General Chemistry: Inorganic section

Instructor: Dr. Prakash Chandra Mondal
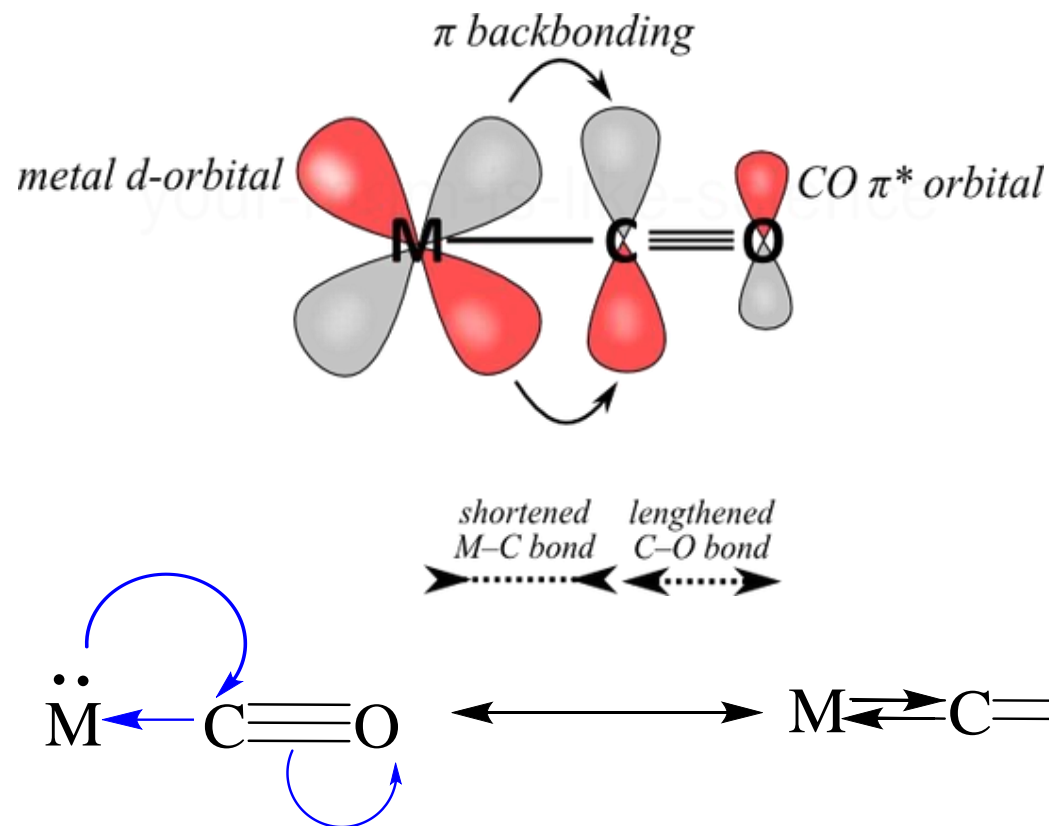
Department of Chemistry

Lecture: 6 (last class of Inorganic Section)
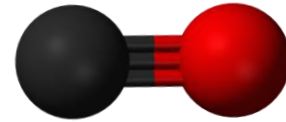
Bonding in Metal Carbonyls

- **M-CO:**

➢ **σ-donation strengthens the M-C bond**

➢ **π-back donation strengthens the M-C bond and weakens C≡O**

As back bonding increases, we would expect the C=O bond strength to decrease

FT-IR Spectroscopy and C=O Bond Strength

- **FT-IR spectra provide important information about the stretching frequency of a bond.**

- **The stronger a bond gets, the higher its stretching frequency.**

- **The υ_{CO} stretching frequency of the coordinated CO is very informative as to the nature of the bonding. Thus, the more important the M=C=O (C=O is a double bond) canonical structure, the lower the υ_{CO} stretching frequency as compared to the M-C≡O structure (C≡O is a triple bond): (Note: υ_{CO} for free C≡O is 2143 cm^{-1}).**

$$\bar{\nu} = 1 / 2\pi c \sqrt{k/\mu}$$

Hooke's Law

M←C≡O ⟷ M⇄C=O
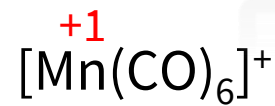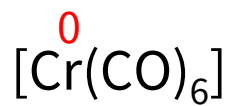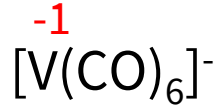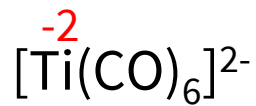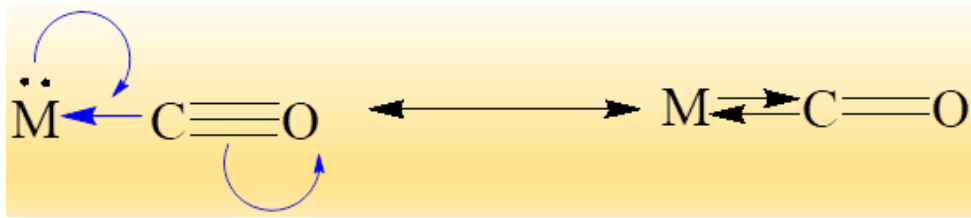
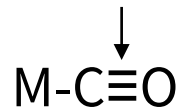|	-2	-1	0	+1
	$[Ti(CO)_6]^{2-}$	$[V(CO)_6]^-$	$[Cr(CO)_6]$	$[Mn(CO)_6]^+$
υ_{CO}	1748	1858	1984	2094 cm^{-1}

increasing M=C double bonding → decreasing M=C double bonding
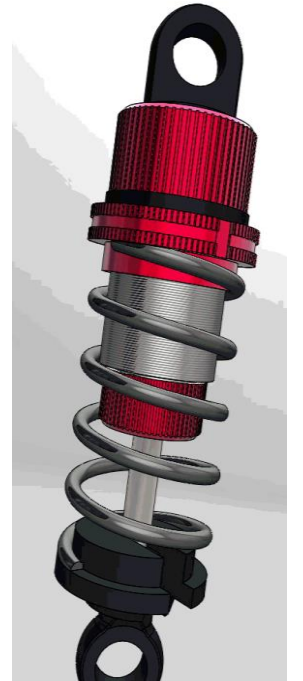
FT-IR Spectra: Bridging vs Terminal Carbonyls

- **Bridging CO groups can be regarded as having a double bond C=O group, as compared to a terminal C≡O, which is more like a triple bond:**

~ triple bond

M-C≡O

~ double bond

$$\underset{M}{\overset{M}{\diagdown}} C=O$$

terminal carbonyl
(~ 1850-2125 cm^{-1})
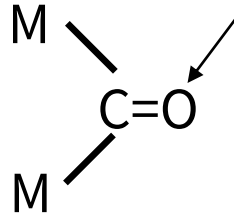
bridging carbonyl
(~1700-1860 cm^{-1})

The C=O group in a bridging carbonyl is more like the C=O in a ketone, which typically has $\upsilon_{C=O}$ = 1750 cm^{-1}.

:O≡C: → M

$$\underset{M\cdots M}{\overset{O}{\underset{\|}{C}}}$$

terminal mode

μ_2– *bridging mode*
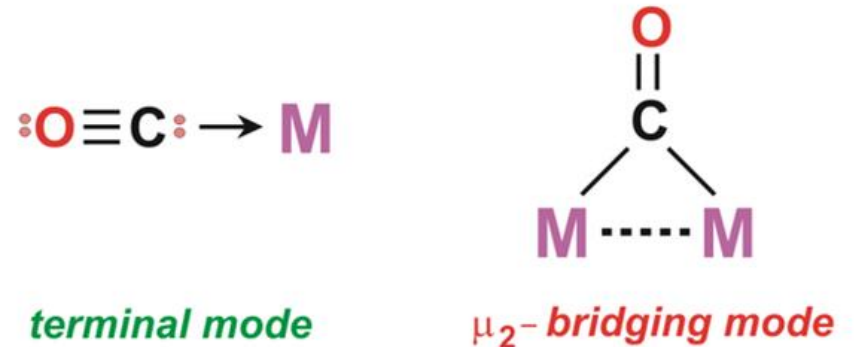
One can thus use the CO stretching frequencies around 1700-2200 cm^{-1} to detect the presence of bridging CO groups.

C=O $\upsilon_{C=O}$ = 1750 cm^{-1}
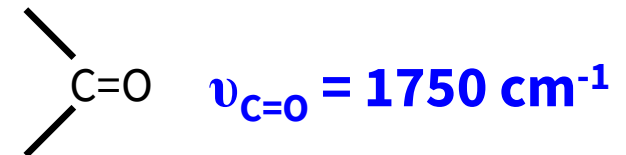
FT-IR Spectra: Bridging vs. Terminal CO
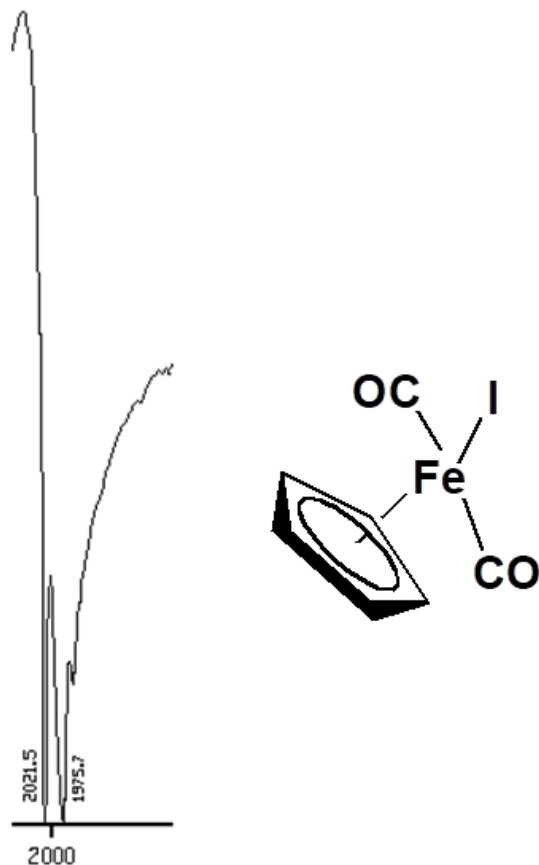
Terminal CO bonding at 2021.5 cm^{-1} and 1975.7 cm^{-1} also, because of very small symmetry differences between carbon monoxides.
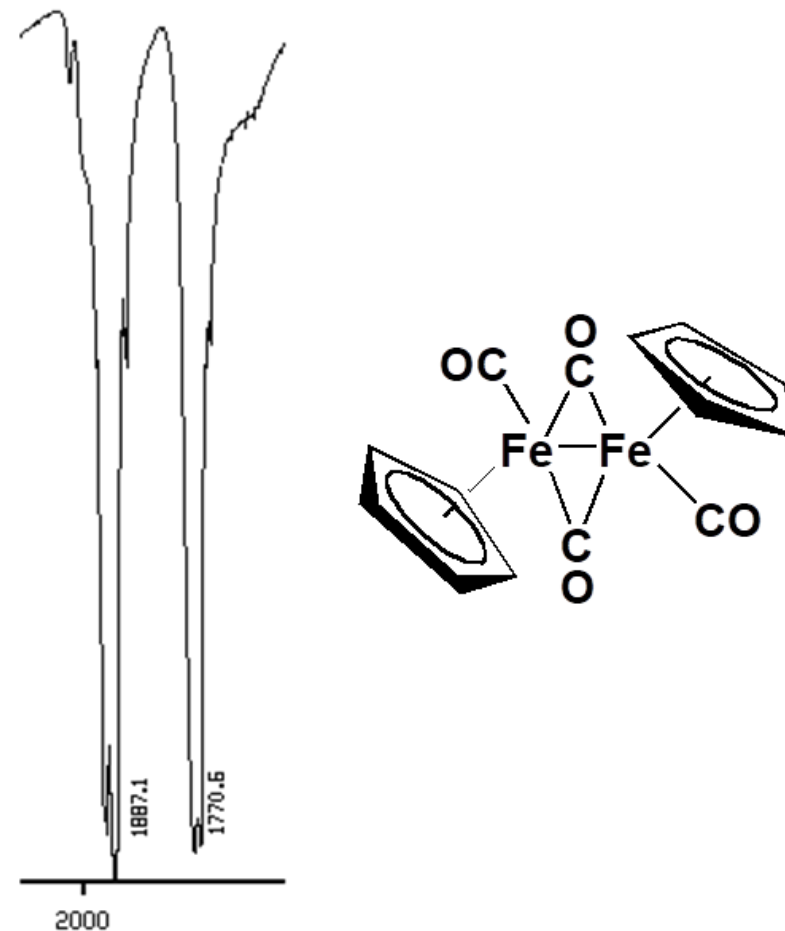
Terminal CO bond 1887 cm^{-1}
Bridging CO bond at 1770 cm^{-1}

5

Types of Organometallic Reactions

$$[M]\!-\!L \quad + \quad = \quad \rightleftarrows \quad [M]\!-\!\| \quad + \quad L$$

ligand exchange

$$[M]^n \quad + \quad A\!-\!B \quad \rightleftarrows \quad [M]^{n+2}\!\!\begin{smallmatrix}A\\ \\B\end{smallmatrix}$$
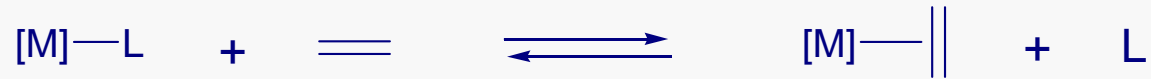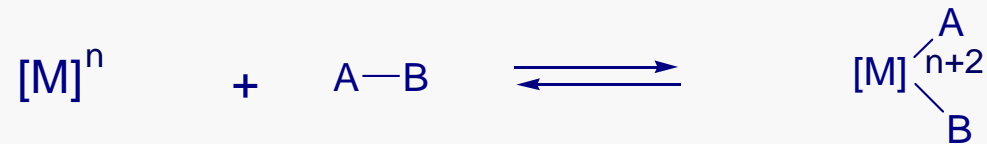
oxidative addition ⟶
reductive elimination ⟵
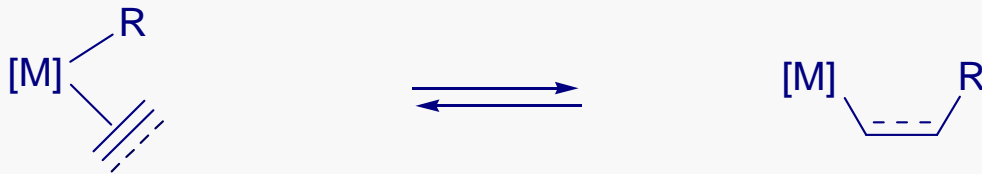
migratory insertion ⟶
(carbo-, hydro-metalation)
β-elimination ⟵
(decarbo-, dehydro-metalation)
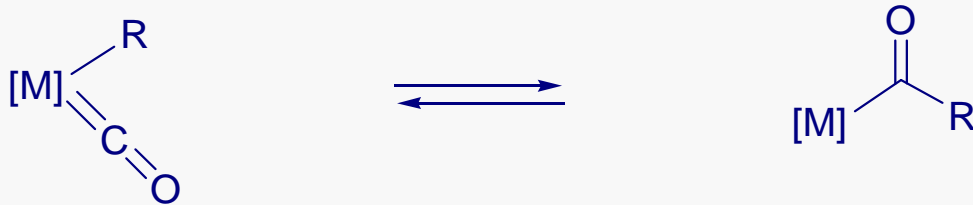
(CO) insertion

Types of Substrates (X-Y)

- **Depending on the nature of the substrate (X-Y), the mechanism of the oxidative addition may differ.**

- **There are different classes of molecules (substrates) that can perform oxidative additions to metal centers: Non-Electrophilic (non-polar) and electrophilic (polar).**

- ***Non-electrophillic*: when A-B (substrate) is a non-polar molecule; such as dihydrogen and hydrocarbons. These molecules usually require the presence of an empty orbital on the metal to pre-coordinate prior to being activated for the oxidative addition. This addition requires low-oxidation metal (electron-rich), sterically unhindered, and open coordination sites.**

two new anionic hydride ligands

Ir(+1)
16e-

Ir(+1)
18e-

Ir(+3)
18e-
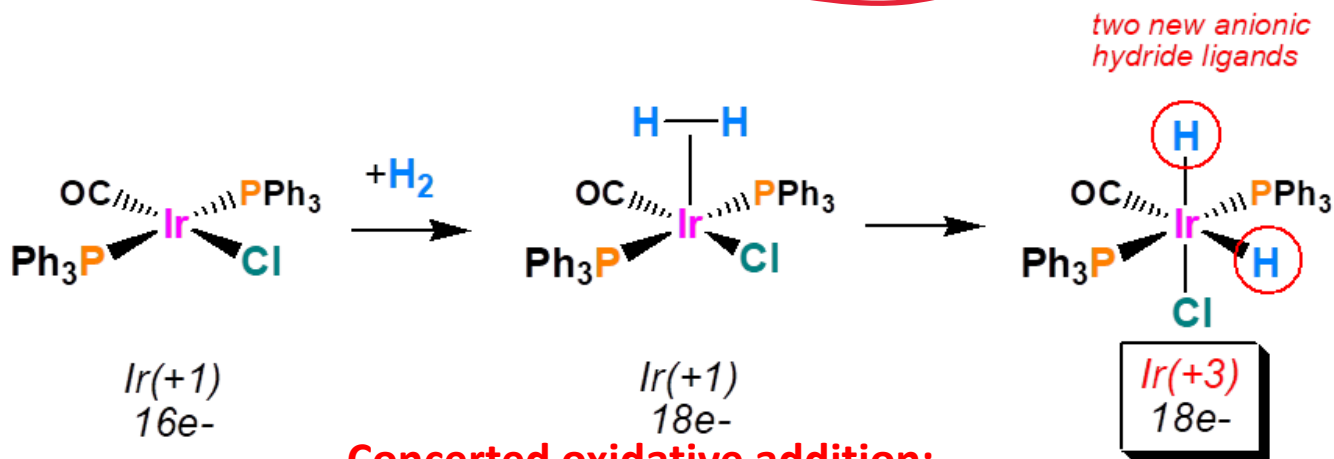
Concerted oxidative addition:
σ complex formation followed by bond-breaking

The OA will be mutually cis

- Δ OS = 2
- Δ EC = 2
- Δ CN = 2

d^9	
27 Co Cobalt	
45 Rh Rhodium	
77 Ir Iridium	

Electrophilic Substrates

Electrophilic (SN²-type Oxidative Addition): when A-B (substrate) is a polar molecule; such as alkyl halides.

S_{N2} nucleophillic attack

δ^+ δ^-

+CH$_3$Br

Ir(+1)
16e-

Ir(+1)
16e-

two new anionic ligands

two new anionic ligands

+Br⁻

Ir(+3)
18e-

Ir(+3)
16e-

+ Br⁻

The OA will be mutually trans

d^9

27
Co
Cobalt

45
Rh
Rhodium

77
Ir
Iridium

- △ OS = 2
- △ EC = 2
- △ CN = 2
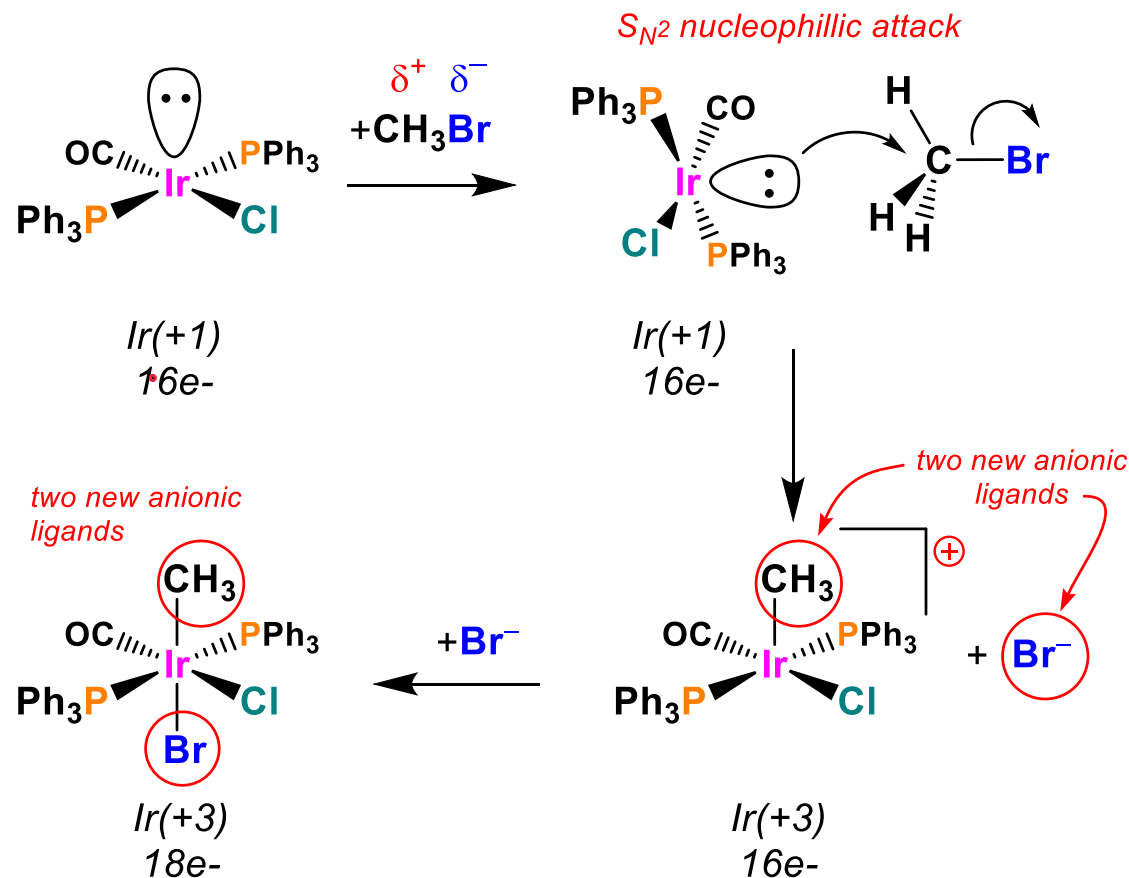
Reductive Elimination

- A *reductive elimination* reaction is the reverse of an **oxidative addition**. It is a reaction in which **two cisoidal anionic ligands** on a metal center couple together. Each anionic ligand pushes **one electron** back onto the metal center (in the case of a monometallic complex) to reduce it by 2e⁻. The coupled anionic ligands then leave as a **neutral** molecule.

two cisoidal anionic ligands that can form a bond between them

and eliminate a neutral ligand

Ir(+1)
18e-

Ir(+1)
16e-
metal reduced by 2 e-

Ir(+3)
18e-

rarely observed intermediate

d^9

27
Co
Cobalt
45
Rh
Rhodium
77
Ir
Iridium

- △ OS = -2
- △ EC = -2
- △ CN = -2

9

Reductive Elimination: Effect of Ligand Dissociation

Sometimes, more than one reductive elimination is possible. An understanding of the electronic requirements can facilitate reaction engineering to favor one option over the other.
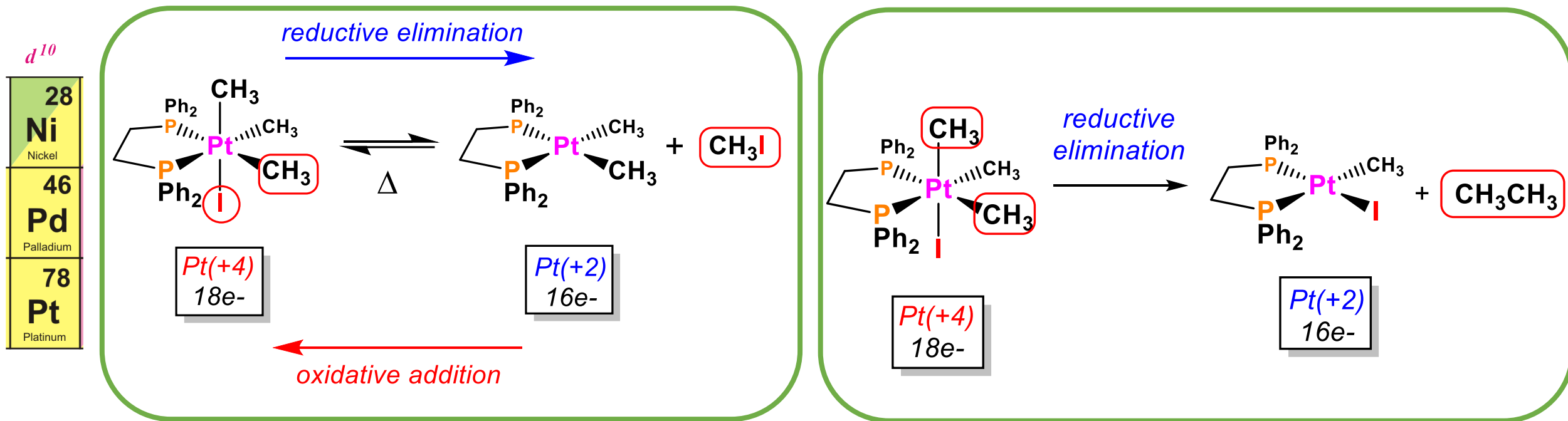
Reductive Elimination

A reductive elimination can be promoted by a ligand dissociation generating an unsaturated and more electron-deficient metal center. Presumably, dissociation to form a distorted TBP geometry brings the eliminating groups closer to one another to facilitate the elimination.

Pt(+4)
18e-

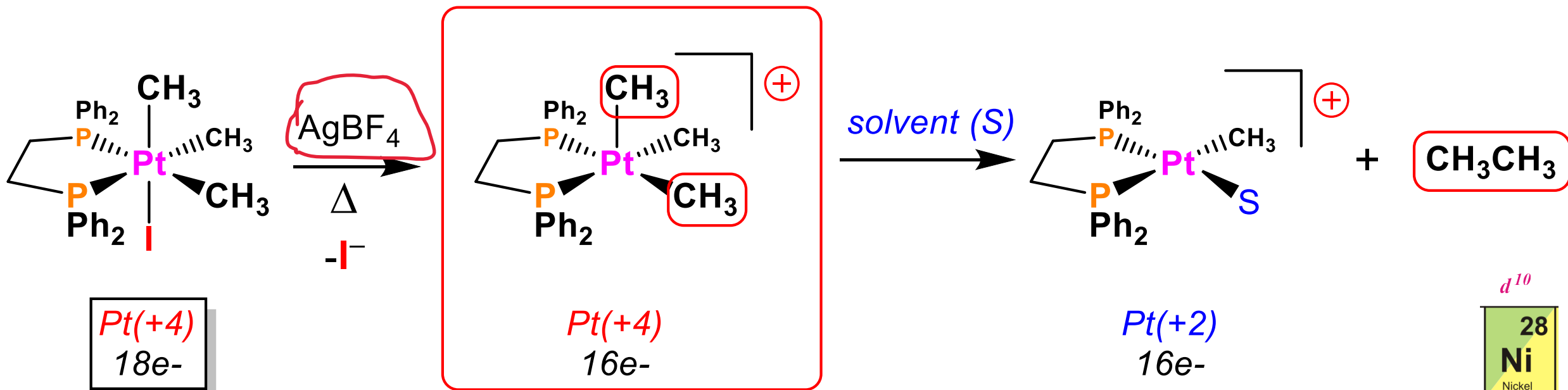Pt(+4)
16e-

Pt(+2)
16e-

$+$ CH_3CH_3

AgBF$_4$
Δ
-I$^-$

solvent (S)

The dissociation of the I- generates a cationic unsaturated complex. This is electron deficient enough to help promote the reductive elimination of ethane (CH$_3$CH$_3$).

Δ OS = -2
Δ EC = -2
Δ CN = -2

d^{10}

28
Ni
Nickel
46
Pd
Palladium
78
Pt
Platinum

11

β Hydride Elimination

It occurs in which an alkyl group bonded to a metal center is converted into the corresponding metal-bonded hydride and an alkene.

The alkyl must have hydrogens on the β carbon.

The metal complex must have an empty (or vacant) site cis to the alkyl group for this reaction to occur.

Migratory Insertion
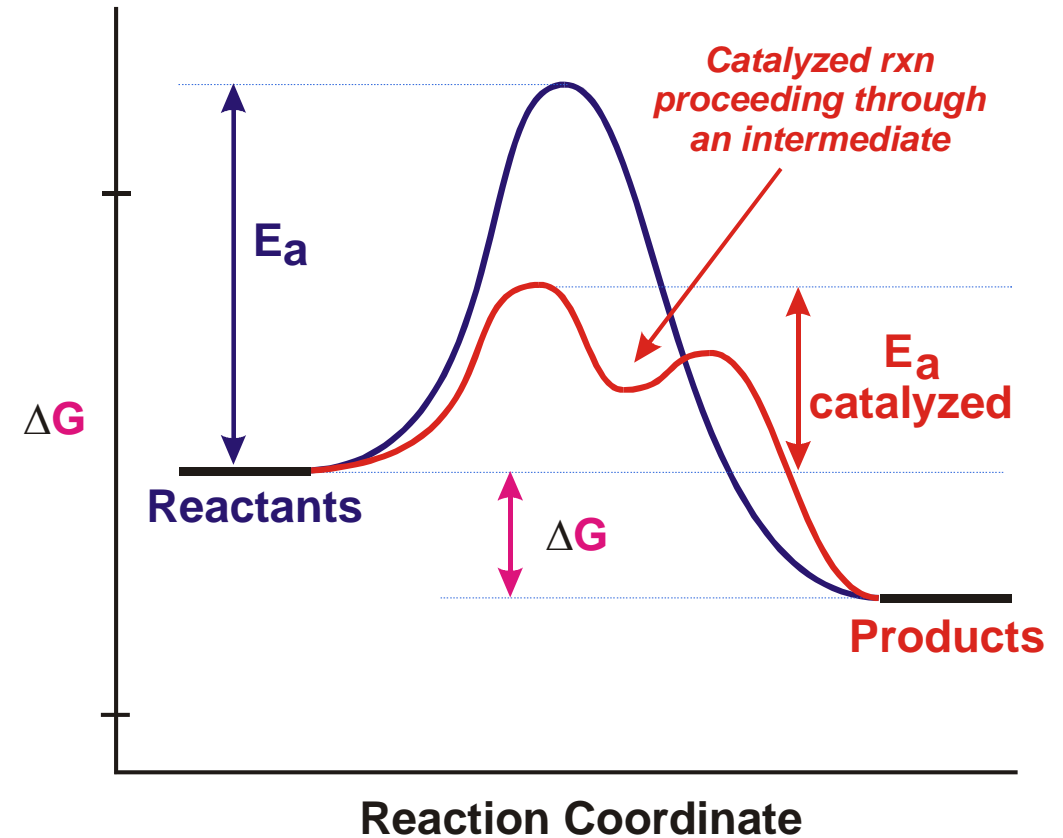
- A *migratory insertion* reaction occurs when a cisoidal anionic and neutral ligand on a metal complex couple together to generate a new coordinated anionic ligand.
- *There is NO change in the oxidation state or d electron-count of the metal center.*
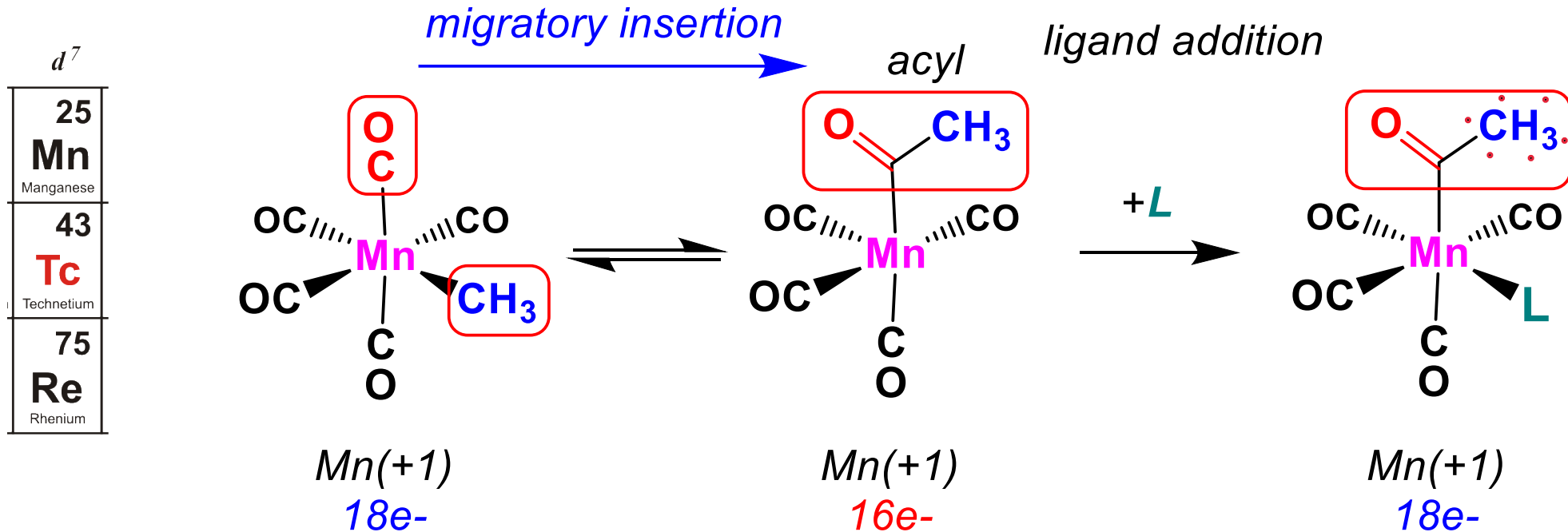
Applications of Organometallic Complexes
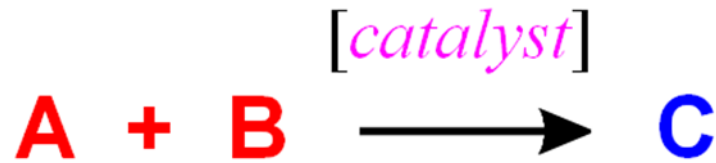
$$A + B \xrightarrow{[\textit{catalyst}]} C$$

A catalyst is a substance that changes the rate of a chemical reaction without itself appearing in the products.

Catalyzed rxn proceeding through an intermediate

E_a

ΔG

Reactants

E_a catalyzed

ΔG

Products

Reaction Coordinate

- **A catalyst**
  - **Speeds up a reaction**
  - **Enables a reaction to proceed that otherwise does not occur without it**
  - **Typically added in non-stoichiometric amounts**
  - **Remains unchanged at the end of the reaction**
    - **Catalysis is a *kinetic* phenomenon.**

Homogeneous Vs. Heterogeneous Catalysis
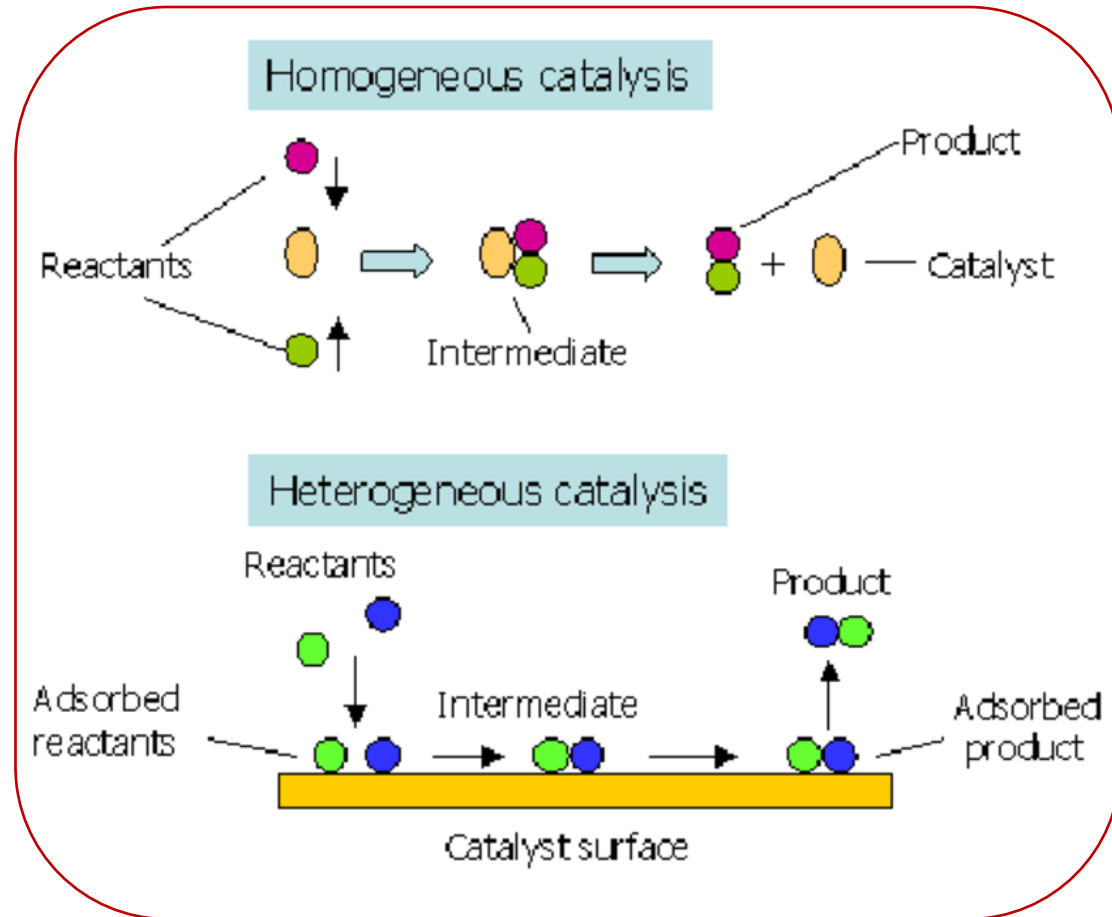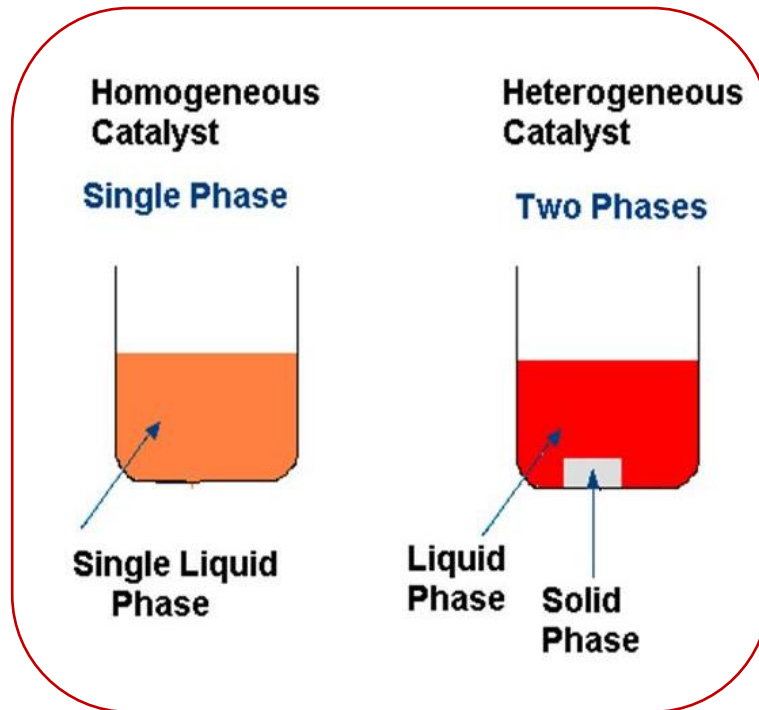
- **Homogeneous catalysis: Catalyst and reactants are in the same phase.**

- **Heterogeneous catalysis: Catalyst and reactants are in the different phase (the catalyst is usually insoluble; reaction occurs on its surface).**

Terminologies in Catalysis : TON and TOF

- **Each time the complete catalyst cycle occurs, we consider one catalytic turnover (one mole of product formed per mole of catalyst) to have been completed.**

- **TOF: The catalytic rate can be conveniently given in terms of the Turnover Frequency (TOF) measured in turnovers per unit time; the lifetime of the catalyst before deactivation is measured in terms of turnover number (TON).**

- **Turnover number (TON): The number of moles of substrate that a mole of catalyst can convert before becoming inactivated.**

- **How many cycles that a catalyst can perform ⟶ TON**

Example: If **0.1 mole** of catalyst converts **100 moles** of substrates in **5 minutes** (**100% yield**) then

TON = 100/0.1 = 1000 (unitless)

TOF = TON/time = 1000/5 min = 200 min^{-1}

Hydrogenation of Alkenes
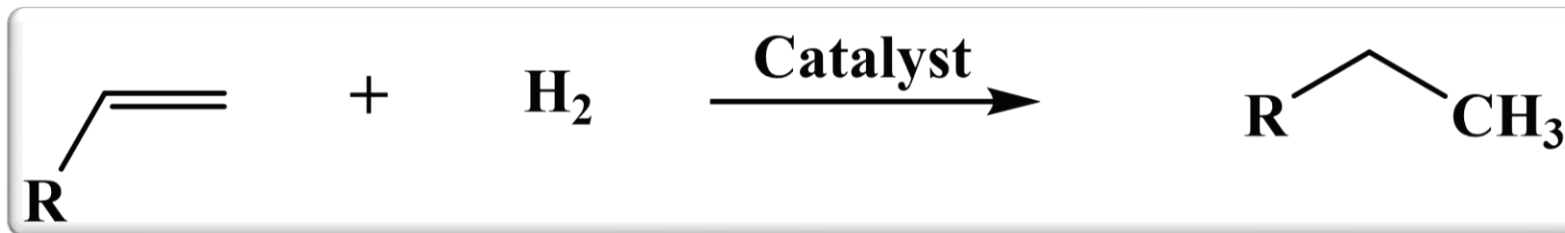
Wilkinson's catalyst

- **The most used catalyst is the Wilkinson's Catalyst**

- **Many alkenes are hydrogenated with hydrogen at 1 atm pressure or less.**

- **Wilkinson's catalyst is highly sensitive to the nature of the phosphine ligand and the alkene substrate.**
- **The stereochemistry of H_2 addition is cis**

d^9

27
Co
Cobalt
45
Rh
Rhodium
77
Ir
Iridium

Wilkinson's Catalyst - Mechanism

Reductive Elimination

Oxidative Addition

Ligand Dissociation

Ligand Association

Alkene Coordination

Migratory Insertion

d^9

27
Co
Cobalt

45
Rh
Rhodium

77
Ir
Iridium

16e⁻

18e⁻

18e⁻

16e⁻

18e⁻

16e⁻

Hydroformylation reaction

$$R{-}CH{=}CH_2 \;+\; CO \;+\; H_2 \xrightarrow{\text{Catalyst}} RCH_2CH_2CHO$$
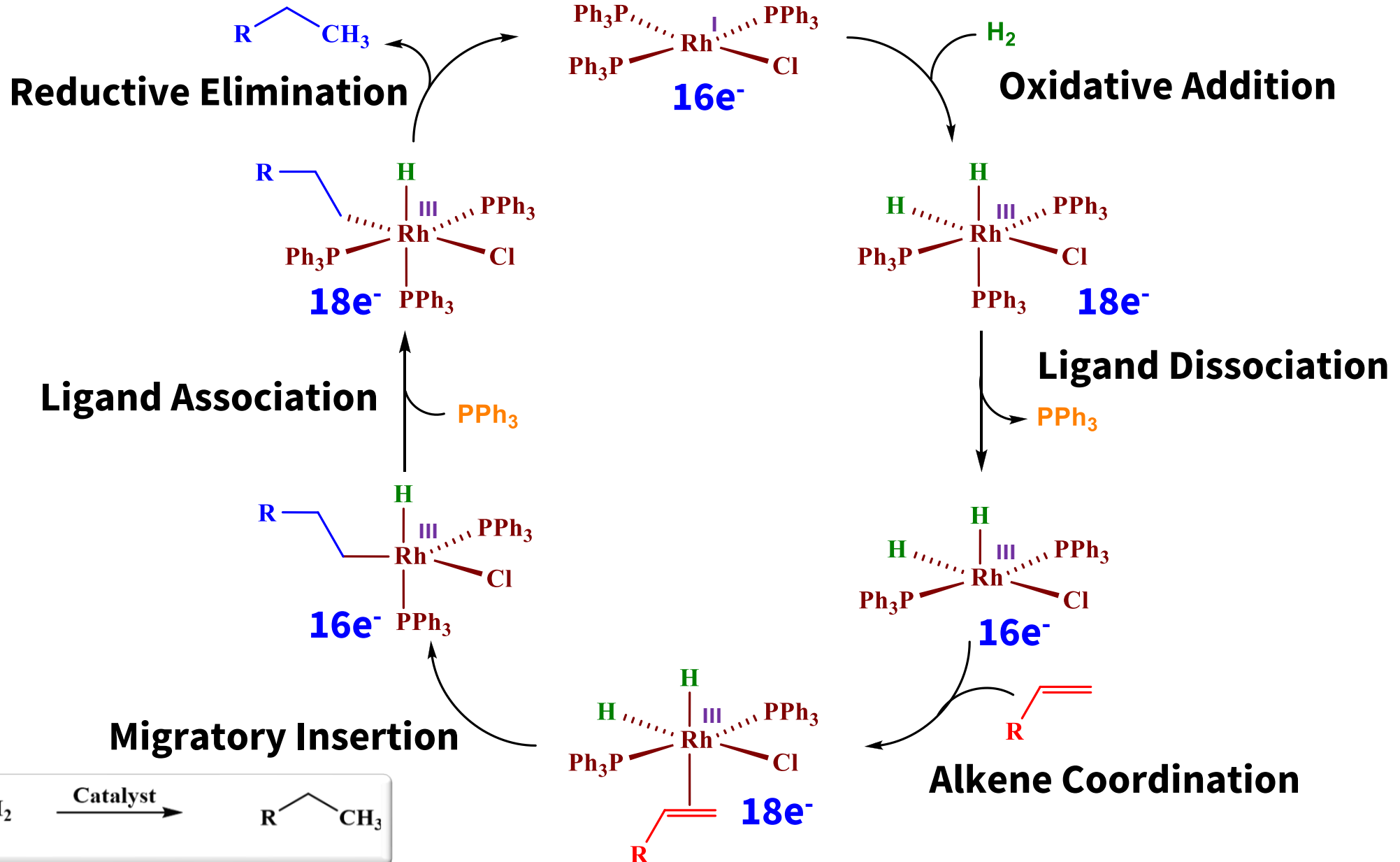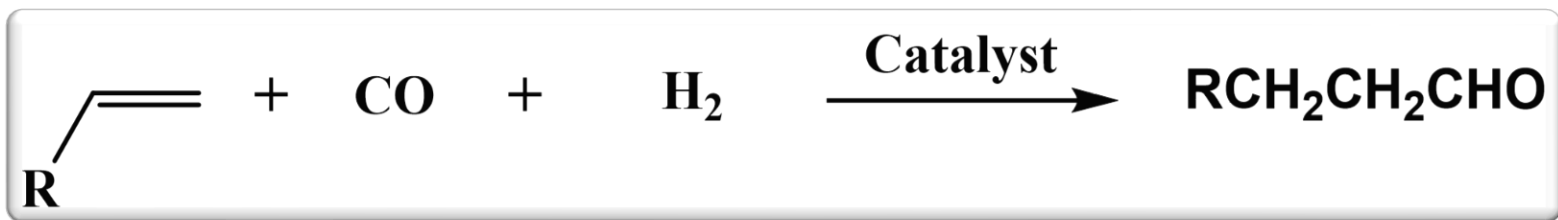
- **It is an industrial process to produce aldehydes from alkenes**

- Both cobalt and rhodium complexes are used as catalysts.

- Alkene isomerization, alkene hydrogenation and formation of branched aldehydes are the possible side reactions.

d^9

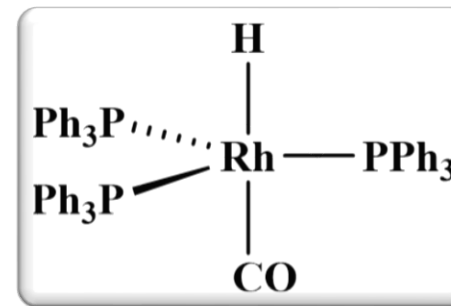| 27 |
|----|
| **Co** |
| Cobalt |
| 45 |
| **Rh** |
| Rhodium |
| 77 |
| **Ir** |
| Iridium |
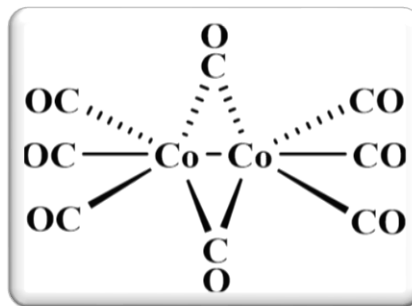
- **Cobalt catalysts operate at 150 ⁰C and 250 atm, whereas Rhodium catalysts operate at moderate temperatures and 1 atm.**

- **Rhodium catalysts promotes the formation of linear aldehydes. Cobalt catalysts do so if modified with alkylphosphine ligands.**

19

Hydroformylation reaction

$R-CH=CH_2$ + CO + H$_2$ $\xrightarrow{\text{Catalyst}}$ RCH$_2$CH$_2$CHO

$Co_2(CO)_8$ + H$_2$

Ligand Dissociation

CH$_3$CH$_2$CH$_2$CH$_2$CHO

Reductive Elimination

Oxidative Addition

Alkene Coordination

Ligand Association
Migratory Insertion

Ligand Association
Migratory Insertion

18e$^-$

16e$^-$

d^9

27
Co
Cobalt

45
Rh
Rhodium

77
Ir
Iridium

Monsanto Acetic Acid Synthesis

$$CH_3OH + CO \xrightarrow{[RhI_2(CO)_2]^-} CH_3COOH$$
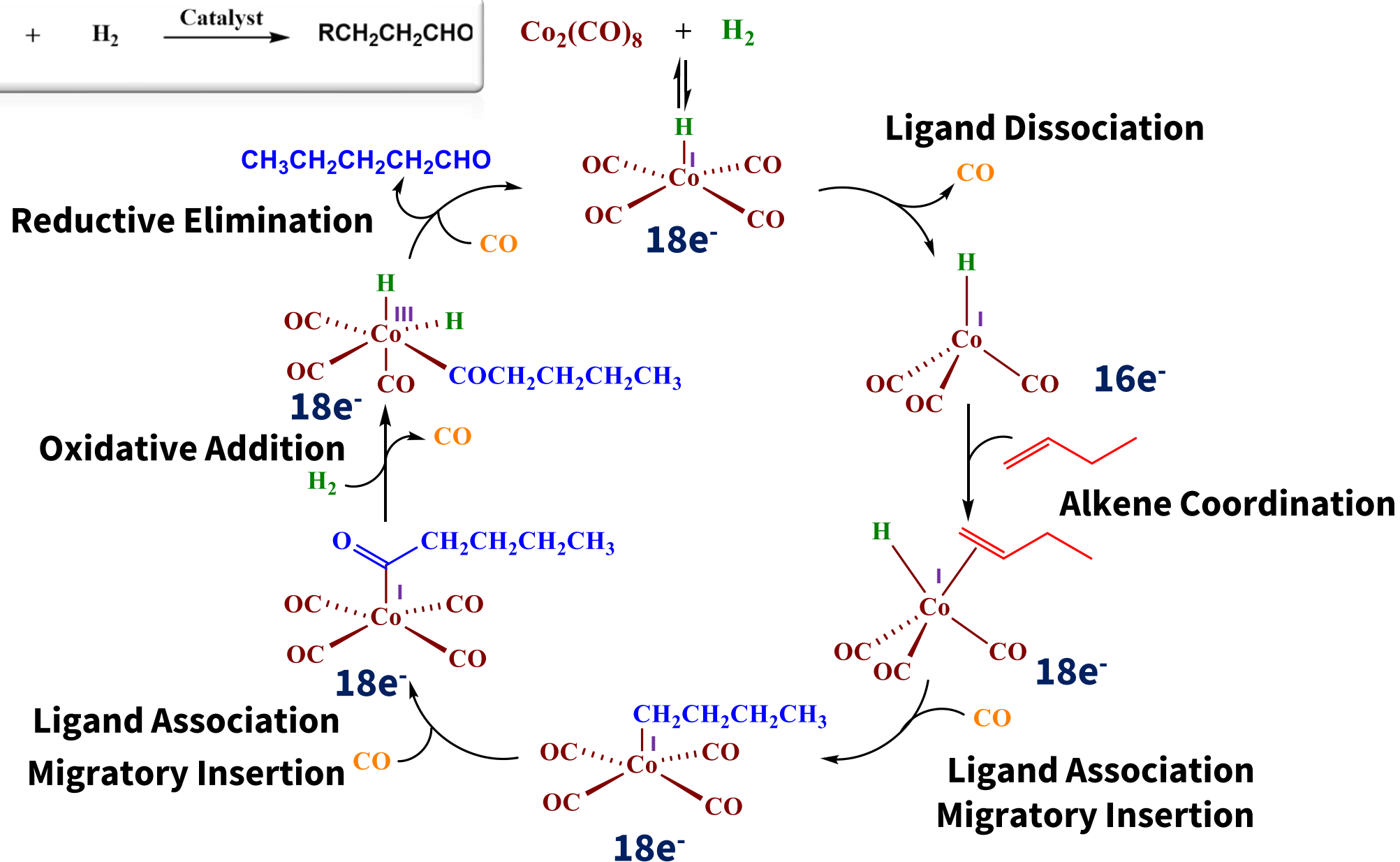
- All three members of the group 9 (Co, Rh and Ir) can catalyze this reaction.

- A cobalt complex was initially used, which was replaced with the rhodium complex later on.

- Methanol initially reacts with hydroiodic acid to give methyliodide and H_2O. Methyl iodide reacts with the 16e$^-$ catalyst, which is the rate-determining step.

$$CH_3OH + HI \longrightarrow CH_3I + H_2O$$

- The final product formed after the catalytic cycle is acetyl iodide, which is hydrolyzed by water to acetic acid and HI.
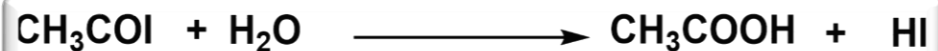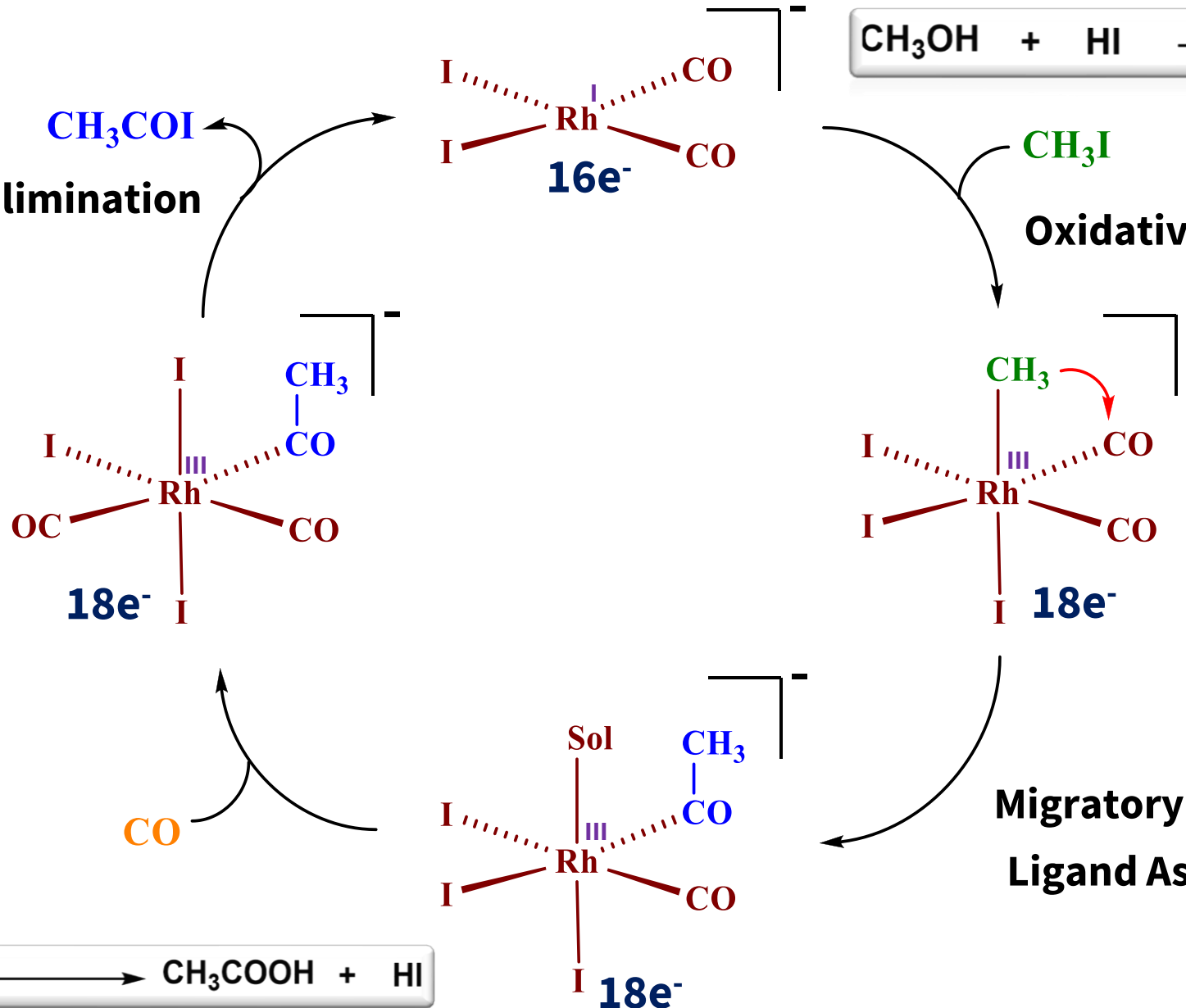
$$CH_3COI + H_2O \longrightarrow CH_3COOH + HI$$

Monsanto Acetic Acid Synthesis

$$CH_3OH + HI \longrightarrow CH_3I + H_2O$$

Reductive Elimination

CH_3COI

Oxidative Addition

CH_3I

$16e^-$

$18e^-$

$18e^-$

Migratory Insertion

Ligand Association

CO

$18e^-$

d⁹

27
Co
Cobalt

45
Rh
Rhodium

77
Ir
Iridium

$$CH_3COI + H_2O \longrightarrow CH_3COOH + HI$$

Alkene Polymerization

$$n \; {=\!\!=} \longrightarrow \left(\!\!\! \bigwedge \!\!\! \right)_n$$
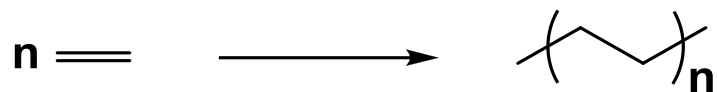
If only a few monomers couple together, the short chains formed are called oligomers.

d^4

| 22 |
|---|
| **Ti** |
| Titanium |
| 40 |
| **Zr** |
| Zirconium |
| 72 |
| **Hf** |
| Hafnium |
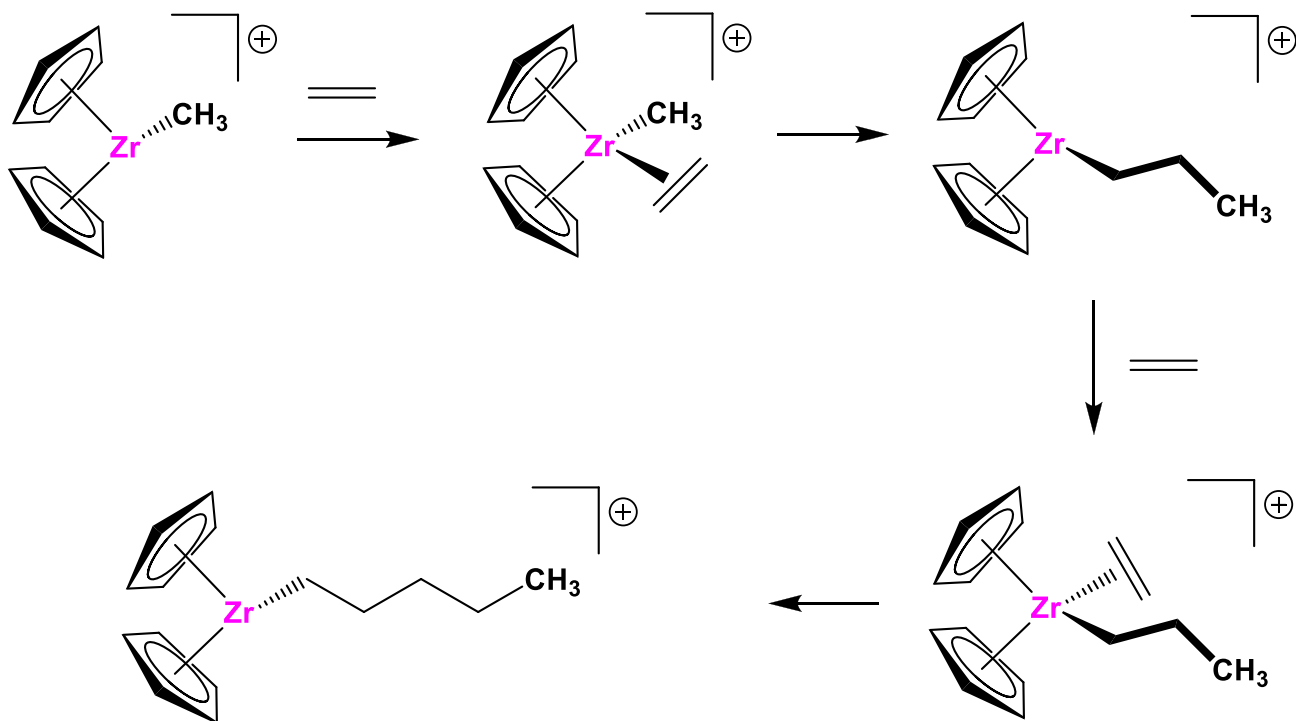
The commonly used catalyst has a tetrahydrofuran molecule occupying the fourth coordination site of zirconium.

Ziegler-Natta Catalyst

- **Karl Ziegler in 1953, discovered a catalyst based on $TiCl_3$ and $AlCl_3$ for the polymerization of ethylene.**

- **Giulio Natta extended the method for the polymerization of other olefins like propylene and made a number of different variations.**

- **The Ziegler-Natta catalyst family includes halides of titanium, chromium, vanadium and zirconium, typically activated by aluminum halide compounds.**

- **Ziegler and Natta received the Nobel Prize in Chemistry in the year 1963.**
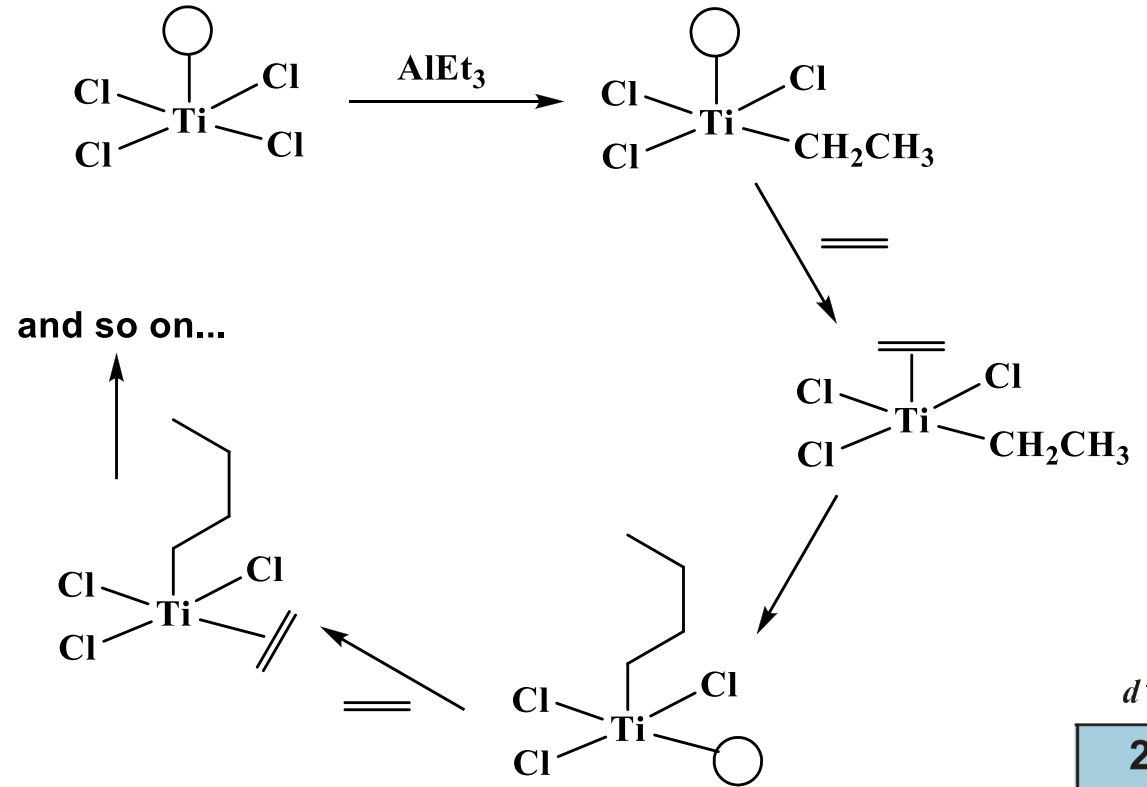
Giulio Natta
1903-1979, Nobel Prize 1963
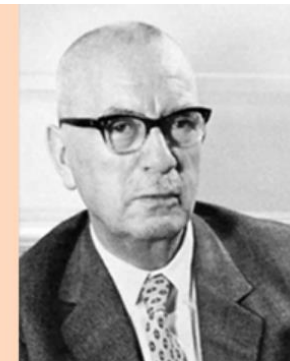
Karl Ziegler
1898-1973, Nobel Prize 1963

d^4

22
Ti
Titanium
40
Zr
Zirconium
72
Hf
Hafnium