

1. (a) Define the following with suitable example : (i) Organometallic compounds and its application

- **Definition:** Organometallic compounds are chemical compounds that contain at least one chemical bond between a carbon atom of an organic group and a metal atom. The metal can be a main group metal, a transition metal, or a lanthanide/actinide.

- **Example:**

- Grignard reagents:  $\text{CH}_3\text{MgBr}$  (Methylmagnesium bromide) - a bond between carbon and magnesium.
- Ferrocene:  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  - Iron bonded to cyclopentadienyl rings.
- Dimethylzinc:  $(\text{CH}_3)_2\text{Zn}$  - Zinc bonded to two methyl groups.

- **Applications:**

- **Catalysis:** Organometallic compounds are widely used as catalysts in various industrial processes. For example, Ziegler-Natta catalysts (e.g.,  $\text{TiCl}_4/\text{Al}(\text{C}_2\text{H}_5)_3$ ) are used for the polymerization of alkenes (like ethene and propene) to produce plastics such as polyethylene and polypropylene. Wilkinson's catalyst ( $\text{RhCl}(\text{PPh}_3)_3$ ) is used for the homogeneous hydrogenation of alkenes.
- **Organic Synthesis:** They are indispensable reagents in organic synthesis for forming new carbon-carbon bonds. Grignard reagents ( $\text{RMgX}$ ) and organolithium reagents ( $\text{RLi}$ ) are classic examples used for the synthesis of alcohols, carboxylic acids, and many other organic compounds.
- **Material Science:** Organometallic compounds are precursors for the synthesis of various materials, including semiconductors, ceramics, and superconductors. For example, metal-organic chemical vapor deposition (MOCVD) uses

organometallic precursors to deposit thin films of metals and metal oxides.

- **Medicine:** Some organometallic compounds have medicinal applications. For example, cisplatin (a platinum complex) is an anticancer drug. Organoarsenic compounds were historically used as antisyphilitic agents.

(ii) Hapticity. Give examples of ligands with hapticities of 3, 4 and 5.

- **Definition:** Hapticity (denoted by the Greek letter eta,  $\eta$ ) is a term used in organometallic chemistry to describe the number of contiguous atoms of a ligand that are simultaneously bonded to a central metal atom. It indicates how many atoms in a delocalized pi-system (like an alkene, allyl, or cyclopentadienyl group) are involved in bonding to the metal.
- **Examples of Ligands with Specific Hapticities:**
  - **Hapticity of 3 ( $\eta^3$ ):**
    - **Ligand:** Allyl group ( $C_3H_5$ )
    - **Example Complex:**  $(\eta^3-C_3H_5)Fe(CO)_3Cl$  (Allyliron tricarbonyl chloride)
    - **Explanation:** In this complex, all three carbon atoms of the allyl group are bonded to the iron metal. The allyl ligand binds in a delocalized fashion, utilizing its pi-system.
  - **Hapticity of 4 ( $\eta^4$ ):**
    - **Ligand:** Butadiene ( $C_4H_6$ )
    - **Example Complex:**  $Fe(\eta^4-C_4H_6)(CO)_3$  (Butadieneiron tricarbonyl)

- **Explanation:** In this complex, all four carbon atoms of the butadiene ligand are bonded to the iron metal, utilizing its conjugated diene pi-system.
- **Hapticity of 5 ( $\eta^5$ ):**
  - **Ligand:** Cyclopentadienyl anion ( $C_5H_5^-$ )
  - **Example Complex:**  $Fe(\eta^5-C_5H_5)_2$  (Ferrocene)
  - **Explanation:** In ferrocene, all five carbon atoms of each cyclopentadienyl ring are symmetrically bonded to the central iron atom, utilizing the delocalized pi-electron system of the aromatic cyclopentadienyl anion.

(b) What is meant by Synergic effect? How does it account for the formation of carbonyl complexes of transition metals in low oxidation states?

- **Synergic Effect (or Pi-Backbonding):**
  - The synergic effect describes a cooperative bonding mechanism between a transition metal and a ligand, particularly common in metal carbonyls. It involves two main components:
    - i. **Sigma ( $\sigma$ ) Donation:** The ligand (e.g., CO) donates electron density from its lone pair (on carbon) to an empty d-orbital of the metal, forming a sigma ( $M \leftarrow L$ ) bond.
    - ii. **Pi ( $\pi$ ) Backdonation (or Pi-Backbonding):** The metal donates electron density from a filled d-orbital into an empty antibonding ( $\pi^*$ ) orbital of the ligand. This forms a pi ( $M \rightarrow L$ ) bond, strengthening the metal-ligand interaction.
  - The term "synergic" implies that these two processes reinforce each other. Sigma donation increases electron density on the metal, making it more willing to donate electrons back into the ligand's antibonding orbitals via pi-backbonding. This pi-

backbonding, in turn, strengthens the M-L bond and makes the ligand a better sigma donor.

- **Accounting for Formation of Carbonyl Complexes in Low Oxidation States:**

- **Low Oxidation States:** Carbonyl complexes (like metal carbonyls) are predominantly formed by transition metals in low (often zero or even negative) oxidation states. The synergic effect is crucial in explaining this.
- **Availability of Electron Density:** For effective pi-backbonding ( $M \rightarrow L$ ), the metal must have filled d-orbitals with sufficient electron density to donate into the ligand's antibonding orbitals. Metals in low oxidation states have a higher electron density on the metal center.
- **Increased Backbonding:** When the metal is in a low oxidation state, its electron density is high, making it a better electron donor (in terms of pi-backbonding). This strong pi-backbonding strengthens the M-C bond, compensating for the relatively weak sigma donation from CO and stabilizing the complex.
- **Stabilization of the Complex:** The synergic bonding (sigma donation + pi-backbonding) creates a very stable metal-carbonyl bond. Without sufficient pi-backbonding, the interaction would be much weaker, and the complex would not be stable, especially in low oxidation states where simple sigma donation might not be enough to satisfy the metal's electron requirements and orbital overlap.
- **Example:** In  $[Ni(CO)_4]$ , nickel is in the zero oxidation state. It has a  $d^{10}$  configuration. The filled d-orbitals readily engage in pi-backbonding with the empty  $\pi^*$  orbitals of CO, leading to a very stable complex. If nickel were in a high oxidation state, its d-orbitals would be less electron-rich, and pi-backbonding would

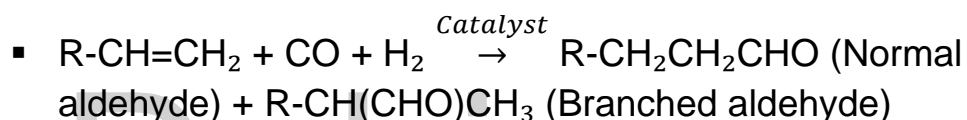
be diminished, leading to instability or non-formation of the carbonyl complex.

(c) Explain hydroformylation? Mention in detail the mechanism for the catalytic cycle of conversion of alkenes to aldehyde.

- **Hydroformylation (Oxo Process):**

- **Definition:** Hydroformylation is an industrial process that converts alkenes into aldehydes by reaction with carbon monoxide (CO) and hydrogen gas ( $H_2$ ) in the presence of a transition metal catalyst (typically cobalt or rhodium complexes).

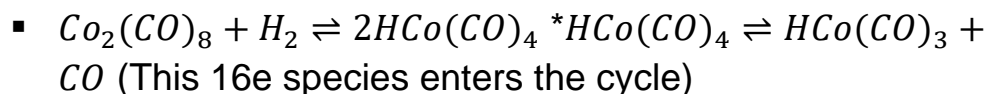
- **Overall Reaction:**



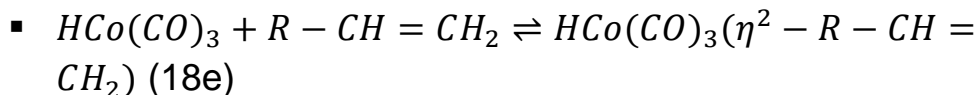
- **Significance:** It is a highly important industrial process for the production of aldehydes, which are precursors for alcohols, carboxylic acids, and polymers. The normal aldehyde is usually the desired product due to its utility.

- **Mechanism for the Catalytic Cycle (using Cobalt Catalyst, e.g.,  $\text{HCo(CO)}_4$ ):**

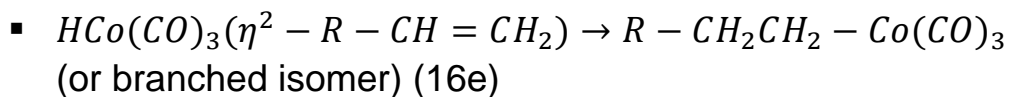
- b. **Catalyst Precursor Formation:** The actual catalyst is often generated in situ from a precursor, such as dicobalt octacarbonyl ( $\text{Co}_2(\text{CO})_8$ ), which reacts with  $\text{H}_2$  to form tetracarbonylhydridocobalt(I) ( $\text{HCo(CO)}_4$ ). This complex is typically 18-electron. It can lose a CO to become 16-electron, which is the active species.



- c. **Alkene Coordination ( $\pi$ -Complex Formation):** The alkene (e.g., propene) coordinates to the 16-electron  $HCo(CO)_3$  complex. This is an associative step.



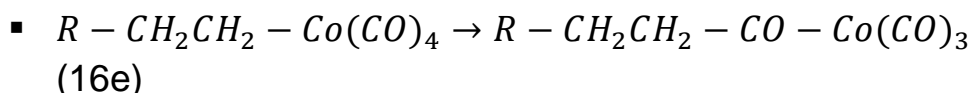
- d. **Migratory Insertion (Hydride Migration):** The hydride ligand migrates from the cobalt to one of the alkene carbon atoms, and simultaneously, the alkene carbon bonds to the cobalt. This results in the formation of an alkyl-cobalt complex. The insertion can be linear (preferred, leading to normal aldehyde) or branched.



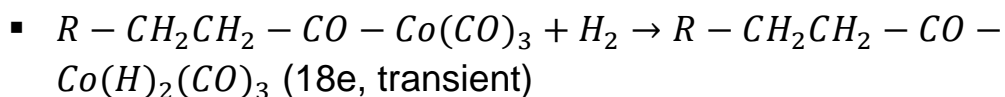
- e. **CO Coordination:** A CO molecule coordinates to the alkyl-cobalt complex. This is an associative step.



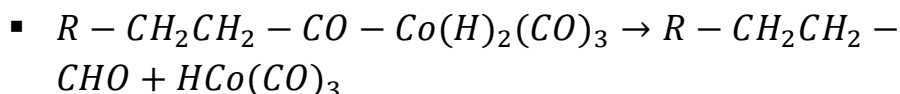
- f. **Migratory Insertion (Alkyl Migration):** The alkyl group ( $R-CH_2CH_2$ ) migrates from the cobalt to the coordinated carbonyl carbon, forming an acyl-cobalt complex and creating a vacant coordination site. This is often considered the rate-determining step.



- g. **Oxidative Addition of  $H_2$ :** An  $H_2$  molecule undergoes oxidative addition to the acyl-cobalt complex.



- h. **Reductive Elimination:** The acyl group and a hydride ligand reductively eliminate to form the aldehyde product ( $R-CH_2CH_2CHO$ ) and regenerate the 16-electron  $HCo(CO)_3$  catalyst, which re-enters the cycle.



- **Summary:** The cycle involves sequential steps of alkene coordination, hydride migration, CO coordination, alkyl migration (CO insertion), oxidative addition of  $H_2$ , and reductive elimination of the aldehyde.
2. (a) How are organometallic compounds classified on the bases of type of bonding. Explain giving example.
- Organometallic compounds can be broadly classified into three main types based on the nature of the metal-carbon bond:

i. **Ionic Organometallic Compounds:**

- **Bonding:** These compounds contain a largely ionic bond between a highly electropositive metal (typically from Group 1 or Group 2, like Na, K, Mg, Li) and a carbon atom. The carbon atom effectively carries a negative charge (carbanionic character).
- **Properties:** They are highly reactive, often pyrophoric (ignite spontaneously in air), and behave as strong bases and nucleophiles. They are usually non-volatile solids with high melting points, often insoluble in nonpolar solvents.
- **Example:**
  - **Methyl lithium ( $CH_3Li$ ):** The bond between carbon and lithium has significant ionic character.  $CH_3Li$  exists as aggregates in solution (e.g., tetramers).

- **Sodium cyclopentadienide ( $\text{Na}^+\text{C}_5\text{H}_5^-$ ):** The sodium ion interacts electrostatically with the delocalized cyclopentadienyl anion.

j. **Covalent Organometallic Compounds:**

- **Bonding:** These compounds contain a covalent bond between the metal and carbon. The metal-carbon bond can be polar covalent, with the carbon often being more electronegative or less electronegative depending on the metal. This category includes compounds of transition metals, Group 13, 14, and 15 elements with carbon.
- **Properties:** They are generally more volatile, soluble in organic solvents, and less reactive than ionic compounds. They can be liquids or solids.
- **Subcategories (based on bond polarity/character):**
  - **Electron-Deficient Compounds (e.g., Al, B):** Where the central atom does not have enough electrons to form simple 2-center-2-electron bonds to all surrounding atoms, leading to bridging bonds (e.g., electron-deficient bridging alkyl groups in aluminum alkyls).
    - **Example:** Triethylaluminum ( $(\text{C}_2\text{H}_5)_3\text{Al}$ ): In the dimeric form ( $(\text{C}_2\text{H}_5)_6\text{Al}_2$ ), there are electron-deficient 3-center-2-electron Al-C-Al bonds.
  - **Electron-Precise Compounds (e.g., Sn, Hg, Si):** Where the central atom has exactly enough electrons to form normal 2-center-2-electron bonds to its substituents.
    - **Example:** Tetramethyltin ( $(\text{CH}_3)_4\text{Sn}$ ): The Sn-C bonds are covalent.



- **Electron-Rich Compounds (not common for simple alkyls, more for complexes):** Metals in low oxidation states with pi-acid ligands (like CO).

k. **Electron-Delocalized (or Non-Classical) Organometallic Compounds:**

- **Bonding:** These compounds involve metals bonded to delocalized pi-electron systems of organic ligands (e.g., alkenes, alkynes, allyl, cyclopentadienyl, benzene). The bonding is described by a combination of sigma donation from the ligand's pi-orbitals to empty metal orbitals and pi-backdonation from filled metal d-orbitals to empty antibonding pi-orbitals of the ligand (synergic bonding). The Hapticity concept is central here.
- **Properties:** They are often relatively stable and widely used in catalysis.
- **Examples:**
  - **Ferrocene ( $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ ):** Iron is bonded to the delocalized pi-systems of two cyclopentadienyl rings. This is a "sandwich" complex.
  - **Zeise's Salt ( $\text{K}[\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_4)]$ ):** Platinum is bonded to the pi-electron system of an ethene molecule.
  - **Chromium tricarbonyl benzene ( $\eta^6\text{-C}_6\text{H}_6$ ) $\text{Cr}(\text{CO})_3$ ):** Chromium is bonded to the delocalized pi-system of a benzene ring.

(b) (i) The V-C bond lengths in  $[\text{V}(\text{CO})_6]$  and  $[\text{V}(\text{CO})_6]^-$  are 200pm and 193pm respectively. Explain.

- **Relevant Concept:** Synergic Bonding (Sigma donation and Pi-Backbonding) and its effect on bond lengths.

- **Metal Carbonyls:** In metal carbonyls, the M-C bond consists of two components:
  - l. **Sigma ( $\sigma$ ) Bond:** Formed by the donation of a lone pair from the carbon of CO to an empty d-orbital of the metal.
  - m. **Pi ( $\pi$ ) Backbond:** Formed by the donation of electron density from a filled d-orbital of the metal to an empty antibonding ( $\pi^*$ ) orbital of the CO ligand. This is the more significant component for stabilization and bond length effects.
- **Explanation for V-C Bond Lengths:**
  - **$[\text{V}(\text{CO})_6]^-$  (Vanadium is in -1 oxidation state):**
    - In this complex, vanadium has a formal oxidation state of -1. This means the vanadium atom has a higher electron density.
    - This high electron density on the metal facilitates **stronger pi-backbonding** from the filled vanadium d-orbitals to the empty  $\pi^*$  orbitals of the CO ligands.
    - Stronger pi-backbonding leads to a **stronger and shorter M-C bond**. This also weakens the C-O bond.
    - Therefore, the V-C bond length in  $[\text{V}(\text{CO})_6]^-$  is shorter (193 pm).
  - **$[\text{V}(\text{CO})_6]$  (Vanadium is in 0 oxidation state):**
    - In this complex, vanadium has a formal oxidation state of 0. Compared to the anionic complex, the vanadium atom has less electron density.
    - Consequently, the pi-backbonding from vanadium to the CO ligands is **weaker** than in  $[\text{V}(\text{CO})_6]^-$ .
    - Weaker pi-backbonding results in a **weaker and longer M-C bond**.

- Therefore, the V-C bond length in  $[V(CO)_6]$  is longer (200 pm).
- **Conclusion:** The difference in V-C bond lengths is a direct consequence of the varying degrees of pi-backbonding, which is influenced by the electron density on the central metal atom. A higher negative charge (lower oxidation state) on the metal leads to stronger backbonding and shorter M-C bonds.
- (b) (ii) Give reason and arrange in order of shortest C-O bond -  $Ni(CO)_4$ ,  $[Co(CO)_4]^-$ ,  $[Fe(CO)_4]^{2-}$ .
- **Relevant Concept:** Synergic Bonding (Pi-Backbonding) and its effect on C-O bond length (or stretching frequency).
- **C-O Bond Length:** In metal carbonyls, pi-backbonding involves the donation of electrons from the metal's d-orbitals into the empty antibonding ( $\pi^*$ ) orbitals of the CO ligand. When electrons enter the antibonding orbitals of CO, the bond order of the C-O bond decreases, making the C-O bond weaker and longer. Conversely, **less pi-backbonding leads to a stronger and shorter C-O bond.**
- **Analyzing the Complexes and Oxidation States:**
  - **$Ni(CO)_4$ :** Ni is in 0 oxidation state. Electron count: 10 (Ni) + 4x2 (CO) = 18e.
  - **$[Co(CO)_4]^-$ :** Co is in -1 oxidation state. Electron count: 9 (Co) + 1 (charge) + 4x2 (CO) = 18e.
  - **$[Fe(CO)_4]^{2-}$ :** Fe is in -2 oxidation state. Electron count: 8 (Fe) + 2 (charge) + 4x2 (CO) = 18e.
- **Reasoning for C-O Bond Length Order:**
  - As the negative charge on the metal carbonyl complex increases (i.e., the metal's oxidation state becomes more negative), the electron density on the central metal atom increases.

- Higher electron density on the metal leads to **stronger pi-backbonding** into the empty  $\pi^*$  orbitals of the CO ligands.
- Stronger pi-backbonding implies more electron density filling the CO antibonding orbitals, which in turn **reduces the C-O bond order and lengthens the C-O bond**.
- Therefore, the C-O bond length will increase as the negative charge on the complex increases.
- **Order of Shortest C-O bond (i.e., weakest backbonding):**
  - n. **Ni(CO)<sub>4</sub>** (Ni is 0 oxidation state, least negative charge, weakest backbonding, shortest C-O bond)
  - o. **[Co(CO)<sub>4</sub>]<sup>-</sup>** (Co is -1 oxidation state, intermediate negative charge, intermediate backbonding, intermediate C-O bond)
  - p. **[Fe(CO)<sub>4</sub>]<sup>2-</sup>** (Fe is -2 oxidation state, most negative charge, strongest backbonding, longest C-O bond)
- **Arrangement in order of shortest C-O bond:**
  - **Ni(CO)<sub>4</sub> < [Co(CO)<sub>4</sub>]<sup>-</sup> < [Fe(CO)<sub>4</sub>]<sup>2-</sup>**
- (c) Explain in details the Wacker Oxidation process for conversion of ethene to acetaldehyde.
- **Wacker Oxidation (or Hoechst-Wacker Process):**
  - **Definition:** The Wacker process is an industrial chemical process for the production of acetaldehyde from ethene (ethylene) using a catalytic system involving palladium chloride ( $PdCl_2$ ) and copper(II) chloride ( $CuCl_2$ ) in aqueous solution. It is a key example of homogeneous catalysis.
  - **Overall Reaction:**
    - $CH_2=CH_2 + \frac{1}{2} O_2 \xrightarrow{PdCl_2/CuCl_2, H_2O} CH_3CHO$

- **Mechanism (Catalytic Cycle):**

- q. **Alkene Coordination and Hydroxypalladation:**

- An ethene molecule coordinates to a  $Pd(II)$  species (e.g.,  $[PdCl_3(H_2O)]^-$ ), forming a  $\pi$ -complex.
- A water molecule attacks the coordinated ethene (or a hydroxide attacks), followed by migration of the OH group to the ethene carbon and formation of a Pd-C bond (hydroxypalladation). This is often viewed as external attack.
- $[PdCl_3(\eta^2 - C_2H_4)]^- + H_2O \rightleftharpoons [Cl_2Pd(CH_2CH_2OH)]^- + H^+ + Cl^-$

- r.  **$\beta$ -Hydride Elimination and Aldehyde Formation:**

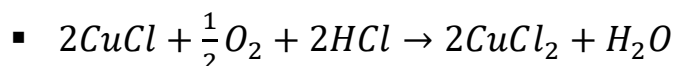
- A hydride from the beta-carbon (the carbon adjacent to the palladium-bonded carbon) migrates to the palladium, and simultaneously, the C-Pd bond breaks. This leads to the formation of vinyl alcohol ( $CH_2 = CHOH$ ) which immediately tautomerizes to acetaldehyde ( $CH_3CHO$ ).
- This step also results in the reduction of  $Pd(II)$  to  $Pd(0)$ .
- $[Cl_2Pd(CH_2CH_2OH)]^- \rightarrow CH_3CHO + Pd(0) + 2Cl^- + H^+$

- s. **Reoxidation of  $Pd(0)$  by  $Cu(II)$ :**

- The  $Pd(0)$  species is reoxidized back to  $Pd(II)$  by  $Cu(II)$  chloride. This is crucial for completing the catalytic cycle.
- $Pd(0) + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl$

- t. **Reoxidation of  $Cu(I)$  by Oxygen:**

- The  $Cu(I)$  chloride generated in step 3 is then reoxidized back to  $Cu(II)$  chloride by oxygen from the air. This ensures that the copper catalyst is regenerated.



- **Summary:** The Wacker process cleverly couples the catalytic activity of palladium for ethene oxidation with a copper redox cycle that continuously reoxidizes the palladium, allowing the overall reaction to proceed with atmospheric oxygen as the terminal oxidant.
3. (a) The cyclopentadienyl rings in ferrocene have aromatic character but cyclopentadiene itself has no such character. Explain. Give two reactions of ferrocene which show it is more reactive than benzene.

- **Aromatic Character Explanation:**

- **Cyclopentadiene ( $\text{C}_5\text{H}_6$ ):**

- Cyclopentadiene is a cyclic hydrocarbon with two double bonds and one  $\text{CH}_2$  group. It contains only 4 pi-electrons in its conjugated system (from the two double bonds).
- According to **Hückel's Rule for aromaticity**, a cyclic, planar, fully conjugated system must have  $(4n + 2)$  pi-electrons (where  $n$  is a non-negative integer, usually 0, 1, 2...).
- With 4 pi-electrons, cyclopentadiene is an **anti-aromatic** compound if it were planar and fully conjugated. However, it is not fully conjugated due to the  $\text{CH}_2$  group, which is  $\text{sp}^3$  hybridized. Thus, it lacks a continuous cyclic delocalization of pi-electrons and is best described as a non-aromatic cyclic diene. It exists as tautomers and readily undergoes Diels-Alder reactions.

- **Cyclopentadienyl anion ( $\text{C}_5\text{H}_5^-$ ) in Ferrocene:**

- Ferrocene contains two cyclopentadienyl (Cp) ligands. These ligands are derived from cyclopentadiene by deprotonation, forming the **cyclopentadienyl anion** ( $\text{C}_5\text{H}_5^-$ ).

- The cyclopentadienyl anion has 5 carbon atoms, and each carbon is  $sp^2$  hybridized. It has 5 pi-electrons from the 5 p-orbitals, plus one additional electron from the negative charge, totaling **6 pi-electrons**.
- This system is cyclic, planar, and fully conjugated, and it satisfies Hückel's rule ( $4n + 2$  where  $n=1$ , so  $4(1) + 2 = 6$  pi-electrons).
- Therefore, the cyclopentadienyl anion is an **aromatic species**.

○ **Ferrocene ( $Fe(\eta^5-C_5H_5)_2$ ):**

- In ferrocene, the iron atom is "sandwiched" between two aromatic cyclopentadienyl anions. The iron atom forms bonds with the delocalized 6 pi-electron system of each Cp ring. The aromatic character of the Cp rings is preserved and contributes significantly to the stability of ferrocene.

• **Reactions of Ferrocene Showing Higher Reactivity than Benzene:**

- Ferrocene undergoes electrophilic aromatic substitution reactions much more readily than benzene, indicating its enhanced reactivity.

u. **Friedel-Crafts Acylation (e.g., Acetylation):**

- Ferrocene reacts with acetic anhydride (or acetyl chloride) in the presence of a mild Lewis acid catalyst (like  $H_3PO_4$  or  $BF_3 \cdot OEt_2$ ) to give acetylferrocene. Benzene requires a strong Lewis acid like anhydrous  $AlCl_3$  and is less reactive.
- $Fe(\eta^5-C_5H_5)_2 + (CH_3CO)_2O \xrightarrow{H_3PO_4} (\eta^5-C_5H_5)Fe(\eta^5-5H-C_5H_4COCH_3) + CH_3COOH$

v. **Metallation (e.g., Lithiation):**

- Ferrocene readily undergoes metallation (deprotonation) by strong bases like butyllithium to form lithioferrocene. This reaction is extremely difficult (or impossible under normal conditions) for benzene.
- $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2 + \text{C}_4\text{H}_9\text{Li} \rightarrow (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Li}) + \text{C}_4\text{H}_{10}$
- The increased reactivity of ferrocene compared to benzene in electrophilic substitution is due to the electron-donating effect of the iron atom to the cyclopentadienyl rings.

(b) Give one method of preparation of Fischer Carbene. Differentiate between Fischer and Schrock Carbene (at least three).

- **Method of Preparation of Fischer Carbene:**

- **From Metal Carbonyls (using organolithium reagents and then alkylation):**
  - i. **Nucleophilic Attack on Metal Carbonyl:** A strongly nucleophilic organolithium reagent (e.g., methyllithium,  $\text{CH}_3\text{Li}$ ) attacks the carbon atom of a metal carbonyl ligand (e.g.,  $\text{Cr}(\text{CO})_6$ ). This creates an anionic acyl metalate intermediate.
    - $\text{Cr}(\text{CO})_6 + \text{CH}_3\text{Li} \rightarrow [(\text{CH}_3\text{CO})\text{Cr}(\text{CO})_5]^- \text{Li}^+$
  - ii. **Alkylation (or Protonation):** The anionic intermediate is then alkylated with a strong electrophile, typically an alkylating agent (e.g., Meerwein's salt,  $(\text{CH}_3)_3\text{O}^+\text{BF}_4^-$ ), or an alkyl halide (e.g.,  $\text{CH}_3\text{I}$ ), which adds an alkyl group to the oxygen.
    - $[(\text{CH}_3\text{CO})\text{Cr}(\text{CO})_5]^- \text{Li}^+ + (\text{CH}_3)_3\text{O}^+\text{BF}_4^- \rightarrow (\text{CH}_3\text{O})\text{Cr}(\text{CO})_5 = \text{C}(\text{OCH}_3)\text{CH}_3$  (Fischer Carbene) +  $\text{LiBF}_4 + (\text{CH}_3)_2\text{O}$



- **Differentiation between Fischer and Schrock Carbene (at least three points):**

Feature	Fischer Carbene	Schrock Carbene
<b>Metal Oxidation State</b>	Typically from metals in low oxidation states (e.g., 0, +1).	Typically from metals in high oxidation states (e.g., +4, +6).
<b>Carbene Carbon</b>	Electrophilic (has electron-withdrawing groups).	Nucleophilic (has electron-donating groups, e.g., H or alkyl).
<b>Heteroatom on Carbene C</b>	Usually has a heteroatom (O, N, S) directly bonded to the carbene carbon.	Usually has no heteroatom directly bonded to the carbene carbon.
<b>Stabilization</b>	Stabilized by the $\pi$ -donating heteroatom and $\pi$ -accepting metal.	Stabilized by strong $\alpha$ -hydrogen donation to the metal.
<b>Synthesis</b>	Formed by nucleophilic attack on metal carbonyls, followed by alkylation.	Formed by $\alpha$ -hydrogen abstraction from alkyl ligands.
<b>Reactivity</b>	Behaves like an acyl equivalent; carbene carbon is electrophilic.	Behaves like an ylide; carbene carbon is nucleophilic.
<b>Bonding Model</b>	C-M bond is primarily single bond with some double bond character from metal-	C-M bond is often considered a double bond, like in alkenes (alkylidene).

Feature	Fischer Carbene	Schrock Carbene
	to-carbene backdonation.	
<b>Example</b>	$\text{Cr}(\text{CO})_5=\text{C}(\text{OCH}_3)\text{CH}_3$ (Methoxy(methyl)carbene chromium(0) pentacarbonyl)	$\text{Ta}(\text{CH}=\text{CH}_2)_3\text{Cl}$ (Tantalum methylene complex)

(c) What is Ziegler Natta catalyst? Explain the active form of this catalyst which is involved in the polymerization of alkenes.

- **Ziegler-Natta Catalyst:**

- **Definition:** Ziegler-Natta catalysts are a class of coordination catalysts used in the polymerization of alkenes (olefins) to produce highly stereoregular polymers (e.g., isotactic or syndiotactic polypropylene) and linear polyethylene.
- **Composition:** They typically consist of two main components:
  - iii. **A Transition Metal Halide:** Usually from Group 4 (Ti, Zr, Hf), most commonly titanium tetrachloride ( $\text{TiCl}_4$ ).
  - iv. **An Organoaluminum Compound:** An alkylaluminum compound, such as triethylaluminum ( $\text{Al}(\text{C}_2\text{H}_5)_3$ ) or diethylaluminum chloride ( $(\text{C}_2\text{H}_5)_2\text{AlCl}$ ).

- **Active Form of the Catalyst:**

- The actual active species in Ziegler-Natta polymerization is not simply  $\text{TiCl}_4$  or  $\text{AlR}_3$ , but rather a complex generated by the reaction between these two components, often at the surface of a heterogeneous solid phase (e.g., crystalline  $\text{TiCl}_3$ ).
- **Formation of Active Site:**

- v. When  $TiCl_4$  (or  $TiCl_3$ ) reacts with the organoaluminum co-catalyst, the alkyl group from aluminum replaces a chloride ligand on the titanium.
  - vi. Simultaneously, the titanium is reduced to a lower oxidation state (e.g., from  $Ti(IV)$  to  $Ti(III)$  or  $Ti(II)$ ) via electron transfer with the alkylaluminum, which acts as a reducing agent.
  - vii. The active site is believed to be a **vacant coordination site** on a titanium atom in a low oxidation state (typically  $Ti(III)$ ), located at the edge or corner of the crystal lattice of the transition metal halide. This vacant site is created when an alkyl ligand from aluminum coordinates and then one of the chloride ligands on titanium is exchanged for an alkyl group.
  - viii. This titanium atom has an alkyl group already bonded to it and a vacant site available for alkene coordination.
- **The Active Site for Polymerization (Cossee-Arman Mechanism):**
- The active site is a **titanium(III) center** (or sometimes  $Ti(IV)$ ) with an alkyl group (R) bonded to it, and a vacant coordination site.
  - **Mechanism:**
    1. **Alkene Coordination:** An alkene molecule (e.g., ethene,  $C_2H_4$ ) coordinates to the vacant site on the titanium.
    2. **Migratory Insertion:** The alkyl group (R) migrates from the titanium to the coordinated alkene carbon, simultaneously forming a new Ti-C bond with the other alkene carbon. This effectively inserts the

alkene into the Ti-R bond. The vacant site is regenerated adjacent to the newly formed longer alkyl chain.

3. **Chain Propagation:** This process repeats, with successive alkene molecules coordinating to the vacant site and inserting into the growing polymer chain.

- **Significance:** The vacant coordination site and the migrating alkyl group are key to the highly controlled and stereospecific polymerization.

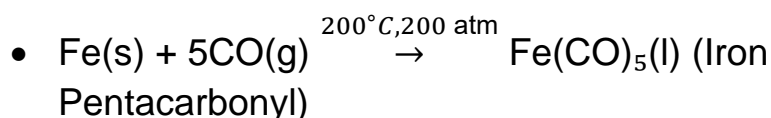
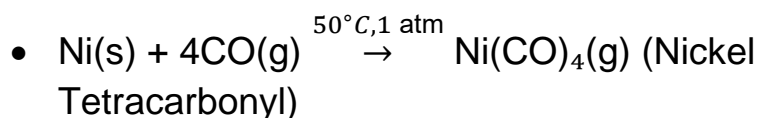
4. (a) Give any two methods of preparation of Metal Carbonyls. What happens when  $\text{Fe}(\text{CO})_5$  react with :

- **Two Methods of Preparation of Metal Carbonyls:**

w. **Direct Carbonylation:**

- **Method:** This is the simplest method, involving the direct reaction of finely divided metal with carbon monoxide gas, usually under elevated temperature and pressure. This method is limited to certain metals that can directly react with CO.

- **Example:**



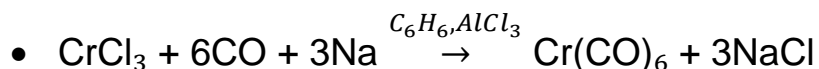
x. **Reductive Carbonylation:**

- **Method:** This involves reducing a metal salt or oxide in the presence of carbon monoxide, often with a reducing

agent. This method is more general and applicable to metals that do not react directly with CO.

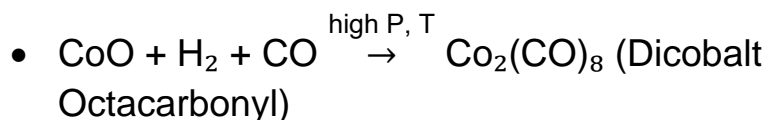
▪ **Example:**

- From metal salt (e.g., anhydrous chloride) with CO and a reducing agent (e.g., Na, Mg,  $\text{AlR}_3$ ):



- (Chromium hexacarbonyl from chromium chloride)

- From metal oxide/salt with CO and hydrogen (a common industrial method, as in Fischer-Tropsch):



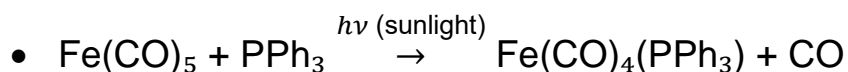
- **Reactions of  $\text{Fe(CO)}_5$ :**

- **$\text{Fe(CO)}_5$  (Iron Pentacarbonyl):** A common 18-electron complex. (i)  **$\text{Fe(CO)}_5$  react with Bromine ( $\text{Br}_2$ ):**

- **Reaction Type:** Oxidative addition or substitution depending on conditions. In the presence of oxidizing agents like halogens, metal carbonyls can undergo oxidative addition, increasing the metal's oxidation state and coordination number, and leading to the replacement of some CO ligands.
- **Product:** Halogenation of metal carbonyls typically leads to the formation of metal carbonyl halides.
- **Reaction:**  $\text{Fe(CO)}_5$  reacts with bromine to form **dibromotetracarbonyliron(II)**, where iron goes from 0 to +2 oxidation state.

- $\text{Fe}(\text{CO})_5 + \text{Br}_2 \rightarrow \text{Fe}(\text{CO})_4\text{Br}_2 + \text{CO}$  (ii)  **$\text{Fe}(\text{CO})_5$  react with  $\text{PR}_3$  (e.g., Triphenylphosphine,  $\text{PPh}_3$ ) in presence of sunlight:**

- **Reaction Type:** Ligand substitution. Metal carbonyls can undergo substitution reactions where CO ligands are replaced by other ligands (L), often promoted by heat or UV light (photolysis).
- **Reagent ( $\text{PR}_3$ ):** A phosphine ligand (e.g., triphenylphosphine,  $\text{PPh}_3$ ), which is a better sigma donor and sometimes a poorer pi-acceptor than CO.
- **Condition:** Sunlight (UV light) assists in the dissociation of a CO ligand, creating a vacant site for the phosphine to coordinate.
- **Product:** Substitution of one or more CO ligands by  $\text{PR}_3$ . Typically, one CO is substituted first.
- **Reaction (monosubstitution):**



- **Explanation:** Photolysis causes the dissociation of one CO ligand from  $\text{Fe}(\text{CO})_5$  to generate a 16-electron intermediate  $\text{Fe}(\text{CO})_4$ , which is then readily attacked by the incoming ligand  $\text{PPh}_3$  to form the more stable 18-electron complex, tetracarbonyl(triphenylphosphine)iron(0).

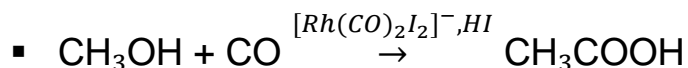
(b) Discuss in detail the Monsanto process for the production of acetic acid from methanol.

- **Monsanto Process:**

- **Definition:** The Monsanto process is a highly efficient and widely used industrial catalytic process for the production of

acetic acid ( $CH_3COOH$ ) from methanol ( $CH_3OH$ ) and carbon monoxide (CO). It is a classic example of homogeneous catalysis.

○ **Overall Reaction:**



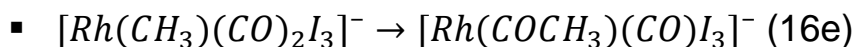
● **Key Features:**

- **Catalyst System:** The active catalyst is a rhodium complex, specifically cis-dicarbonyl diiodorhodate(I) anion ( $[\text{Rh}(\text{CO})_2\text{I}_2]^{-}$ ), in the presence of iodide ions (e.g., from HI, methyl iodide, or an iodide salt).
- **Conditions:** Typically operates at moderate temperatures (150-200°C) and pressures (30-60 atm).
- **High Selectivity and Yield:** The process is highly selective for acetic acid, with yields often exceeding 99%.

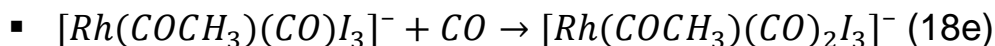
● **Mechanism (Catalytic Cycle):**

- y. **Formation of Active Catalyst:** The active catalytic species is the 16-electron  $[\text{Rh}(\text{CO})_2\text{I}_2]^{-}$  complex. This is formed in situ from a rhodium precursor (e.g.,  $\text{RhCl}_3$ ) in the presence of iodide.
- z. **Oxidative Addition of Methyl Iodide:** Methanol is first converted to methyl iodide ( $\text{CH}_3\text{I}$ ) by reaction with hydrogen iodide (HI) which is present as a promoter. The  $\text{CH}_3\text{I}$  then undergoes oxidative addition to the  $\text{Rh(I)}$  catalyst. This increases the oxidation state of rhodium from +1 to +3 and its coordination number by two.
  - $[\text{Rh}(\text{CO})_2\text{I}_2]^{-} + \text{CH}_3\text{I} \rightarrow [\text{Rh}(\text{CH}_3)(\text{CO})_2\text{I}_3]^{-}$  (18e)
- aa. **Migratory Insertion (Methyl Migration/CO Insertion):**  
The methyl group migrates from rhodium to a coordinated

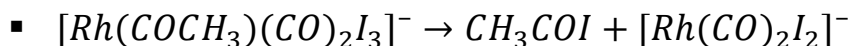
carbonyl ligand, forming an acyl group (acetyl,  $\text{CH}_3\text{CO}$ ). This creates a vacant coordination site on the rhodium.



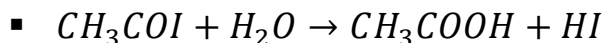
bb. **CO Coordination:** A new molecule of carbon monoxide coordinates to the vacant site on the rhodium center.



cc. **Reductive Elimination of Acetyl Iodide:** The acetyl group ( $\text{CH}_3\text{CO}$ ) and an iodide ligand reductively eliminate from the rhodium(III) complex, forming acetyl iodide ( $\text{CH}_3\text{COI}$ ) and regenerating the  $\text{Rh(I)}$  catalyst ( $\text{[Rh(CO)}_2\text{I}_2\text{]}^-$ ).



dd. **Hydrolysis of Acetyl Iodide:** The acetyl iodide then reacts with water (present in the reaction mixture) to hydrolyze and produce acetic acid and regenerate hydrogen iodide. The regenerated HI re-enters the cycle to convert more methanol to methyl iodide.



- **Summary:** The Monsanto process efficiently converts methanol to acetic acid via a rhodium-catalyzed carbonylation, where methyl iodide acts as a key intermediate for oxidative addition and subsequent migratory insertion.

(c) Using the 18-electron rule as a guide, find the number of metal-metal bonds in  $\text{Fe}_3(\text{CO})_{12}$ , and the charge on the species  $\text{[Co(CO)}_4\text{]}^x$ .

- **(i) Number of metal-metal bonds in  $\text{Fe}_3(\text{CO})_{12}$ :**
  - **Step 1: Calculate the total valence electrons (TVE) for the cluster.**
    - Fe is in Group 8, so 8 valence electrons per Fe atom.



- CO is a 2-electron donor ligand.
- $TVE = (3 * 8) + (12 * 2) = 24 + 24 = 48$  electrons.
- **Step 2: Calculate the number of electrons required for all metals to obey the 18-electron rule.**
  - For 3 Fe atoms, the ideal electron count =  $3 * 18 = 54$  electrons.
- **Step 3: Calculate the number of electrons involved in metal-metal bonding.**
  - Electrons involved in M-M bonding = (Ideal electrons) - (Actual TVE)
  - Electrons involved in M-M bonding =  $54 - 48 = 6$  electrons.
- **Step 4: Determine the number of M-M bonds.**
  - Each metal-metal single bond contributes 2 electrons.
  - Number of M-M bonds = (Electrons involved in M-M bonding) / 2
  - Number of M-M bonds =  $6 / 2 = 3$  metal-metal bonds.
- **Conclusion:** There are **3 metal-metal bonds** in  $Fe_3(CO)_{12}$ .  
(This is consistent with its triangular structure with one bridging CO and two terminal COs per Fe, forming three Fe-Fe single bonds).
- **(ii) Charge on the species  $[Co(CO)_4]^x$ :**
  - **Step 1: Assume the complex obeys the 18-electron rule.**
  - **Step 2: Count valence electrons contributed by Co and CO.**
    - Co is in Group 9, so 9 valence electrons.
    - CO is a 2-electron donor, so  $4 * 2 = 8$  electrons.

- **Step 3: Set up the equation for the 18-electron rule.**
  - Metal electrons + Ligand electrons + (or -) Charge = 18
  - $9 + 8 + x = 18$
- **Step 4: Solve for x (the charge).**
  - $17 + x = 18$
  - $x = 18 - 17$
  - $x = +1$
- **Correction:** For  $[\text{Co}(\text{CO})_4]^x$ , if Co is +1, then it's a 16e complex. The question is asking to find the charge for it to obey the 18e rule.
- **Re-evaluating the charge based on 18e rule:**
  - Co (Group 9) = 9 valence electrons.
  - 4 CO ligands =  $4 * 2 = 8$  electrons.
  - Total electrons without charge =  $9 + 8 = 17$  electrons.
  - To obey the 18-electron rule, the complex needs 1 more electron. This means it must have a negative charge of 1.
  - So,  $17 + (\text{charge}) = 18 \Rightarrow \text{charge} = -1$ .
- **Conclusion:** The charge on the species  $[\text{Co}(\text{CO})_4]^x$  is **-1**. (This is the stable tetracarbonylcobaltate(I) anion,  $[\text{Co}(\text{CO})_4]^-$ ).

5. (a) (i) Give reasons  $\text{Fe}(\text{CO})_5$  is known while  $\text{Fe}(\text{CO})_6$  is not.

- **$\text{Fe}(\text{CO})_5$  (Iron Pentacarbonyl):**
  - Iron (Fe) is a Group 8 metal.
  - In  $\text{Fe}(\text{CO})_5$ , Fe is in the 0 oxidation state.
  - Electron count using the 18-electron rule:

- Valence electrons from Fe = 8
  - Electrons from 5 CO ligands =  $5 * 2 = 10$
  - **Total electrons =  $8 + 10 = 18$  electrons.**
  - According to the 18-electron rule, compounds with 18 valence electrons are highly stable.  $\text{Fe}(\text{CO})_5$  perfectly satisfies the 18-electron rule, which contributes to its stability and existence.
  - **$\text{Fe}(\text{CO})_6$  (Hypothetical Iron Hexacarbonyl):**
    - If  $\text{Fe}(\text{CO})_6$  were to exist, Fe would still be in the 0 oxidation state.
    - Electron count using the 18-electron rule:
      - Valence electrons from Fe = 8
      - Electrons from 6 CO ligands =  $6 * 2 = 12$
      - **Total electrons =  $8 + 12 = 20$  electrons.**
    - A 20-electron complex is generally unstable because it violates the 18-electron rule. The 18-electron rule predicts stability for transition metal complexes, analogous to the octet rule for main group elements. Having more than 18 electrons would mean filling higher energy antibonding orbitals, leading to destabilization.
  - **Conclusion:**  $\text{Fe}(\text{CO})_5$  exists and is stable because it obeys the 18-electron rule.  $\text{Fe}(\text{CO})_6$  does not exist (or would be extremely unstable) because it would have 20 valence electrons, violating the 18-electron rule and destabilizing the complex.
- (a) (ii) Explain the structure and hybridization in Potassium trisoxalatoferrate(III).
- **Compound:** Potassium trisoxalatoferrate(III)
  - **Formula:**  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$

- **Central Metal Ion:**  $\text{Fe}^{3+}$  (Iron in +3 oxidation state)
- **Ligand:** Oxalate ion ( $\text{C}_2\text{O}_4^{2-}$ )
  - The oxalate ion is a bidentate ligand, meaning it can form two coordinate bonds with the central metal ion. It coordinates through two oxygen atoms.
  - Since there are three oxalate ligands, and each is bidentate, the total coordination number of iron is  $3 \times 2 = 6$ .
- **Structure:**
  - With a coordination number of 6, the most common and stable geometry is **octahedral**.
  - The central  $\text{Fe}^{3+}$  ion is at the center, and the six oxygen atoms from the three oxalate ligands occupy the six vertices of an octahedron.
  - Since the oxalate ligand is symmetrical and bidentate, it forms chelate rings (five-membered rings) with the iron atom.
  - The complex exists as **optical isomers (enantiomers)**, denoted as  $\Delta$  and  $\Lambda$ , because the chelate rings introduce chirality.
- **Hybridization:**
  - **$\text{Fe}^{3+}$  electronic configuration:**  $[\text{Ar}]3d^5$
  - **Oxalate as Ligand:** Oxalate is a relatively weak field ligand.
  - **High Spin vs. Low Spin:** For a  $d^5$  ion in an octahedral field, it can be either high spin or low spin, depending on the ligand field strength. Oxalate is typically considered a weak to moderate field ligand.
  - **Most Common State for Fe(III) with Oxalate:** It is generally a **high spin complex**.

- In a high spin octahedral complex, the 3d orbitals are split into  $t_{2g}$  (lower energy) and  $e_g$  (higher energy).
- The five electrons occupy these orbitals according to Hund's rule, filling all five 3d orbitals ( $t_{2g}^3, e_g^2$ ), resulting in 5 unpaired electrons.
- For a high spin complex, the inner 3d orbitals are not used for bonding. Instead, the hybridization involves the outer d-orbitals.
- **Hybridization:**  $sp^3d^2$  (**Outer orbital complex**)
- This hybridization leads to an octahedral geometry.
- **Note on Fe(III) complexes:** Some Fe(III) complexes can be low spin with strong field ligands (e.g., cyanide), leading to  $d^2sp^3$  hybridization. However, with oxalate, it is typically high spin.
- **Summary:**  $K_3[Fe(C_2O_4)_3]$  has an octahedral structure. The central  $Fe^{3+}$  ion is  $sp^3d^2$  hybridized (an outer orbital complex) and is typically high spin. The complex exhibits optical isomerism.

(b) Give a possible mechanism of conversion of synthesis gas to synthetic gasoline by Fischer Tropsch method.

- **Fischer-Tropsch Method:**
  - **Definition:** The Fischer-Tropsch (FT) process is a catalytic chemical reaction that converts a mixture of carbon monoxide (CO) and hydrogen ( $H_2$ ), known as synthesis gas or syngas, into various liquid hydrocarbons (including synthetic gasoline, diesel, and waxes) and oxygenates.
  - **Catalysts:** Typically heterogeneous catalysts based on iron (Fe), cobalt (Co), or ruthenium (Ru), often supported on metal oxides (e.g., alumina, silica).

○ **Overall Reaction (General):**

- $n\text{CO} + (2n+1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{(2n+2)} + n\text{H}_2\text{O}$  (for alkanes)
- $n\text{CO} + 2n\text{H}_2 \rightarrow \text{C}_n\text{H}_{(2n)} + n\text{H}_2\text{O}$  (for alkenes)

● **Possible Mechanism (Surface Polymerization on Catalyst):**

- The mechanism is complex and still debated, involving surface chemistry on heterogeneous catalysts. It is generally believed to proceed via **polymerization of surface methylene ( $-\text{CH}_2-$ ) or formyl ( $-\text{CHO}$ ) species**. Here's a simplified view based on common proposals:

ee. **Adsorption and Dissociation of CO and  $\text{H}_2$ :**

- CO and  $\text{H}_2$  molecules adsorb onto the active sites of the metal catalyst surface.
- CO can dissociate into adsorbed carbon ( $\text{C}_{ads}$ ) and oxygen ( $\text{O}_{ads}$ ) atoms.
- $\text{H}_2$  dissociates into adsorbed hydrogen atoms ( $\text{H}_{ads}$ ).

ff. **Formation of Methylene/Methyl Radicals:**

- Adsorbed carbon atoms are hydrogenated to form methylene ( $-\text{CH}_2$ ) or methyl ( $-\text{CH}_3$ ) surface species. These are key building blocks.
- $\text{C}_{ads} + \text{H}_{ads} \rightarrow \text{CH}_{ads} \quad \text{CH}_{ads} + \text{H}_{ads} \rightarrow \text{CH}_{2,ads} \quad \text{CH}_{2,ads} + \text{H}_{ads} \rightarrow \text{CH}_{3,ads}$

gg. **Chain Initiation:**

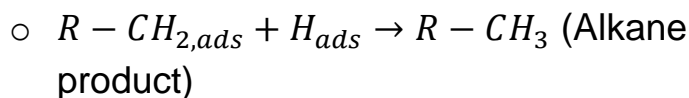
- A growing hydrocarbon chain starts from a surface-bound methyl ( $\text{CH}_3$ ) group or methylene ( $\text{CH}_2$ ) group. This is considered the initiation step.

hh. **Chain Propagation (Carbon-Carbon Bond Formation):**

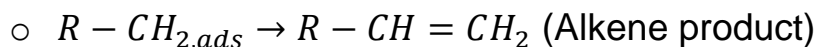
- This is the core of the polymerization. New methylene ( $CH_2$ ) units are generated (likely from CO and  $H_2$ ) and inserted into the existing metal-alkyl bond.
- A common proposal is that a surface-bound alkyl chain ( $R - CH_{2,ads}$ ) reacts with an adsorbed CO to form an acyl intermediate ( $R - CH_2 - CO_{ads}$ ).
- This acyl intermediate is then hydrogenated, leading to the migration of hydrogen, and loss of oxygen (as  $H_2O$  or  $CO_2$ ) eventually forming a longer alkyl chain attached to the metal.
- Another view is that adsorbed  $CH_2$  groups insert into metal-alkyl bonds, lengthening the chain.
- $R - CH_{2,ads} + CH_{2,ads} \rightarrow R - CH_2 - CH_{2,ads}$  (Chain growth)

## ii. Chain Termination:

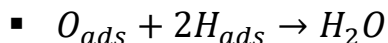
- The growing hydrocarbon chain can detach from the catalyst surface through various termination pathways:
  - **Hydrogenation:** The surface alkyl species picks up an additional hydrogen atom to form an alkane (paraffin).



- **$\beta$ -Hydride Elimination:** The surface alkyl species undergoes  $\beta$ -hydride elimination to form an alkene (olefin).



- jj. **Water Formation:** Adsorbed oxygen from CO dissociation reacts with hydrogen to form water, which desorbs from the catalyst.



- **Summary:** The Fischer-Tropsch mechanism involves the initial dissociation of CO and H<sub>2</sub>, followed by the formation and propagation of surface methylene or alkyl chains through repeated insertions and hydrogenation steps, leading to the formation of various hydrocarbons depending on the catalyst and conditions.

(c) Which of the following are organometallic compounds and why :

- **Criterion:** An organometallic compound must contain at least one direct chemical bond between a carbon atom of an organic group and a metal atom.

(i) (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Zn

- **Is it organometallic?** Yes.
- **Reason:** It contains a direct covalent bond between carbon atoms of the ethyl groups and the zinc (Zn) metal atom. Zinc is a metal.

(ii) Ti(OEt)<sub>4</sub>

- **Is it organometallic?** No.
- **Reason:** Titanium (Ti) is a metal, but the ethoxy groups (–OEt or –OC<sub>2</sub>H<sub>5</sub>) are bonded to titanium through oxygen atoms (Ti–O–C<sub>2</sub>H<sub>5</sub>), not directly through carbon atoms. Therefore, it is a metal alkoxide, not an organometallic compound.

(iii) CH<sub>3</sub>MgBr

- **Is it organometallic?** Yes.
- **Reason:** It is a Grignard reagent, which contains a direct bond between the carbon atom of the methyl group and the magnesium (Mg) metal atom. Magnesium is a metal.

(iv) (η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>Cr



- **Is it organometallic?** Yes.
- **Reason:** Chromium (Cr) is a transition metal. The complex contains a benzene ligand ( $\eta^6\text{-C}_6\text{H}_6$ ) where the chromium atom is directly bonded to all six carbon atoms of the benzene ring through a delocalized pi-electron system. The  $\text{PPh}_3$  ligands are phosphine ligands, which bond through phosphorus, so they are not organometallic. However, the presence of the benzene ligand makes the entire complex organometallic.

(v) LiBr

- **Is it organometallic?** No.
  - **Reason:** Lithium (Li) is a metal, but it is bonded to bromine (Br), which is a halogen, not a carbon atom from an organic group. It is an ionic salt.
6. (a) Draw and explain the structure of the following metal carbonyls using VBT.
- **Note:** Valence Bond Theory (VBT) is less commonly used to explain the intricate bonding in metal carbonyls, especially pi-backbonding. Molecular Orbital Theory (MOT) provides a more comprehensive explanation. However, if VBT is specifically requested for structure and hybridization, we can explain it in terms of formal coordination and geometry.

(i)  $\text{Co}_2(\text{CO})_8$

- **Structure:** Dicobalt octacarbonyl
  - It exists in two isomeric forms:
    - Non-bridged (or Open-chain) Form:** This form predominates in solution and at higher temperatures.
      - It consists of two cobalt atoms linked by a single Co-Co bond.

- Each cobalt atom has four terminal CO ligands.
- Structure:  $(CO)_4Co - Co(CO)_4$  (linear arrangement of two Co atoms with terminal COs).
- Hybridization (VBT): Each cobalt atom can be considered as  $sp^3$  hybridized (tetrahedral geometry around each Co, but overall structure is complex).

ii. **Bridged Form:** This form predominates in the solid state.

- It consists of two cobalt atoms bridged by two carbonyl ligands. There is also a direct Co-Co bond.
- Each cobalt atom has three terminal CO ligands and shares two bridging CO ligands.
- Structure: Two Co atoms with a direct bond. Two COs bridge the two Co atoms. Three terminal COs are attached to each Co.
- **Bridging CO:** The CO ligand bridges between two metal centers, with its carbon atom simultaneously bonded to both metals. The oxygen atom typically points away from the metal-metal bond.
- **Overall Geometry around each Co (approximate, considering bridging):** Each cobalt can be considered to have a distorted trigonal bipyramidal or square pyramidal geometry, achieving 18-electron rule.

• **Explanation (VBT based on idealized structure):**

○ **Electron Count (18-electron rule for each Co):**

- Total valence electrons for  $Co_2(CO)_8 = (2 * 9) + (8 * 2) = 18 + 16 = 34$  electrons.

- For a M-M bond, subtract 2 electrons:  $34 - 2 = 32$  electrons.
- Electrons per Co =  $32 / 2 = 16$  electrons (if no bridging).
- This indicates that a simple non-bridged structure would not obey 18e rule without some additional interaction.
- **Re-evaluating with Bridging (Solid State Structure):**
  - Each Co is bonded to another Co (1 electron from Co-Co bond).
  - Each Co has 3 terminal COs ( $3 * 2 = 6$  electrons).
  - Each Co is bonded to 2 bridging COs. Bridging COs typically donate 1 electron to each metal. So,  $2 * 1 = 2$  electrons.
  - Total electrons for each Co = 9 (from Co) + 1 (from Co-Co) + 6 (from 3 terminal COs) + 2 (from 2 bridging COs) = 18 electrons.
  - This makes the bridged structure stable.
- **Hybridization (simplified for 18e complex):**
  - For an 18-electron complex with 6 bonds (3 terminal CO, 2 bridging CO, 1 Co-Co), the geometry around each Co atom is distorted octahedral. The hybridization would involve d-orbitals, often approximated as  $d^2sp^3$ .

(ii)  $\text{Cr}(\text{CO})_6$ 

- **Structure:** Chromium hexacarbonyl
  - **Geometry:** The complex has an **octahedral** geometry.
  - The central chromium (Cr) atom is located at the center, and the six carbon monoxide (CO) ligands are arranged

symmetrically around it, pointing to the six vertices of an octahedron.

- **Explanation (using VBT concepts):**

- **Electron Count (18-electron rule):**

- Chromium (Cr) is a Group 6 metal, so it contributes 6 valence electrons.
    - Each CO ligand is a 2-electron donor, so 6 CO ligands contribute  $6 \times 2 = 12$  electrons.
    - **Total electrons =  $6 + 12 = 18$  electrons.**

- **Stability:** Since  $\text{Cr}(\text{CO})_6$  has 18 valence electrons, it is a highly stable complex, obeying the 18-electron rule.

- **Hybridization:**

- For an octahedral geometry and to accommodate 18 electrons, the chromium atom undergoes  $d^2sp^3$  **hybridization**.
    - This hybridization involves two (n-1)d orbitals, one ns orbital, and three np orbitals. These six hybrid orbitals overlap with the lone pair orbitals of the six carbon monoxide ligands to form six sigma ( $\text{Cr} \leftarrow \text{CO}$ ) coordinate bonds.
    - In addition to these sigma bonds, there is significant pi-backbonding from the filled d-orbitals of Cr to the empty  $\pi^*$  orbitals of the CO ligands, further strengthening the Cr-C bond (though pi-bonding is not explicitly part of basic VBT hybridization diagrams).

- **Conclusion:**  $\text{Cr}(\text{CO})_6$  is an 18-electron, highly stable octahedral complex with Cr undergoing  $d^2sp^3$  hybridization.

(b) Draw and explain the structure and bonding of metal with alkyl and allyl group.

• **Structure and Bonding of Metal with Alkyl Group (e.g., Methyl,  $R = CH_3$ ):**

- **Structure:** Alkyl ligands typically bind to metals as **sigma ( $\sigma$ ) ligands**. This means they form a classical two-electron, two-center single bond between the metal atom and one carbon atom of the alkyl group.
- **Bonding:**
  - The bonding involves the overlap of an  $sp^3$  hybrid orbital of the alkyl carbon with a suitable empty hybrid or d-orbital on the metal atom.
  - The alkyl group acts as a **1-electron donor** in the neutral ligand counting method, or a **2-electron donor** in the electron pair donation method (where it's treated as  $R^-$  anion bonding to  $M^+$ ).
  - The M-C bond in metal alkyls is generally polar, with electron density usually shifted towards the carbon (due to carbon being more electronegative than many metals), making the carbon somewhat nucleophilic.
- **Example:** In  $Ti(CH_3)_4$  (Tetramethyltitanium), each methyl group forms a sigma bond with the central titanium atom, resulting in a tetrahedral geometry around titanium.
- **Draw:**  $R-M$  (where R is an alkyl chain, and the bond is a single bond).

• **Structure and Bonding of Metal with Allyl Group ( $\eta^1$  and  $\eta^3$ ):**

- The allyl group ( $CH_2 = CH - CH_2$ ) is an interesting ligand because it can bind to a metal in two common ways, exhibiting different hapticities:

### kk. Monohapto ( $\eta^1$ ) Allyl:

- **Structure:** In this mode, the allyl group binds to the metal via a **single sigma ( $\sigma$ ) bond** between one of its terminal carbon atoms (an  $sp^3$  hybridized carbon) and the metal. The double bond remains uncoordinated or coordinated as a separate  $\pi$ -complex.
- **Bonding:** It acts as a **1-electron donor** (or 2-electron donor if treated as allyl anion with 2e from C-M bond). The carbon atom is typically  $sp^3$  hybridized, and the bonding is similar to an alkyl group.
- **Example:** ( $\eta^1$ -C<sub>3</sub>H<sub>5</sub>)Mn(CO)<sub>5</sub> (Monohapto allyl manganese pentacarbonyl).
- **Draw:** M - CH<sub>2</sub>-CH=CH<sub>2</sub> (showing the single bond to one CH<sub>2</sub> group).

### II. Trihapto ( $\eta^3$ ) Allyl:

- **Structure:** In this more common bonding mode, all **three carbon atoms** of the allyl group are simultaneously bonded to the metal atom. The allyl group is treated as a delocalized three-carbon  $\pi$ -system. The carbon atoms are all considered  $sp^2$  hybridized, forming a bent or U-shaped structure.
- **Bonding:** The bonding involves the overlap of the delocalized  $\pi$ -molecular orbitals of the allyl system (specifically, the lowest energy bonding orbital and the non-bonding orbital) with suitable d-orbitals on the metal. This is a form of  **$\pi$ -complexation** involving a three-electron donation (neutral ligand method) or a four-electron donation (electron pair method, treating it as an allyl anion).

- **Example:**  $(\eta^3\text{-C}_3\text{H}_5)\text{Co}(\text{CO})_3$  (Trihapto allyl cobalt tricarbonyl).
- **Draw:** A "U" shaped allyl group with the metal atom typically above or below the plane of the carbons, indicating interaction with all three carbons. (Often drawn as an arc connecting the three carbons with the metal atom in the center).

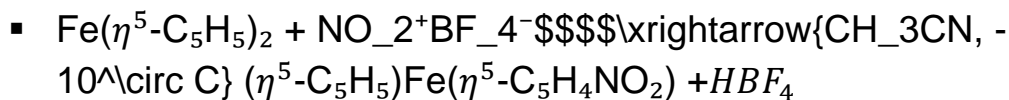
(c) (i) Explain why direct nitration of ferrocene is not possible? How can you get nitro derivative of ferrocene?

• **Why Direct Nitration is Not Possible:**

- **Oxidation by Nitrating Agents:** Direct nitration of ferrocene using standard nitrating mixtures (e.g., concentrated nitric acid and sulfuric acid) is not possible because ferrocene is readily oxidized by these strong oxidizing agents.
- Ferrocene is an electron-rich organometallic compound, and its iron center is easily oxidized from Fe(II) to Fe(III). Strong nitrating agents act as oxidizing agents, causing the ferrocene to be oxidized to the ferrocenium cation ( $\text{Fe}(\text{C}_5\text{H}_5)_2^+$ ), which is not susceptible to electrophilic aromatic substitution. Instead of nitration, oxidation occurs, often leading to decomposition.

• **How to Get Nitro Derivative of Ferrocene:**

- To synthesize nitroferrocene, an indirect method must be used that avoids direct contact with strong oxidizing nitrating agents. One common method involves the reaction with a nitronium salt or a milder nitrating reagent.
- **Method:** Reaction of ferrocene with **nitronium tetrafluoroborate** ( $\text{NO}_2^+\text{BF}_4^-$ ) in acetonitrile.
- **Reaction:**



- **Explanation:** Nitronium tetrafluoroborate provides a source of the nitronium ion ( $\text{NO}_2^+$ ), which is the electrophile for nitration, but it is not as strong an oxidizing agent as nitric acid. The reaction is typically carried out at low temperatures to minimize side reactions and oxidation. This method allows for the electrophilic substitution of a hydrogen atom on the cyclopentadienyl ring by a nitro group without oxidizing the iron center.

(c) (ii) Explain the following term used in a catalytic process: Catalyst Poison, Catalyst Promotor.

- **Catalyst Poison:**

- **Definition:** A catalyst poison is a substance that inhibits or reduces the activity of a catalyst. It does this by binding strongly to the active sites on the catalyst surface, preventing the reactant molecules from adsorbing and reacting.
- **Mechanism of Action:**
  - **Strong Adsorption:** Poisons typically form very strong bonds (often covalent or coordination bonds) with the active sites of the catalyst.
  - **Blocking Active Sites:** This strong adsorption blocks the active sites, making them unavailable for the reactants.
  - **Altering Catalyst Structure:** In some cases, poisons can chemically alter the structure of the catalyst, leading to irreversible deactivation.
- **Examples:**
  - **Sulfur compounds (e.g.,  $\text{H}_2\text{S}$ , thiols):** Common poisons for metal catalysts (like Ni, Pt, Pd) used in hydrogenation



and reforming processes. They bind strongly to the metal surface.

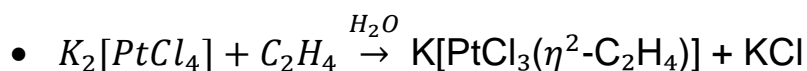
- **Carbon monoxide (CO):** A poison for many transition metal catalysts in reactions other than carbonylations (e.g., in ammonia synthesis or fuel cells).
- **Lead and heavy metals:** Poisons for catalytic converters in automobiles.
- **Consequences:** Reduced reaction rate, lower yield, increased production costs.
- **Catalyst Promotor:**
  - **Definition:** A catalyst promotor is a substance that, when added in small amounts to a catalyst, enhances its activity, selectivity, or stability, but is not itself a catalyst for the main reaction. Promoters do not directly participate in the reaction as catalysts do.
  - **Mechanism of Action:** Promoters work by:
    - **Modifying Catalyst Structure:** They can alter the electronic or geometric properties of the active sites, making them more effective.
    - **Improving Dispersion:** They might help disperse the active catalyst particles more evenly on a support material, increasing the number of accessible active sites.
    - **Stabilizing the Catalyst:** They can prevent sintering (agglomeration) of catalyst particles at high temperatures, thus maintaining surface area.
    - **Facilitating Adsorption/Desorption:** They might enhance the adsorption of reactants or the desorption of products.
  - **Examples:**

- **Alumina ( $Al_2O_3$ ) in Haber-Bosch process:** While the main catalyst is iron, the addition of small amounts of alumina acts as a structural promoter, preventing the sintering of iron particles and maintaining their surface area.
  - **Potassium oxide ( $K_2O$ ) in Haber-Bosch process:** Acts as an electronic promoter, increasing the electron density on the iron catalyst, which enhances the adsorption of nitrogen.
  - **Manganese oxides:** Can promote oxidation reactions catalyzed by transition metals.
  - **Consequences:** Increased reaction efficiency, longer catalyst lifespan, better product yield, improved selectivity towards desired products.
7. (a) Give any three methods of synthesis of metal alkene complexes. What happens when a metal alkene complex  $[CpW(CO)_3(\pi-C_2H_4)]^+$  reacts with triphenylphosphine.

• **Three Methods of Synthesis of Metal Alkene Complexes:**

mm. **Direct Reaction of Alkene with Metal Salt/Complex:**

- **Method:** This is the most straightforward method, involving the direct coordination of an alkene to a suitable metal center, often an electrophilic metal complex or a metal salt.
- **Example:**
  - Reaction of potassium tetrachloroplatinate(II) with ethene to form Zeise's salt.



nn. **Reduction of Metal Salts in the Presence of Alkene:**

- **Method:** A metal salt is reduced in the presence of an alkene, where the metal (often in a higher oxidation state) is reduced to a lower oxidation state suitable for alkene coordination.
- **Example:**
  - Reduction of  $Ni(acac)_2$  (nickel(II) acetylacetonate) with an aluminum alkyl (e.g.,  $Al(C_2H_5)_3$ ) in the presence of cyclooctadiene (COD) to form  $Ni(COD)_2$ .
  - $Ni(acac)_2 + 2Al(C_2H_5)_3 + 2COD \rightarrow Ni(COD)_2 + \dots$

oo. **Ligand Substitution Reactions:**

- **Method:** An existing ligand (often CO or another weak ligand) in a metal complex is replaced by an alkene ligand, often facilitated by heat or light.
- **Example:**
  - $Fe(CO)_5 + C_2H_4 \xrightarrow{h\nu} (\eta^2-C_2H_4)Fe(CO)_4 + CO$
- **Reaction of  $[CpW(CO)_3(\pi-C_2H_4)]^+$  with Triphenylphosphine ( $PPh_3$ ):**
  - **Reactants:**
    - Metal alkene complex:  $[CpW(CO)_3(\pi-C_2H_4)]^+$  (Cationic complex of Tungsten with cyclopentadienyl, carbonyls, and ethene).
    - Nucleophile: Triphenylphosphine ( $PPh_3$ ) - a strong electron-pair donor.
  - **Reaction Type:** This is a **nucleophilic attack on the coordinated alkene**. Coordinated alkenes in cationic complexes are often activated towards nucleophilic attack due

to the electron-withdrawing effect of the positively charged metal center.

- **Mechanism:** The triphenylphosphine nucleophilically attacks one of the carbon atoms of the coordinated ethene ligand. This breaks the pi-bond between the ethene and the tungsten, and the ethene becomes an alkyl ligand (specifically, a phosphoethyl group) bonded to the metal via a single sigma bond.
  - **Product:** The tungsten complex will have a sigma-bonded alkyl ligand (containing the phosphine group) instead of the pi-bonded ethene.
  - **Reaction:**
    - $[\text{CpW}(\text{CO})_3(\pi\text{-C}_2\text{H}_4)]^+ + \text{PPh}_3 \rightarrow [\text{CpW}(\text{CO})_3(\sigma\text{-CH}_2\text{CH}_2\text{PPh}_3)]^+$
  - **Name of Product:** Cyclopentadienyl(tricarbonyl)(2-(triphenylphosphonio)ethyl)tungsten(II) cation.
- (b) Explain the following : (i) Migratory insertion of Carbonyl.
- **Definition:** Migratory insertion (also known as 1,1-insertion or carbonyl insertion) is a fundamental reaction in organometallic chemistry where a ligand (typically an alkyl or aryl group, R) migrates from the metal center to a coordinated carbonyl (CO) ligand. This results in the formation of an acyl (RCO) ligand and simultaneously creates a vacant coordination site on the metal.
  - **Process:**

pp.      **Prerequisite:** The metal complex must have an alkyl/aryl ligand and a carbonyl ligand coordinated to the same metal center. It must also have a vacant coordination site, or one must be created (e.g., by dissociation of another ligand or by the migration itself).

- qq. **Ligand Migration:** The alkyl/aryl group (R) moves from its direct bond with the metal and forms a new bond with the carbon atom of the adjacent coordinated CO ligand.
- rr. **Vacant Site Creation:** As the R group moves, the original coordination site it occupied becomes vacant.
- **General Reaction:**
    - $R-M(CO)L_n \rightarrow (RCO)-M(L_n)(\text{vacant site})$
  - **Mechanism (Two common views):**
    - **Alkyl Migration (More commonly accepted for CO insertion):** The alkyl group actually migrates to the coordinated CO ligand. This is usually concerted.
    - **CO Migration (less common for CO):** The CO ligand moves towards the alkyl group.
  - **Significance:**
    - **C-C Bond Formation:** Migratory insertion is a crucial step in many industrially important catalytic processes because it forms a new carbon-carbon bond (between the alkyl carbon and the carbonyl carbon).
    - **Examples in Catalysis:**
      - **Hydroformylation (Oxo Process):** The alkyl group generated from alkene hydroformylation migrates to a CO, forming an acyl intermediate that is then hydrogenated to an aldehyde.
      - **Monsanto and Cativa Processes for Acetic Acid Synthesis:** The methyl group migrates to a CO ligand, forming an acetyl group, which eventually leads to acetic acid.

- **Vacant Site Generation:** The vacant site created by the migration is often essential for the next step in the catalytic cycle, allowing another substrate molecule to coordinate to the metal.

(ii) The Carbonyls of 4d metals are less stable than the corresponding carbonyl of 3d metals.

- **General Trend:** This statement is generally incorrect or at least misleading in many contexts of transition metal chemistry. **For most organometallic complexes (including carbonyls), the stability usually increases down a group (i.e., 4d and 5d metals often form more stable complexes than their 3d counterparts).**
- **Re-evaluating the Question/Common Misconception:**
  - Perhaps the question refers to thermal stability in some specific conditions or kinetic stability against substitution.
  - **Common Observation:** 4d and 5d transition metals (e.g., Ru, Os, Rh, Ir, Pd, Pt) generally form **more stable** metal-carbon and metal-ligand bonds compared to 3d metals (e.g., Fe, Co, Ni). This is often attributed to:
    - **Larger Orbitals:** 4d and 5d orbitals are more diffuse and extended in space, allowing for better overlap with ligand orbitals, leading to stronger sigma bonds.
    - **More Efficient Pi-Backbonding:** The 4d and 5d metals have more accessible and extended d-orbitals, which can engage in stronger pi-backbonding with pi-acceptor ligands like CO. Stronger pi-backbonding leads to stronger M-C bonds and overall more stable complexes.
    - **Relativistic Effects:** For 5d metals, relativistic effects can further stabilize complexes.
- **Possible Exception/Context where 3d might seem "more stable" or more reactive for synthesis:**

- **Kinetic Lability:** 3d metal carbonyls might be more kinetically labile (undergo ligand exchange more easily) than 4d/5d counterparts, but this doesn't mean less thermodynamic stability. Some 3d carbonyls (like  $\text{Fe}(\text{CO})_5$ ) are volatile liquids at room temperature, while their 4d/5d analogues might be solids. This volatility might be perceived as less "stability" in terms of handling.
- **Accessibility:** 3d metals are cheaper and more abundant, so their carbonyl chemistry might be more extensively studied and applied in some areas.
- **Correction:** Based on standard organometallic principles, metal-ligand bonds generally strengthen and complexes become more thermodynamically stable down a group. Therefore, **carbonyls of 4d metals (and 5d metals) are typically MORE stable than the corresponding 3d metals.**
- **If the question implies a different type of "stability" or a specific example, it needs clarification.** Without further context, the premise is generally contradicted by common chemical principles.

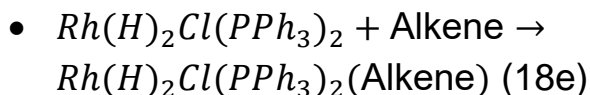
(c) What is Wilkinson's Catalyst? Explain its structure and how it is an effective homogenous catalyst for hydrogenation of alkenes.

- **Wilkinson's Catalyst:**
  - **Definition:** Wilkinson's catalyst is a well-known homogeneous catalyst used for the hydrogenation of alkenes and alkynes. Its full chemical name is **chlorotris(triphenylphosphine)rhodium(I).**
  - **Formula:**  $\text{RhCl}(\text{PPh}_3)_3$  (where  $\text{PPh}_3$  is triphenylphosphine)
- **Structure:**
  - The rhodium (Rh) atom is at the center.

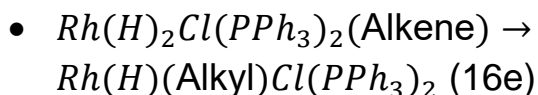
- It is coordinated to three bulky triphenylphosphine ( $\text{PPh}_3$ ) ligands and one chloride ( $\text{Cl}$ ) ligand.
- The rhodium atom is in the **+1 oxidation state**.
- The complex typically adopts a **square planar geometry**.
- **Electronic Configuration:**  $\text{Rh(I)}$  is a  $d^8$  metal ion. In a square planar field,  $d^8$  complexes are often 16-electron species and kinetically stable.
- **How it is an Effective Homogeneous Catalyst for Hydrogenation of Alkenes:**
  - Wilkinson's catalyst is highly effective due to its ability to undergo facile oxidative addition and reductive elimination steps, its solubility in organic solvents (homogeneous catalysis), and its high selectivity.
  - **Catalytic Cycle (Simplified):**
    - i. **Ligand Dissociation (Formation of Active Species):**  
The 16-electron  $\text{RhCl(PPh}_3)_3$  complex is in equilibrium with a 14-electron species,  $\text{RhCl(PPh}_3)_2$ , formed by the dissociation of one  $\text{PPh}_3$  ligand. This 14-electron species is the highly active catalyst.
      - $\text{RhCl(PPh}_3)_3 \rightleftharpoons \text{RhCl(PPh}_3)_2 + \text{PPh}_3$
      - 2. **Oxidative Addition of Hydrogen ( $\text{H}_2$ ):** The 14-electron  $\text{RhCl(PPh}_3)_2$  complex undergoes oxidative addition with hydrogen gas ( $\text{H}_2$ ). This adds two hydride ligands to the rhodium, increasing its oxidation state from +1 to +3 and its coordination number from 3 to 5.
      - $\text{RhCl(PPh}_3)_2 + \text{H}_2 \rightarrow \text{Rh(H)}_2\text{Cl(PPh}_3)_2$  (16e, square pyramidal or trigonal bipyramidal)



- ii. **Alkene Coordination:** The alkene to be hydrogenated coordinates to the rhodium complex. This is an associative step, leading to an 18-electron species.

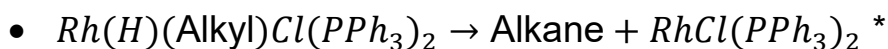


- iii. **Migratory Insertion (Hydride Migration):** One of the hydride ligands migrates from the rhodium to one of the alkene carbon atoms, forming a sigma-bonded alkyl group and creating a vacant coordination site.



- iv. **Second Migratory Insertion/Reductive Elimination:**

The second hydride ligand then migrates to the alkyl group, or the alkyl group undergoes reductive elimination with the second hydride, leading to the formation of the alkane product. This also regenerates the 14-electron  $\text{RhCl(PPh}_3)_2$  species (after a  $\text{PPh}_3$  re-associates to form  $\text{RhCl(PPh}_3)_3$ ).



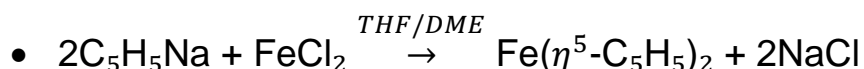
**Effectiveness:** Its effectiveness comes from the facile nature of the oxidative addition and reductive elimination steps, which are characteristic of  $d^8$  square planar complexes. The bulky phosphine ligands also play a role in directing the stereochemistry and selectivity of the hydrogenation.

8. (a) Give two methods of synthesis of ferrocene and how does it react with the following :

- **Two Methods of Synthesis of Ferrocene:**

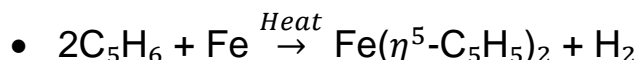
**ss. From Cyclopentadienyl Sodium and Iron(II) Chloride (Most Common Method):**

- **Method:** This involves the reaction of cyclopentadienyl sodium (prepared from cyclopentadiene and sodium metal/hydride) with anhydrous iron(II) chloride. This is a very common and high-yielding method.
- **Reaction:**



**tt. From Cyclopentadiene and Iron Powder/Reduced Iron (Direct Method, Less Common Industrially):**

- **Method:** Cyclopentadiene can react directly with finely divided or freshly reduced iron, often under high temperature (e.g., 300°C) and sometimes with a hydrogen atmosphere. This method is less common for laboratory synthesis due to harsher conditions but represents a direct combination.
- **Reaction:**

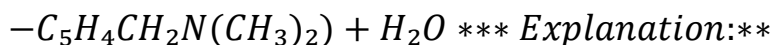
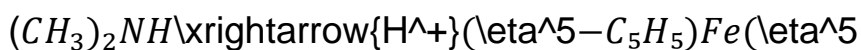
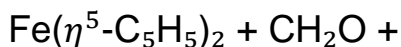


- **Reactions of Ferrocene: (i) Ferrocene with Butyl Lithium (n-BuLi):** \* **Reaction Type:** Metallation (deprotonation). Ferrocene is an electron-rich aromatic system, and its cyclopentadienyl protons are acidic enough to be removed by strong bases like butyllithium. \* **Product:** Lithioferrocene (or 1,1'-dilithioferrocene with excess n-BuLi). \* **Reaction (Monolithiation):** \*  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2 + \text{n-BuLi} \rightarrow (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Li}) + \text{n-Butane}$  \* **Reaction (Dilithiation with excess n-BuLi):** \*  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2 + 2\text{n-BuLi} \rightarrow (\eta^5\text{-C}_5\text{H}_4\text{Li})\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Li}) + 2\text{n-Butane}$  \* **Significance:** Lithioferrocene is a versatile intermediate for further functionalization of the ferrocene core (e.g., reaction with electrophiles, carbonylation, etc.).

(ii) **Ferrocene with Formaldehyde and Secondary Amine****(Mannich Reaction):** \* **Reaction Type:** Mannich reaction

(aminomethylation). This is an electrophilic aromatic substitution reaction. \* **Reagents:** Formaldehyde ( $CH_2O$ ) and a secondary amine (e.g., dimethylamine,  $(CH_3)_2NH$ ) in the presence of an acid catalyst (like acetic acid or phosphoric acid). \* **Product:**

Ferrocenyl(dimethylamino)methane (a Mannich base). \* **Reaction:** \*



The formaldehyde and secondary amine react in situ to form an iminium ion ( $R_2N^+=CH_2$ ), which acts as the electrophile and attacks the activated cyclopentadienyl ring of ferrocene.

(b) Predict whether the following obey the EAN rule :

- **EAN Rule (Effective Atomic Number Rule):** A stable organometallic complex often has an effective atomic number (EAN) equal to that of the next noble gas (e.g., 18-electron rule for 3d metals, 36 for Kr, 54 for Xe, 86 for Rn). This means the central metal atom effectively achieves a noble gas electron configuration by counting its own valence electrons plus all electrons donated by the ligands and any charge.

(i)  $[Mn(\eta^2-C_2H_4)(CO)_2]^+$  \* **Metal:** Mn (Manganese) - Group 7, 7 valence electrons. \* **Charge:** +1 (subtract 1 electron). \* **Ligands:** \*  $\eta^2-C_2H_4$  (Ethene): 2-electron donor (pi-bond). \* CO (Carbonyl): 2-electron donor. (There are 2 COs, so  $2 * 2 = 4$  electrons). \* **EAN Calculation:** \* Electrons from Mn = 7 \* Electrons from  $C_2H_4 = 2$  \* Electrons from 2 CO = 4 \* Adjust for charge = -1 (since it's a cation) \* **Total EAN = 7 + 2 + 4 - 1 = 12 electrons.** \* **Prediction: Does NOT obey the EAN rule.** (It has 12 electrons, far from 18). This complex would likely be highly reactive or unstable, or the formula is incorrect for a stable species. (A common stable Mn complex is  $[Mn(CO)_5H]$  or  $Mn_2(CO)_{10}$ , both 18e). There might be a typo, e.g., if it was  $Mn(CO)_5$ .

(ii)  $\text{Mn}_2(\text{CO})_{10}$  \* **Metal:** Mn (Manganese) - Group 7, 7 valence electrons. \* **Number of Metals:** 2 \* **Ligands:** 10 COs ( $10 * 2 = 20$  electrons for both Mn, so 10 electrons per Mn if distributed equally). \* **Metal-Metal Bond:** This is a dimer with a single Mn-Mn bond. This bond contributes 1 electron to each Mn. \* **EAN Calculation (for each Mn):** \* Electrons from Mn = 7 \* Electrons from 5 terminal CO ligands =  $5 * 2 = 10$  \* Electrons from Mn-Mn bond = 1 (each Mn gets 1 electron from the shared bond) \* **Total EAN per Mn =  $7 + 10 + 1 = 18$  electrons.** \* **Prediction: Obeys the EAN rule.** (Each manganese atom achieves an 18-electron configuration).

(iii)  $[\text{Fe}(\text{CO})_4]^{2-}$  \* **Metal:** Fe (Iron) - Group 8, 8 valence electrons. \* **Charge:** -2 (add 2 electrons). \* **Ligands:** 4 CO ligands ( $4 * 2 = 8$  electrons). \* **EAN Calculation:** \* Electrons from Fe = 8 \* Electrons from 4 CO = 8 \* Adjust for charge = +2 (since it's an anion) \* **Total EAN =  $8 + 8 + 2 = 18$  electrons.** \* **Prediction: Obeys the EAN rule.** (It has 18 electrons and is a stable species).

(iv)  $[\text{Cr}(\text{CO})_3(\text{NO})_2]$  \* **Metal:** Cr (Chromium) - Group 6, 6 valence electrons. \* **Ligands:** \* CO (Carbonyl): 2-electron donor. (3 COs, so  $3 * 2 = 6$  electrons). \* NO (Nitrosyl): Can be a 3-electron donor (linear NO) or 1-electron donor (bent NO). For transition metal carbonyls, it's often a 3e donor. Assuming linear NO (common for 18e complexes). (2 NOs, so  $2 * 3 = 6$  electrons). \* **EAN Calculation:** \* Electrons from Cr = 6 \* Electrons from 3 CO = 6 \* Electrons from 2 NO (as 3e donor) = 6 \* **Total EAN =  $6 + 6 + 6 = 18$  electrons.** \* **Prediction: Obeys the EAN rule.** (Assuming NO is a 3-electron donor).

(v)  $[\text{Co}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_3]$  \* **Metal:** Co (Cobalt) - Group 9, 9 valence electrons. \* **Ligands:** \*  $\eta^3\text{-C}_3\text{H}_5$  (Allyl): A 3-electron donor (neutral ligand method). \* CO (Carbonyl): 2-electron donor. (3 COs, so  $3 * 2 = 6$  electrons). \* **EAN Calculation:** \* Electrons from Co = 9 \* Electrons from  $\eta^3\text{-C}_3\text{H}_5 = 3$  \* Electrons from 3 CO = 6 \* **Total EAN =  $9 + 3 + 6 = 18$  electrons.** \* **Prediction: Obeys the EAN rule.** (It has 18 electrons and is a stable species).

(c) How to synthesized Zeise's salt? Discuss the bonding in Zeise's salt on the basis of Dewar-Chatt-Duncanson model.

- **Synthesis of Zeise's Salt:**

- **Compound:** Potassium trichloro( $\eta^2$ -ethene)platinate(II) ( $K[PtCl_3(\eta^2-C_2H_4)]$ )
- **Method:** Zeise's salt can be synthesized by bubbling ethene gas ( $C_2H_4$ ) through an aqueous or alcoholic solution of potassium tetrachloroplatinate(II) ( $K_2[PtCl_4]$ ).
- **Reaction:**
  - $$K_2[PtCl_4] + C_2H_4 + H_2O \rightarrow K[PtCl_3(\eta^2 - C_2H_4)] \cdot H_2O + KCl$$
- **Conditions:** The reaction is typically carried out at room temperature. The complex often crystallizes as a hydrate.

- **Bonding in Zeise's Salt on the Basis of Dewar-Chatt-Duncanson Model:**

- The Dewar-Chatt-Duncanson (DCD) model is the widely accepted model for explaining the bonding in metal-alkene (and metal-alkyne) complexes. It describes a synergic (two-way) bonding interaction between the metal and the alkene.
- **Components of Bonding:**
  - i. **Sigma ( $\sigma$ ) Donation (Ligand  $\rightarrow$  Metal):**
  - The ethene molecule acts as a Lewis base. It donates electron density from its filled pi ( $\pi$ ) bonding orbital to an empty  $d_{x^2-y^2}$  (or other suitable empty) orbital of the platinum(II) ion.
  - This forms a sigma-type coordinate bond, oriented perpendicular to the Pt-Cl plane.

- This donation slightly weakens the C=C bond of the alkene as electrons are removed from its bonding orbital.

ii. **Pi ( $\pi$ ) Backdonation (Metal  $\rightarrow$  Ligand):**

- The platinum(II) ion acts as a Lewis base. It donates electron density from a filled d-orbital (specifically, the  $d_{xz}$  or  $d_{yz}$  orbital, which has the correct symmetry) into the empty pi antibonding ( $\pi^*$ ) orbital of the ethene molecule.
- This forms a pi-type backbond, oriented perpendicular to the sigma bond, and parallel to the original C=C bond.
- This backdonation strengthens the M-C bond and significantly weakens the C=C bond of the alkene (due to electrons going into an antibonding orbital), effectively increasing its bond length and decreasing its stretching frequency.

○ **Consequences of DCD Bonding:**

- **Shortened M-C bond:** Both sigma donation and pi backdonation contribute to strengthening the metal-carbon bond(s).
- **Lengthened C=C bond:** The pi backdonation into the antibonding orbital of ethene reduces its bond order, causing the C=C bond to lengthen (approaching a single bond character). This is experimentally observed as an increase in C=C bond length in the complex compared to free ethene.
- **Planar to Non-Planar Alkene:** The carbon atoms of the ethene molecule in the complex are slightly bent away from the metal, changing from  $sp^2$  hybridization

toward  $sp^3$  character, particularly due to the backbonding. The hydrogens of the ethene are bent back from the metal.

- **Stability:** The synergic nature of the DCD model explains the unexpected stability of transition metal-alkene complexes, where both components reinforce each other.

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