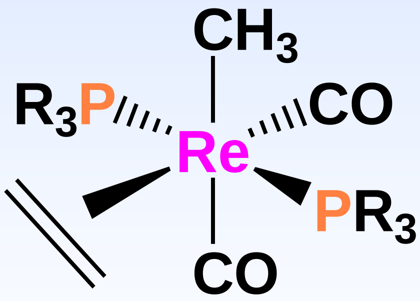
Transition metal:

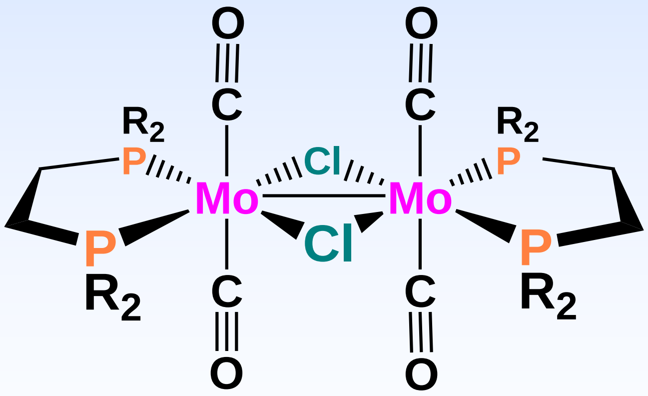
Organometallic compounds
&
Catalysis

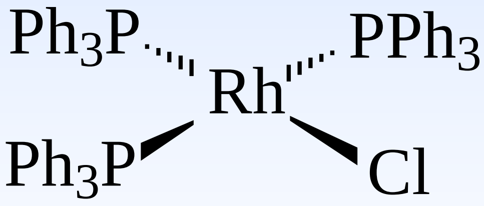
Transition metal organometallic compounds & Catalysis

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

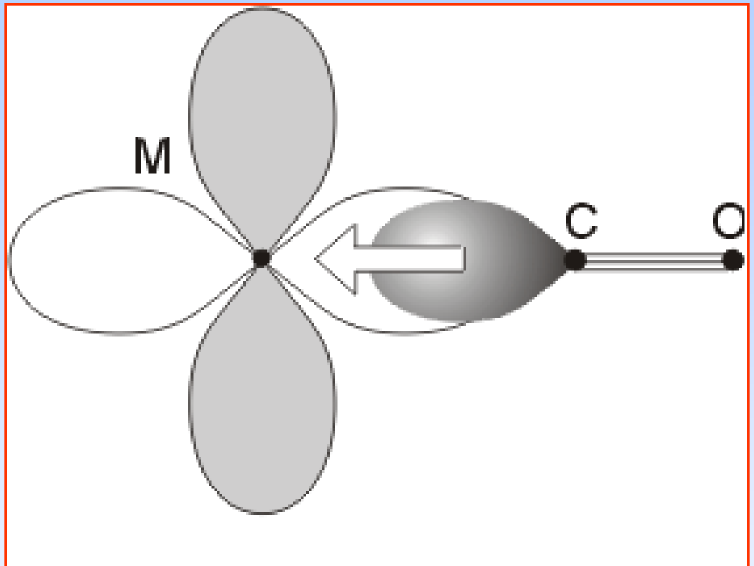
Metal-carbon bond should be present.







Stabilizing Low Oxidation State: CO Can Do the Job



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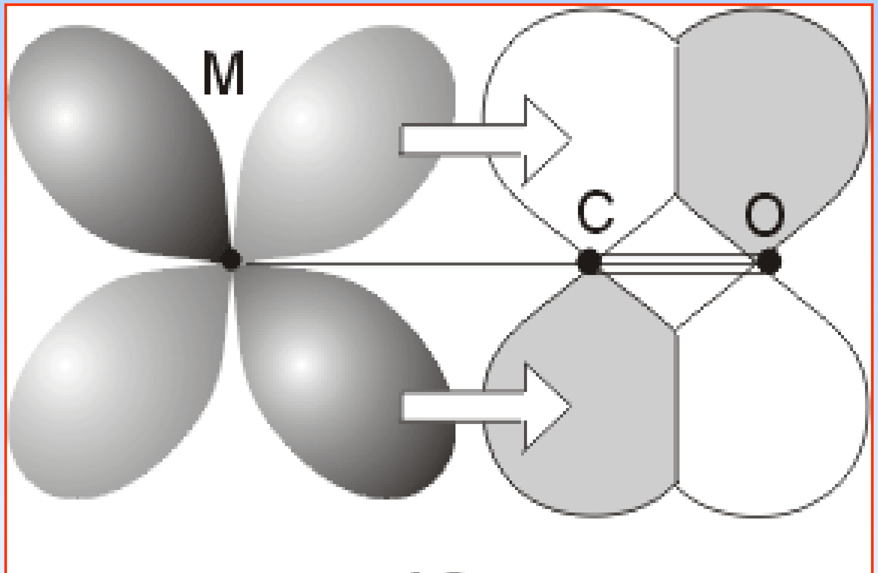
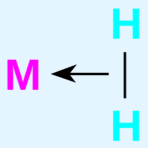
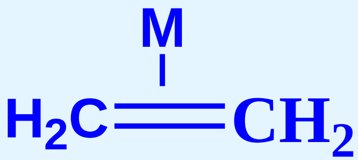


13

$Ni(CO)_4]$, $[Fe(CO)_5]$, $[Cr(CO)_6]$, $[Mn_2(CO)_{10}]$, $[Co_2(CO)_8]$, $Na_2[Fe(CO)_4]$, $Na[Mn(CO)_5]$

Organometallic Compound: Looking closer

Ligand Name	**Bonding Type**
Molecular Hydrogen: H_2	 $M \leftarrow \begin{matrix}H\\ \vert \\H\end{matrix}$
Hydride H^-	**M-H**
Phosphine: PR_3	**$M-PR_3$**
Carbonyl: C≡O	$M-C\equiv O$
Alkyl , Aryl	**M-CR M-Ph**
Alkene	 $H_2C\overset{\overset{M}{\vert}}{=}CH_2$

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

Counting the number of electrons

To determine the electron count for a metal complex:

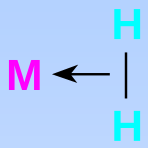
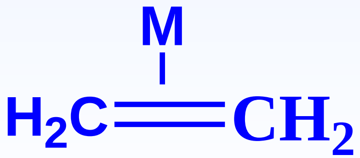
Determine the oxidation state of the transition metal center(s) and the metal centers resulting *d*-electron count.

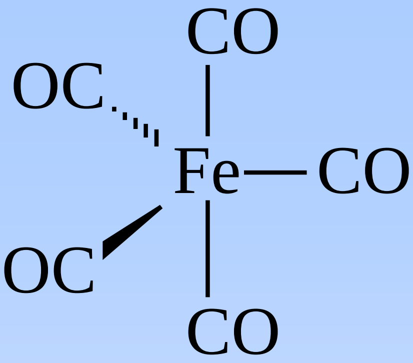
To do this one must:

- 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**

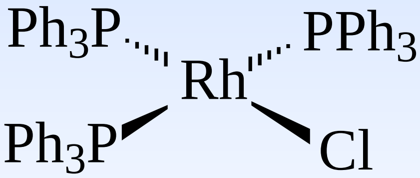
2) Add up the electron counts for the metal center and ligands

Counting the number of electrons

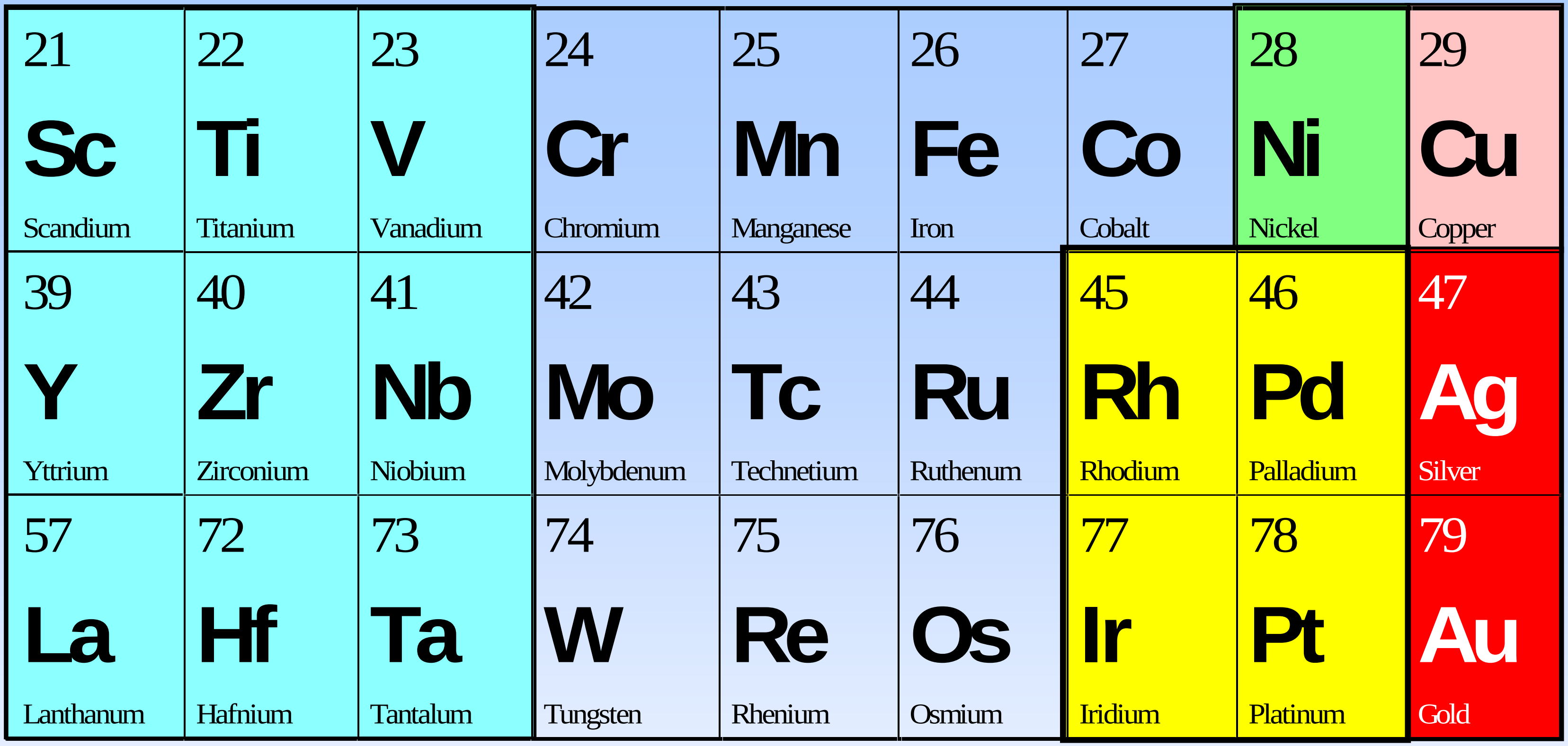
Ligand Name	Bonding Type	Formal Charge	Electrons donated
Molecular Hydrogen: H_2		0	2
Hydride H^-	M-H	-1	2
Halide X^-	M-X	-1	2
Amine, phosphine, arsine: NR_3, PR_3, AsR_3	M-NR3 M-PR3	0	2
Carbonyl: $C\equiv O$	$M-C\equiv O$	0	2
Alkyl , Aryl	M-CR M-Ph	-1	2
Alkene		0	2



coordinately saturated



therefore coordinately **unsaturated**



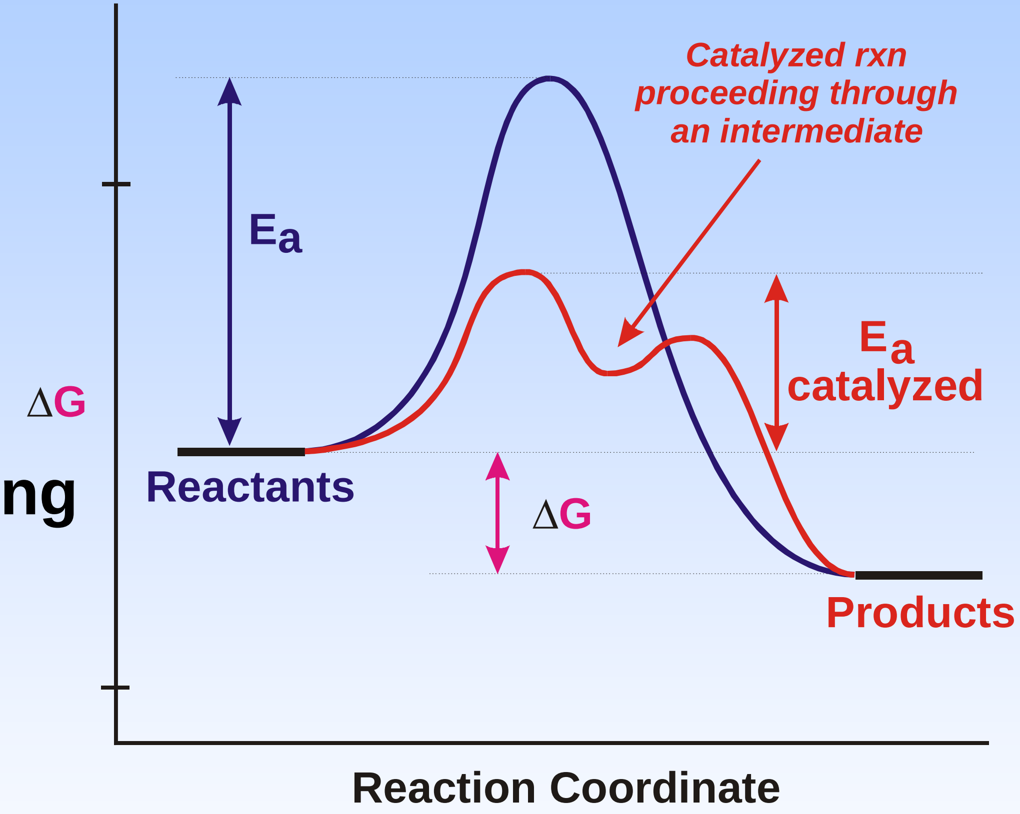
21 **Sc** Scandium	22 **Ti** Titanium	23 **V** Vanadium	24 **Cr** Chromium	25 **Mn** Manganese	26 **Fe** Iron	27 **Co** Cobalt	28 **Ni** Nickel	29 **Cu** Copper
39 **Y** Yttrium	40 **Zr** Zirconium	41 **Nb** Niobium	42 **Mo** Molybdenum	43 **Tc** Technetium	44 **Ru** Ruthenum	45 **Rh** Rhodium	46 **Pd** 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	**Middle Transition Metals**	**Late Transition Metals**
16e and sub-16e configurations are common	***18e configurations are common***	***16e and sub-16e configurations are common***
Coordination geometries higher than 6	***Coordination geometries of 6 are common***	***Coordination geometries of 5 or lower***

Catalysis

$$A + B \xrightarrow{\text{Catalyst}} C$$

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



It does not change the thermodynamics!!

Heterogeneous **Homogeneous**

Catalysis : Why?

Synthesis of chemicals… pharmaceutical, agricultural

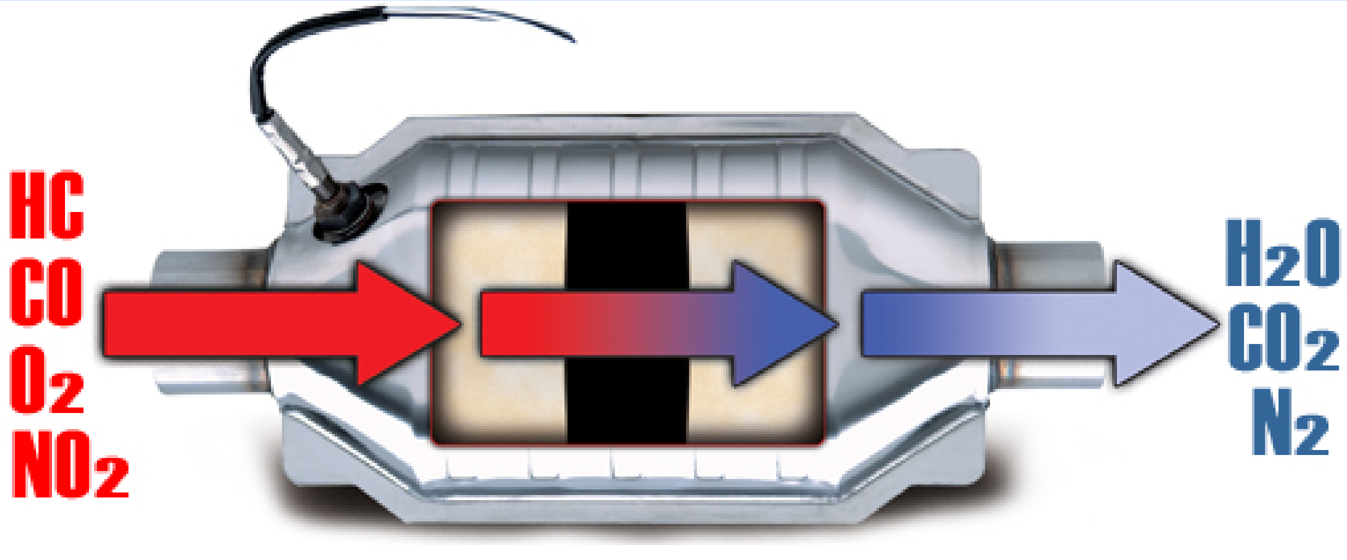
Catalytic converter … environmental

Biology: Enzymes

Biological system – efficient catalyst

Organometallic compounds, metals etc.

Catalytic Converter



How to select an efficient catalyst?

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

efficient catalyst: good activity

Turnover frequency (N)

Large turnover frequency – efficient catalyst

Selectivity: Byproducts should be minimized

Lifetime: It is costly to replace the catalyst frequently

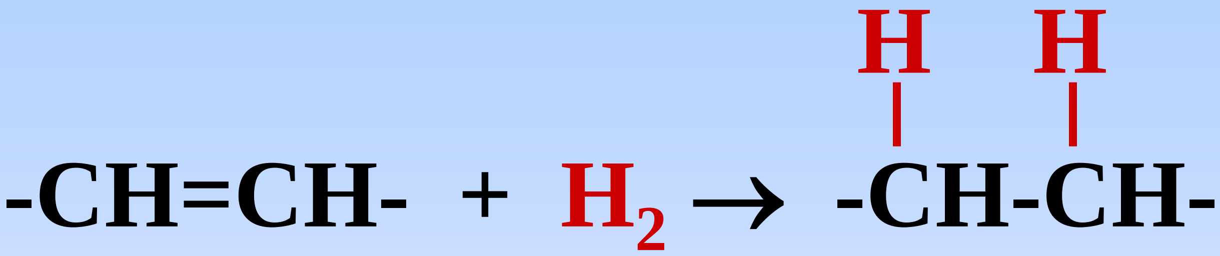
Cost: The acceptable cost depends upon the catalyst lifetime, product value lifetime and product value

Poisoning: decomposition of catalyst, adsorption of reactant/product

Coordination compounds in catalysis
Nobel Prizes

2005	***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



$$\text{-CH=CH-} + H_2 \rightarrow \text{-}\overset{\overset{H}{|}}{C}H\text{-}\overset{\overset{H}{|}}{C}H\text{-}$$

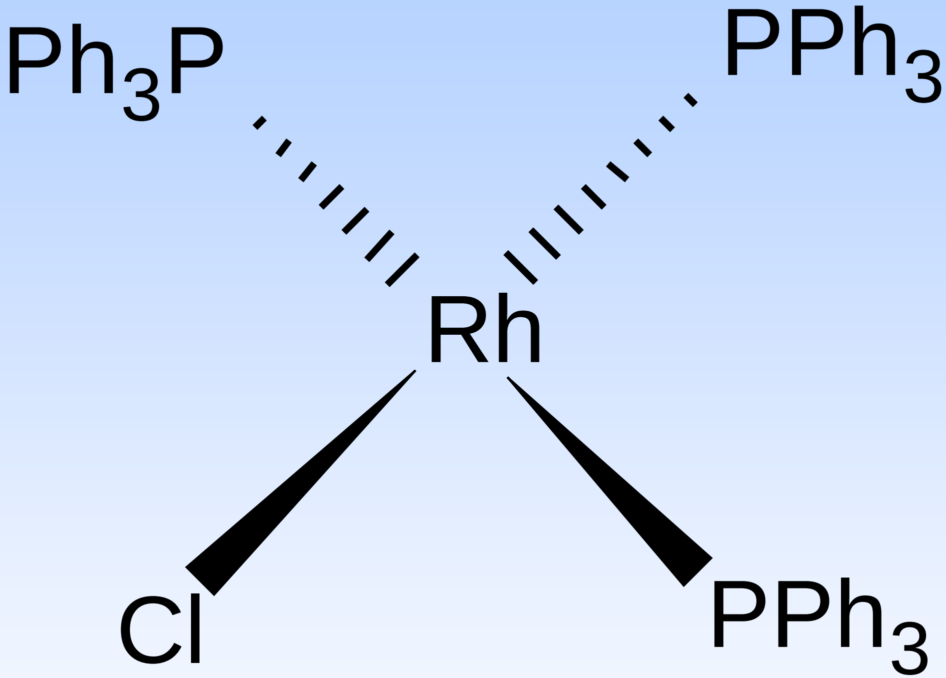
NOBEL : 1973

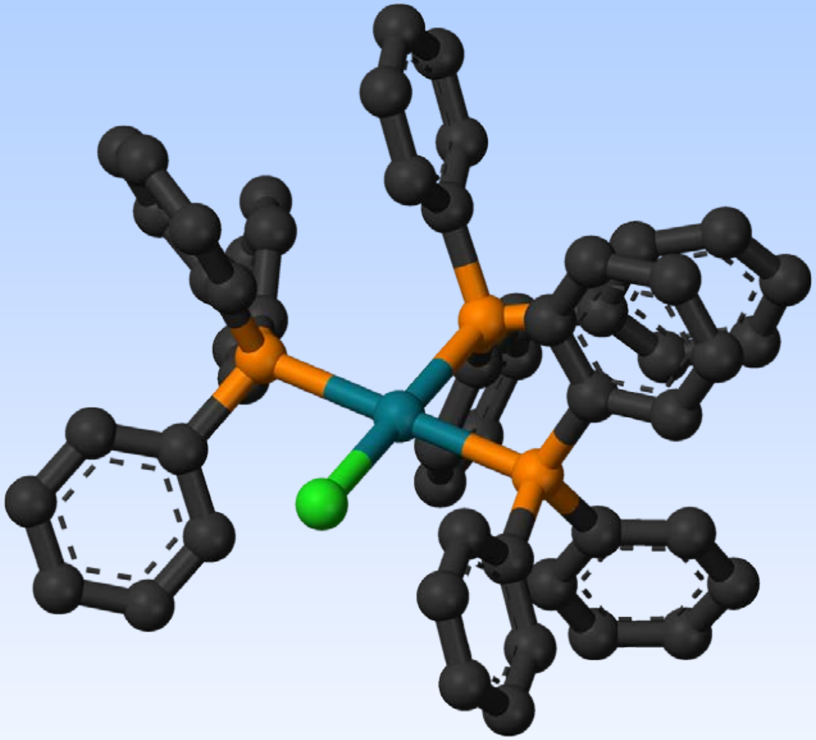
The most common catalyst

⇓

Wilkinson's Catalyst, $[RhCl(PPh_3)_3]$

Wilkinson's Catalyst (WC)





Chlorotris(triphenylphosphine)rhodium(I)

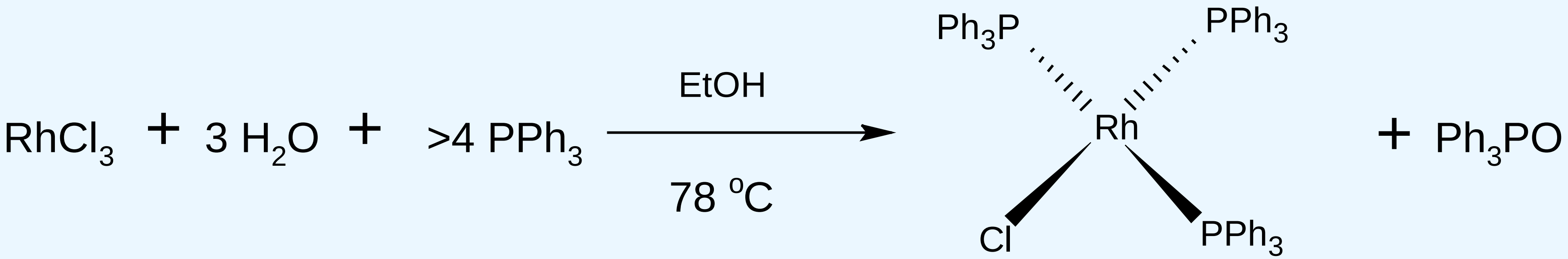
square planar **d^8 configuration**

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

Catalytic steps

(a) Ligand coordination and dissociation

Facile coordination of the reactant and facile loss of products.

Coordinatively unsaturated - 16-electron complexes

(b) Oxidative addition

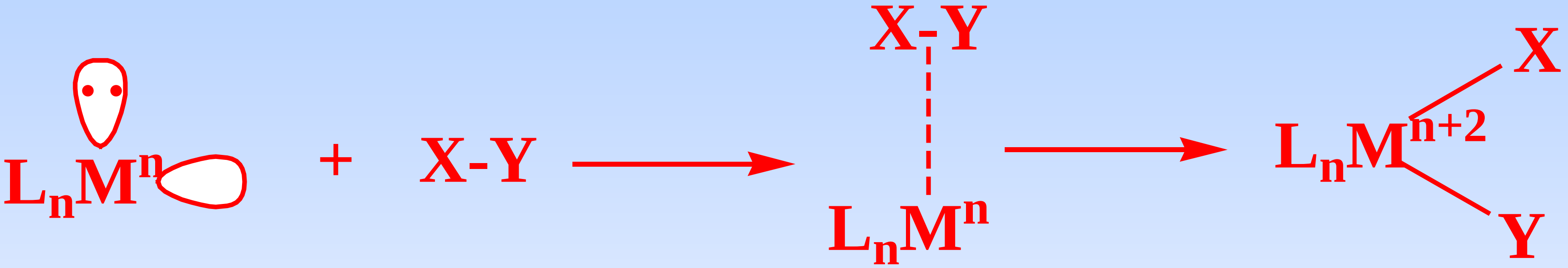
-occurs when a complex behaves simultaneously as a Lewis base and a Lewis acid

Metal must possess a non-bonding electron pair

Coordinatively unsaturated

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

Oxidative addition…



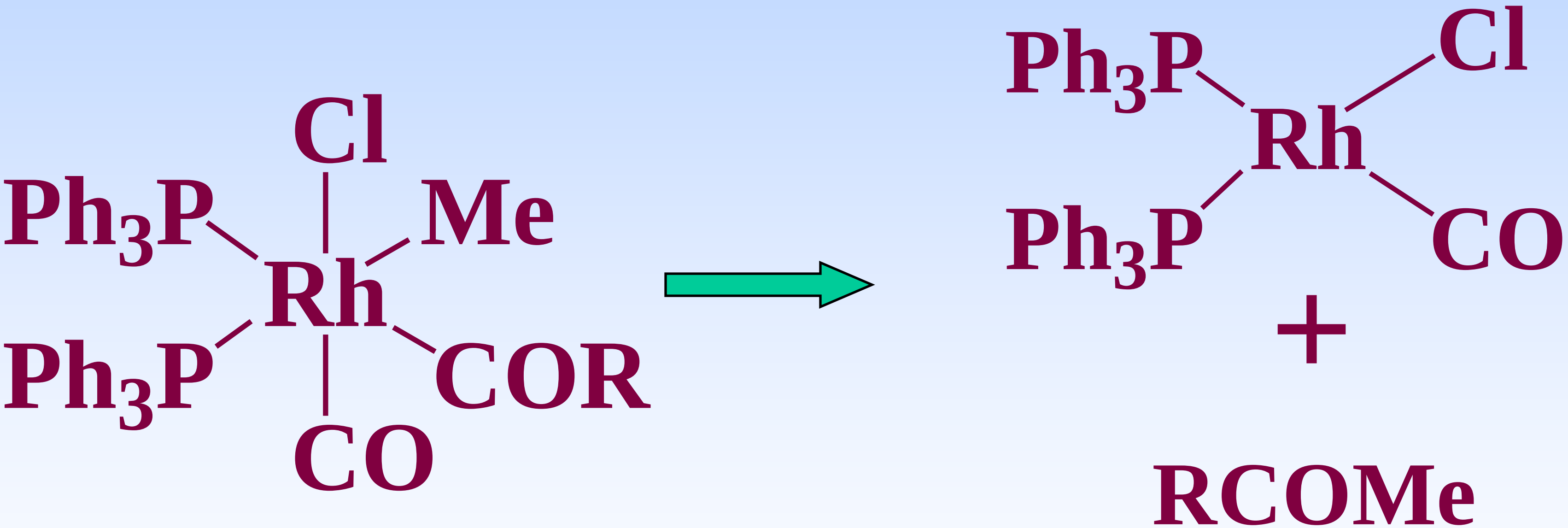
L_nM^n + X-Y $\longrightarrow$ X-Y L_nM^n $\longrightarrow$ L_nM^{n+2} X Y

(c) Insertion or migration

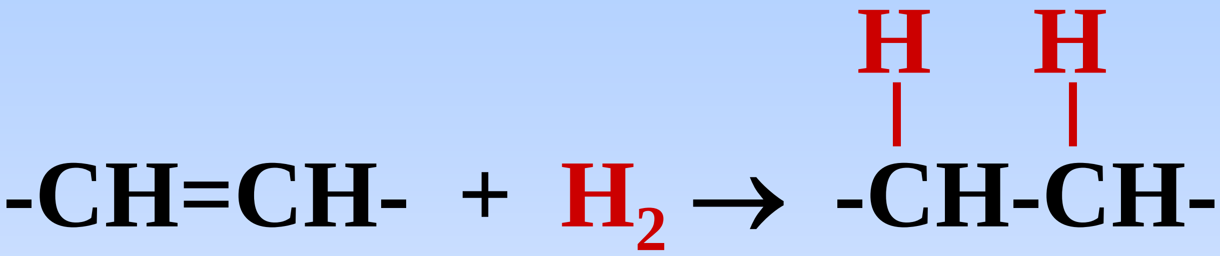
Migration of alkyl and hydride ligands

(d) Reductive elimination

Involves decrease in the oxidation and coordination number



Hydrogenation of Unsaturated Hydrocarbons

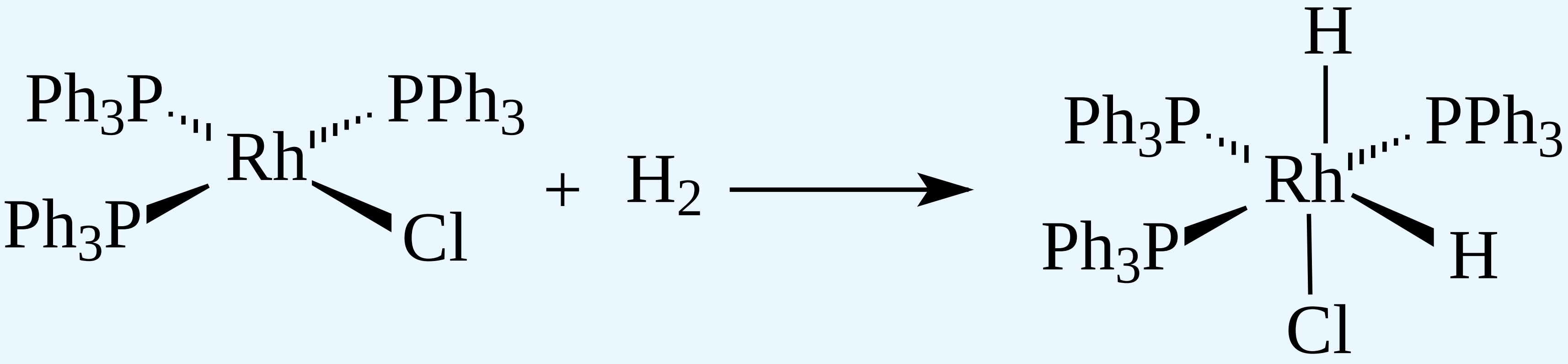


$$-CH=CH- + H_2 \rightarrow -\overset{\overset{H}{|}}{C}H-\overset{\overset{H}{|}}{C}H-$$

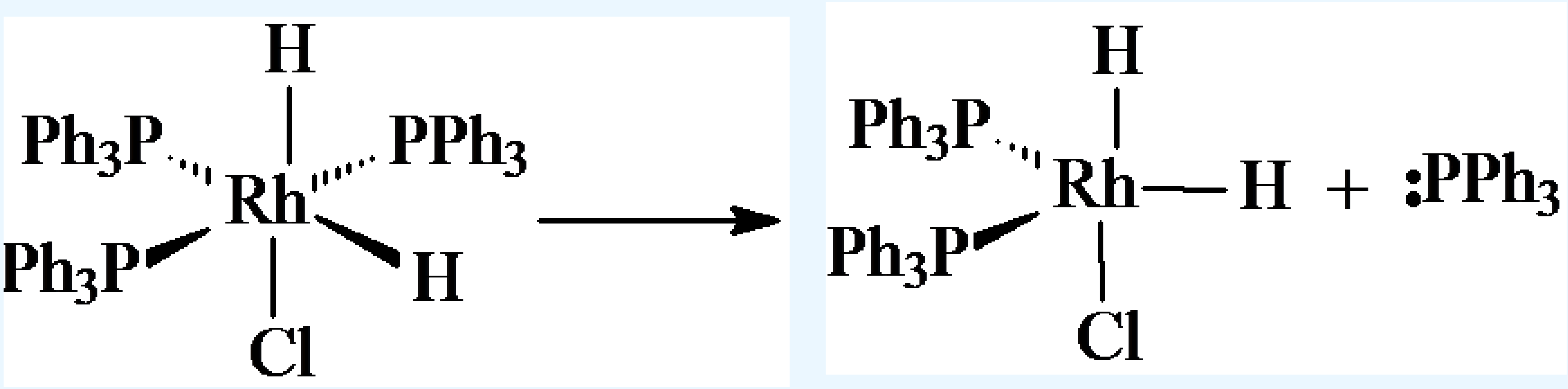
$\Delta G^0 = -101$ kJ/mol

WC in alkene Hydrogenation: Catalytic Steps

(1) Oxidative addition

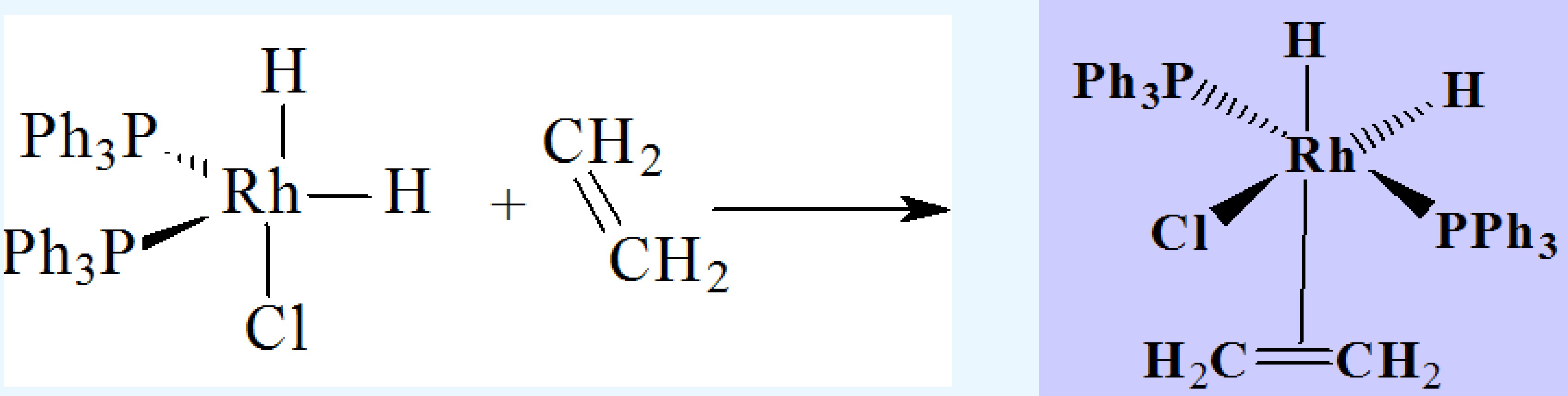


(2) Ligand Dissociation

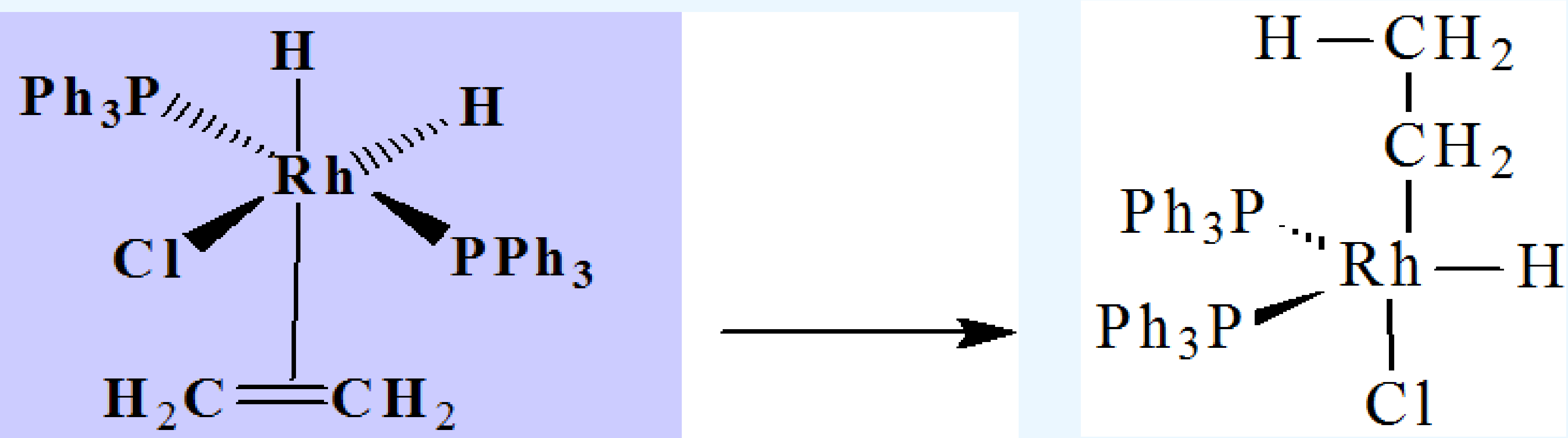


WC in alkene Hydrogenation: Catalytic Steps

(3) Ligand Association

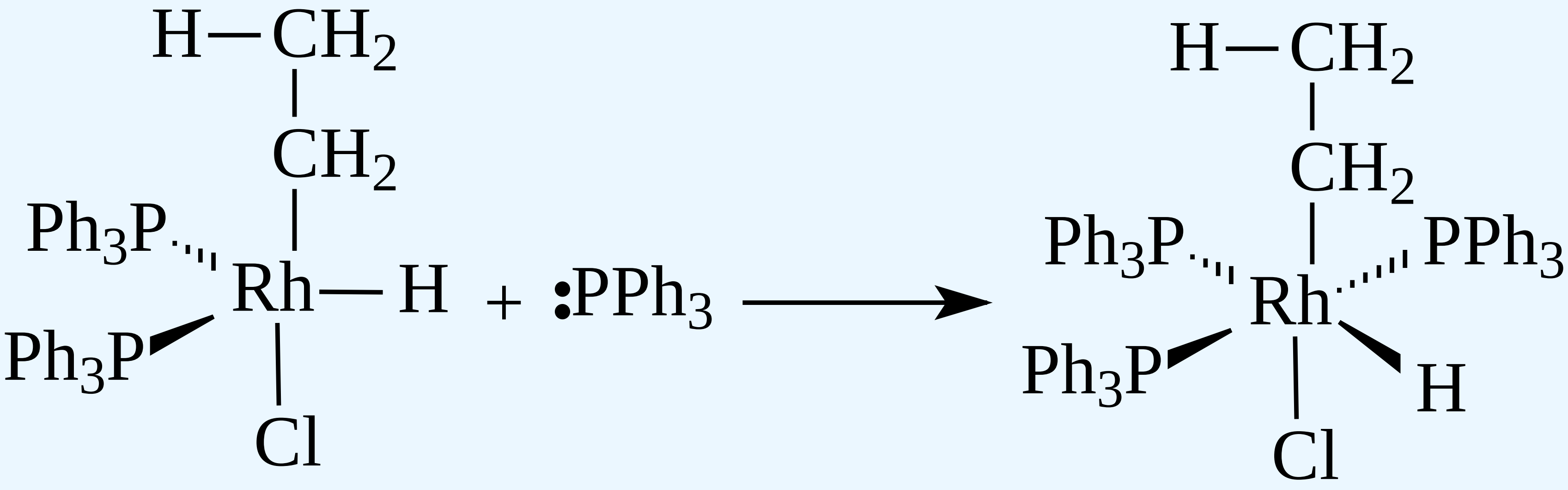


(4) Migration/Insertion



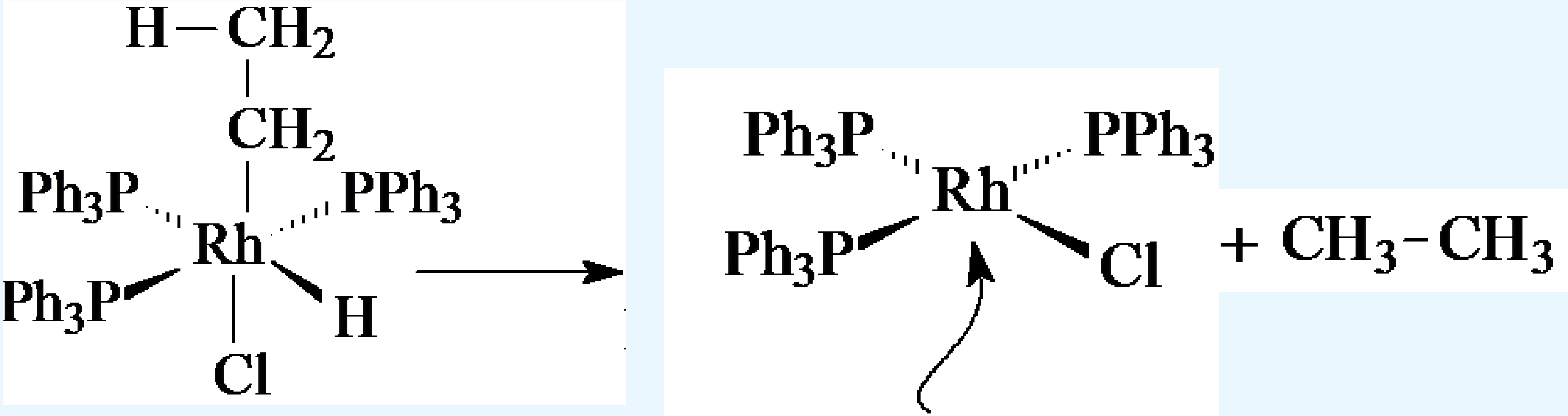
WC in alkene Hydrogenation: Catalytic Steps

(5) Ligand association



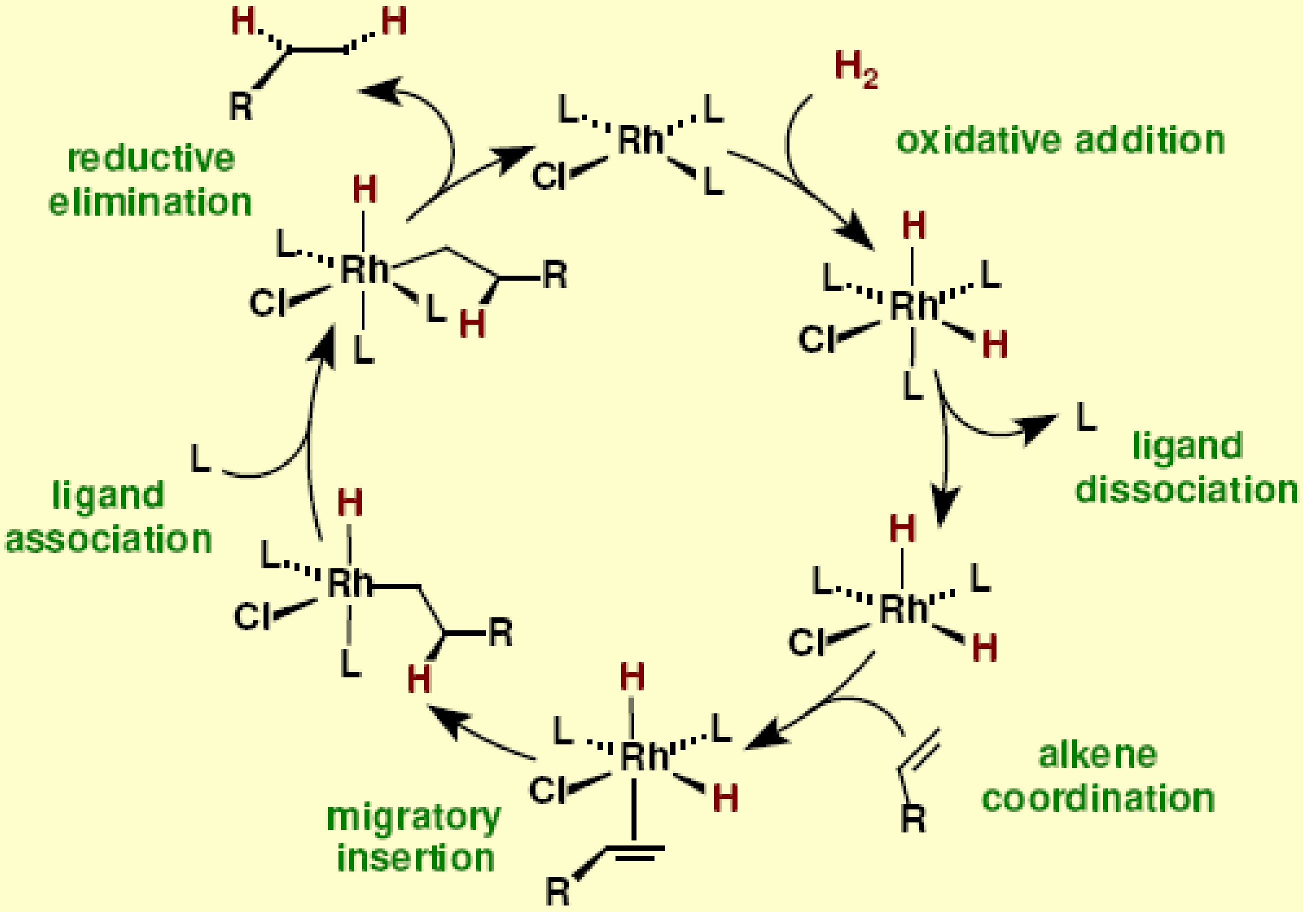
WC in alkene Hydrogenation: Catalytic Steps

(6) Reductive elimination



(note: regeneration of the catalyst)

Homogeneous Hydrogenation



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.