# M.Sc. Part I

# Inorganic Chemistry (Paper I-CHT101)

## UNIT-III

## ORGANOMETALLIC CHEMISTRY

**Syllabus** **15 Hrs**

- Definition and criteria of organometallic compounds.
- Classification of organometallic compounds based on hapticity and polarity of the M-C bond.
- Nomenclature and general characteristics.
- 18 electron rule-applications and exceptions.
- Synthesis, bonding, properties, and reactivity of representative organometallic compounds (-CO, -NO, -alkene, -alkyne),
- Reactions of organometallic compounds: Oxidative addition, reductive elimination, Insertion, and elimination.
- Organometallics in homogeneous catalysis: Hydrogenation of olefins, hydroformylation reaction, Monsanto Acetic Acid, and polymerization of olefins.

**Expected Learning Outcomes**

- Study the synthesis, bonding, and catalytic applications of organometallic compounds
- Study of organometallic reactions and their mechanisms.

## Definition & Criteria of Organometallic Compounds

Organometallic compounds are compounds containing at least one metal-carbon bond between a metal and carbon in an organic molecule

- **Metal-Carbon Bond:**The defining characteristic is a bond between a metal (which can be a main group element, transition metal, or even a metalloid) and a carbon atom.
- **Organic Moiety:**The organic part can be an alkyl group, an aryl group, or any other organic fragment
- **Examples:**Common examples include organolithium compounds $CH_3Li$, Grignard reagents $CH_3MgBr$, and various transition metal complexes with carbon-containing ligands, such as Metal carbonyls like $NiCO_4$

Metal cyanides (like KCN, NaCN) are not organometallic compounds, despite having a metal-carbon bond

### Significance of Organometallic Compounds

- **Catalysis:** Organometallic compounds act as catalysts in numerous industrial processes, including the production of plastics, pharmaceuticals, and fuels.
- **Organic Synthesis:** They facilitate the formation of new carbon-carbon bonds, which are essential for building complex organic molecules.
- **Materials Science:** These compounds are used in the synthesis of nanomaterials and microelectronic materials.
- **Medicine:** Organometallic compounds are used as drugs and diagnostic agents, with applications in cancer therapy and MRI contrast agents.
- **Biological Systems:** They can interact with biological macromolecules like DNA, proteins, and enzymes, offering unique therapeutic potential.

### History of Organometallic Compounds

- In1760, the first organometallic compound $[(CH_3)_2As]_2O$ was prepared. This compound is called cacodyl oxide because it has a very bad smell.
- In 1827, the first olefin complex called Ziese's salt, having the formula $Na[Cl_3Pt(C_2H_4)]$ was prepared.
- In 1840, R. W. Bunsen synthesized $R_2As\text{-}AsR_2$.
- In 1849, E. Frankland, a student of Bunsen, synthesized $Et_2Zn$.
- In 1852, E. Frankland synthesized $(CH_3)HgI$,
- In 1852 C. J. Lowing and E. Schweizer prepared $(Et)_4Pb$,
- In 1859, W. Hallwachs and A. Schafarik generated aluminum alkyl halide, $R_2AlI$ and $RAlI_2$.
- In 1863, the famous Friedel C. Friedel and J. M Crafts prepared organochlorosilane compounds by the reaction of $SiCl_4$ with $R_2Zn$, giving RZnCl and $ZnCl_2$.

- In 1866, J. A. Wanklyn prepared halide-free magnesium alkyls, and this was done by reaction of $Et_2Hg$ with Mg, giving $Et_2Mg$ and Hg.
- In 1868, M. P. Schutzenberger prepared the first metal carbonyl complex $[(CO)PtCl_2]$.
- In 1890, L. Mond prepared the first binary metal carbonyl compound in the form of $Ni(CO)_4$. This compound is very toxic and has to be handled with care. This discovery led to the formation of a large chemical company, which came to be known as ICI.
- In 1909, W. J. Pope prepared the first transition metal complex in the form of $(CH_3)_3PtI$.
- In 1917, W. Schlenk prepared RLi. The reaction used was a trans metalation reaction using mercury alkyls.
- In 1927, A. Job and A. Cassal prepared $Cr(CO)_6$. This was an important reaction, and turned out to be a big hit in industry, producing tons of aldehyde by using this method, and came to be later known as the hydroformylation reaction.
- In 1951, M. J. S. Dewar proposed the theory of alkene binding to transition metal complexes.
- In 1951, P. Pauson and S. A. Miller prepared the first sandwich complex in the form of ferrocene, $(C_5H_5)2Fe$. The overall stability of this complex arises from the 18 valence electrons of this metal center.
- In 1952, H. Gilman prepared organocuprates in the form of $LiCu(CH_3)_2$
- In 1953. Wittig prepared the olefins from phosphonium ylides and carbonyl compounds. The impact of this discovery was recognized by the fact that the Nobel Prize for 1979 was awarded for this reaction.
- In 1955 Karl Ziegler and Giulio Natta found that olefins in the presence of $Al(Et)_3$ and $TiCl_4$ give very long-chain polymers. It is an important discovery in terms of olefin polymerization
- In 1956, another Nobel Prize-winning discovery was made by H. C. Brown when he discovered the hydroboration reaction.
- In 1964, E. O. Fischer prepared the first carbene complex in the form of $(CO)_5WC(OMe)Me$.
- In 1965, G. Wilkinson and R. S. Coffey reported the first homogeneous olefin hydrogenation catalyst in the form of $(PPh_3)_3RhCl$.
- In 1973, E. R. Fischer prepared the first carbine complex in $I(CO)_4Cr(CR)$. In this way, Fischer was instrumental not only in making the metal-carbon double bond, but also in making the metal-carbon triple bond, and this led to him is receiving the Nobel Prize

**9 Nobel Prizes in the area of organometallic chemistry**

1. Ehrlich in 1908 for organ arsenic compounds.
2. Grignard and Sabatier in 1912 for the Grignard reagent.
3. Ziegler-Natta in 1963 for Ziegler-Natta catalysts for olefin polymerization.
4. Fischer and Wilkinson in 1973 for sandwich compounds,
5. Brown in 1979 for the hydroboration reaction.

6. Hoffmann and Fukui got it in 1981 for the Woodward-Hoffmann rule,
7. Knowles, Noyori, and Sharpless in 2001 for asymmetric hydrogenation,
8. Chauvin, Schrock, and Grubbs in 2005 for alkene metathesis.
9. Heck, Negishi, and Suzuki in 2010 for palladium-catalyzed cross-coupling reactions.

## Classification of Organometallic Compounds

### *A. Based on nature of Metal Carbon bond polarity*

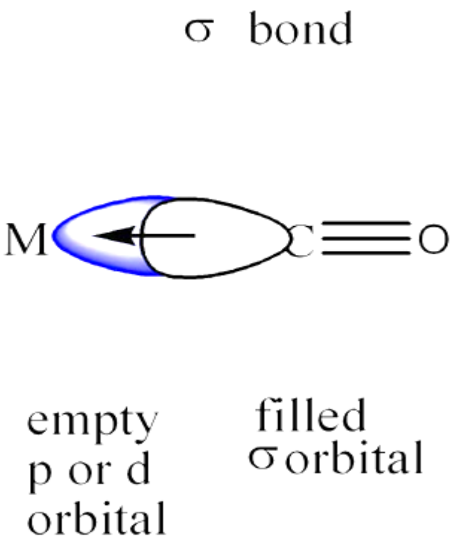
1. **Ionic M–C Bond** (Highly Polarized, Carbanionic Carbon)

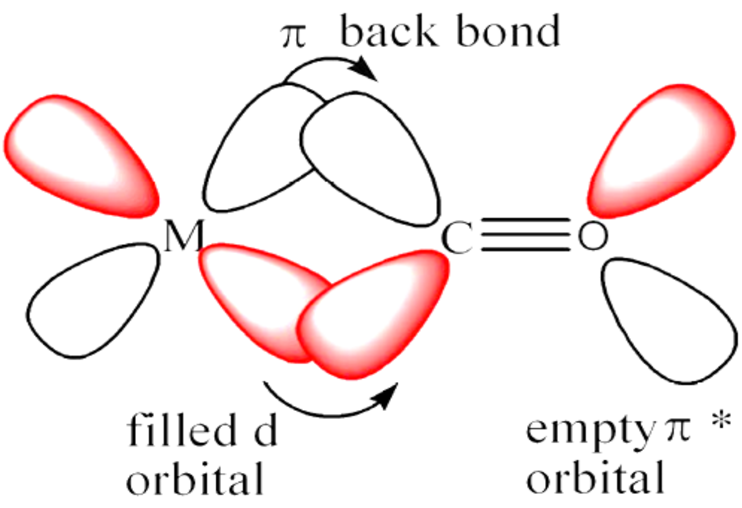
- The metal is very electropositive, and the carbon is a negatively charged stable group.
- Common with Group 1 and 2 metals (Li, Na, K, Mg, Ca).
- Examples:Organolithium: $CH_3Li$, Grignard reagents: $CH_3MgBr$, Organosodium: PhNa
- Properties:
    - Highly reactive (nucleophilic) more ionic.
    - Sensitive to air/moisture.

Used in organic synthesis (nucleophilic addition to carbonyls).

2. **Covalent M–C Bond**

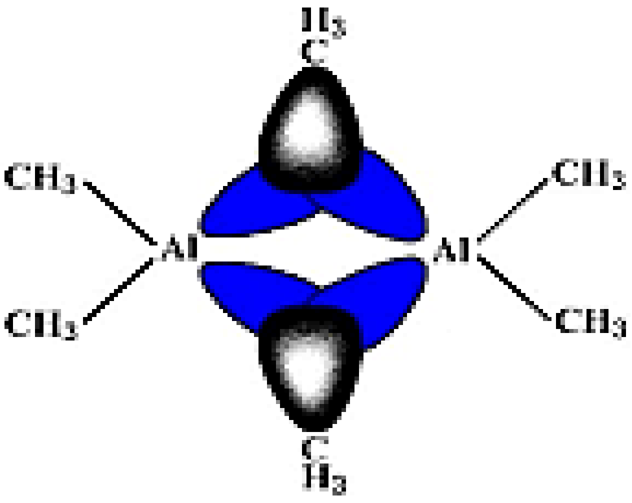
- The metal and carbon share electrons, but the bond has some polarity.
- Typically found with **transition metals**.
- **Examples**:Metal-alkyl/aryl complexes like **$(CH_3)_2Pd(PPh_3)_2$**, Metal-carbene complexes: **$M=CR_2$**
- **Properties**:
    - Moderate reactivity, Contains σ as well as Л bonds.
    - Important in catalysis (e.g. olefin polymerization, cross-coupling).
    - Reactivity depends on the metal, oxidation state, and ligands.
- Covalent bond is of two types: **Polar** Covalent Bond and **Nonpolar** Covalent Bond

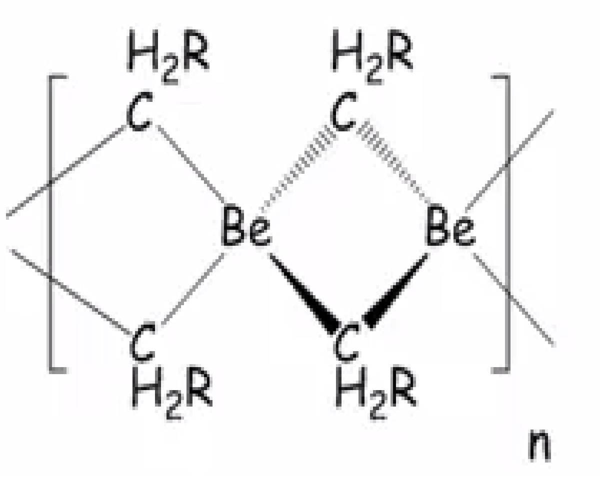




### 3. Non-Classical Covalent M–C Bond

- In some organometallic compounds, the metal atom interacts with multiple carbon atoms simultaneously.
- This is often seen in alkyl compounds of alkali and alkaline earth metals, such as lithium, beryllium, and aluminum. For example, in dimeric trialkylaluminum ($Al_2R_3$), the alkyl groups act as bridging ligands, forming **three-center two-electron bonds** with the aluminum atoms. Similarly, polymeric dimethylberyllium (($BeMe_2$)n





## B. *Classification Based on Hapticity (η)*

**Hapticity (η)**. It indicates the number of contiguous atoms in a ligand that are coordinated to the metal

### 1. $\eta^1$ (Monohapto) Ligands

Only one atom of the ligand is bonded to the metal.

These are usually σ-bonded carbon atoms like alkyl, aryl, or carbanions.

Examples:

- M–$CH_3$ (methyl group)
- M–Ph (phenyl group)

Eg.$CH_3Li$, PhMgBr, $(CH_3)_2Zn$

**2. $\eta^2$ (Dihapto) Ligands**

Two adjacent atoms of a ligand are bonded to the metal, typically seen in **π-bonded alkenes or alkynes**.

Indicates metal interaction with a π-bond.

Examples:

Zeise's salt: $[PtCl_3(C_2H_4)]^-$

Metal-alkene complexes like $(C_2H_4)PdCl_2$

3. **$\eta^3$ (Trihapto) Ligands**

Three adjacent atoms bonded to the metal.

Seen in allyl ligands.

Examples: $\eta^3$-allyl complexes like $(\eta^3\text{-}C_3H_3)Fe(CO)_3$

4. **$\eta^4$ (Tetrahapto) Ligands**

Four contiguous atoms involved in bonding.

Common in 1,3-butadiene complexes.

Example:

$(\eta^4\text{-}C_4H_6)Fe(CO)_3$

5. **$\eta^5$ (Pentahapto) Ligands**

Five contiguous atoms are coordinated.

Typical in cyclopentadienyl (Cp) complexes.

Examples: Ferrocene: $(\eta^5\text{-}C_5H_5)_2Fe$

$(\eta^5\text{-}C_5H_5)Mo(CO)_3$

6. **$\eta^6$ (Hexahapto) Ligands**

Six contiguous atoms participate in bonding.

Found in arene complexes like benzene.

Examples: $(\eta^6\text{-}C_6H_6)Cr(CO)_3$

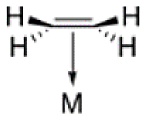
7. **$\eta^7$ to $\eta^8$ and higher**

Seen in polycyclic or highly conjugated ligands.

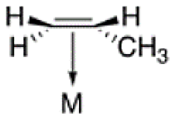
$\eta^8$: Often in complexes of $C_8H_8$ (cyclooctatetraene)

$\eta^6$ to $\eta^8$ can be found in sandwich and half-sandwich complexes.

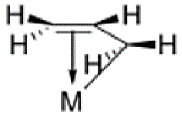
**Some common organic groups with Hapticity**



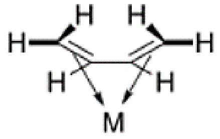
$\eta^2$



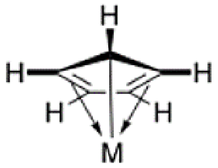
$\eta^2$



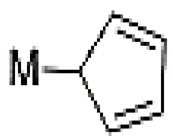
$\eta^3$



$\eta^4$



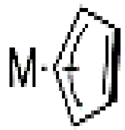
$\eta^5$



$\eta^1$-$C_5H_5$

**monohaptocyclopentadienyl**

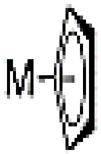
(1-bonding C)



$\eta^3$-$C_5H_5$

**trihaptocyclopentadienyl**

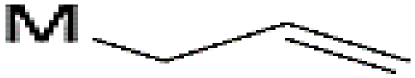
(3-bonding C)



$\eta^5$-$C_5H_5$

**pentahaptocyclopentadienyl**

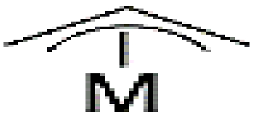
(5-bonding C)



$\eta^1$-$C_3H_5$

**monohaptoallyl**

(1-bonding C)



$\eta^3$-$C_3H_5$

**trihaptoallyl**

(3-bonding C)

## Nomenclature of Organometallic Compounds

### 1.Binary type nomenclature

- Used for salt-like ionic species.
- From its predominant use for simple salts consisting of a cation and anion, it may be extended to more complicated compositions.

1. diethylaluminium bromide $Al(C_2H_5)_2Br$
2. phenylmercury acetate $CH_3CO_2HgC_2H_5$
3. methylmagnesium chloride $CH_3MgBr$
4. sodium cyclopentadienide $C_5H_5Na$

### 2. Substitutive Nomenclature

- This system has its origin in organic nomenclature.
- It has been extended to the naming of organometallic compounds of some main-group elements, which in their bonding modes and properties closely resemble organic molecules.
- The system is based on the concept of a parent hydride (an alkane in organic nomenclature), e.g. $SiH_4$. silane, $AsH_3$. arsane etc., whose hydrogen atoms have partially or completely been replaced by organic groups (substituents).
- This system is used for naming compounds of group 13, 14, 15, and 16.

1. dicyclohexylborane $B(C_6H_{ll})_2H$
2. chlorotrimethylsilane $Si(CH_3)_3Cl$
3. triethylarsane $As(C_2H_5)_3$
4. diphenylselane $Se(C_6H_5)_2$

- Organometallic compounds with double bonds between the main-group elements may also be similarly named to alkenes,

e.g. tetramesityldisilene for $[2,4,6\text{-}(CH_3)_3C_6H_2]_2Si.Si[2,4,6\text{-}(CH_3)_3C_6H_2]_2$.

### 3. Coordination Nomenclature

$CH_3$ methyl $CH_3CH_2$ ethyl $CH_2{=}CHCH_2$ allyl $C_6H_{11}$ Cyclohexyl $C_6H_5$ Phenyl

$K[PtCl_3(C_2H_4)]$ potassium trichloro(ethene)platinate

2. $[Ni(C_5H_5)_2]$ bis(cyclopentadienyl)nickel (nickelocene)

3. $[FeC_4H_6(CO)_3]$ (butadiene)tricarbonyliron

4. $[Cr(C_3H_5)_3]$ tris(allyl)chromium

5. $[Ti(CH_3)Cl_3]$trichloro(methyl)titanium

Bridging ligands are indicated by the Greek letter **μ** appearing before the ligand name and separated by a hyphen. The whole term, e.g. **μ**-chloro

If all unsaturated carbon atoms are coordinated to metal, the name of ligand is preceded by η.

The number of coordinated carbon atoms is indicated by a numerical superscript (e.g. η3 . eta three or trihapto, η4 . eta four or tetrahapto, η5 pentahapto

## Properties of Organometallic Compounds

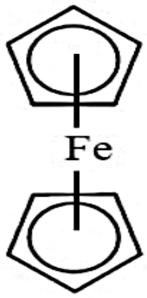
1. The nature of the metal-carbon bond (e.g., covalent or ionic) can significantly affect the compound's properties, including its reactivity and stability.
2. Many organometallic compounds are solids, especially those with aromatic or ring-structured hydrocarbon groups. Some are liquids or gases, particularly metal carbonyls.
3. Organometallic compounds generally exhibit poor solubility in water due to the covalent nature of the metal-carbon bond. They are typically soluble in nonpolar organic solvents like ethers. Solubility in polar solvents can vary depending on the polarity of the ligands attached to the metal.
4. Many organometallic compounds are highly reactive and air and moisture-sensitive, especially those formed with highly electropositive metals like lithium or sodium.
5. Many organometallic compounds act as catalysts in various chemical reactions.
6. They can be paramagnetic or diamagnetic depending on the presence of unpaired electrons.
7. Some organometallic compounds can be toxic, particularly volatile ones.

## 18 Electron Rule-applications and Exceptions

- The 18-electron rule, a guideline in organometallic chemistry, predicts the stability of transition metal complexes by suggesting that those with 18 valence electrons are most stable, analogous to a noble gas configuration.
- This rule is a useful tool for understanding the structure and reactivity of these compounds, but it does have exceptions.
- **The Rule**: Transition metals tend to have 18 valence electrons, including those donated by ligands, to achieve a stable electron configuration.
- This configuration is achieved by filling the ns, np, and (n-1)d orbitals, which can hold a total of 18 electrons.
- Organometallic compounds that follow this rule are often more stable and less reactive

| **Valence Electrons** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** | **12** |
|---|---|---|---|---|---|---|---|---|---|---|
| 3d transition series | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
| 4d transition series | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
| 5d transition series | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg |

**Ferrocene**



**Neutral atom method**

Fe = 8 = 8

2Cp = 5 = 10

$18\ e^-$

**Oxidation state method**

Fe = 6 $(Fe^{++})$

2Cp = 12

$18\ e^-$

Ferrocene follows 18 electron rule

**$Mn(CO)_5CH_3$**

Neutral atomic method: 7 + 10 + 1 = 18 electron (Mn)

Oxidation state method: 6 + 2 + 10 = 18 electron $(Mn^+)$

**$Ni(CO)_4$**

Valence electrons of Ni = 10

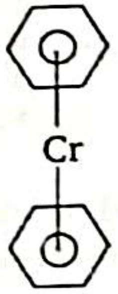
Electrons donated by four CO ligands = 2 x 4 = 8

Thus, total outer electrons in $Ni(CO)_4$ = 10 + 8 = 18 electrons

Hence, $Ni(CO)_4$ exists as stable compound.

$HMn(CO)_5$

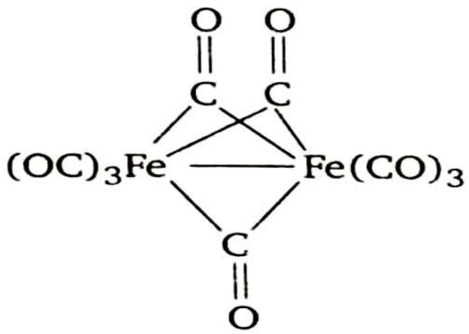
| | Neutral atom method | | Oxidation state method | |
|---|---|---|---|---|
| | Mn | 7$e$ | $Mn^+$ | 6$e$ |
| | H | 1$e$ | $H^-$ | 2$e$ |
| | 5CO | 10$e$ | 5CO | 10$e$ |
| | | 18$e$ | | 18$e$ |



| | | | | |
|---|---|---|---|---|
| | Cr | 6$e$ | Cr | 6$e$ |
| | $2C_6H_6$ | 12$e$ | $2C_6H_6$ | 12$e$ |
| | | 18$e$ | | 18$e$ |

| | | | | |
|---|---|---|---|---|
| $(OC)_5—Mn—Mn(CO)_5$ | Mn | 7$e$ | Mn | 7$e$ |
| | Mn—Mn | 1$e$ | Mn—Mn | 1$e$ |
| | 5CO | 10$e$ | 5CO | 10$e$ |
| | | 18$e$ | | 18$e$ |

| | | | | |
|---|---|---|---|---|
| ) $[PtCl_4]^{--}$ | $Pt^{++}$ | 8$e$ | Pt | 10$e$ |
| | $4Cl^-$ | 8$e$ | 4Cl | 4$e$ |
| | | | Charge | 2$e$ |
| | | 16$e$ | | 16$e$ |
| $[Cr(CO)_6]$ | Cr | 6$e$ | Cr | 6$e$ |
| | 6CO | 12$e$ | 6CO | 12$e$ |
| | | 18$e$ | | 18$e$ |
| $[Fe(CO)_5]$ | Fe | 8$e$ | Fe | 8$e$ |
| | 5CO | 10$e$ | 5CO | 10$e$ |
| | | 18$e$ | | 18$e$ |



| | |
|---|---|
| Fe | $8e$ |
| 3CO | $6e$ |
| Fe—Fe | $1e$ |
| $3(\mu\text{-CO})$ | $3e$ |
| | $18e$ |

| | |
|---|---|
| Fe | $8e$ |
| 3CO | $6e$ |
| Fe—Fe | $1e$ |
| $3(\mu\text{-CO})$ | $3e$ |
| | $18e$ |

$[Co(CO)_4]^{\ominus}$

| | |
|---|---|
| Co | $9e$ |
| 4CO | $8e$ |
| Charge | $1e$ |
| | $18e$ |

| | |
|---|---|
| Co | $9e$ |
| 4CO | $8e$ |
| Charge | $1e$ |
| | $18e$ |

$[Co(NH_3)_6]^{+++}$

| | |
|---|---|
| Co | $9e$ |
| $6NH_3$ | $12e$ |
| Charge | $-3e$ |
| | $18e$ |

| | |
|---|---|
| Co | $9e$ |
| $6NH_3$ | $12e$ |
| Charge | $-3e$ |
| | $18e$ |

**Applications**

1. In the determination of the total number of metal-metal bonds
2. Used to predict the stability of various organometallic compounds.
3. To know the reactivity of transition elements.
4. In the determination of the formula of organometallic compounds.
5. By understanding the rule, chemists can design and synthesize new organometallic compounds with specific properties

**Exceptions**

1. 16 electron compounds (both high spin octahedral and low spin square planar) fail to obey this rule.
2. High-spin compounds usually do not follow this rule as they lack vacant orbitals to gain electrons in their valence shell.
3. The metal complexes containing bulky ligands violate the 18-electron rule by interfering with the ligands for bonding.
4. **π**-donating ligands do not follow the 18-electron rule.
5. When an organometallic compound consists of more than 6 metal atoms, the 18-electron rule does not apply.
6. Most organometallic compounds can be synthesized by using one of four M-C bond-forming reactions of a metal with an organic halide, metal displacement, metathesis, and hydrometallation.

# General Methods of Preparation

## a. Reaction with metal and Transmetallation

The net reaction of an electropositive metal M and a halogen-substituted hydrocarbon is

$2M+RX(\text{alkyl or aryl})\longrightarrow MR+MX$

For example

$8Li+4CH_3Cl\longrightarrow Li_4(CH_3)_4+4LiCl$

$Mg+CH_3Br\longrightarrow CH_3MgBr$ (organometallic halide with Mg, Al, Zn)

If one metal atom takes the place of another, it is called **Transmetallation**

$M+M'R\longrightarrow M'+MR$

$2Ga+3CH_3{-}Hg{-}CH_3\longrightarrow 3Hg+2Ga(CH_3)_3$

Transmetallation is favorable when the displacing metal is higher in the electrochemical series than the displaced metal

## b. Metathesis

The metathesis of an organometallic compound MR and a binary halide $EX_n$ is a widely used synthetic route in organometallic chemistry.

$MR+EX\longrightarrow ER+MX$

$Li_4(CH_3)_4+SiCl_4\longrightarrow 4LiCl+Si(CH_3)_4$

$Al_2(CH_3)_6+2BF_3\longrightarrow 2AlF_3+2B(CH_3)_3$

Metathesis reaction can frequently be predicted from electronegativity or HSAB Principle.

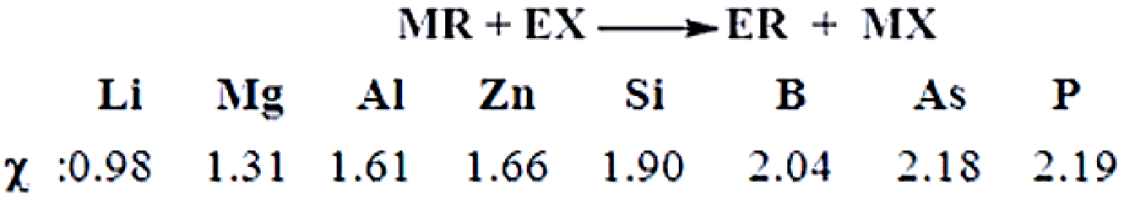
In brief, the alkyl and aryl group tends to migrate from the less to the more electronegative element.

Metathesis reactions involving the same central element are often referred to as redistribution reactions.

$SiCl_4+SiMe_4\longrightarrow Me_3SiCl+Me_2SiCl_2+\cdots$

$3GeCl_4+2AlMe_6\longrightarrow 3GeMe_4+4AlCl_3$

Al is more electropositive than Ge, this reaction occurs as it is thermodynamically favorable



$$MR + EX \longrightarrow ER + MX$$

| | Li | Mg | Al | Zn | Si | B | As | P |
|---|---|---|---|---|---|---|---|---|
| χ | :0.98 | 1.31 | 1.61 | 1.66 | 1.90 | 2.04 | 2.18 | 2.19 |

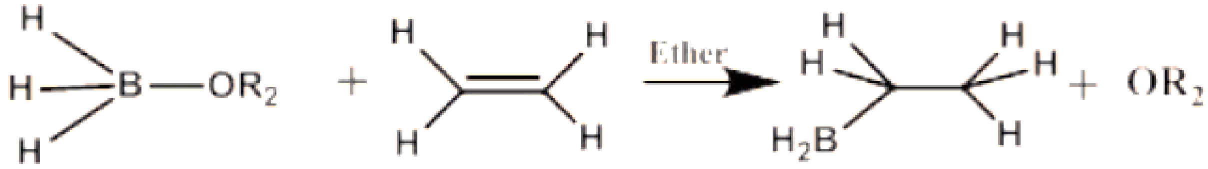
## C. Hydrometallation/ Alkene Insertion

The net outcome of the addition of a metal hydride to an alkene is an alkylmetal compound.

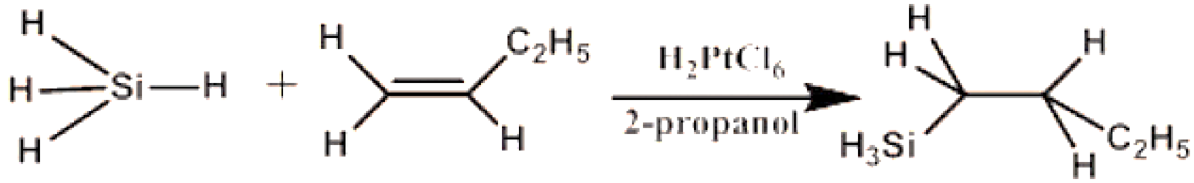
$EH+H_2C{=}CH_2 \longrightarrow E{-}CH_2{-}CH_3$

The reaction is driven by the high strength of E-C bond relative to that of most E-H bonds, and occurs with a wide variety of compounds that contain E-H bonds.

Hydroboration



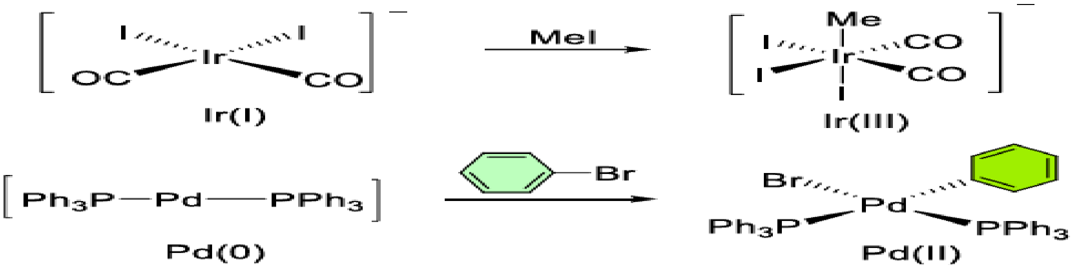
Hydrosilation



## Reactions of organometallic compounds:

### 1. Oxidative addition

- This unique reaction observed for organometallic compounds involves oxidation by 2 units of the metal atom, with an increase in coordination number by 2 with the addition of two new anionic ligands, with an increase in electron count.
- The reaction of a neutral molecule ($H_2$, $Cl_2$, $Me_3SiH$, $CH_3Cl$, etc.) with an oxidatively unsaturated metal complex (such as a square planar complex, complex with CN less than 6 with a metal ion in a low oxidation state).
- The addition can be cis (for homonuclear molecules, nonpolar, or slightly polar group, e.g., $Cl_2$) or trans (for a heteronuclear reactant, polar group, e.g., MeI).
- The metal should be in a low coordination number i.e., the metal should be co-coordinatively unsaturated (C.N. less than 6), and the metal should be electron-rich.
- Metals with $d^8$, $d^{10}$ configuration undergoes oxidative addition. Metals with $d^0$ configuration do not undergo oxidative addition. EWG or Pi acceptor ligands decrease the rate of oxidative addition



- **Factors Influencing Oxidative Addition**

1. Oxidation State & Electron Count of Metal: Metals in low oxidation states (0, +1). Electron-rich metals are more likely to undergo oxidative addition. 16-electron or 14-electron complexes are ideal as they can accept new ligands to form 18-electron species.  Metal exists in two stable oxidation states

2. Ligand Effects:  Electron-rich ligands (e.g., phosphines) stabilize low oxidation states and facilitate oxidative addition. Steric bulk can either hinder or direct selectivity; EWG or Pi acceptor ligands decrease the rate of oxidative addition.

3. Nature of Substrate: Bond strength (e.g., H–H < C–H < C–Cl) Polarity (polar bonds often react via $SN_2$-type mechanisms)

- **Mechanisms**

1. Concerted (Non-polar) Mechanism: Typical for H–H, C–H, Si–H bonds. Requires an empty orbital and a low oxidation state metal

2. $SN_2$-Type (Nucleophilic): Mechanism Common for polar bonds like C–X (X = Cl, Br, I). The metal acts as a nucleophile, displacing the leaving group.

## 2. Reductive Elimination:

- This unique reaction observed for organometallic compounds involves the Reduction of the metal atom, with a decrease in coordination number by 2, with the loss of two new anionic ligands, with a decrease in electron count.
- Requirements: Eliminating groups must be adjacent to each other (cis position)

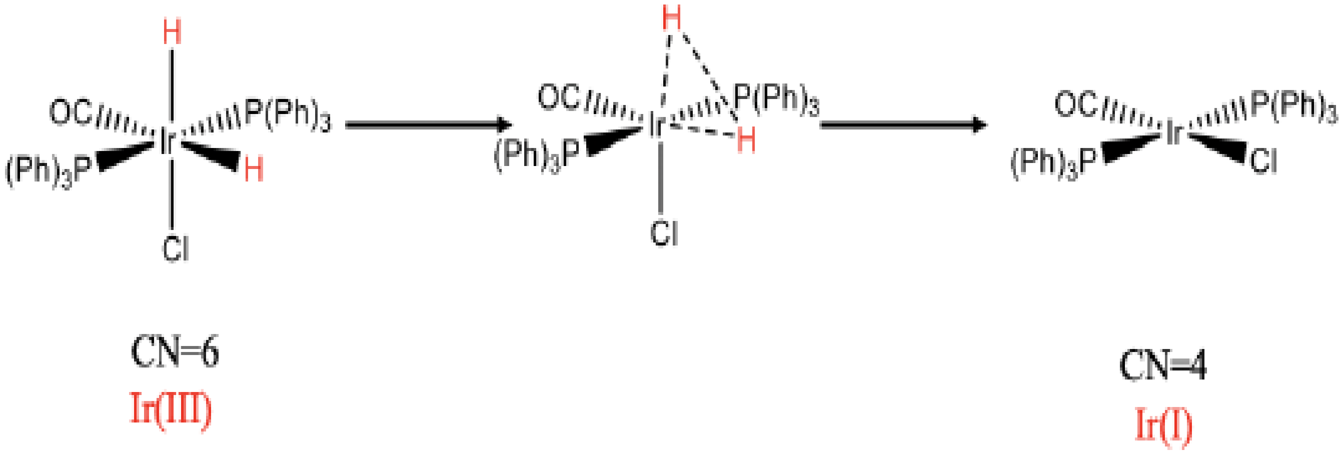
  High formal positive charge (Oxidation State) on metal

  Presence of a bulky group on the metal.

  Electronically stable organic group

  Pi-accepting ligands attached to metal generally accelerate the reaction

  Note: reductive elimination is exactly opposite to oxidative addition



## 3. Insertion

An insertion reaction involves the migration of a ligand (typically an alkyl or hydride) from a metal center to an unsaturated ligand (like an alkene, alkyne, or CO) that is also coordinated to the same metal. This results in the formation of a new M–C bond and a C–C or C–H bond in the product.

$$LnM{-}R+L'{-}{>}LnM{-}L'{-}R$$

Alkene Insertion (Olefin Insertion)

A metal–alkyl or metal–hydride complex reacts with a coordinated alkene, forming a new C–C or C–H bond.

$L_nM{-}H+CH_2{=}CHR{-}{>}\ L_nM{-}CH_2CH_2R$

Migratory insertion of the alkene into the M–H bond.

Common in alkene polymerization and hydrofunctionalization reactions.

2. CO Insertion (Carbonyl Insertion)

Carbon monoxide (CO) inserts between the metal and the alkyl group to form an acyl complex.

$L_nM{-}R+CO\ \ {-}{>}L_nM{-}C(O)R$

Key in hydroformylation and carbonylation reactions.

Often followed by reductive elimination to release an aldehyde or ketone.

3. Alkyne Insertion:

Similar to Alkene Insertion, but with Alkynes. It can lead to vinyl or allyl products depending on subsequent steps.

$L_nM–R + RCCR' \text{->} L_nM–CH=CHR$

Used in hydroalkynylation, cyclization, and ligand-directed C–C bond formation.

4. Heteroatom Insertion

Insertions involving heteroatoms like $CO_2$, $SO_2$, isocyanides, etc., into M–R bonds.

$L_nM–R+CO_2–>L_nM–OC(O)R$

Important in $CO_2$ utilization and green chemistry.

## 4. Elimination

An elimination reaction involves the loss of a small molecule (like $H_2$, alkene, or alkyne) from a metal complex, leading to:

1. A decrease in coordination number.
2. Often the formation of unsaturated organic molecules (like alkenes or alkynes).
3. Often a precursor step to the formation of new metal-ligand species or to the regeneration of a catalytically active metal center.
4. Unlike reductive elimination, which involves the formation of a bond between two ligands, elimination usually involves breaking bonds within a single ligand or between a ligand and the metal to generate a small molecule.

1. β-Hydride Elimination

- A hydrogen atom on the β-carbon of an alkyl ligand migrates to the metal center, leading to:
- Formation of a metal hydride.
- Formation of an alkene (from the alkyl group).

$[M]–CH_2–CH_2R–>[M]–H+CH_2=CHR$

- The metal must have a vacant site cis to the β-hydrogen.
- Common in alkene isomerization, hydrogenation, and olefin metathesis.
- Requirements:

The β-hydrogen must be geometrically accessible.

Metal center should have an empty orbital to accept the hydride.

2. α-Elimination

A hydrogen (or another group) on the α-carbon of a ligand is eliminated, often resulting in the formation of carbenes, vinylidenes, or metal-carbynes.

General Reaction:

$[M]–CH_2–X \longrightarrow [M]=CH_2+HX$

Less common than β-elimination.

Often used to generate metal–carbene complexes.

Important in Fischer and Schrock-type carbenes

# Organometallics in homogeneous catalysis

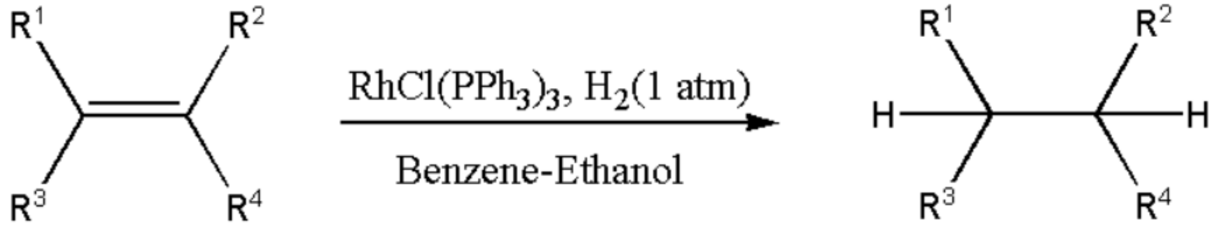
- Hydrogenation of olefins
- Hydroformylation reaction
- Monsanto Acetic Acid
- Polymerization of olefins

**Conditions to be satisfied by the metal to act as a catalyst**

1. Metal should have at least two stable oxidation states
2. It should be capable of forming complexes with a range coordination number
3. Must have the ability to match substrate orbitals

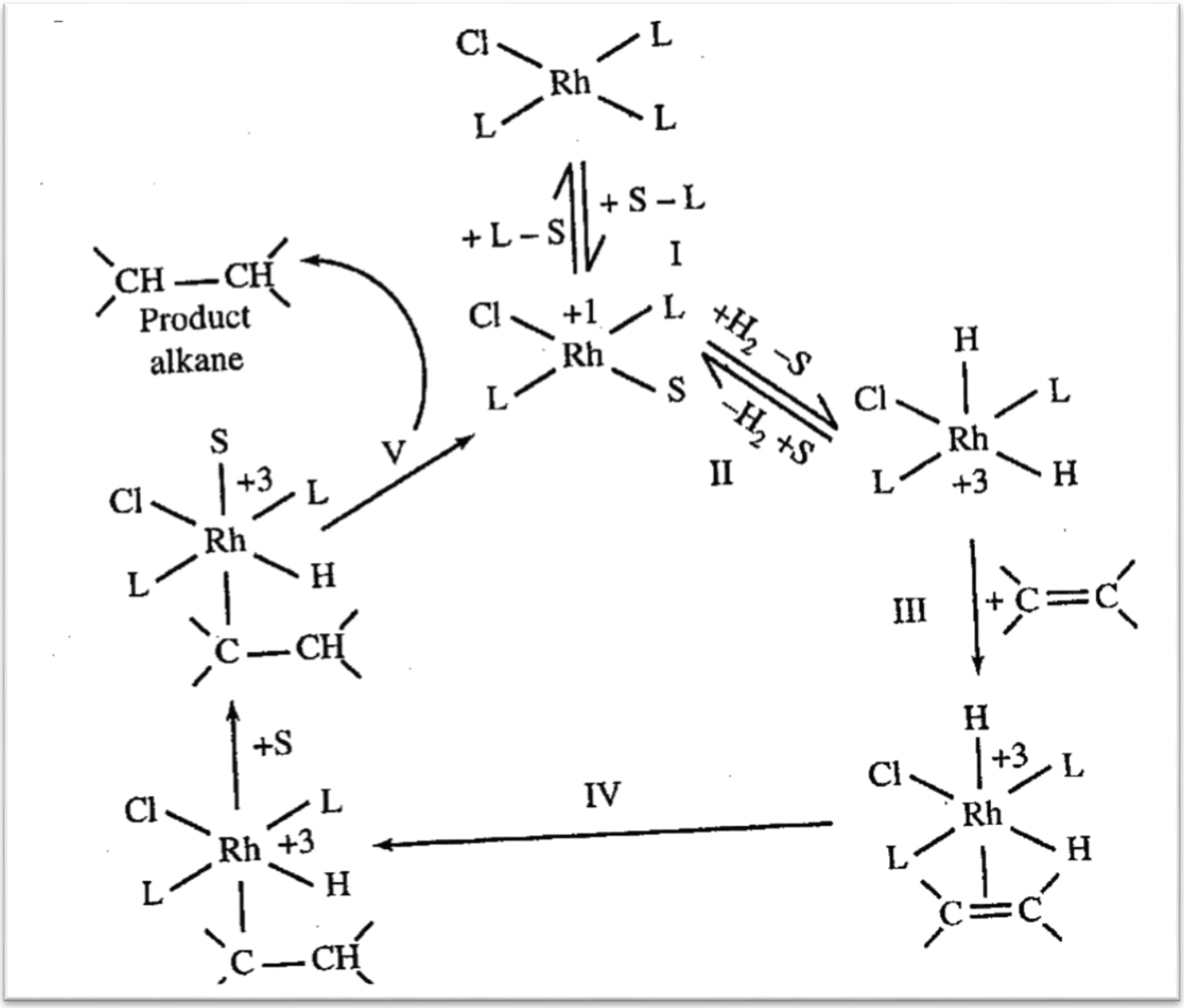
## 1. Hydrogenation of olefins

- Hydrogenation of olefins is a reaction of major industrial importance, used in the petrochemical industry and in the pharmaceutical industry, where the preparation of drugs often involves the hydrogenation of specific double bonds.
- In this Process [$Rh(Cl)(PPh_3)_3$],chlorotris(triphenylphosphine)rhodium(I) is an effective homogeneous catalyst in solutions of aromatic hydrocarbons such as benzene and toluene.
- It is often referred to as Wilkinson's catalyst.
- This catalyst is very important because it carries out the hydrogenation of an isolated double bond at normal temperature and pressure
- This red violet colored compound prepared by refluxing ethanolic $RhCl_3$. $3H_2O$ with excess $PPh_3$



**Mechanism:**

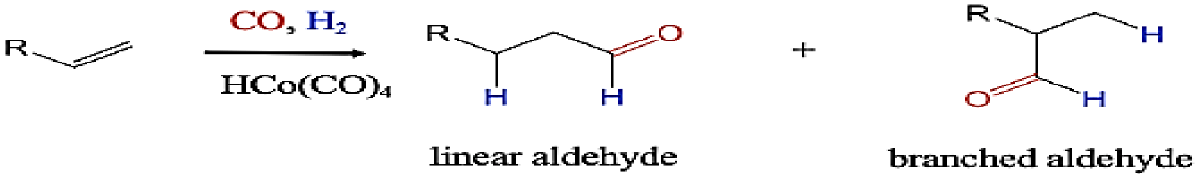
1. Reversible loss of one $PPh_3$.
2. Oxidative addition of $H_2$ followed by formation of five-coordinated complex.
3. Coordination of alkene to form 6-coordinated species.
4. Insertion of olefin into metal metal-hydrogen bond.
5. Addition of substrate to form 6 coordinated complex.
6. The last step, reductive elimination of the alkyl and hydride ligands to yield the alkane, is totally irreversible.



- **Advantages**: Operates at milder Conditions, selectively hydrogenates biologically active substrates like steroids, and selectively works for the hydrogenation of terminal olefins
- **Disadvantages:** Difficult to separate the catalyst, Rhodium metal is very costly

## 2. Hydroformylation reaction

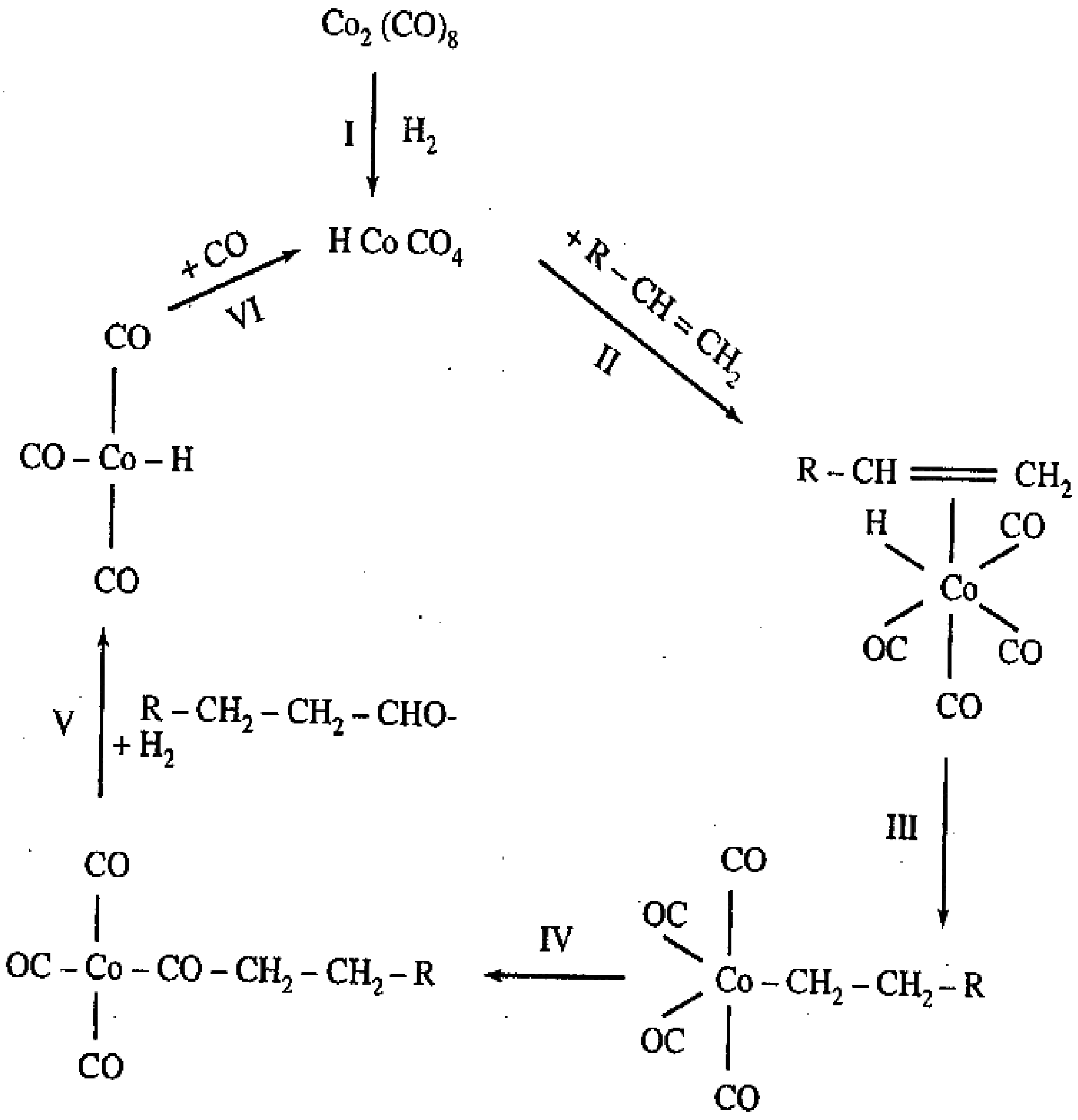
- Hydroformylation reaction involves the addition of $H_2$ and CO (formally H and CHO) to a terminal alkene to yield an aldehyde.
- Since it is used to make oxygen-containing compounds from hydrocarbons, it is also known as the oxo process
- A kinetic study of the oxo reaction reveals that it is first order in olefin and approximately first order in the amount of the catalyst used. The reaction rate increases with increasing hydrogen pressure and decreases with increasing carbon monoxide pressure. The rate is virtually independent of the nature of the solvent used. It is faster for terminal olefins than for internal olefins.
- Since olefins are isomerised under the conditions of oxo reaction, a mixture of linear and branched aldehydes and ketones is often produced.



100°C, up to 100 atm of CO and $H_2$

**Mechanism**

- Step 1 involves the generation of the active catalyst, $HCo(CO)_4$ from $Co_2(CO)_8$ and $H_2$
- Step 2 is the addition of olefin to the coordinatively unsaturated $HCo(CO)_4$, to form a coordinatively saturated 6-coordinated alkene complex.
- Step 3 involves the insertion of an alkene into the Co-H bond to give an alkyl intermediate
- Step 4 is another insertion reaction, namely carbonyl insertion to give an acyl complex
- Step 5 is the reaction of gaseous hydrogen with the acyl complex to yield an aldehyde and $HCo(CO)_3$
- Step 6 is the rapid absorption of CO molecule by $HCo(CO)_3$, to regenerate the active catalyst. $HCo(CO)_4$ which will restart the whole catalytic cycle


$Co_2(CO)_8$
I
$H_2$
$HCoCO_4$
+CO
VI
$+R-CH=CH_2$
II
$R-CH=CH_2$
H
CO
Co
OC
CO
CO
III
CO
OC
$Co-CH_2-CH_2-R$
OC
CO
IV
CO
$OC-Co-CO-CH_2-CH_2-R$
CO
V
$R-CH_2-CH_2-CHO$-
$+H_2$
CO
$CO-Co-H$
CO

### 3. Monsanto Acetic Acid Process

- The Monsanto process is an industrial method to produce acetic acid by methanol carbonylation, reacting methanol and carbon monoxide using a rhodium catalyst and an iodine promoter under high pressure and moderate temperature.
- Developed by Monsanto in the 1960s, the process involves a catalytic cycle where the active catalyst, an iododicarbonyldihydrorhodate anoin, is used as a catalyst

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

$$CH_3I + CO \xrightarrow{\text{cata Rh}^{I}} CH_3COI$$

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

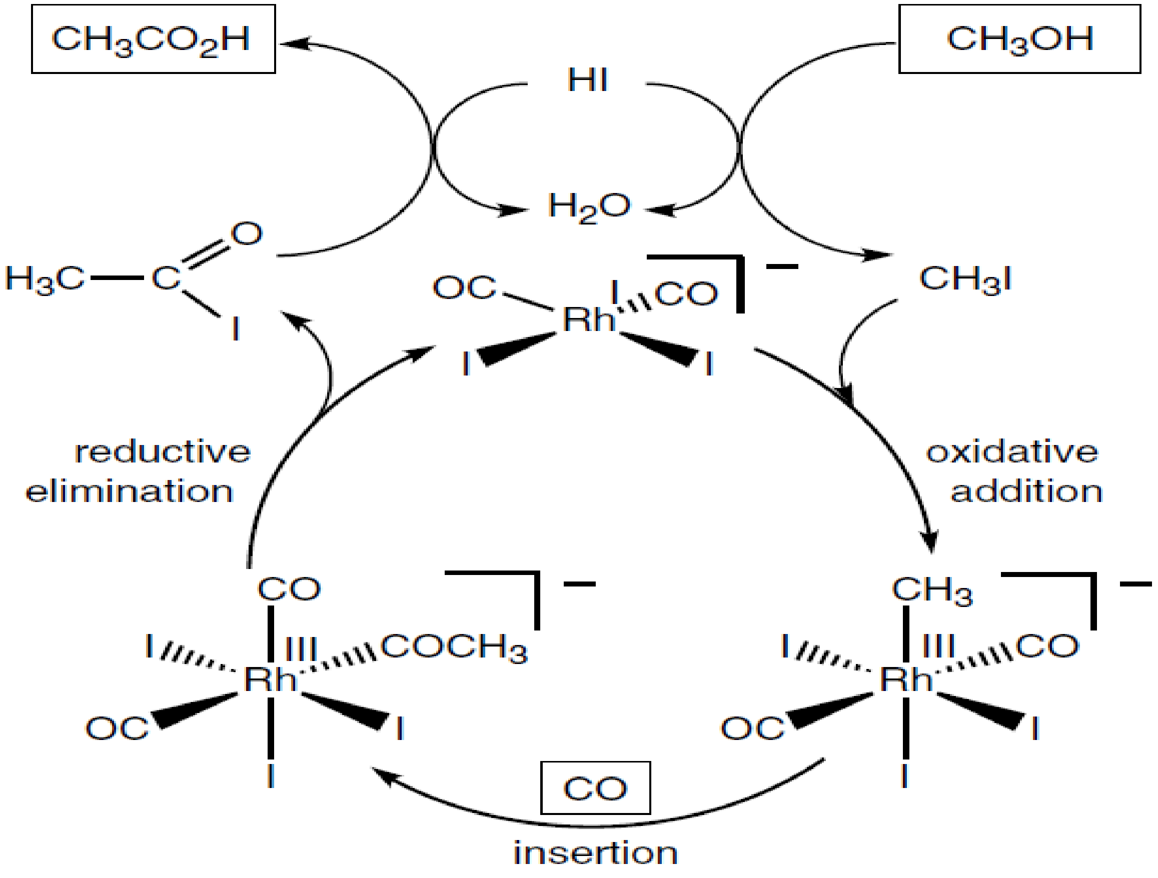
**Mechanism**

Step 1 Oxidative Addition: Methyl iodide adds to the rhodium catalyst, forming a hexacoordinate intermediate.

Step 2 Methyl Migration: A methyl group migrates from the rhodium metal to an adjacent carbonyl ligand, creating an acetyl complex.

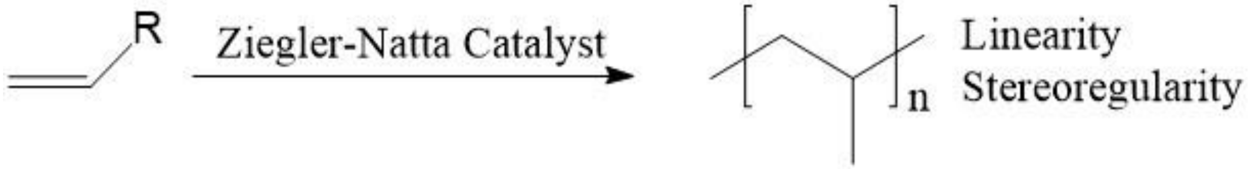
Step 3 Reductive Elimination: The acetyl complex reacts with another carbon monoxide molecule and then undergoes reductive elimination to release acetyl iodide ($CH_3C(O)I$).

Step 4 Hydrolysis: The acetyl iodide then reacts with water in the reaction mixture to produce acetic acid and hydrogen iodide (HI), which regenerates the iodide promoter needed for the cycle.

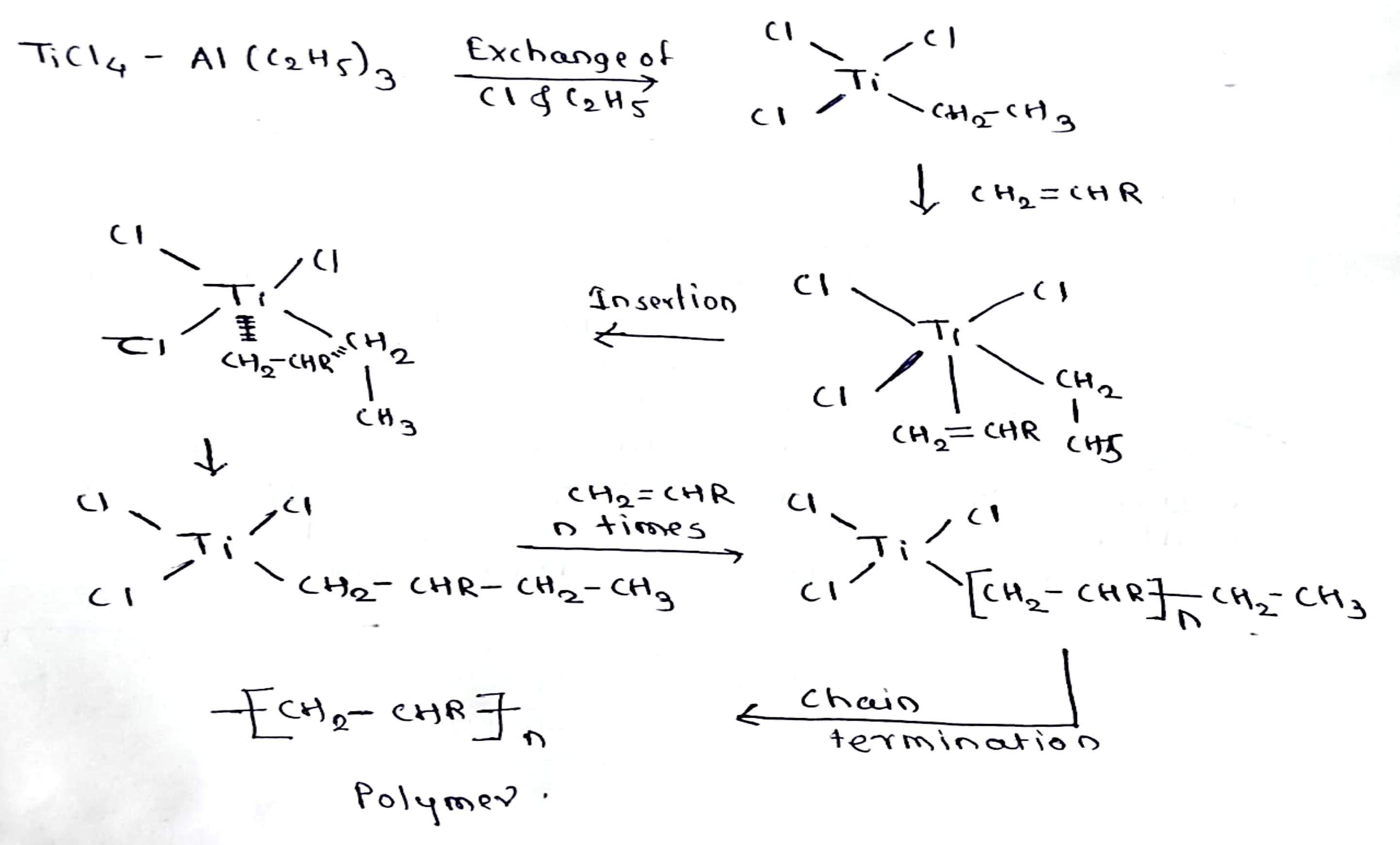


## 4. Polymerization of olefins: Ziegler-Natta polymerization

- Ziegler-Natta polymerization is a coordination polymerization method that utilizes transition metal catalysts and co-catalysts to produce high-quality polyolefins, such as polyethylene and polypropylene.
- This process was discovered by Karl Ziegler and Giulio Natta (won the 1963 Nobel Prize in Chemistry for their work),
- This catalyst is obtained by the combination of $TiCl_4$ with triethylaluminum
- It is used for the creation of stereoregular polymers with controlled physical properties, such as isotactic or syndiotactic polypropylene, which are harder and stronger than their atactic
- Important Characteristics of Ziegler-Natta Catalyst Include
  1. Polymer Chain Grows linearly due to Head-to-Tail Linkage
  2. Polymerization can be carried out at relatively mild conditions of temperature (313-353K) and pressure 1-25 bar
  3. Polymers of desired stereochemistry can be obtained

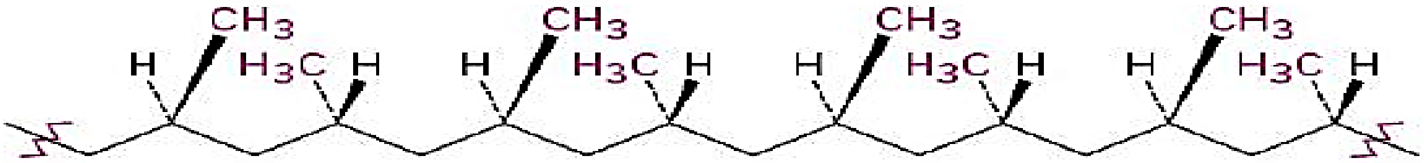


**Mechanism**

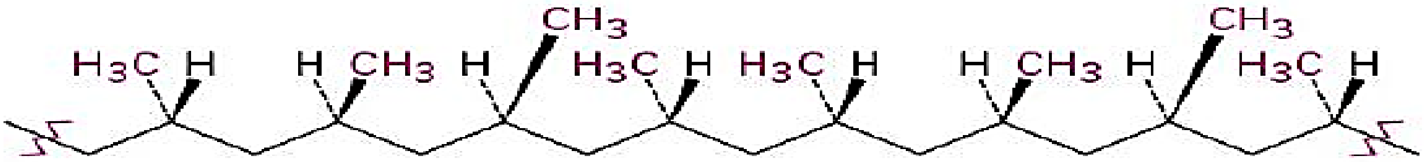


- **Achiral monomer may polymerize to generate stereocentres, it may give three types of polymers**

**Isotactic (same side)**



**Syndiotactic (alternating sides)**



**Atactic (random)**