

ORGANOMETALLIC COMPOUNDS

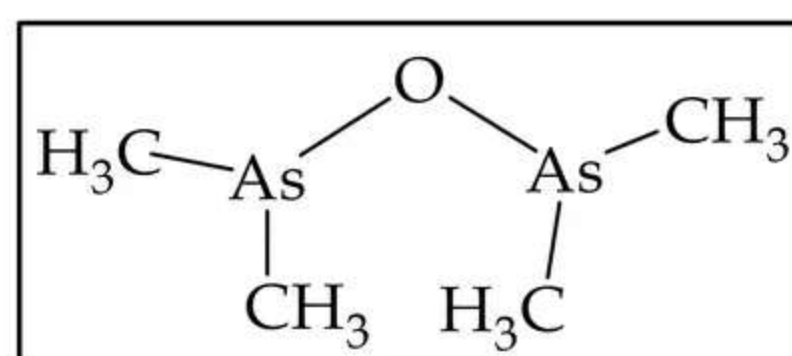
SEM-IV_PAPER-IV: UNIT-I

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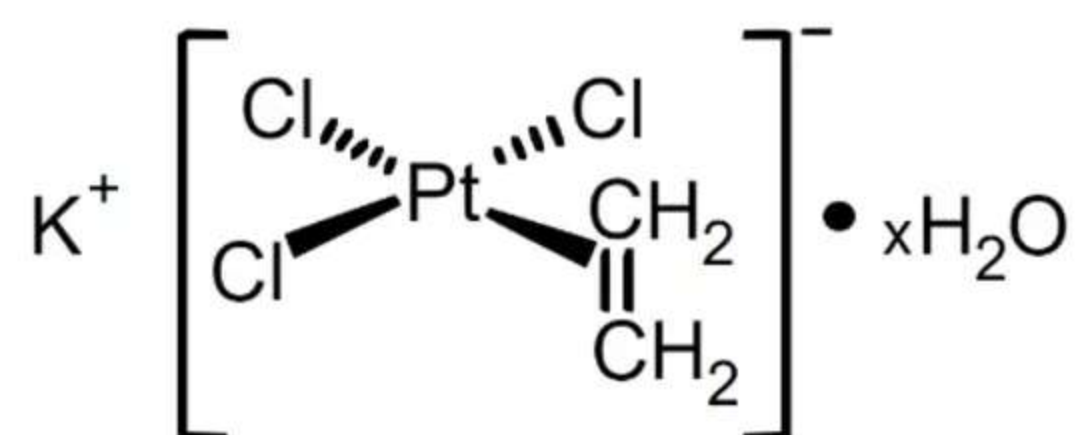
Definition and classification of organometallic compounds on the basis of bond type, Concept of hapticity of organic ligands. Metal Carbonyls: 18 electron rule, electron count of mononuclear, poly nuclear and substituted metal carbonyls of 3d series. General methods of preparation of mono and binuclear carbonyls of 3d series.

Introduction:

- An organometallic compound is the one that possesses a metal-carbon bond.
- In (1760) a French Chemist, Louis Claude Cadet of Paris military pharmacy, prepared first organometallic compound (even though arsenic is not a true metal), when he was working on invisible inks based on cobalt salt solutions containing arsenic, $[(CH_3)_2As]_2O$ (Cacodyl oxide), often called Cadet's fuming liquid.



- The **first olefin complex** synthesized in (1827) by William Christopher Zeise (Danish Organic chemist), who obtained yellow needle-like crystals after refluxing a mixture of $PtCl_4$ and $PtCl_2$ in ethanol, followed by addition of KCl solution. It is an ionic compound of formula $K[Pt(C_2H_4)Cl_3] \cdot H_2O$ [Potassium trichloro(ethene)platinate(II)].

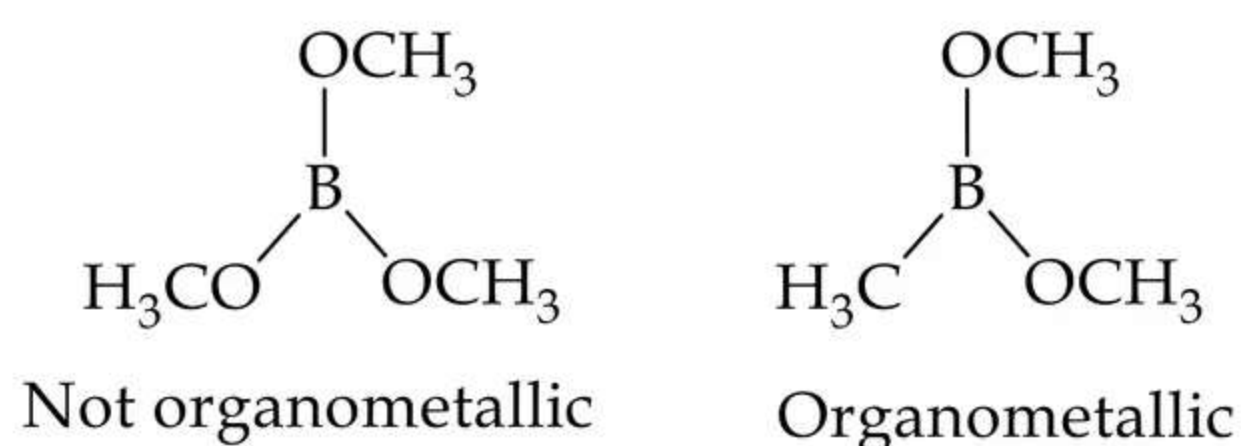
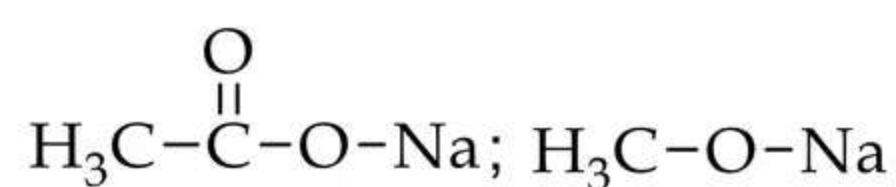


Zeise's salt

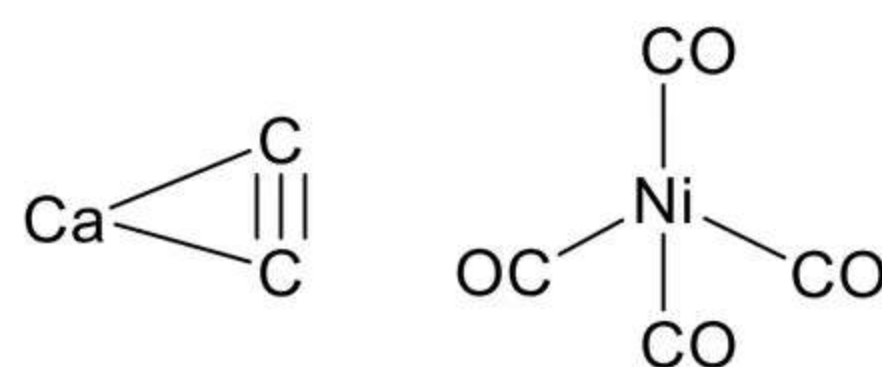


William Christopher Zeise

- *“Organometallic compounds are those in which a metal atom (including non-metals such as B, Si, P, As, Se etc. which are less electronegative than carbon) is bonded directly to at least one carbon atom of a hydrocarbon radical or molecule”*
- The compounds like acetates and alkoxides are not covered under this definition because in these compounds metal is not directly attached to carbon.



- Besides, bonds to 'inorganic' carbon, like carbon monoxide (metal carbonyls), cyanide, or carbide, are generally considered to be organometallic as well.



- Usually, the organometallic compounds are grouped under two classes viz., **"simple"** and **"mixed"**.
- **Simple** organometallic compounds are one in which a metal-carbon bond is typically similar with respect to the derivative of associated component.
- **Simple** organometallic compounds are further divided into two types:
 - i. Symmetrical: Example: [Hg (C₂H₅)₂] (Diethyl mercury), (CH₃)₂ Zn, (C₂H₅)₄Pb
 - ii. Unsymmetrical: Example: CH₃-Hg-C₂H₅ (Ethyl methyl mercury)
- **Mixed organometallic compounds:**

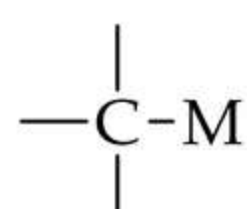
Mixed organometallic compounds are those in which a metal atom is bonded with more than one identity of organic or inorganic constituent.

Example: C₂H₅-Mg-Br (Ethyl magnesium bromide)

Q. What are organometallic compounds? Explain the classification of Organometallic compounds on the basis of bond type.

Definition:

“Organometallic compounds are those in which a metal atom (including non-metals such as B, Si, P, As, Se etc. which are less electronegative than carbon) is bonded directly to at least one carbon atom of a hydrocarbon radical or molecule”



M= Mg, Na, Mn, Fe, Ni, Zn, Pb, Cd etc.

- The bonding is ionic or covalent or delocalized between organic groups and a metal atom.

Classification of organometallic compounds on the basis of bond type:

On the basis of nature of metal- carbon bond organometallic compounds are classified as follows:

1. Ionic bonded organometallic compounds
2. σ -Bonded covalent organometallic compounds
3. π -Bonded organometallic compounds
4. Bridge or multicenter-bonded organometallic compounds

1. Ionic bonded organometallic compounds:

- i. The organometallic compounds of highly electropositive metals are usually ionic in nature.
- ii. In these compounds, the hydrocarbon residue exists as a carbanion, bearing negative charge, is attracted to the metal atom by non-directional electrostatic forces.

- iii. The organometallic compounds of alkali (except lithium), alkaline earth metals, Lanthanides and Actinides are predominantly form ionic compounds.
- iv. These are generally colourless compounds, extremely reactive, non-volatile solids and insoluble in organic solvents.

Examples: $\text{Ph}_3\text{C}^-\text{Na}^+$, Cp_2Ca , Cs^+Me^- , $\text{Na}^+\text{Cp}^- \equiv \left[\text{Cyclopentadienyl} \right]^- \text{Na}^+$

2. σ -Bonded covalent organometallic compounds:

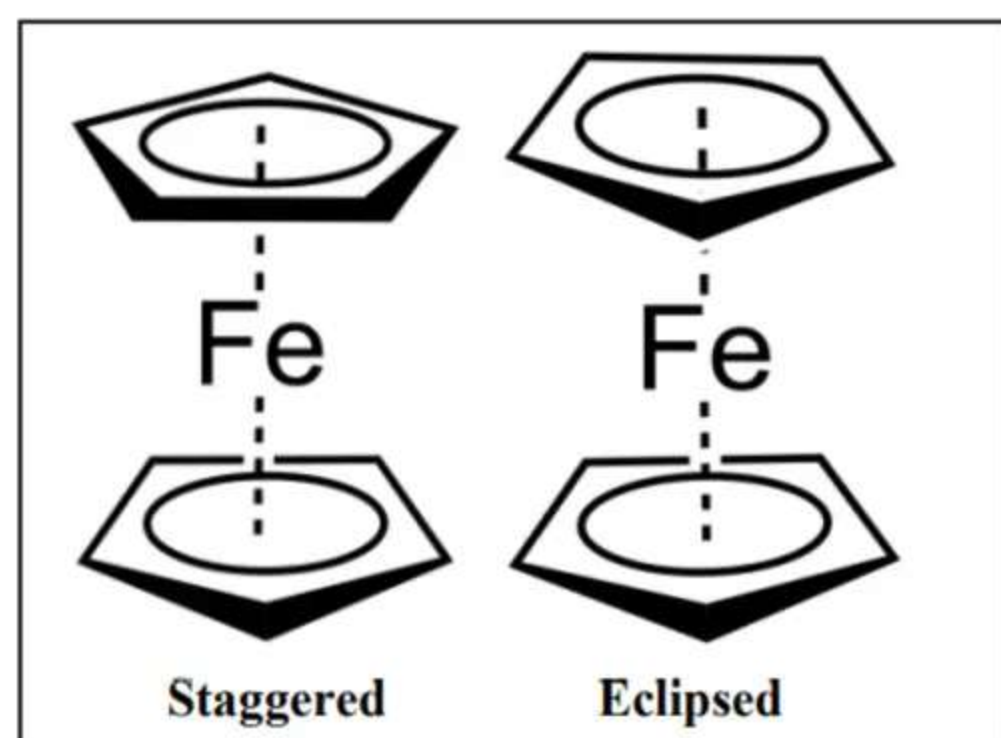
- i. These are the compounds in which carbon atom of the organic ligand is bonded to the metal by a 2 electron, 2 centered (2e-2c) covalent bond.
- ii. A σ -bonded covalent bond is formed between the metal atom and the carbon atom of an organic group.
- iii. Metals with a low electropositive nature form this kind of bond.
- iv. Generally formed by most of the elements with values of electronegativity are higher than 1.
- v. Non-metal atoms and weakly electropositive metal atoms form these types of compounds.
- vi. A metal atom and a carbon atom share a pair of electrons, forming a σ - bond in these compounds.

Examples: $(\text{CH}_3)_3\text{SnCl}$; $(\text{CH}_3)_2\text{SiCl}_2$; $(\text{C}_2\text{H}_5)_4\text{Pb}$; $(\text{CH}_3)_2\text{Zn}$, $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$

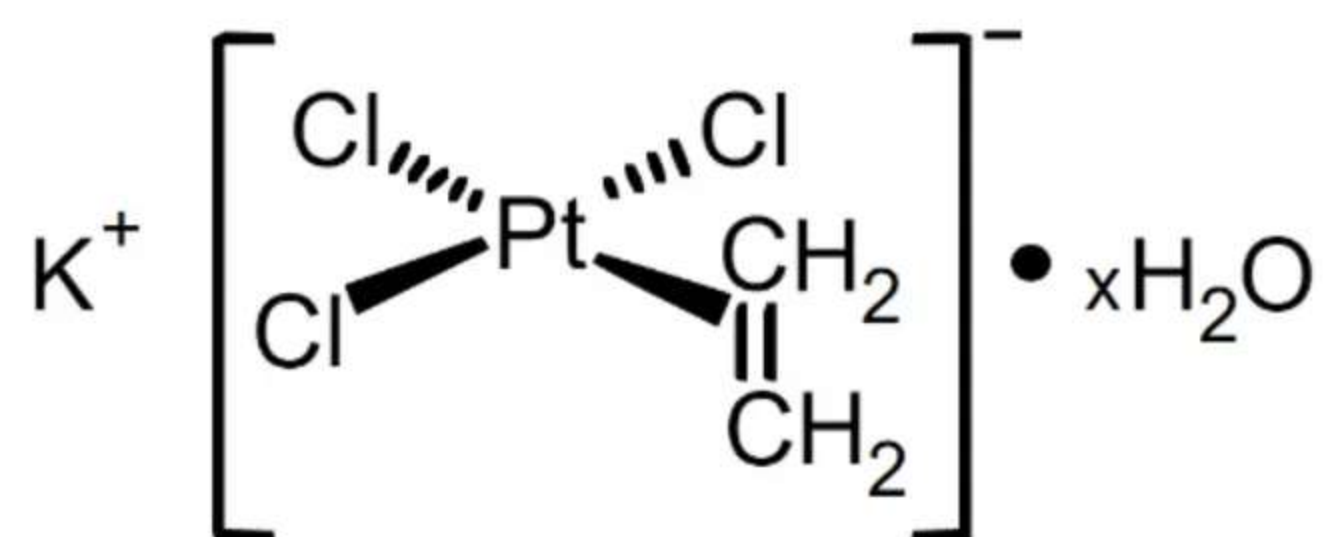
3. π -Bonded organometallic compounds:

- i. Organometallic compounds of this type are specific to transition metals.
- ii. The first π -bonded organometallic compound prepared was bi(cyclopentadienyl) iron or ferrocene, $(\text{C}_5\text{H}_5)_2\text{Fe}$.
- iii. Ferrocene has a '*sandwich*' structure in which the iron atom lies between two planar C_5H_5 rings.
- iv. The bonding involves overlap of π -electrons of the cyclopentadienyl rings with unfilled d -orbitals of the metal, and thus called π -bonding.

Examples: $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]$, $\text{K}[\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_2)]$ (Zeise's salt), acetylenes, dienes such as butadiene, and aromatic molecules.



Ferrocene

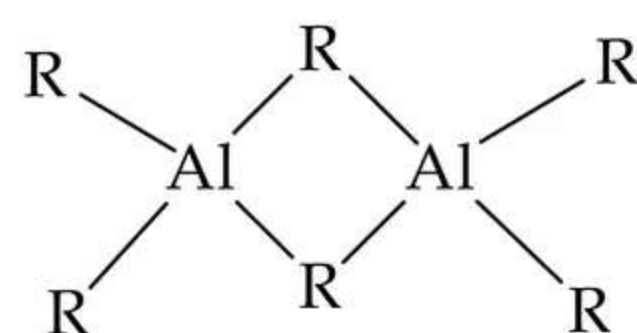


Zeise's salt

4. Bridge or multicenter-bonded alkyl compounds:

- The compounds in which a loosely bonded electron deficient species exist with the coordination of metals like Li, Be, Al etc.
- This group includes the organometallic compounds having bridging alkyl groups.

Examples: MeLi or $(\text{CH}_3)_4\text{Li}_4$, Al_2Me_6 (dimeric trialkyl aluminium) etc.




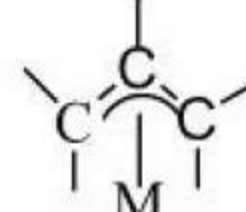
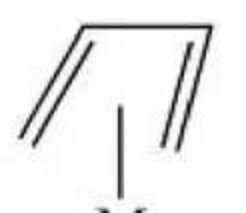
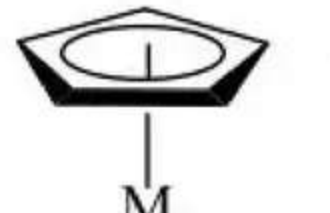

Q. Define hapticity. Discuss the hapticity of ligands with examples.

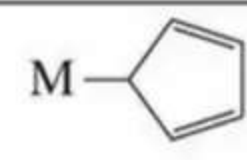
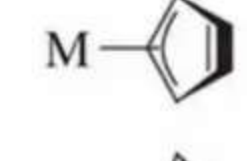

Concept of hapticity of organic ligands:

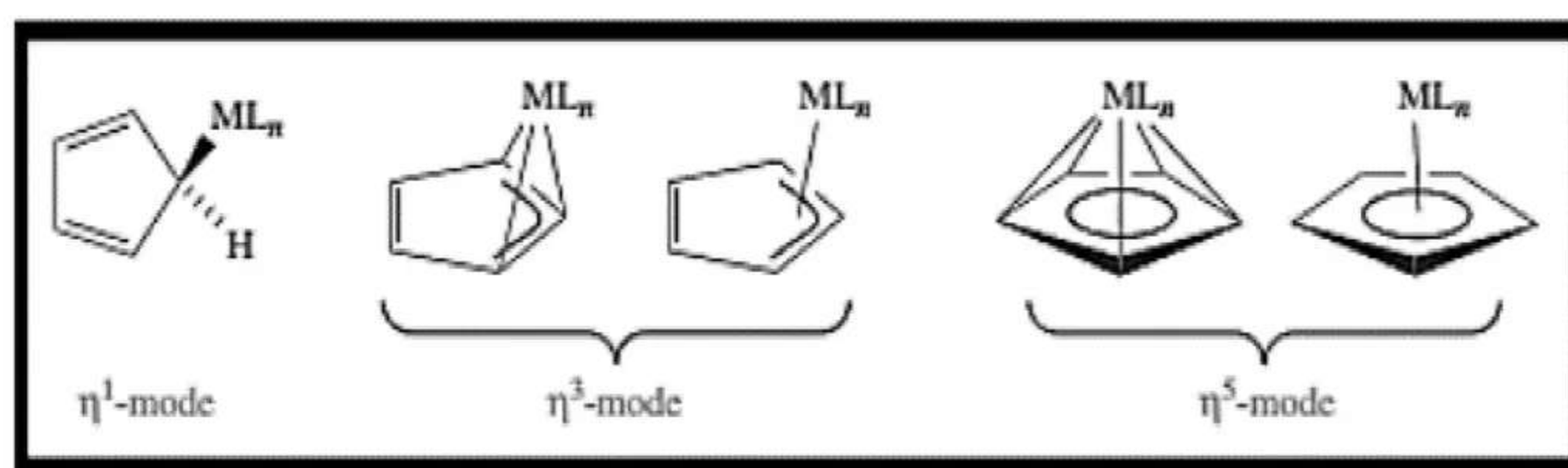
“The number of contiguous carbon atoms through which a ligand is attached to a central metal atom” is known as “hapticity”.

- Hapticity of a ligand is indicated by the Greek letter 'eta' (η).
- The word *hapto* comes from the Greek word for **fasten**; therefore, **pentahapto** means “**fastened in five places**”.

- In η^n where, 'n' represents the number of contiguous carbon atoms of the ligand that are bound to the metal.
 - Monohapto ligands (η^1):** Organic ligands attached to the metal through one carbon.
Ex: $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{CO}$
 - Dihapto ligands (η^2):**
Example: $\text{CH}_2=\text{CH}_2$, $\text{K}[\text{PtCl}_3(\eta^2-\text{C}_2\text{H}_2)]$ (Zeise's salt)
 - Trihapto ligands (η^3):**
Example: Allylic radical $\text{CH}_2=\text{CH}-\text{CH}_2\cdot$
 - Tetrahapto ligands (η^4):**
Example: Butadiene $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
 - Pentahapto ligands (η^5):**
Example: Metallocene $\text{M}(\eta^5-\text{C}_5\text{H}_5)_2$
 - Hexahapto ligands (η^6):**
Example: Dibenzene Chromium $\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2$

Ligand	Hapticity, η	Electrons donated
CO	$\text{M}-\text{CO} \quad \eta^1$	2
Alkene $\text{H}_2\text{C}=\text{CH}_2$	 η^2	2
Π -Allyl $\eta^3-\text{C}_3\text{H}_5$ $\text{CH}_2=\text{CH}-\text{CH}_2\cdot$	 η^3	3
1,3-Butadiene C_4H_6	 η^4	4
Cyclopentadienyl C_5H_5 (Cp)	 η^5	5
Benzene C_6H_6	 η^6	6

Number of Bonding Positions	Formula	Name	
1	$\eta^1-\text{C}_5\text{H}_5$	Monohaptocyclopentadienyl	
3	$\eta^3-\text{C}_5\text{H}_5$	Trihaptocyclopentadienyl	
5	$\eta^5-\text{C}_5\text{H}_5$	Pentahaptocyclopentadienyl	



METAL CARBONYLS

Q. What are metal carbonyls? Illustrate the concept of 18 electron rule with examples.

"Metal Complexes in which Carbon monoxide (CO) acts as a ligand are called metal carbonyls"

Example: $\text{Cr}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$, $\text{Ni}(\text{CO})_4$. etc.

Theory:

- 1) The first attempt to account for the bonding in transition metal complexes was made by Sidgwick.
- 2) Sidgwick extended the octet theory of G.N. Lewis to coordination compounds.
- 3) In coordination compounds, ligands have been considered as Lewis bases which donate electrons (usually one pair per ligand) to the metal ion.
- 4) The metal ion in turn acts as a Lewis acid to assume stability of noble gas configuration.
- 5) **Effective Atomic Number (EAN):**
"The sum of the electrons on the metal plus the electrons donated by the ligands is known as the Effective Atomic Number (EAN)"
- 6) When the sum of electrons is equal to 36 [Kr], 54 [Xe], or 86 [Rn], then the EAN rule was said to be obeyed.

The 18-electron rule:

An alternate statement to EAN is 18e⁻ rule which says that

"when the metal achieves an outer shell configuration of $ns^2 (n-1)d^{10} np^6$ there will be 18 electrons in the valence orbitals and a closed, stable configuration is attained." This rule is known as 18-electron rule.

Examples: $\text{Cr}(\text{CO})_6$, $\text{V}(\text{CO})_6$, $[\text{V}(\text{CO})_6]^-$, $\text{Fe}(\text{CO})_5$ etc.

- The 18-electron rule has the advantage of eliminating the need to remember a different EAN for each noble gas.
- The number is easy to remember since it is simply the total capacity of nine orbitals, i.e., s(2) , p(6) , and d(10) = maximum of 18 electrons.

- However, 18-electron rule is not always strictly obeyed, stable complexes with both more than as well as fewer than 18 outer shell electrons are fairly common.

Examples: .

1. $[\text{OsCl}_6]^{2-}$ (16 electrons)
2. $[\text{PtF}_6]^-$ (17 electrons)
3. $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ (19 electrons)
4. $[\text{Ni}(\text{en})_3]^{2+}$ (20 electrons)
5. $[\text{Cu}(\text{NH}_3)_6]^{2+}$ (21 electrons)

Q. What is 18 electron rule? Discuss the methods for 18 electron counting in metal carbonyls.

Counting Electrons in Complexes:

- The 18-electron rule has remarkable utility for predicting the stabilities and structures of organometallic compounds.
- The 18-electron rule not only predicts the stability of metal complexes, but in some cases, it also predicts the presence of metal-metal bonding and bridging ligands or terminal ligands.
- There are two popular procedures for electron counting:
 - i. Neutral atom method or covalent method**
 - ii. Oxidation state method or ionic method**
- Both the methods are quite useful; however, care must be taken not to mix the two.
- The neutral atom method is more foolproof because it does not require correct assignment of oxidation states, which sometimes difficult to predict in organometallic compounds.
- In both the procedures, it is necessary to know how many electrons each ligand is donated to the central metal atom.
- The below table shows the ligand contribution to electron counting:

Ligand	Neutral atom electron count (Covalent model)	Oxidation state electron count (Ionic Model)
H	1	2 (H ⁻)
Cl, Br, I	1	2 (X ⁻)
OH, OR	1	2 (OH ⁻ , OR ⁻)
CN	1	2 (CN ⁻)
CH ₃ , CR ₃	1	2 (CH ₃ ⁻ , CR ₃ ⁻)
CO, PR ₃	2	2
NH ₃ , H ₂ O	2	2
H ₂ C=CH ₂	2	2
η^3 -C ₃ H ₅ (π -allyl)	3	4 (C ₃ H ₅ ⁻)
Butadiene	4	4
Ethylenediamine (en)	4	4
η^5 -C ₅ H ₅ (cyclopentadienyl)	5	6 (C ₅ H ₅ ⁻)
η^6 -C ₆ H ₆ (benzene)	6	6
η^7 -C ₇ H ₇ (cycloheptatrienyl)	7	6 (C ₇ H ₇ ⁺)

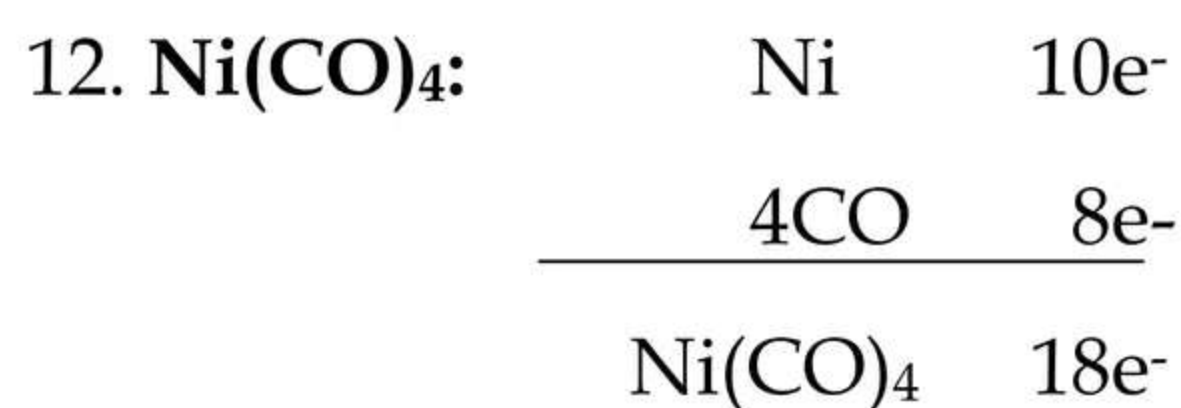
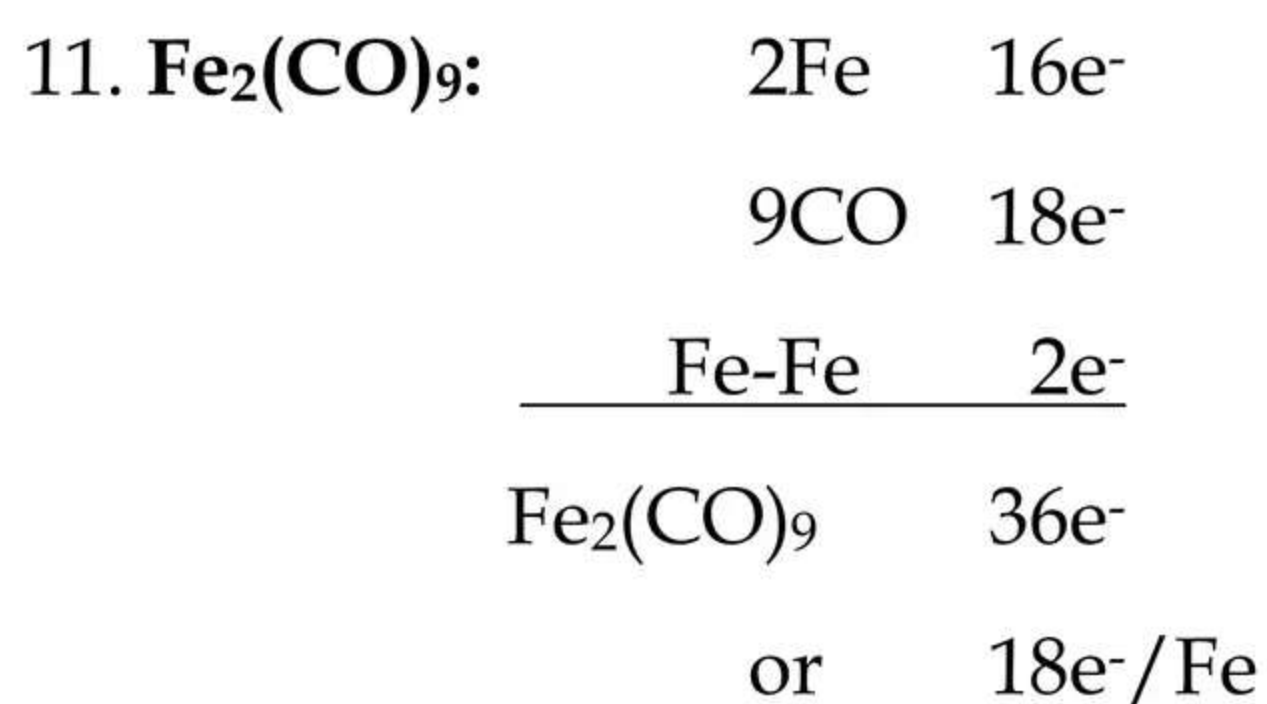
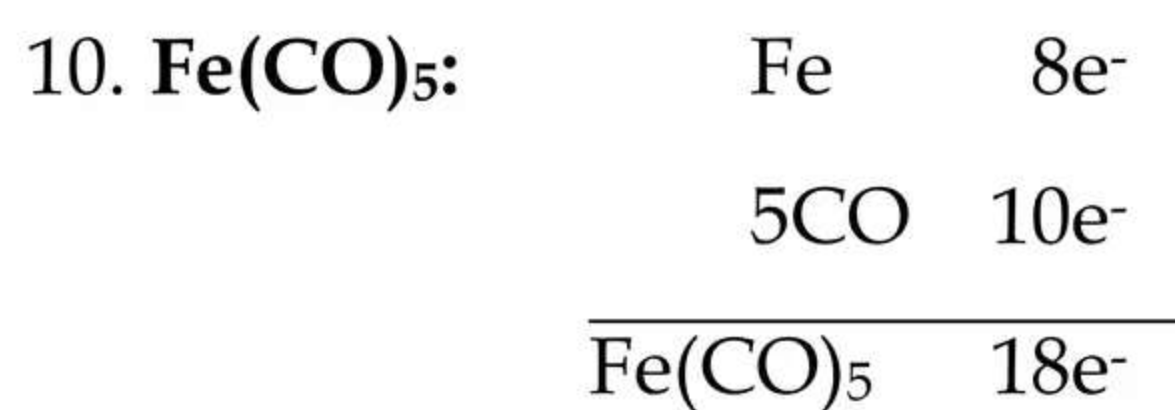
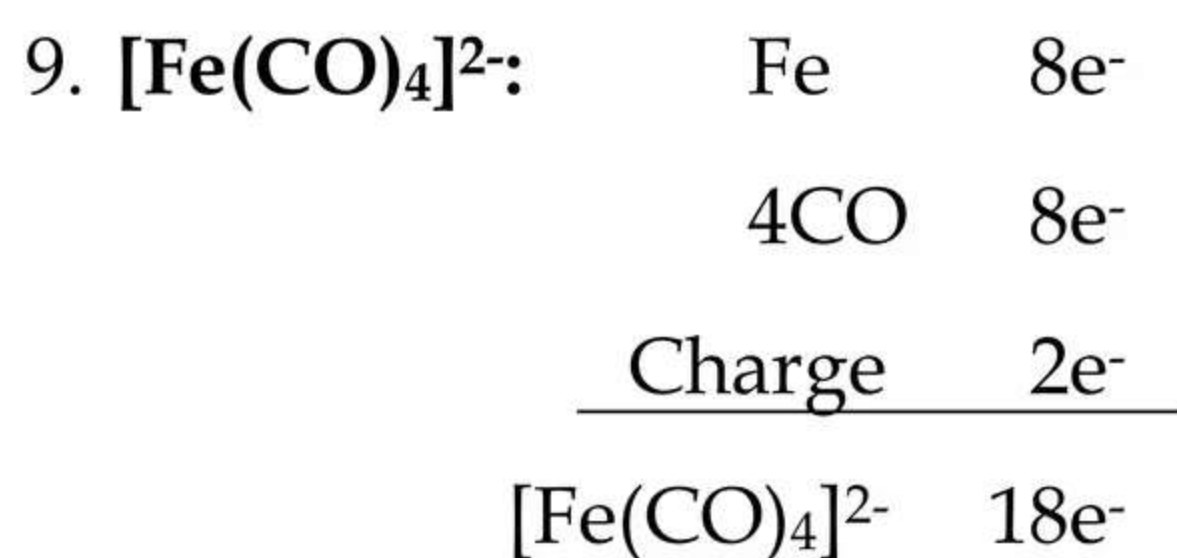
The steps for counting the electrons present in the valence shell of central metal in a metal carbonyl:

- The electrons present in the valence shell of the central metal atom are counted and then electrons are added to it or subtracted from it depending upon the nature of charge (negative or positive) present on it.
- Each terminal carbonyl group contributes **2e** to the valence shell of the central metal.

- iii. The bridging carbonyl group (M – CO – M) contributes **1e** to the valence shell of each metal atom.
- iv. The metal-metal (M –M) bond contributes **1e** to the valence shell of each metal atom.

Some examples of 18-electron count in the metal carbonyls:

1. Cr(CO)_6 :	Cr	6e ⁻	2. $\text{Fe(CO)}_4\text{PPh}_3$:	Fe	8e ⁻
	6CO	12e ⁻		4CO	8e ⁻
	<u>Cr(CO)₆</u>	18e ⁻		Ph ₃ P	2e ⁻
				<u>Fe(CO)₄PPh₃</u>	18e ⁻
3. $[\text{Mn(CO)}_5]^-$:	Mn	7e ⁻	4. $[\text{Co(CO)}_4]^-$:	Co	9e ⁻
	5CO	10e ⁻		4CO	8e ⁻
	Charge	1e ⁻		Charge	1e ⁻
	<u>Mn(CO)₅</u>	18e ⁻		<u>[Co(CO)₄]⁻</u>	18e ⁻
5. $\text{Mn}_2(\text{CO})_{10}$:	2Mn	14e ⁻	6. $\text{Co}_2(\text{CO})_8$:	2Co	18e ⁻
	10CO	20e ⁻		8CO	16e ⁻
	<u>Mn-Mn</u>	2e ⁻		<u>Co-Co</u>	2e ⁻
	<u>Mn₂(CO)₁₀</u>	36e ⁻		<u>Co₂(CO)₈</u>	36e ⁻
	or	18e ⁻ /Mn		or	18e ⁻ /Co
7. V(CO)_6 :	V	5e ⁻	8. $[\text{V(CO)}_6]^-$:	V	5e ⁻
	<u>6CO</u>	12e ⁻		6CO	12e ⁻
	<u>V(CO)₆</u>	17e ⁻ (stable - exception)		Charge	1e ⁻
				<u>[V(CO)₆]⁻</u>	18e ⁻



13. $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$: Neutral counting: C_5H_5 5e + Fe 8e + 2CO 4e + Cl 1e = 18e

Ionic counting: C_5H_5^- 6e + Fe(II) 6e + 2CO 4e + Cl⁻ 2e = 18e

14. $\text{Fe}(\text{C}_5\text{H}_5)_2$ or FeCp_2 : Neutral counting: Fe 8e, C_5H_5 5e: $8 + 2(5) = 18$ electrons

Ionic counting: Fe^{2+} 6e, C_5H_5^- 6e: $6 + 2(6) = 18$ electrons

15. $[\text{CpFe}(\text{CO})_2]_2$: Neutral counting: Cp 10e + Fe 16e + 4 CO 8e + Fe-Fe 2e = 36e (18e/Fe)

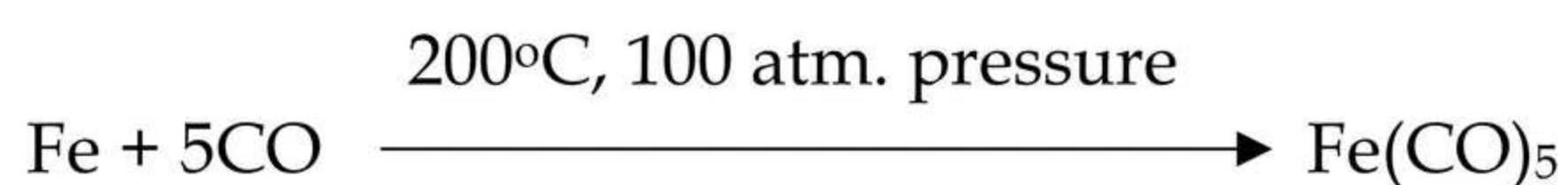
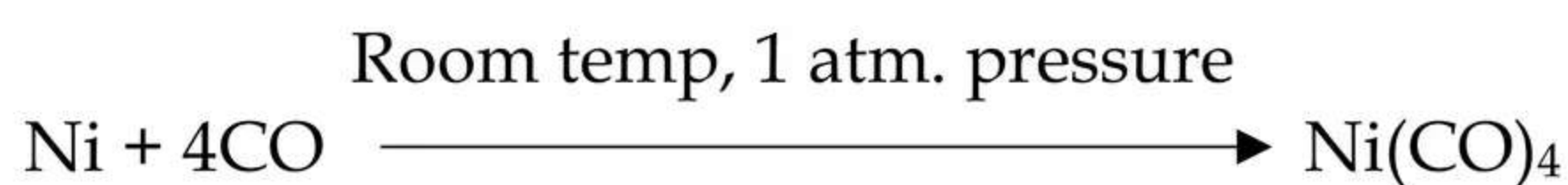
16. $\text{CpFe}(\text{CH}_3)(\text{CO})_2$: Neutral counting: Cp 5e + Fe 8e + CH_3 1e + 2 CO 4e = 18e

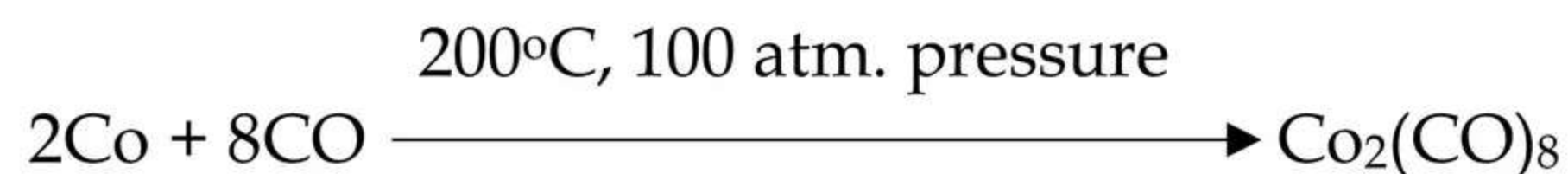
Q. Write any two methods for the preparation of mono and binuclear carbonyls of 3d transition series.

Preparation of mono and binuclear carbonyls of 3d series:

1. By direct synthesis:

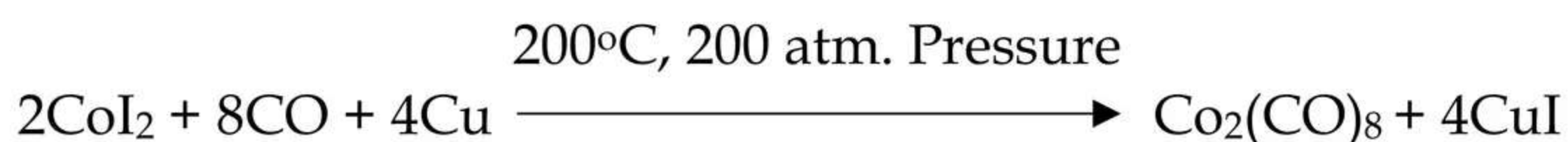
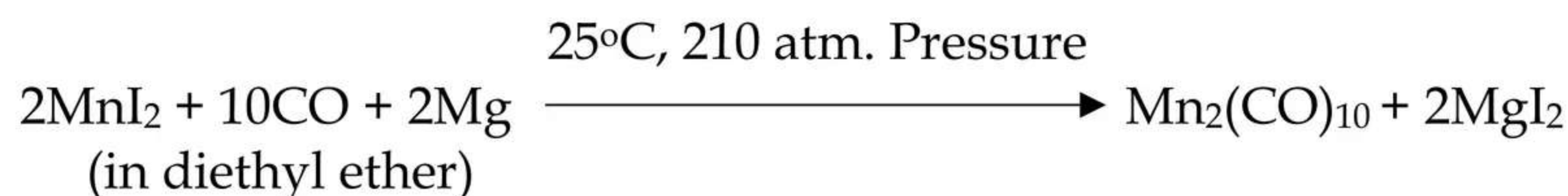
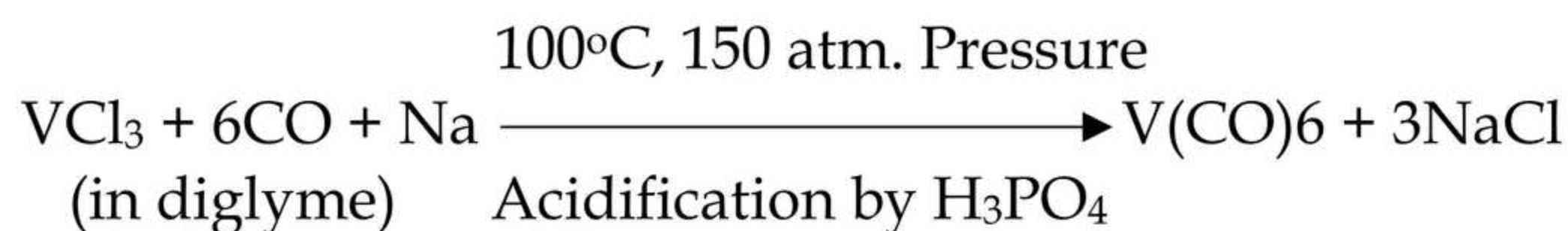
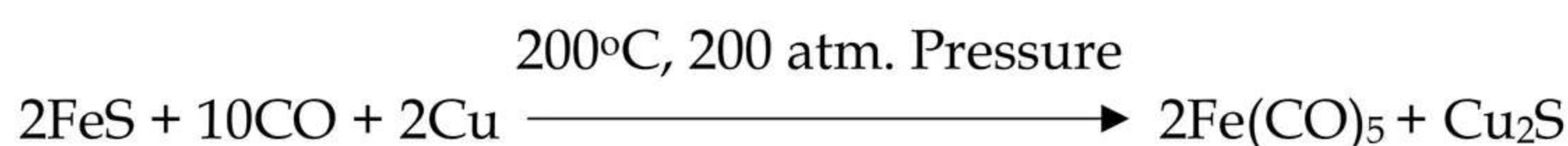
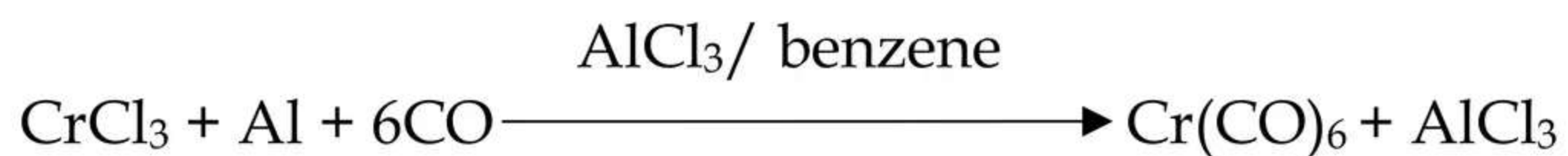
The carbonyls such as $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Co}_2(\text{CO})_8$ can be prepared by the direct combination of CO with finely-divided metals at suitable temperature and pressure.





2. Reductive carbonylation:

When salts like CrCl_3 , VCl_3 , CoS , CoCO_3 , CoI_2 etc., are treated with CO (carbonylation) in presence of a suitable reducing agent like LiAlH_4 , Mg , Cu , etc., metallic carbonyls are obtained.



3. Preparation of $\text{Fe}_2(\text{CO})_9$ from $\text{Fe}(\text{CO})_5$ by photolysis:

When cooled solution of $\text{Fe}(\text{CO})_5$ in glacial acetic acid is irradiated with ultra-violet light, $\text{Fe}_2(\text{CO})_9$ is obtained.