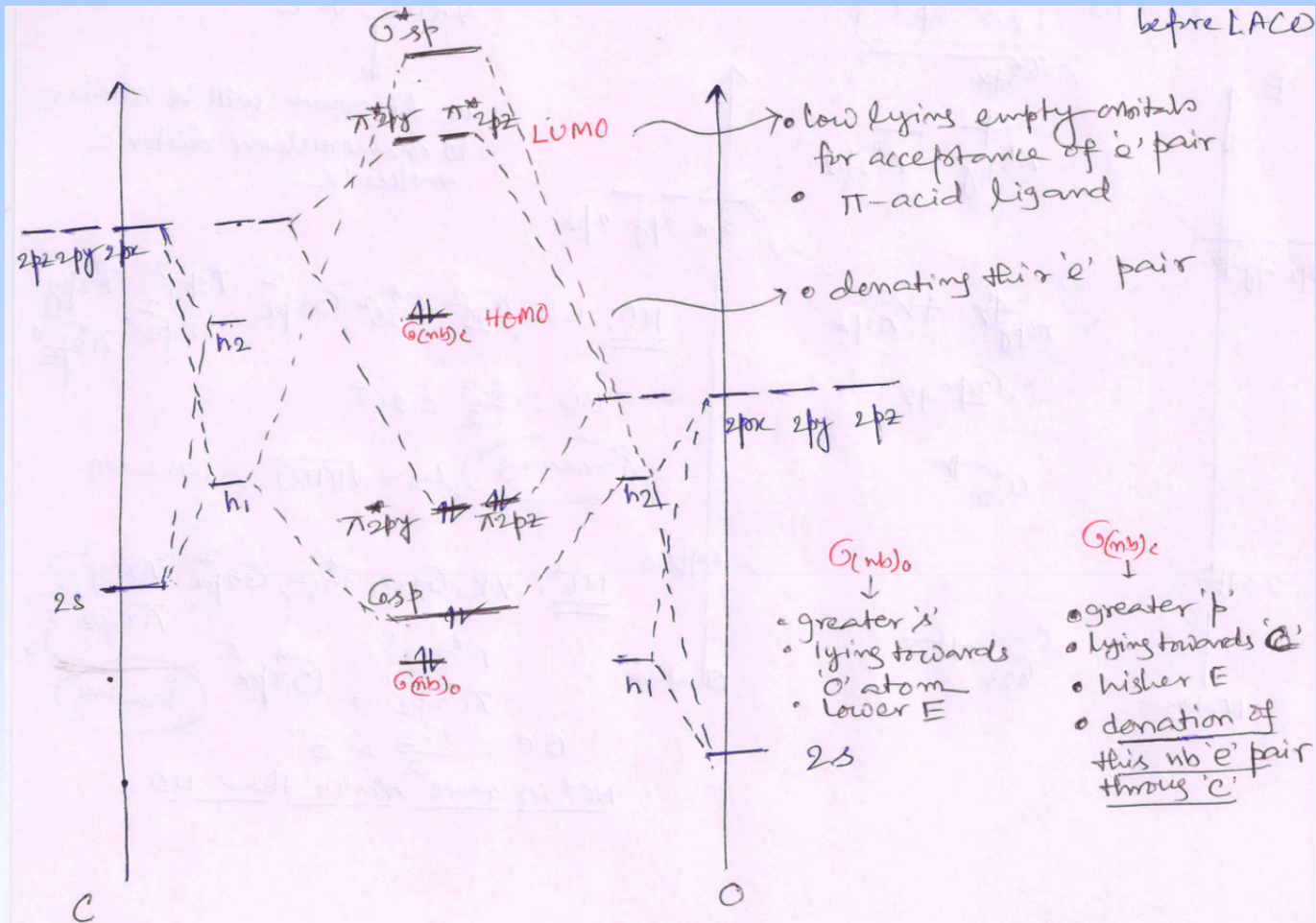
The term “organometallic” is rather loosely defined

Metals in Low Oxidation States

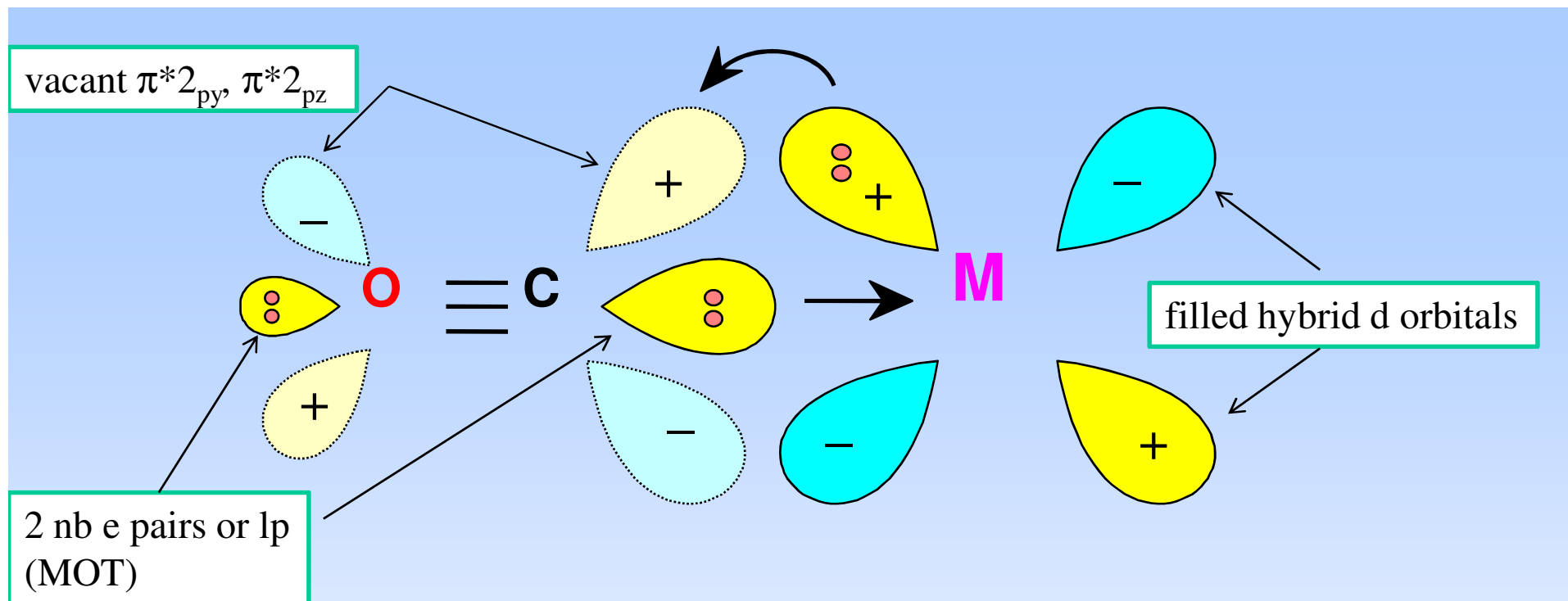
- In low oxidation states, the electron density on the metal ion is very high.
- To stabilize low oxidation states, we require ligands, which can simultaneously bind the metal center and also withdraw electron density from it.



CO does the job (already discussed in Chemical Bonding Part-II)



- Thus CO is reactive & readily forms complex compounds by donating (nb) σ 'e' pair through 'C'



**σ orbital (nb) serves as a donor to a metal atom (M)
&
M to CO pi backbonding**

σ donor + π acceptor

18 electron rule (EAN Rule)

1920

British Chemist Sidgwick

Organic compounds – Octet rule

Organometallic – 18 electron rule (EAN rule for next inert gas)

- predicting stabilities and structures of organometallic compounds

Counting electrons: 1) Oxd state method ✓
2) Neutral atom method

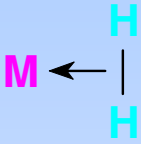
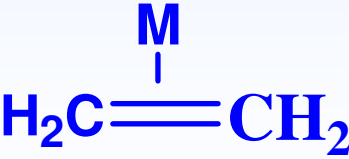
Counting the number of electrons

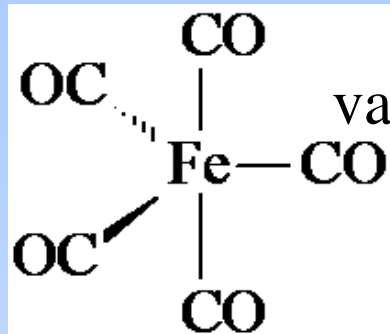
Determine the oxidation state of the transition metal center(s)

To do this one must:

- a) note any overall charge on the metal complex**
 - b) know the charges of the ligands bound to the metal center**
 - c) know the number of electrons being donated to the metal center from each ligand**
- 2) Add up the electron counts for the metal center and ligands**

Counting the number of electrons

Ligand Name	Bonding Type	Formal Charge	Electrons donated
Molecular Hydrogen: H ₂		0	2
Hydride H ⁻	M-H	-1	2
Halide X ⁻	M-X	-1	2
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 M-Ph	-1	2
Alkene		0	2



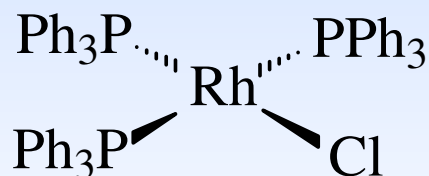
valance cell e of Fe is $4s^2 3d^6 = 8e$

each CO is neutral so Fe^0

each CO donates 2 e = $10e$

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

coordinately 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 coordinately **unsaturated**

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

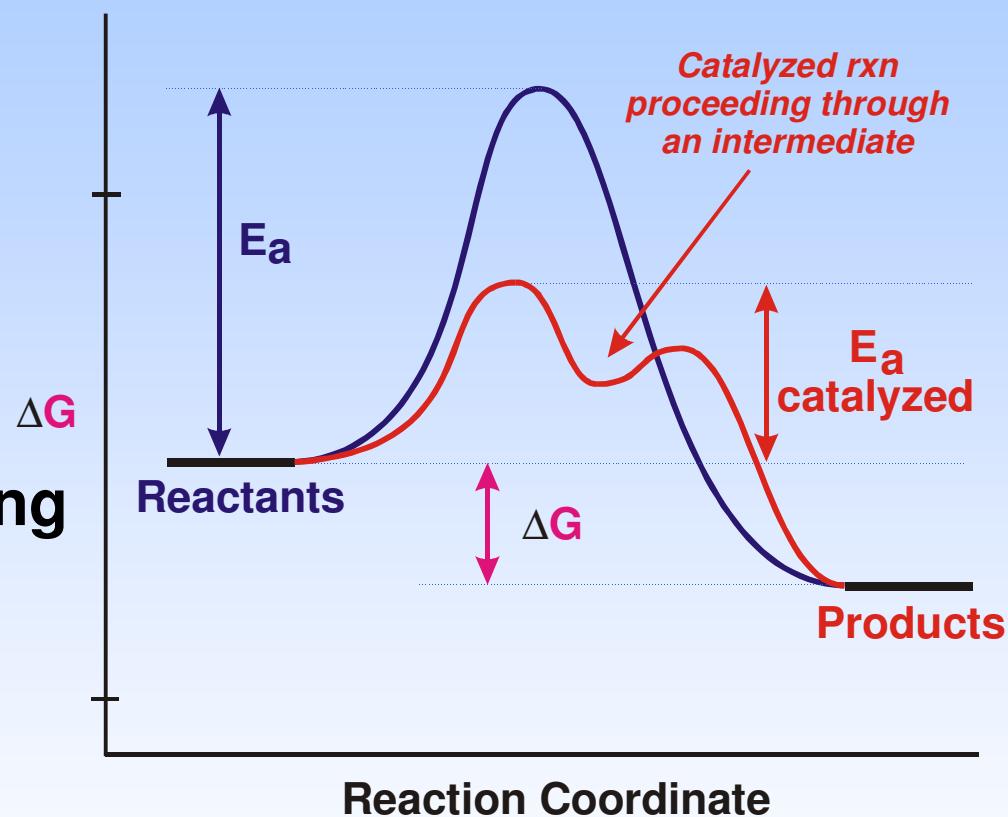
16e and sub-16e configurations are common

Coordination geometries of 5 or lower

Catalysis



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



Heterogeneous

Homogeneous

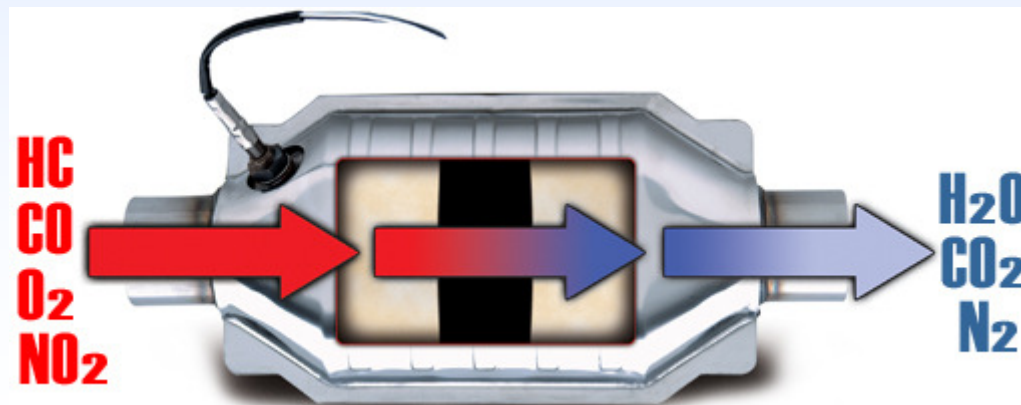
Catalysis : Why?

Synthesis of chemicals... pharmaceutical, agricultural

Catalytic converter ... environmental

Biology: Enzymes

Catalytic Converter



How to select an efficient catalyst?

Activity: related to rate of reaction (also called turnover)

efficient catalyst: good activity

Turnover frequency (N): catalytic cycles/unit time

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 and product value

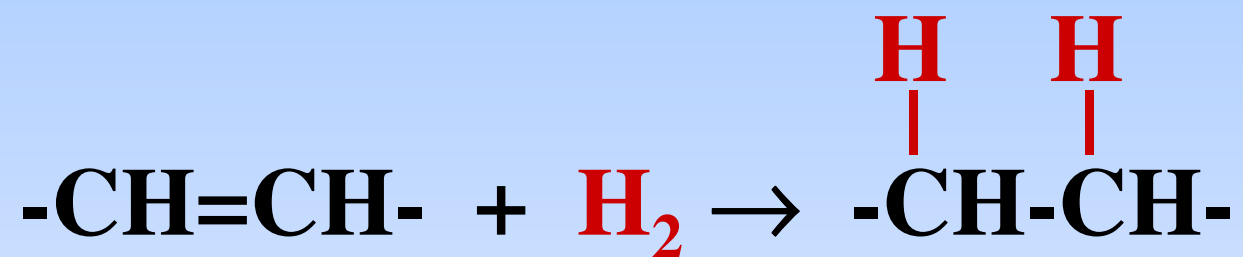
Poisoning: decomposition of catalyst, adsorption of reactant/product

Coordination compounds in catalysis

Nobel Prizes

- 2010** Richard F. Heck, Ei-ichi Negishi, Akira Suzuki
- 2005** *Yves Chauvin, Robert H. Grubbs and Richard R. Schrock.*
- 2001** KNOWLES, NOYORI, SHARPLESS
- 1973** **WILKINSON**
- 1963** ZIEGLER, NATTA
- 1918** HABER
- 1909** OSTWALD

Hydrogenation of Unsaturated Hydrocarbons



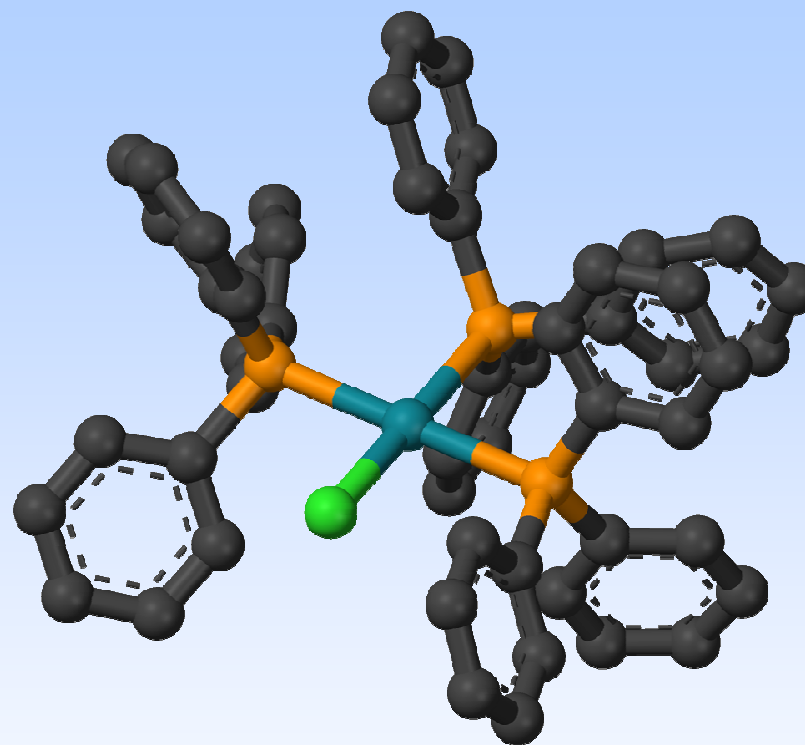
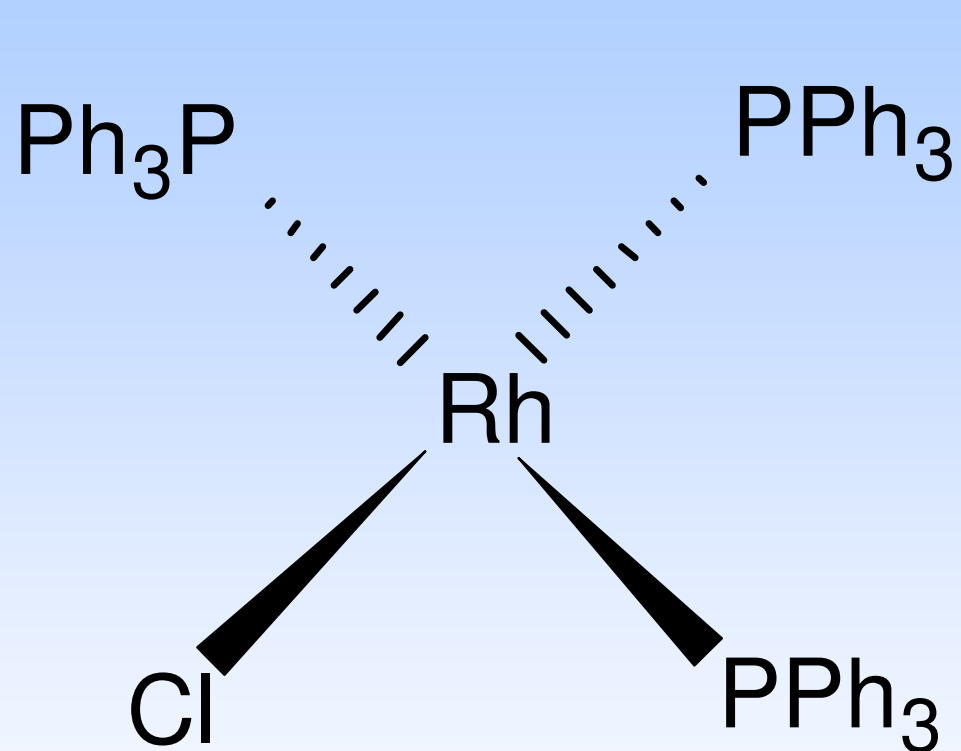
NOBEL : 1973

The most common catalyst



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

Wilkinson's Catalyst (WC)



Chlorotris(triphenylphosphine)rhodium(I)

square planar 16 e d⁸ configuration

Geoffrey Wilkinson

- Born July 14, 1921, Yorkshire, England
- Ph.D from UC 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 organometallics



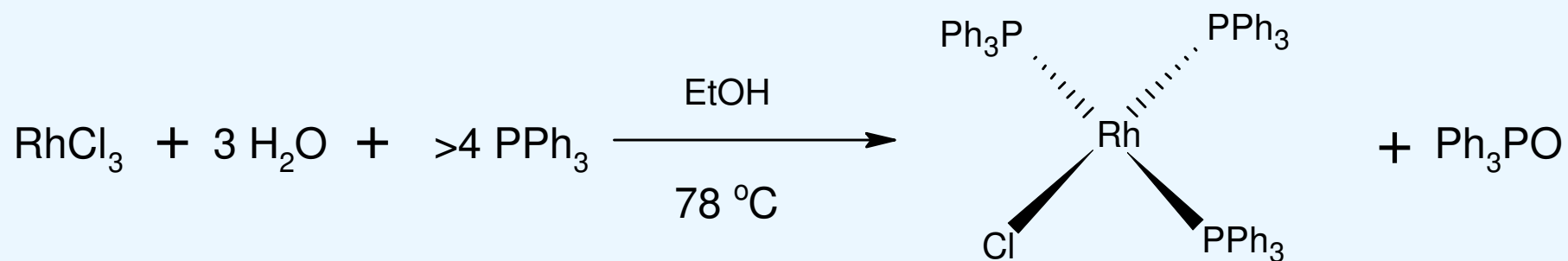
Organometallic compounds prepared by
Wilkinson in display at Harvard Univ.



"Advanced Inorganic Chemistry", often referred
to simply as "Cotton and Wilkinson"



Synthesis of WC



Commercially available

Few Common Organometallic Catalytic Steps

(a) Ligand coordination and dissociation

Facile coordination of the reactant and facile loss of products.

Coordinationally unsaturated - 16-electron complexes

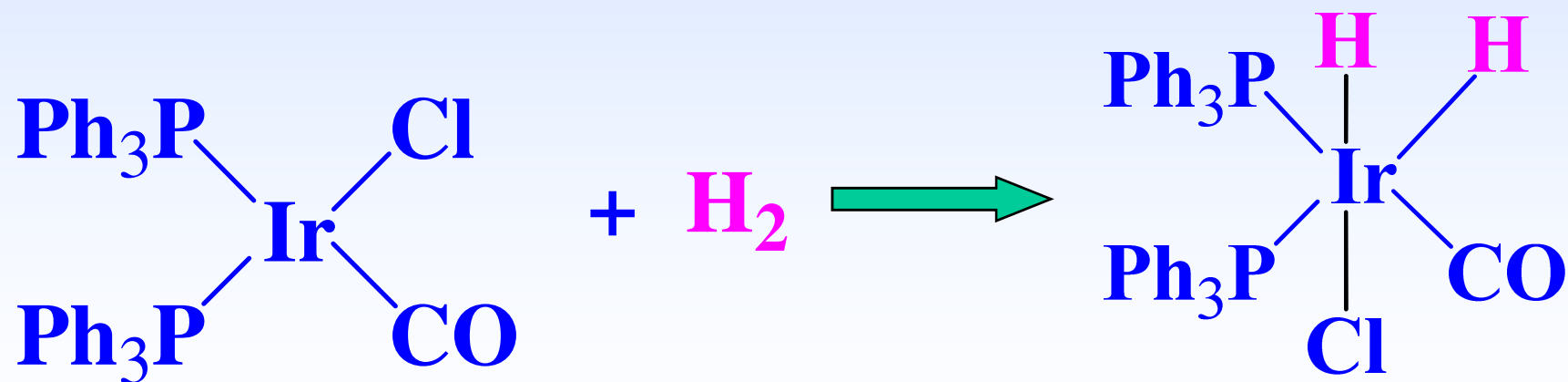
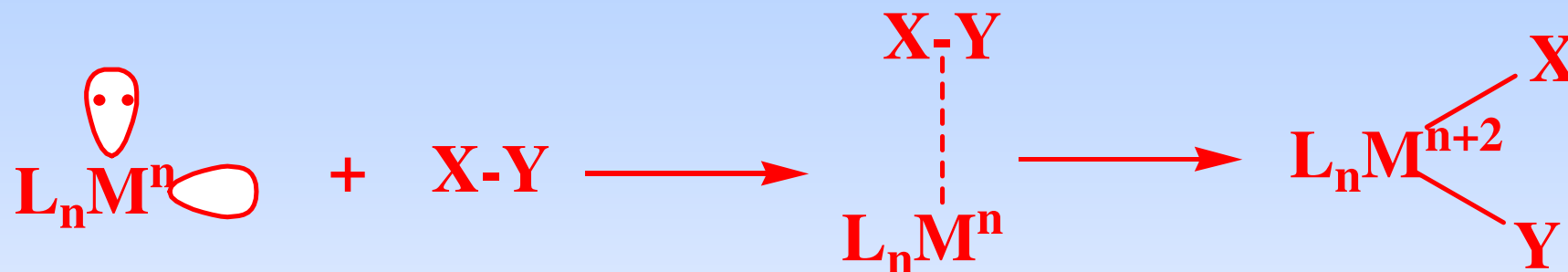
(b) Oxidative addition

Coordinationally unsaturated complex in a low OS undergoes a formal oxdn by 2 units (loss of 2 e) & at the same time increases CN by 2.

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

CN of metal by two units: 4 to 6 (in general)

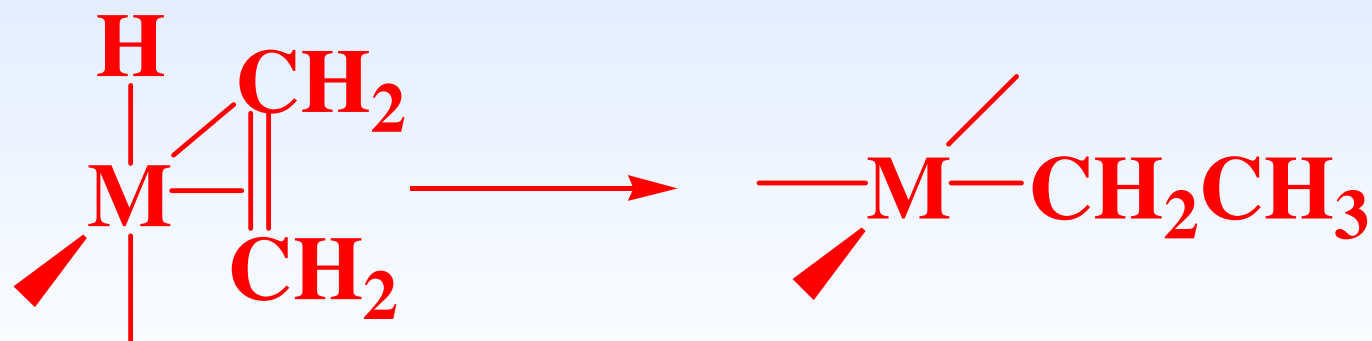
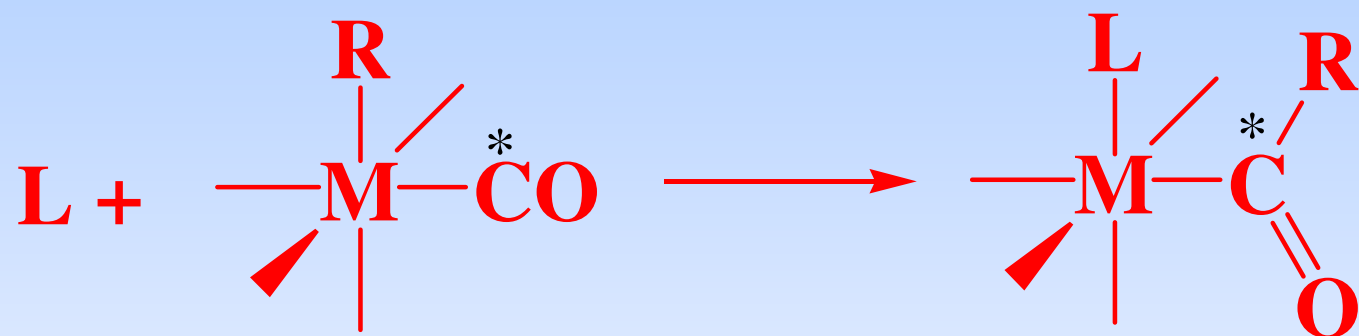
Oxidative addition...



Vaska's complex

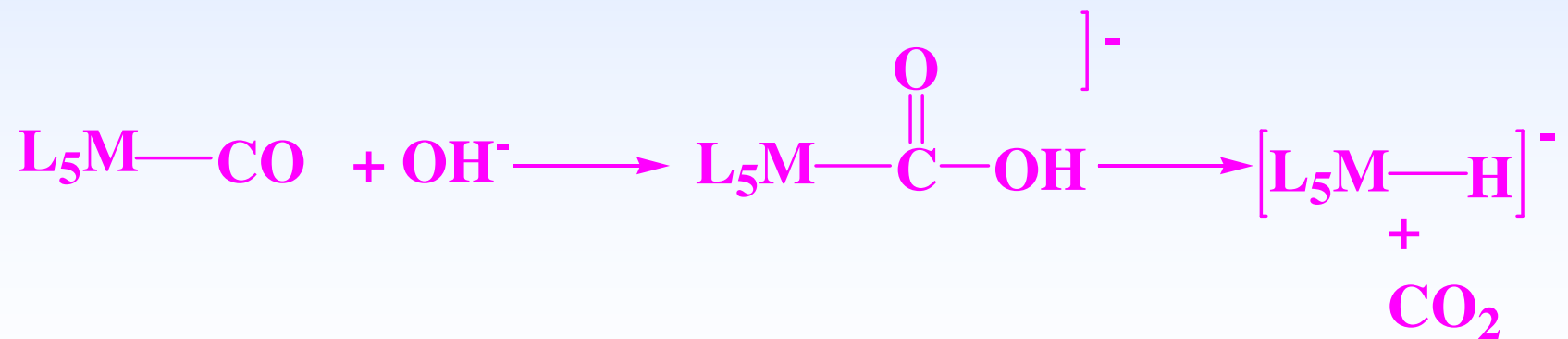
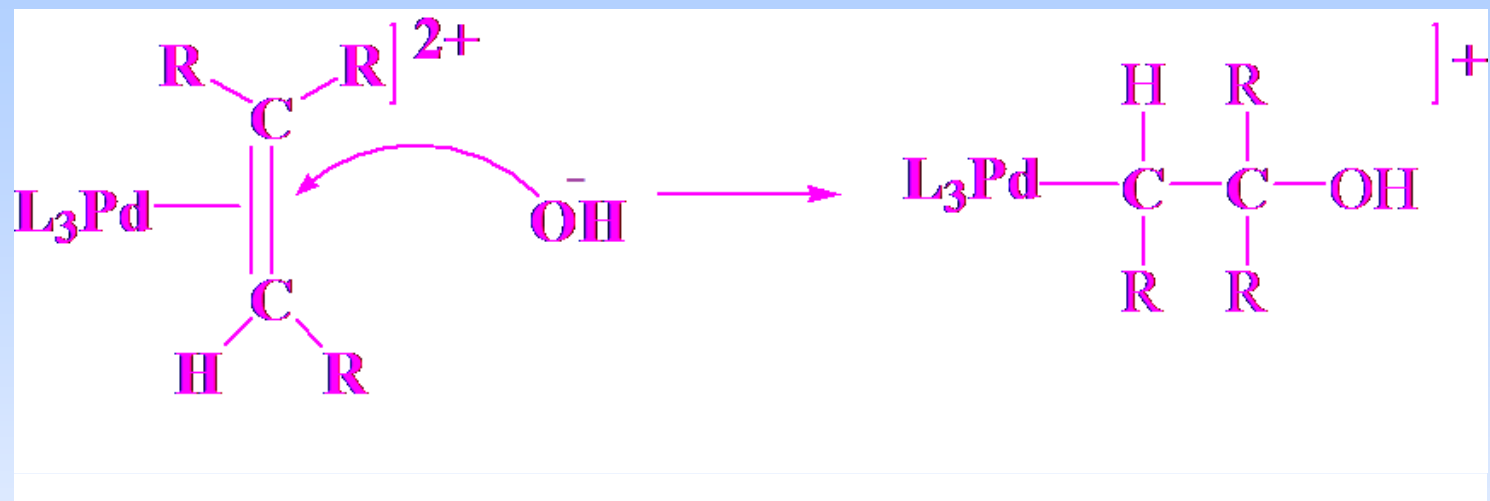
(c) Insertion or migration

Migration of alkyl and hydride ligands



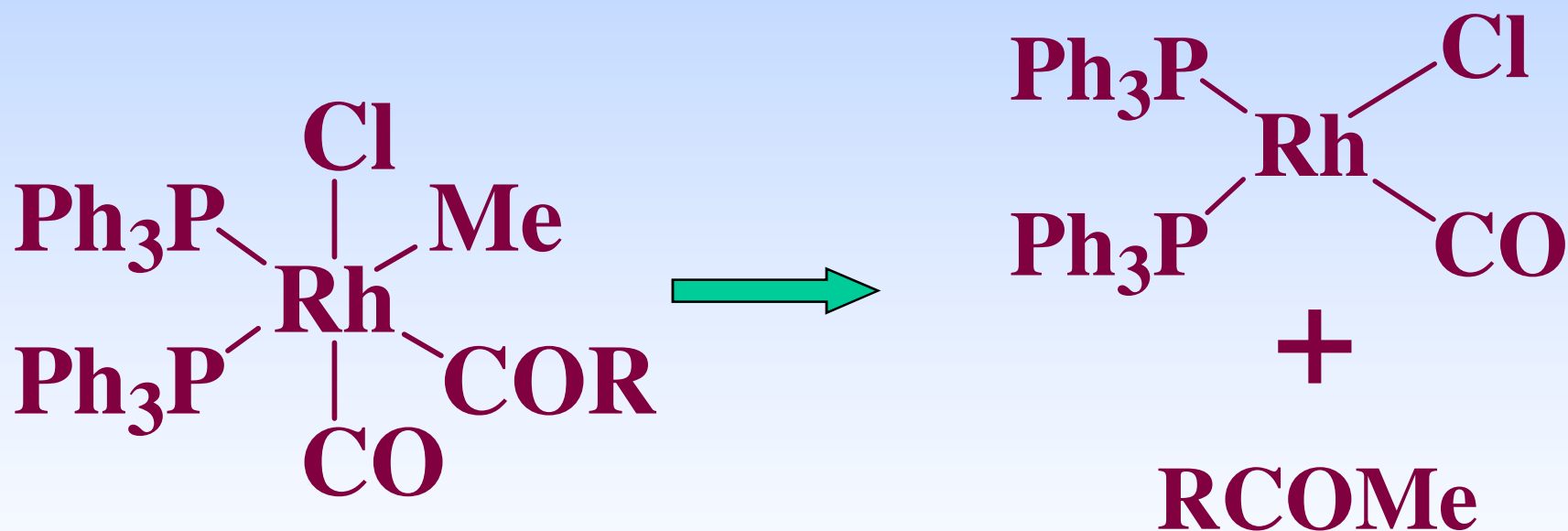
L is generally solvents

(d) Nucleophilic attack

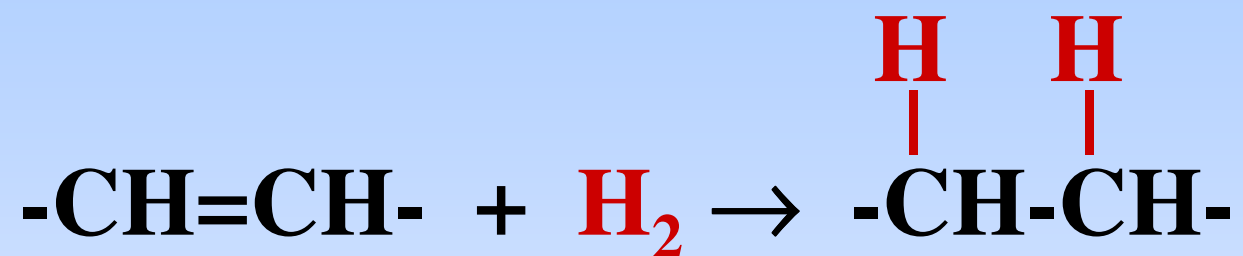


(d) Reductive elimination

Involves decrease in the oxidation and coordination number



Hydrogenation of Unsaturated Hydrocarbons

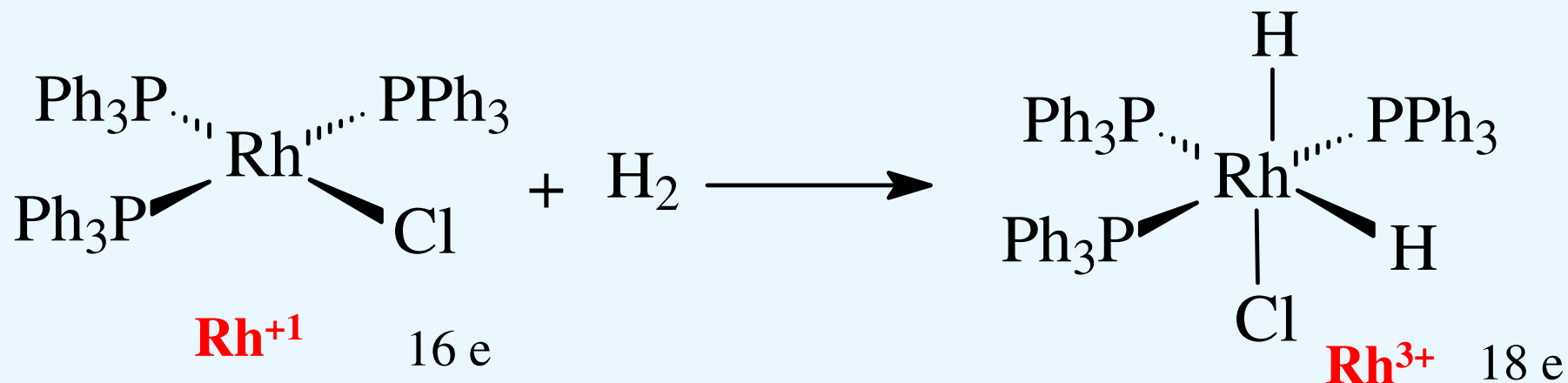


$$\Delta G^0 = -101 \text{ kJ/mol}$$

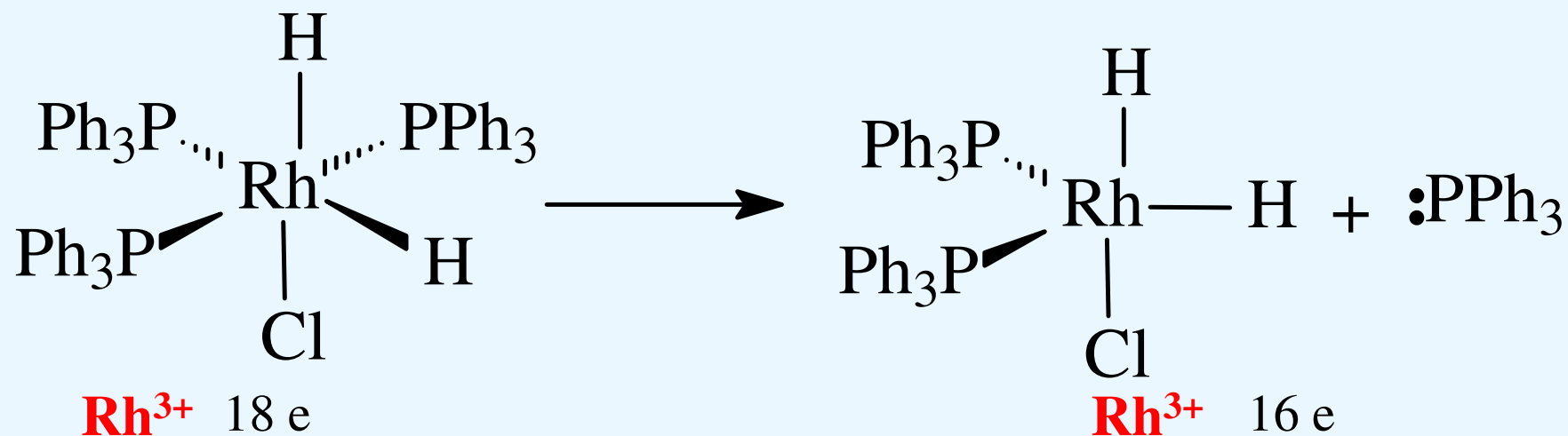
thermodynamically favourable but does not occur at RT and P

WC in alkene Hydrogenation: Catalytic Steps

(1) Oxidative addition

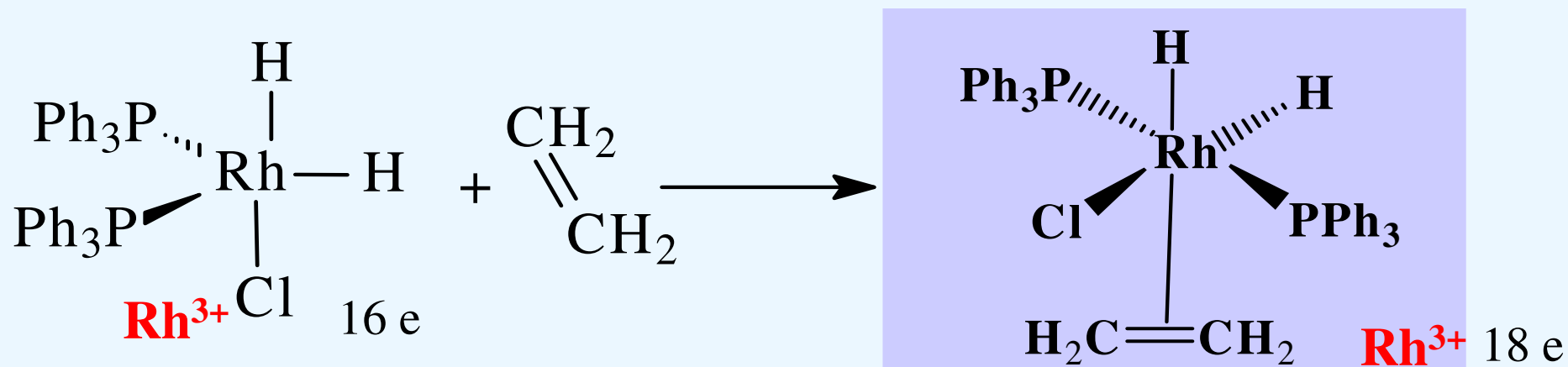


(2) Ligand Dissociation

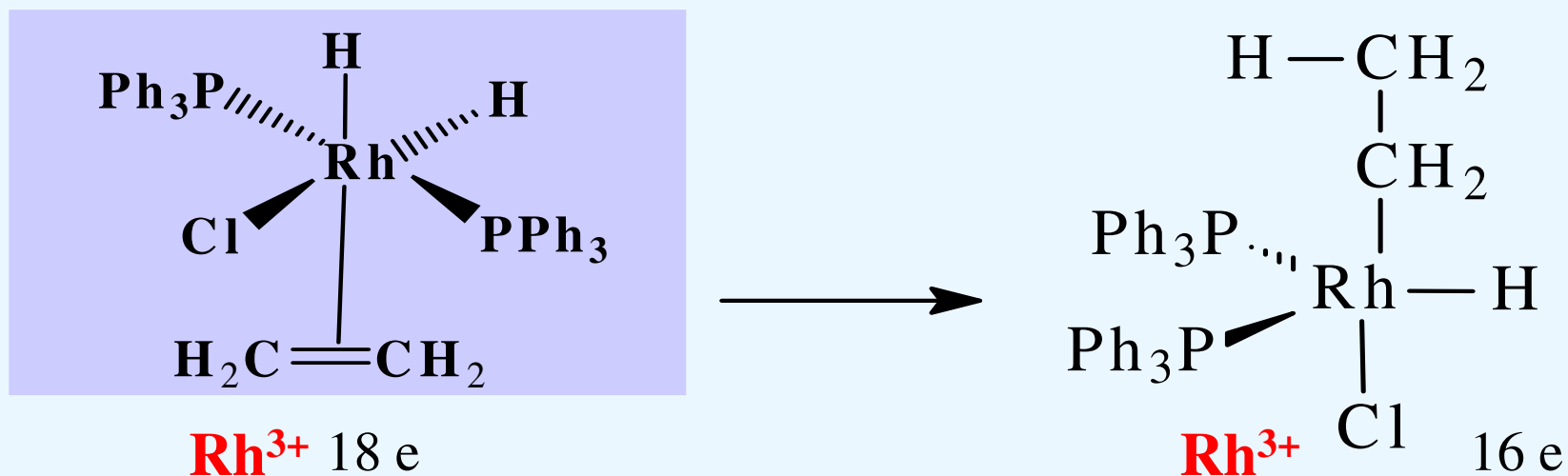


WC in alkene Hydrogenation: Catalytic Steps

(3) Ligand Association

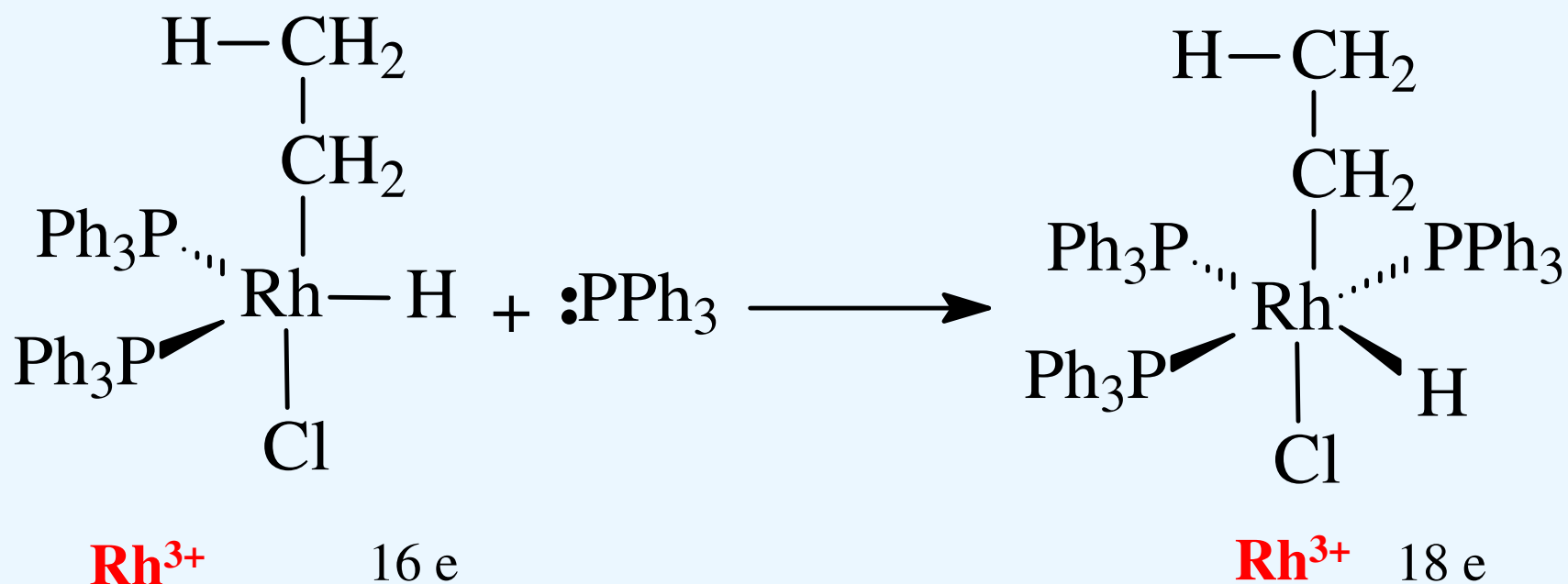


(4) Migration/Insertion



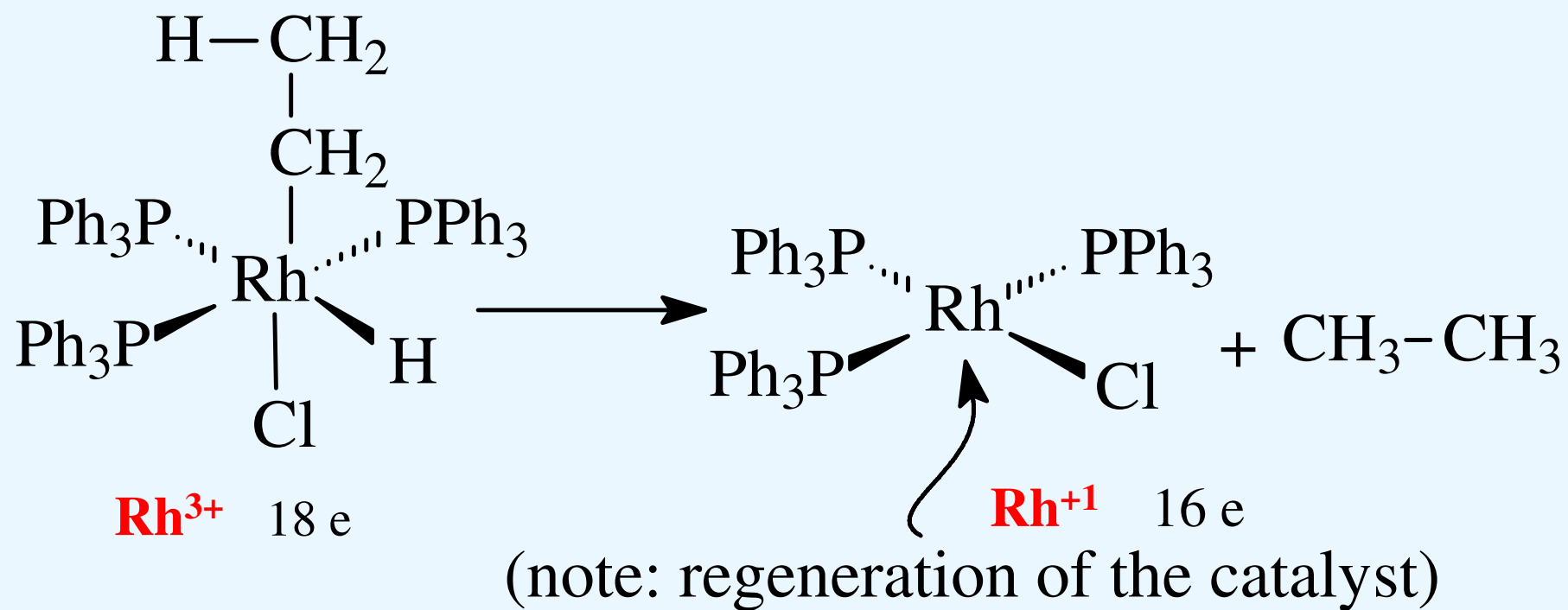
WC in alkene Hydrogenation: Catalytic Steps

(5) Ligand association

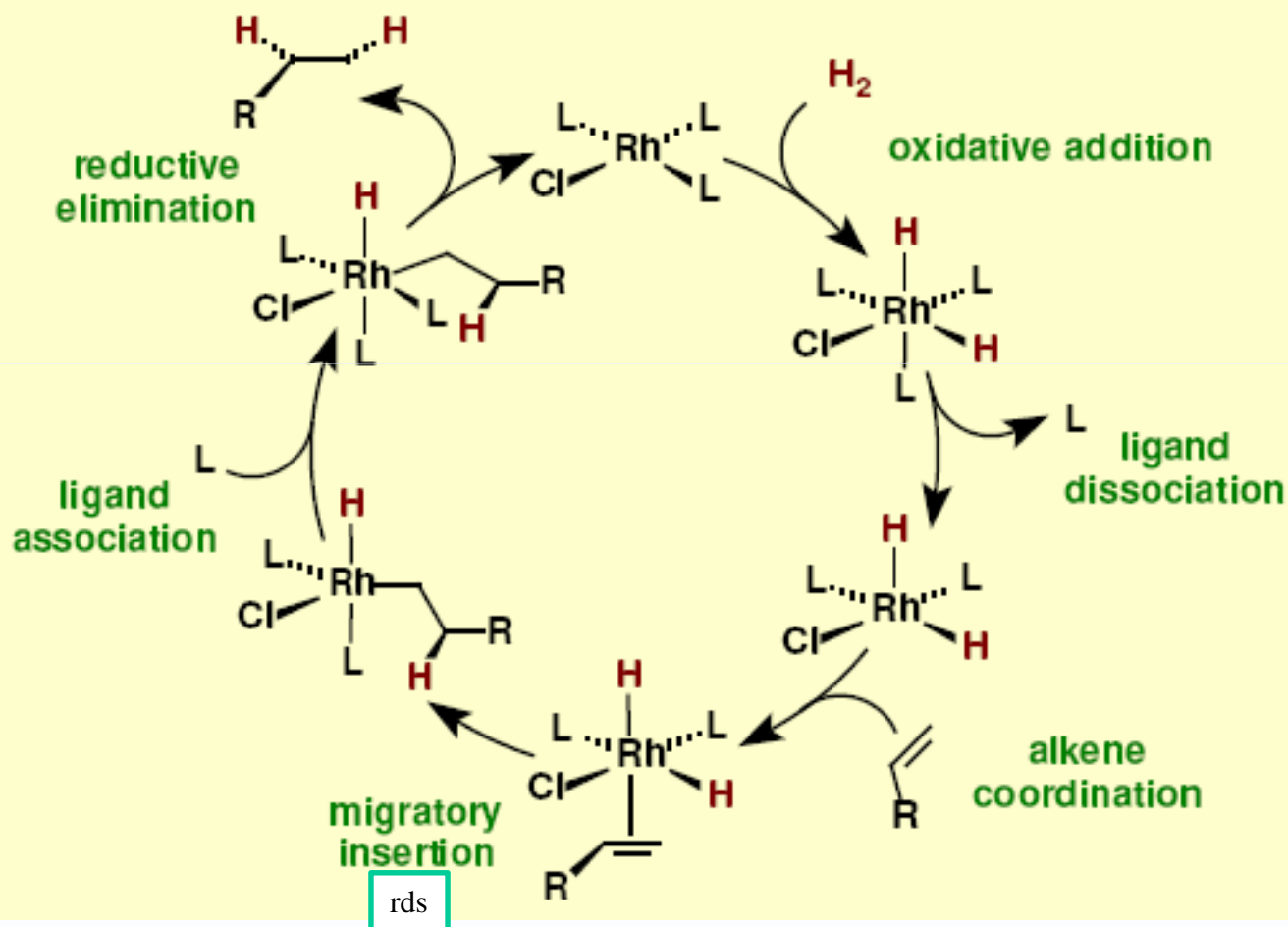


WC in alkene Hydrogenation: Catalytic Steps

(6) Reductive elimination



Homogeneous Hydrogenation



$\text{L} = \text{PPh}_3$

WC in alkene Hydrogenation: Additional Notes

Highly sensitive to the nature of the phosphine ligand

Highly selective for C=C over C=O

It is used in the selective hydrogenation of alkenes and alkynes without affecting the functional groups like: C=O, CN, NO₂, Aryl, CO₂R etc.

Applications

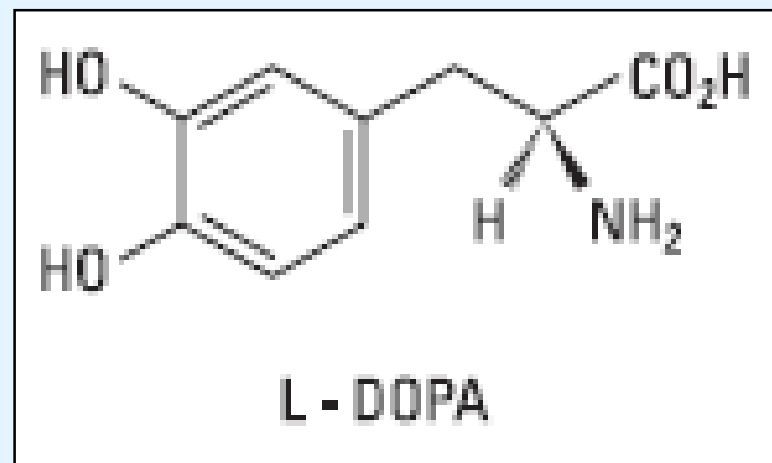
- * **Laboratory scale organic synthesis**
- * **Production of fine chemicals**

Alkene Hydrogenation & Chirality & Nobel

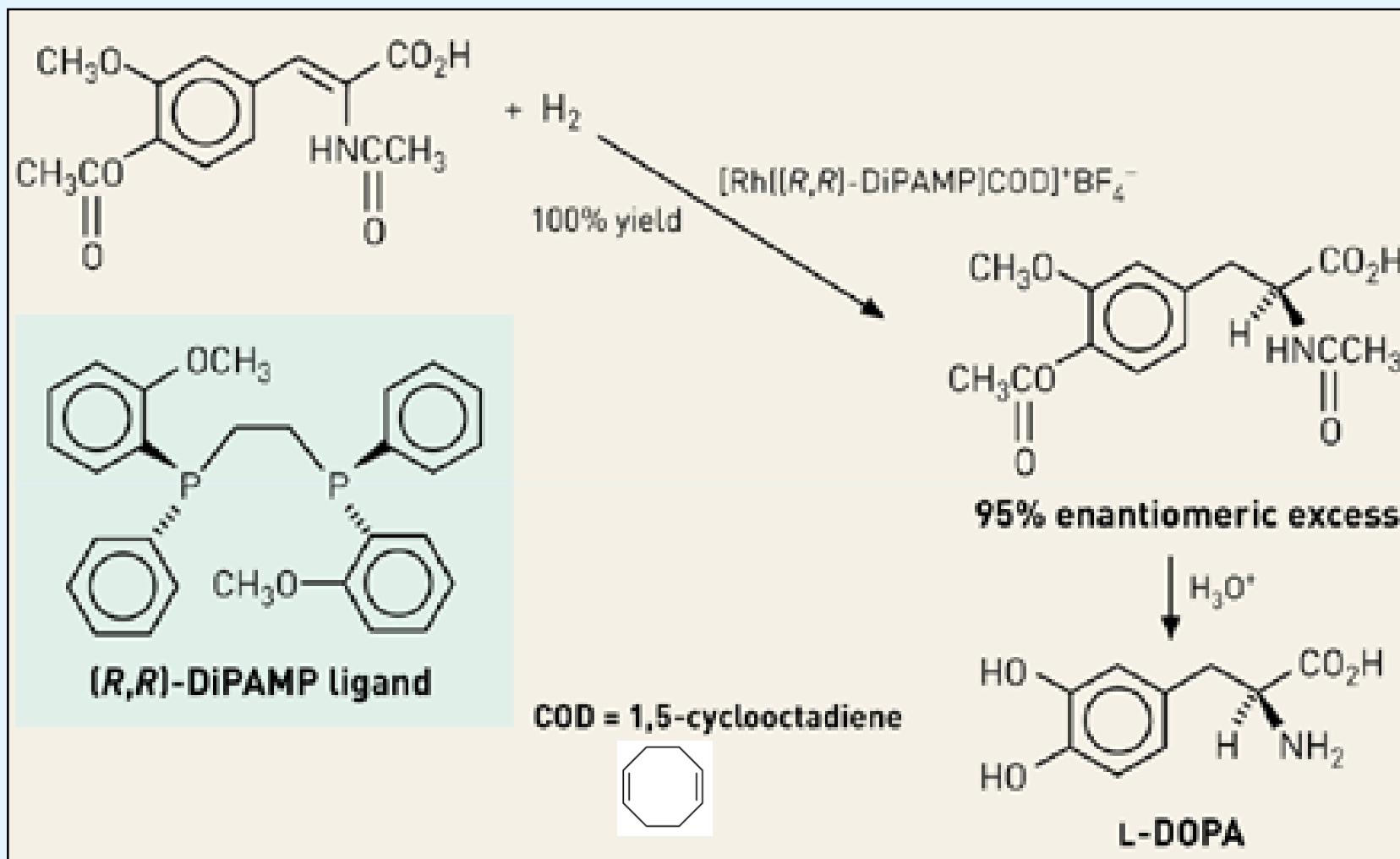
Chiral phosphine ligands have been developed to synthesize optically active products.

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 Prize

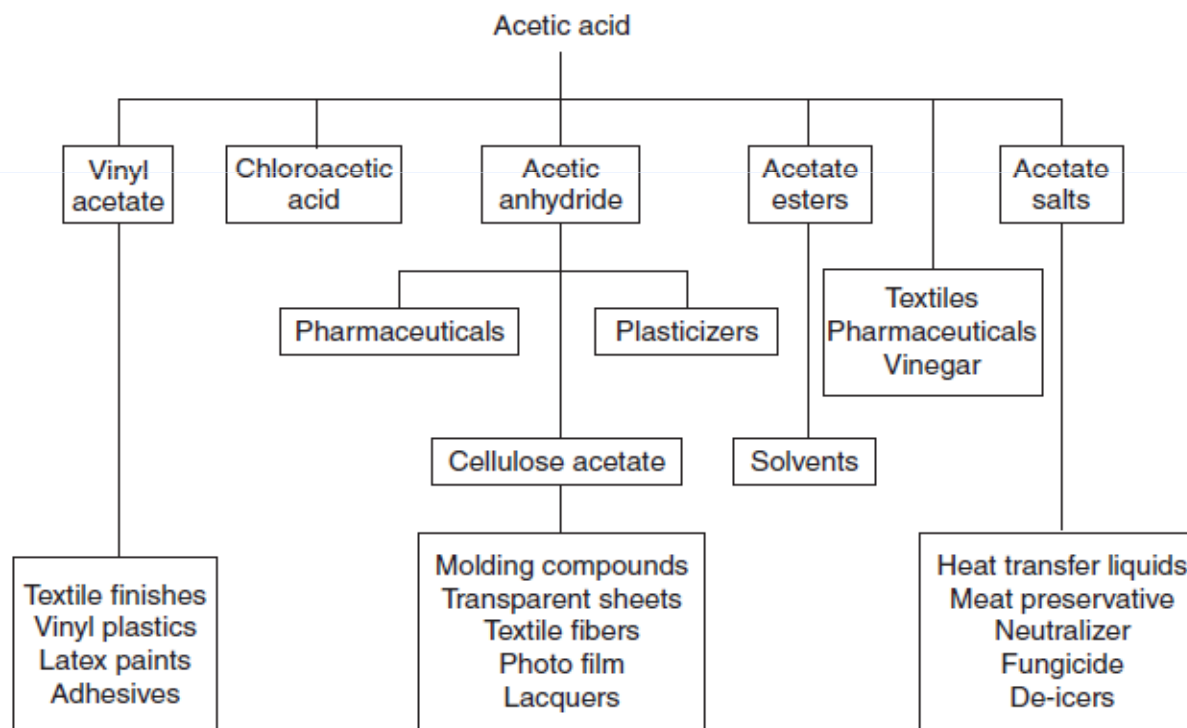


This reaction, developed by Knowles, Vineyard, and Sabacky, was used at Monsanto as a commercial route to the Parkinson's drug L-DOPA.

Acetic Acid

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

vinegar



de-icing chemicals are efficient freezing-point depressants

Synthesis of Acetic Acid

The traditional synthesis uses bio-oxidation of ethanol obtained via fermentation:



This is *not* a clean and efficient process! (need **conc EtOH**)

Industrial acetic acid synthesis:

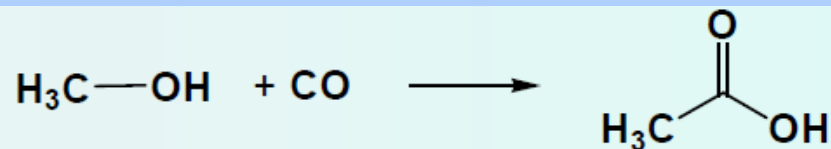


Prior to 1970, acetic acid was made using cobalt catalysts (BASF process)

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

Enormous quantity of MeOH is produced commercially from syn gas: $\text{CO} + 2\text{H}_2 \xrightarrow{\text{Zn/CuO}} \text{CH}_3\text{OH}$

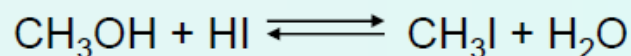
Monsanto Acetic Acid Process (carbonylation of methanol)



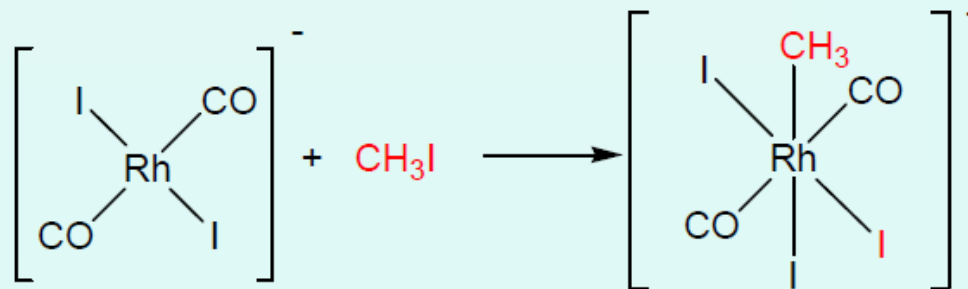
Active/pre- catalyst: $[\text{Rh}(\text{CO})_2\text{I}_2]^-$

The rkn can be initiated with any Rh salt eg RhCl_3 & source of iodine (HI), the two combining the CO to produce the active catalyst $[\text{Rh}(\text{CO})_2\text{I}_2]^-$

1. CH_3I generation:

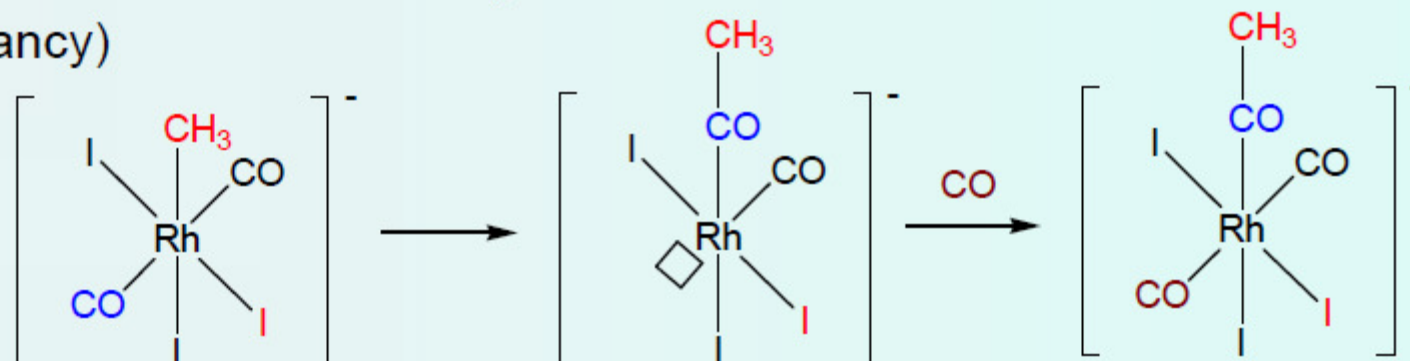


2. Oxidative addition of CH_3I to the Rh^{I} -complex

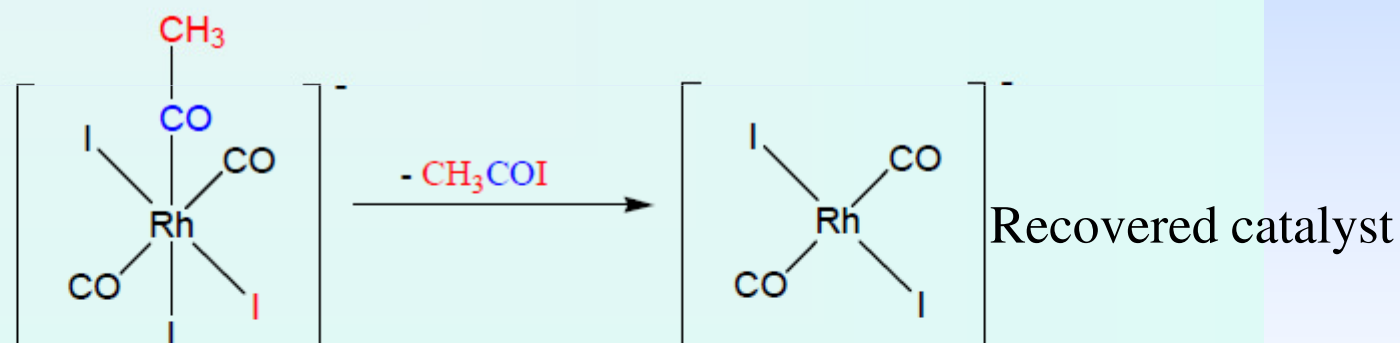


This is the slowest stage of the process

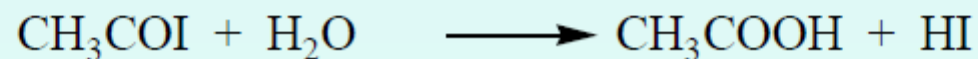
3. Migration insertion of CO (plus new CO addition to the coordination vacancy)



4. Reductive elimination of CH_3COI

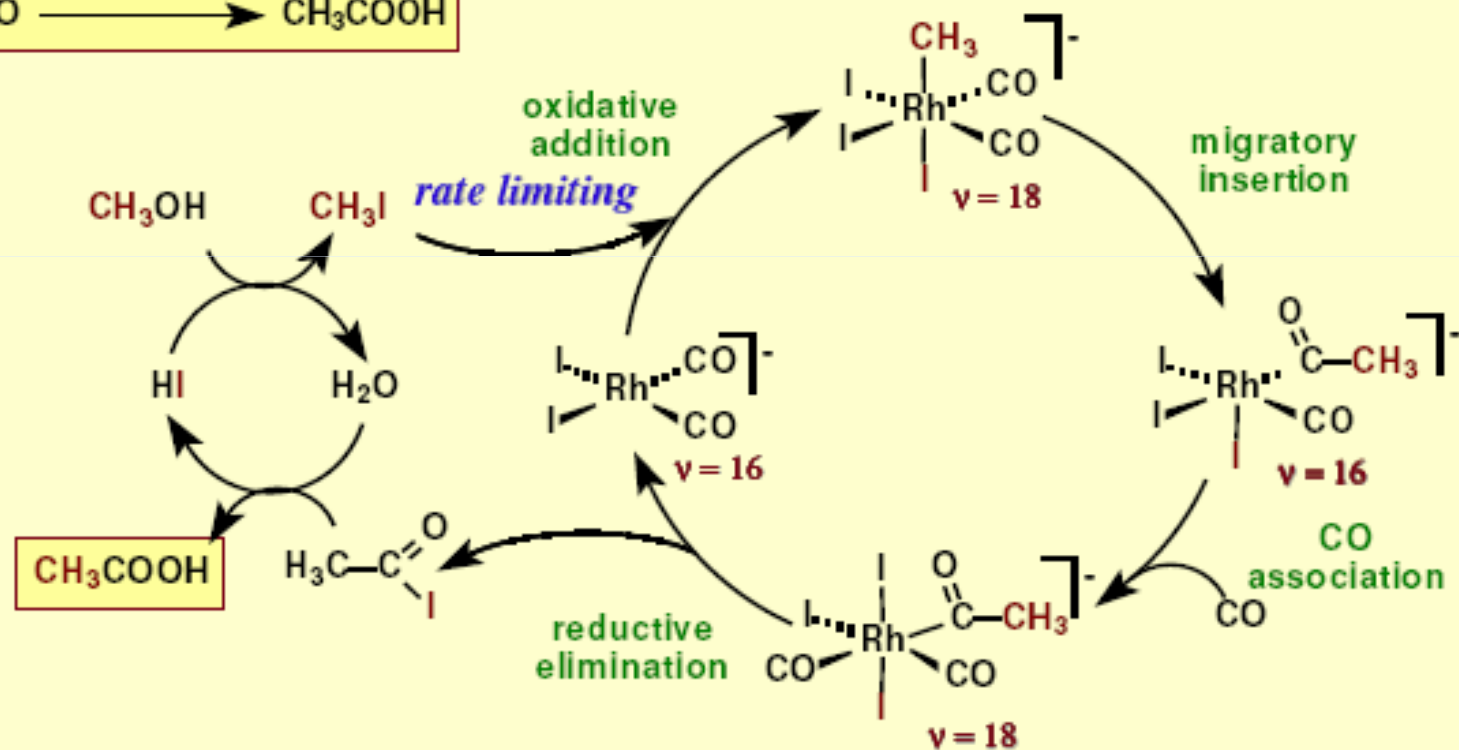
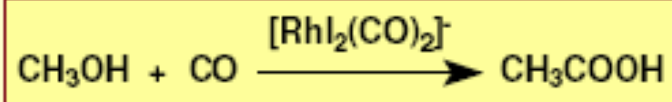


5. Formation of acetic acid through the following processes:



Monsanto Acetic Acid Process

Carbonylation of Methanol



OS of Rh: = +1 & +3