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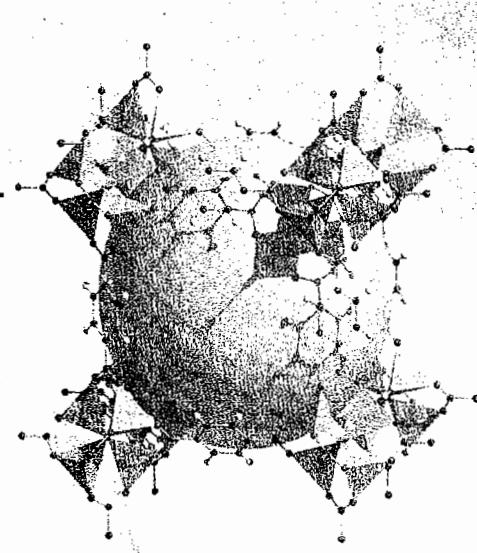
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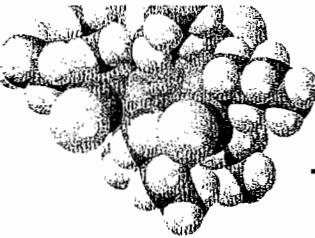
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*To the memory  
of my mother*

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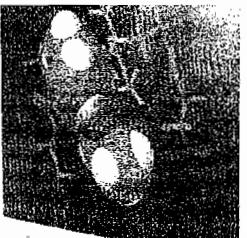
## **Foreword**

I feel pleasure to introduce this book. The content given in the book will be invaluable to teaching and learning concept of Organometallic & Bioinorganic Chemistry. I also feel pleasure that this book is written by my colleague. We (myself, Ajai Kumar and Meenu Srivastava) normally share and discuss the fundamentals of inorganic chemistry including Organometallic & Bioinorganic Chemistry when we are in laboratory, staff room or the teacher's room.

The questions, objective and subjective have the levels of various competition exams like IIT-JAM, CSIR-UGC (JRF/NET), GATE, IISc, BARC, TIFR, DRDO, ONGC, NTPC, NBRC etc. The fundamentals of Organometallic & Bioinorganic Chemistry are written according to the need of the students. I wish that this book may give a way of sure success.

### **Dr. Ram Sharan**

Associate Professor (Dept. of Chemistry)  
Hindu College, University of Delhi, Delhi



## **Preface**

In this book I have attempted to highlight the concepts of **Organometallic & Bioinorganic Chemistry** relevant to students of undergraduate and postgraduate levels of all Indian universities. I have written this book in a readable and easily understandable way. Numerous examples are provided throughout the text.

I hope that this book will be very helpful for the aspirants of all competitive exams related to chemistry like IIT-JAM, CSIR-UGC (NET/JRF), GATE, TIFR, BARC, IISc, DRDO, ONGC, NTPC etc.

I have incorporated large number of objective questions asked in the past competitive exams to know the level of question paper for future competitive examinations.

I have taken particular care to ensure that the text is free of errors.

This edition is successfully produced with the help of Mr. Prakash Arora.

I express my sincere thanks to my daughters—Apeksha and Aradhya, my son—Aaryush and my wife—Mrs. Archana and my other family members. Without the help of my wife Mrs. Archana, writing of this book would only be a dream, not reality.....

I thank to Mr. Gulam Nabi Yatoo and Mr. Vikas Yadav Koslia for their most valuable support and suggestions.

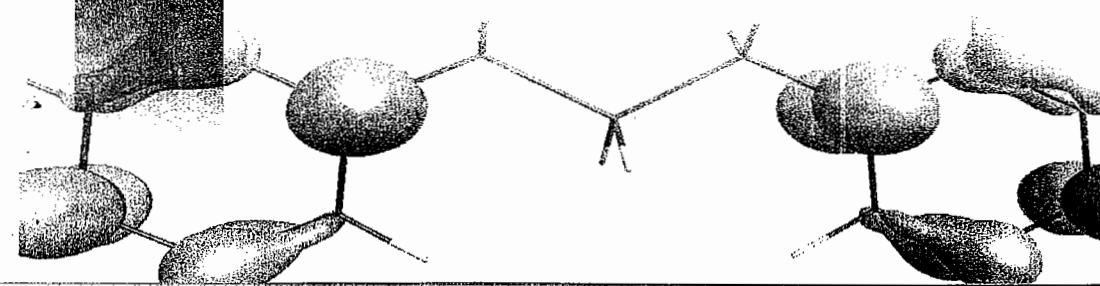
I thank to Dr. Meenu Srivastava, Dr. Sudarshan, Mr. Kuldeep Garg, Dr. Raghvi Khattar, Mr. Gobind Goyat and Mr. Vipin Khoker for their constructive suggestions.

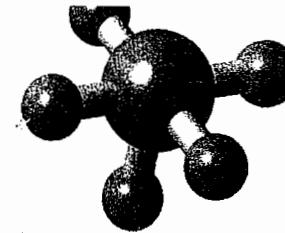
If a learner found any error in the text, please send your constructive criticism and suggestions to update the book time to time. The criticism will be gratefully received and acknowledged.

**—Ajai Kumar**

21-June-2014

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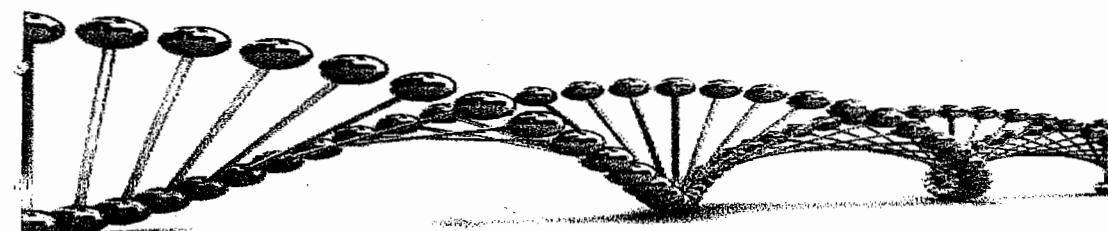


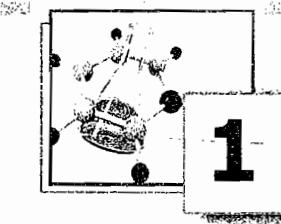
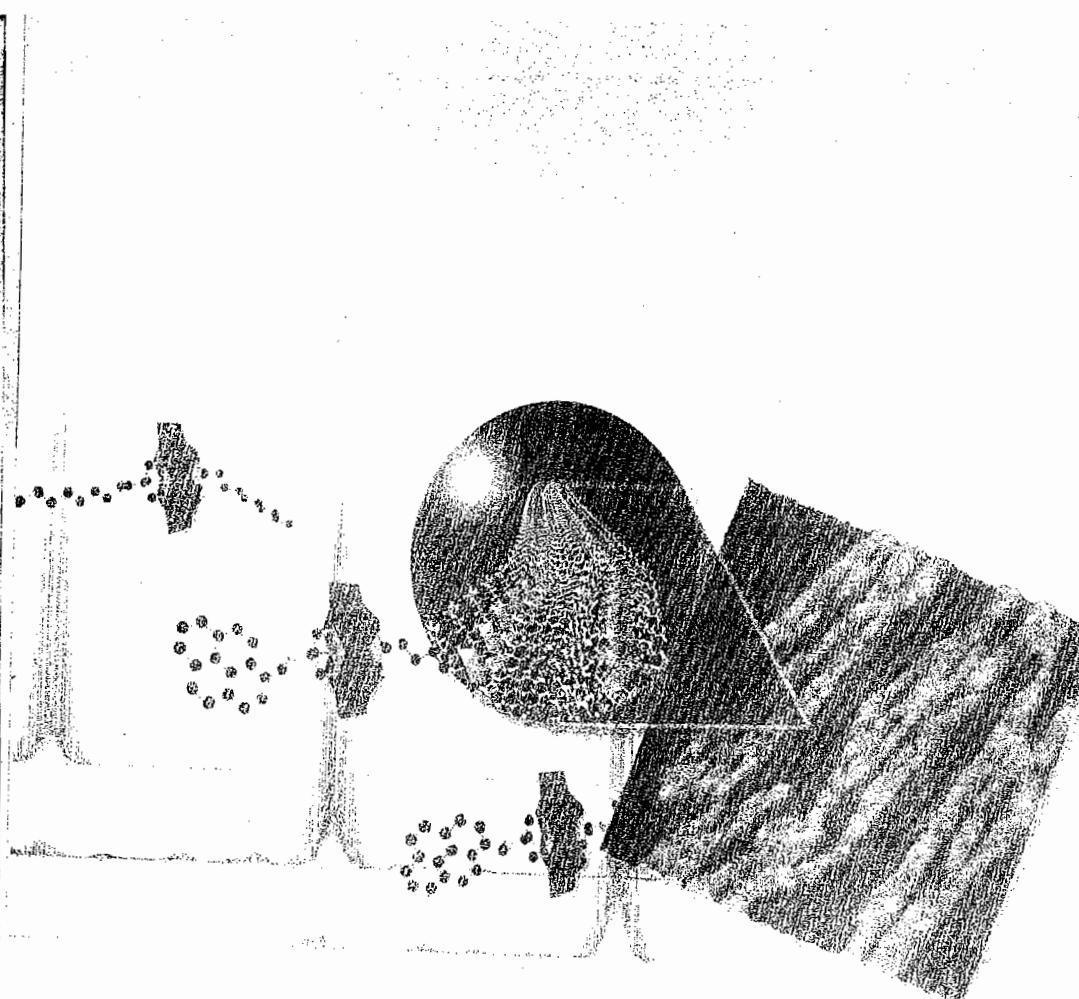


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# Organometallic & Bioinorganic Chemistry

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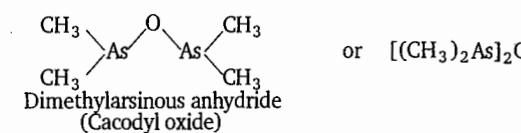


## An Introduction to Organometallic Compounds

An organometallic compound is defined as one that contains atleast one direct metal-carbon bond. This excludes some carbon compounds which are considered to be inorganic such as carbides, e.g.,  $\text{CaC}_2$  and cyanides e.g.,  $\text{NaCN}$ . The carbon containing groups may be carbonyl, alkyl, alkene, aromatic, cyclic or heterocyclic. The various ligands that are attached to metal in organometallic compounds are summarized in Table 1.1.

There are some complexes which do not contain any M—C bonds but are considered to be the members of organometallic compounds. For example, Wilkinson catalyst  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  which is used for hydrogenation of alkenes and alkynes. There is no metal-carbon bond. However, it is an organometallic compound. During catalytic cycle of hydrogenation of alkenes a stage comes when alkene is attached to the metal and forms metal-carbon bond. Due to this reason it is a member of organometallic compounds. According to leading journals of organometallic compounds, the bonding interaction is ionic or covalent, localized or delocalized between atleast one carbon atom of an organic group or molecule and a main group, transition, lanthanide or actinide metal atom. Exceptionally binary metal carbonyls like  $\text{Ni}(\text{CO})_4$  are considered as organometallic compounds even though CO is an inorganic compound. Similarly organic derivatives of the metalloids such as boron, silicon, germanium, arsenic and tellurium are considered to be organometallic compounds.

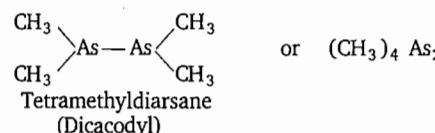
Organometallic compounds straddle both inorganic and organic chemistry. The first organometallic compound of main group elements was cacodyl oxide which has repulsive smell and is a toxic liquid.



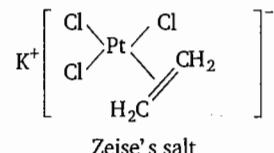
This compound was originally synthesized by heating arsenic trioxide with potassium acetate.



Dicacodyl is also considered one of the earliest organometallic compounds ever discovered. It was investigated by Edward Frankland and Robert Bunsen. It was originally made from arsenic distilled with potassium acetate.



The first organometallic compound of the transition metals was Zeise's salt,  $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ .



Unlike conventional transition metal complexes, the central metal atom in an organometallic compound is often in a low oxidation state (i.e., -1, 0 or +1 or sometime + 2).

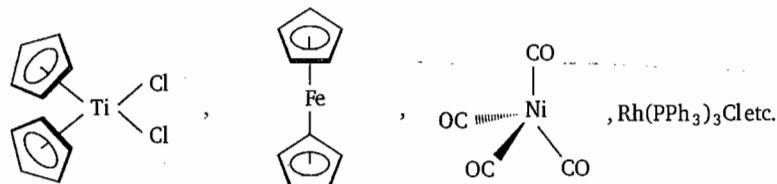
On the basis of periodic table, organometallic compounds can be classified into main group, transition metal and lanthanide/actinide organometallic compounds.

### Main Group Organometallic Compounds

Examples :  $\text{Na}^+\text{C}_5\text{H}_5^-$ ,  $n\text{-BuLi}$ ,  $\text{B}(\text{CH}_2\text{CH}_3)_3$ ,  $\text{Li}_4(\text{CH}_3)_4$ ,  $R_4\text{Pb}$  ( $R = \text{CH}_3, \text{C}_2\text{H}_5$ ),  $\text{RMgX}$  ( $R = \text{alkyl or aryl group}$ ,  $X = \text{Cl}, \text{Br}, \text{I}$ ,  $\text{Al}_2(\text{CH}_3)_6$  etc.

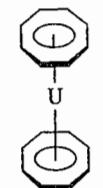
### Transition Metal Organometallic Compounds :

Examples :



### Lanthanide/actinide organometallic compounds :

Example :



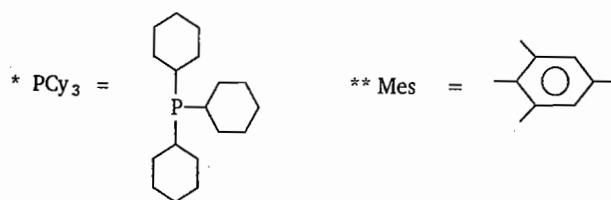
### Applications of Organometallic Compounds

**(1) Organometallic Compounds as Reagents :** Some organometallic compounds especially the alkali and alkaline earth metal compounds such as  $n\text{-BuLi}$ ,  $s\text{-BuLi}$ ,  $t\text{-BuLi}$ , Grignard reagent ( $\text{RMgX}$ ), Gilman's reagent ( $\text{R}_2\text{CuLi}$ ) etc are used as reagents.

**(2) Organometallic Compounds as Catalysts :** The organometallic compounds are being routinely used as catalysts for the synthesis of organic compounds. Some well known organometallic homogeneous catalysts are given in Table 1.1:

Table 1.1 Homogeneous Catalysts

Catalyst	Process
$\text{Rh}(\text{PPh}_3)_3\text{Cl}$	Hydrogenation
$\text{Co}_2(\text{CO})_8$	Hydroformylation
$[\text{Rh}(\text{CO})_2\text{I}_2]^-$	Methanol carbonylation
$[\text{Ir}(\text{CO})_2\text{I}_2]^-$	Methanol carbonylation
 (Grubbs' first generation catalyst)	Olefin metathesis
 (Second generation catalyst, N-heterocyclic carbene)	Olefin metathesis



Vitamin B<sub>12</sub> (known as coenzyme B<sub>12</sub>) is the only known organometallic compound in nature. It incorporates cobalt into a corrin ring and has been found to have many catalytic properties.

**Organometallic Compounds as Drugs :** The first organometallic compound found for anticancer activity was  $\text{Cp}_2\text{TiCl}_2$  [Fig. 1.1(a)]. An another important organometallic compound is ferroquine (FQ) [Fig. 1.1(b)] which is used as antimalarial drug.

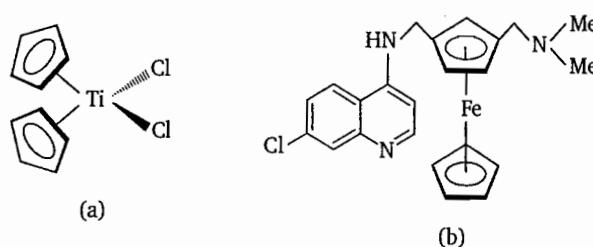


Fig. 1.1 Structure of (a)  $\text{Cp}_2\text{TiCl}_2$ , (b) Ferroquine

**(3) Organometallic compounds as additives :** Organometallic compounds have find applications as bulk additives for modifying the existing properties of compounds. Ferrocene is readily soluble in liquid fuels, air stable, non-toxic and usually thermally stable. Ferrocene is, therefore, added to liquid fuel to reduce carbonaceous particulate matter like soot emitted by diesel engines. The carbonaceous particulates are health hazard. Tetraethyllead [Fig. 1.2(b)] was used as antiknocking agent in the gasoline. TEL helps the gasoline to burn slowly and smoothly and prevents knocking. Combustion of TEL along with gasoline forms particles of Pb and PbO which are very harmful for health. Now, therefore methylcyclopentadienylmanganese tricarbonyl (MMT) [Fig. 1.2(c)] is used in place of TEL as anti-knocking agent.

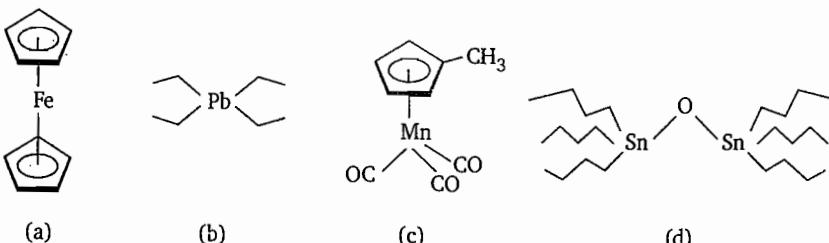


Fig. 1.2

It was found that MMT is harmless for automobiles. Bistributyltinoxide (TBT) Fig. 1.2 (d) is an anti-foulant. It is used for coating outside of ships.

### Organic Ligands and Nomenclature

According to IUPAC recommendation in the formulas of organometallic compounds metal is written first followed by formally anionic ligands in alphabetical order, the neutral ligands are then listed in alphabetical order based on their chemical symbol. A number of unsaturated organic ligands such as allyl, cyclopentadienyl, ethylene, benzene etc. can interact with metal in more than one mode.

### Hapticity

A single organic ligand may interact with a central metal atom using one or more of its atoms simultaneously. The number of atoms in a ligand attached to the metal atom is denoted by the prefix  $\eta$  (the Greek letter eta) followed by a superscript indicating the number of ligand atoms attached to the metal atom. This is called hapticity. Most ligands attach through one atom only, therefore, they are called as monohapto ( $\eta^1$ ). Cyclopentadienyl ligand,  $\text{C}_5\text{H}_5^-$  or Cp, for example, can attach to metal atom through one, three or five carbon atoms. Therefore, it may act as mono ( $\eta^1$ ), tri ( $\eta^3$ ) or pentahapto ( $\eta^5$ )-ligand (Fig. 1.3).

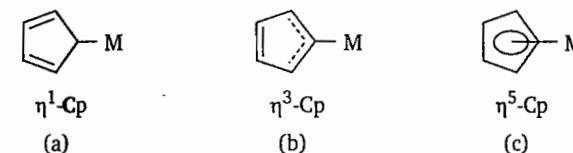
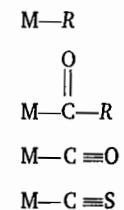


Fig. 1.3

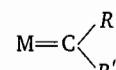
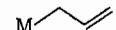
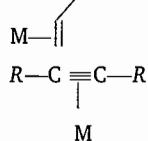
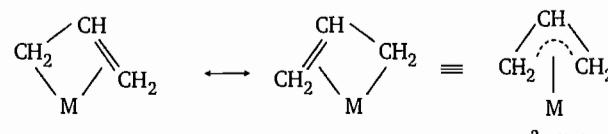
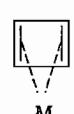
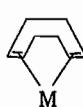
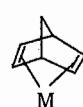
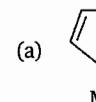
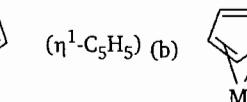
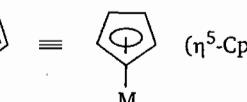
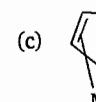
The term hapto comes from the Greek word haptein meaning to fasten. Therefore, pentahapto means fastened in five places.

The hapticity of various ligands is shown below :

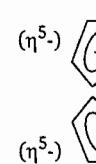
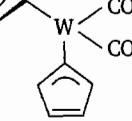
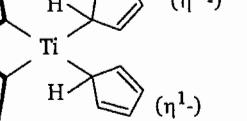
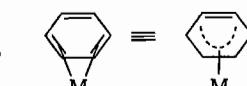
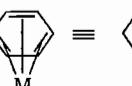
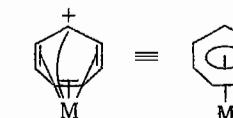
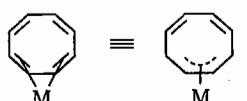
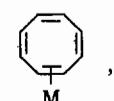
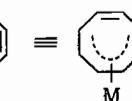
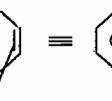
#### (1) $\eta^1$ -monohapto ligands :



(where R =  $-\text{CH}_3$ ,  $-\text{CH}_2\text{—CH}_3$ ,  $-\text{C}_6\text{H}_5$  etc.)

(η<sup>1</sup>-carbene)(η<sup>1</sup>-carbyne)(η<sup>1</sup>-allyl)**(2) η<sup>2</sup>-(Dihapto ligands) :**(η<sup>2</sup>-ethylene)(η<sup>2</sup>-C<sub>3</sub>H<sub>6</sub>)(η<sup>2</sup>-alkyne)**(3) η<sup>3</sup>-(Trihapto ligands) :**(η<sup>3</sup>-allyl)(η<sup>3</sup>-C<sub>3</sub>H<sub>3</sub>)**(4) η<sup>4</sup>-(Tetrahapto ligands) :**η<sup>4</sup>-C<sub>4</sub>H<sub>6</sub>η<sup>4</sup>-C<sub>4</sub>H<sub>4</sub>(η<sup>4</sup>-COD) (where COD = cyclooctadiene)(η<sup>4</sup>-C<sub>7</sub>H<sub>8</sub>)C<sub>7</sub>H<sub>8</sub> → Norbornadiene**(5) η<sup>5</sup>-(Pentahapto ligands) :**(η<sup>1</sup>-C<sub>5</sub>H<sub>5</sub>)(η<sup>3</sup>-C<sub>5</sub>H<sub>5</sub>)

Cyclopentadienyl can also behave monohapto and trihapto.

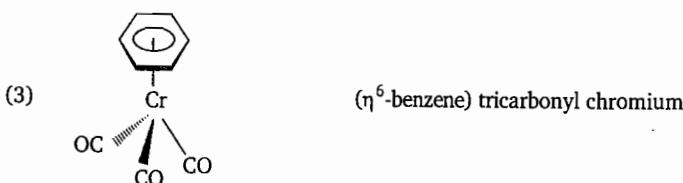
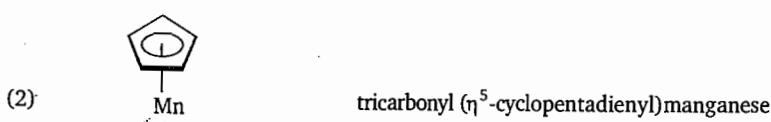
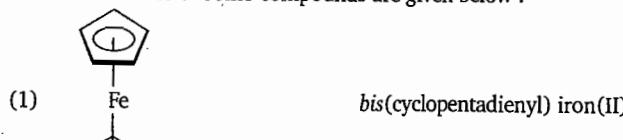
(η<sup>1</sup>-)**(6) η<sup>6</sup>-(Hexahapto ligands) :**(η<sup>2</sup>-C<sub>6</sub>H<sub>6</sub>)(η<sup>4</sup>-C<sub>6</sub>H<sub>6</sub>)(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)(η<sup>6</sup>-C<sub>7</sub>H<sub>8</sub>)**(7) η<sup>7</sup>-(Heptahapto ligands) :**(η<sup>7</sup>-C<sub>7</sub>H<sub>7</sub><sup>+</sup>)**(8) η<sup>8</sup>-(Octahapto ligands) :**(η<sup>2</sup>-COT)(η<sup>4</sup>-COT)(η<sup>6</sup>-COT)(η<sup>8</sup>-COT)

where COT = cyclooctatetraene

The ligand which can change its hapticity is called a fluxional ligand.

If hapticity of a ligand is not given, then the ligand has to be assume in its highest hapticity, e.g.,  $\text{Cp} \rightarrow \eta^5$ , allyl  $\rightarrow \eta^3$ .

The IUPAC name of some compounds are given below :



### Eighteen Electron Rule

The main group element such as lead uses its four valence electrons for the formation of four  $\sigma$  bonds and as a result a stable compound such as  $\text{PbEt}_4$  is obtained. In such compounds, the total number of valence electrons becomes equal to 8, i.e., these compounds obey octet rule. On the other hand  $\text{PbEt}_3$  contains only six valence electrons and therefore does not obey octet rule and is unstable. However there are some complexes which do not obey the octet rule and are unstable.

In general organometallic compounds of transition metals are formed with metals that are in low oxidation states (-1, 0 and +1). According to Sidwick's effective atomic number (EAN) rule, the EAN of a metal is equal to the sum of electrons on metal plus the electrons donated by the ligands and EAN is equal to the atomic number of next noble gas, [i.e., equal to 36 (Kr), 54 (Xe) or 86 (Rn)].

An alternate and more general rule is the 18-electron rule. According to this rule, in an organometallic compounds and other complexes the sum of valence shell electrons of transition metal or metal ion and electrons donated by the ligands is equal to 18. It provides a closed and stable valence shell configuration  $(n-1)d^{10}ns^2np^6$ . In transition metals, the electrons of  $(n-1)d$  and  $ns$  electrons are considered to be valence electrons. The complexes which obey the EAN or 18-electron rule are considered to be stable. The EAN and 18-electron rules are similar. The 18-electron rule is a

rule of thumb and is more advantageous than EAN because there is no need to remember the atomic number of the noble gases. However, there are some exceptions which obey neither EAN nor 18-electron rule. The mononuclear compounds in which the number of total valence electrons is odd never obey either EAN or 18-electron rule.

The first row transition metal carbonyls mostly obey the 18-electron rule. Each metal contributes the same number of electrons as its group number and each CO ligand contributes two electrons,  $\pi$ -back bonding makes no difference to the electron count for the metal. In cases of transition metals with odd electrons, even number of electron 18 is never obtained by adding two electron ligands such as CO. In each case the system resolves this problem in a different way. The complex  $\text{V}(\text{CO})_6$  has 17 valence electron and easily reduced to the 18-electron  $[\text{V}(\text{CO})_6]^-$  anion. In  $\text{V}(\text{CO})_6$ , the vanadium is too small to permit a seventh coordination site because there would be strong steric hindrance. Therefore, no metal-metal bonded dimer is formed which would give an 18-electron configuration. Unlike  $\text{V}(\text{CO})_6$ , the  $\text{Mn}(\text{CO})_5$  species which is also a 17-electron species, does dimerize with the formation of M—M bond. This is due to the reason that the coordination of the 5-coordinate species has more space available to make the M—M bond. Each metal atom in the dimer obeys 18-electron rule because the unpaired electron in each 5-coordinate species is shared with the other in forming the M—M bond much as the 7-electron methyl radical dimerizes to give the 8-electron compound,  $\text{C}_2\text{H}_6$ . Similarly, the 17-electron  $\text{Co}(\text{CO})_4$  species dimerizes with the formation of M—M bond but a pair of CO ligands also form bridges with metals. This makes no difference in the electron count because the bridging CO shares one electron with each metal, thus an M—M bond is still required to attain 18-electron. The even electron transition metal complexes achieve 18-electrons without M—M bond formation and they achieve 18-electrons by binding the appropriate number of CO ligands. For example, Cr Fe and Ni metals bond with 6, 5 and 4 CO ligands respectively to attain 18-electrons. The odd electron transition metals need to form M—M bonds. The complexes with coordination number 6, 5 and 4 adopt octahedral, trigonal or square pyramidal and tetrahedral or square planar geometries respectively.

In most of the transition metal complexes electrons are filled in the bonding molecular orbitals leaving the antibonding molecular orbitals vacant. Since there are nine bonding molecular orbitals in transition metal complexes, maximum 18-electrons will be filled in them as predicted by the 18 electron rule. Thus according to 18-electron rule, these complexes are considered to be stable.

### Electron Count in Complexes

By counting number of valence electrons surrounding each metal atom or metal ion, in a complex it is possible not only to predict the complex would be stable but also in some cases, whether there will be M—M bonds, or not or the ligands will be terminal or bridging etc.

There are two methods for counting electrons :

- (1) Oxidation state or ionic method
- (2) Neutral ligand or covalent method

Both the methods have roughly the equal number of supporters and lead to exactly the same net results. They differ only in the way that the electrons are considered as coming from the metal or from the ligands. Either of the methods can be used quite successfully but care must be taken not to

mix the two. The neutral atom method will be more useful because it does not require the correct assignment of oxidation states, which may be some times difficult for organometallic compounds. The oxidation state method is widely used for the reactions in which oxidation state of the central metal atom is changed. For both the electron counting methods, it is necessary to know how many electrons each ligands in a complex donates to the metal. The contribution of electrons for a variety of ligands for both the neutral atom and the oxidation state methods is shown in Table 1.2. It is to be noted that the electron count for neutral ligands is the same for either of the two methods. Therefore, CO and phosphine ligands behave as two electron donors for both neutral atom and oxidation state methods. The neutral atom method is probably more appropriate for low valent transition metal complexes, especially with the unsaturated ligands. On the other hand, the oxidation state method is more appropriate for high-valent complexes with N, O or  $X^-$  ( $X = Cl, Br, I$ ) ligands, such as are found in coordination as well as organometallic compounds.

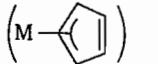
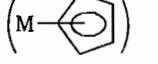
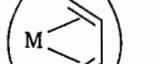
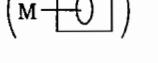
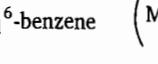
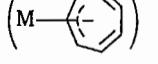
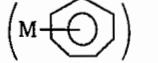
In the neutral atom method, each metal atom and ligand is treated as neutral. If the complex is charged the appropriate number of electrons are added (if the complex has negative charge) or subtracted (if the complex has positive charge) to the total. In this method, the ligands are considered to donate the number of electrons equal to their negative charge as free ions.

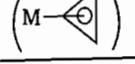
In oxidation state method, to determine the total valence electron count, it must be taken into account the charge on each ligand and determine the formal oxidation of metal.

Table 1.2 : Electron Count for Common Ligands

Ligand	Neutral Atom Method	Oxidation State Method
Carbonyl (M—CO)	2	2
Thiocarbonyl (M—CS)	2	2
Phosphine (M—PR <sub>3</sub> )	2	2
Amine (M—NR <sub>3</sub> )	2	2
Amide (M—NR <sub>2</sub> )	1	2 (NR <sub>2</sub> <sup>-</sup> )
Nitrosyl, bent (M—N <sup>+</sup> =O <sup>-</sup> )	1	2
Nitrosyl, linear (M—N ≡ O)	3	2
Halogen (M—X)	1	2 (X <sup>-</sup> )
Hydrogen (M—H)	1	2 (H <sup>-</sup> )
Alkyl (M—R)	1	2 (R <sup>-</sup> )
Aryl (M—Ph)	1	2 (Ph <sup>-</sup> )

Ligand	Neutral Atom Method	Oxidation State Method
Acyl $\left( \begin{array}{c} O \\    \\ M-C-R \end{array} \right)$	1	2 (C—R <sup>-</sup> )
Alkoxide (M—OR)	1	2 (OR <sup>-</sup> )
Phosphide (M—PR <sub>2</sub> )	1	2 (PR <sub>2</sub> <sup>-</sup> )
Thiolate (M—SR)	1	2 (SR <sup>-</sup> )
Isocyanide (M—CNR)	2	2
Dihydrogen $\left( \begin{array}{c} H \\   \\ M-H \end{array} \right)$	2	2
Dinitrogen (M—N ≡ N)	2	2
Alkene $\left( \begin{array}{c} C \\    \\ M-C \end{array} \right)$	2	2
Alkyne $\left( \begin{array}{c}   \\ C \\    \\ M-C \\   \end{array} \right)$	2	2
Carbene or Alkylidene (M = CR <sub>2</sub> )	2	4 (CR <sub>2</sub> <sup>2-</sup> )
Carbyne or alkylidyne (M ≡ CR)	3	6 (CR <sup>3-</sup> )
$\eta^1$ -allyl (M—CH <sub>2</sub> $\nwarrow$ )	1	2 (CH <sub>2</sub> $\nwarrow$ )
$\eta^3$ -allyl (M— $\rangle\!\rangle$ )	3	4 ( $\langle\!\langle$ ) or 2(C <sub>3</sub> H <sub>5</sub> <sup>+</sup> )
$\eta^1$ -cyclopentadienyl $\left( \begin{array}{c} M \\   \\ \text{C}_5\text{H}_5 \end{array} \right)$	1	2 (C <sub>5</sub> H <sub>5</sub> <sup>-</sup> )

Ligand	Neutral Atom Method	Oxidation State Method
$\eta^3$ -cyclopentadienyl 	3	$4(C_5H_5^-)$
$\eta^5$ -cyclopentadienyl 	5	$6(C_5H_5^-)$
$\eta^4$ -1,3-butadiene 	4	4
$\eta^4$ -cyclobutadiene 	4	$6(C_4H_4^{2-})$
$\eta^6$ -benzene 	6	6
$\eta^3$ -C <sub>7</sub> H <sub>7</sub> (Cycloheptatrienyl) 	3	$4(C_7H_7^-)$
$\eta^4$ -C <sub>7</sub> H <sub>8</sub> (Cycloheptatriene) 	4	4
$\eta^6$ -C <sub>7</sub> H <sub>8</sub> (Cycloheptatriene) 	6	6
$\eta^7$ -Cycloheptatrienyl 	7	$6(C_7H_7^+)$

Ligand	Neutral Atom Method	Oxidation State Method
$\eta^8$ -Cyclooctatetraenyl 	8	$10(C_8H_8)^{2-}$
$\eta^6$ -Cyclooctatetraene	6	8
$\eta^4$ -Cyclooctatetraene	4	6
$\eta^3$ -C <sub>3</sub> H <sub>3</sub> (Cyclopropenyl) 	3	$2(C_3H_3^+)$

Bridging Ligand	Neutral Atom Method	Oxidation State Method
Carbonyl (M—C=O—M)	2	2
Halogen (M—X—M)	3	4
Hydrogen (M—H—M)	1	2
Alkyl [M—(CR <sub>3</sub> )—M]	2	2
Alkyne M—C≡C—M	4	4
Amide [M—(NR <sub>2</sub> )—M]	3	4
Phosphide [M—(PR <sub>2</sub> )—M]	3	4

**Contribution of Electron in M—M Bonds**

M—M bond	Contribution of electrons
M—M	2
M=M	4
M≡M	6
M≡M	8

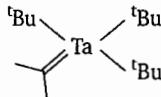
## Sixteen Electron Rule

An important class of organometallic compounds follow a  $16e^-$  rather than  $18e^-$  rule because one of the nine orbitals is very high in energy and usually vacant. These complexes with 16 valence electrons are common for  $d^8$  transition metals, particularly of groups 9 and 10. These complexes are usually square planar. Examples of these complexes are :  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ ,  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ , anion of Zeise's salt  $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$  etc. Square planar 16 electron complexes are usually common for the  $d^8$  metal atoms or ions of the heavier elements of group 9 and 10 especially for Rh(I), Ir(I), Pd(II), Pt(II).

The combination of eight metal  $d$ -electrons and two electrons from each of the four ligands gives a total valence electrons of 16. The  $16e^-$  complexes can often be just as stable as or even more stable than  $18e^-$  complexes of the same metal.

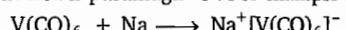
## Exception to 18/16-Electron Rule

There are many complexes which do not follow the 18/16-electron rule but are stable. These complexes are common for transition metals which lie on the left of the periodic table. Here the electronic and steric factors prevent the increasing coordination number or to permit dimerization. To attain  $18e^-$  they may require more ligands or dimerization which can be sterically impossible and 18/16 electron rule is violated. Some examples are given below :



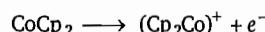
,  $\text{Me}_3\text{TiCl}_3(8e^-)$ ;  $\text{Me}_2\text{NbCl}_3(10e^-)$ ;  $\text{WMe}_6(12e^-)$ ,  $\text{Pt}(\text{PCy}_3)_2(14e^-)$ ;  $(\eta^5-\text{Cp})\text{Cr}(\text{CO})_2(\text{PPh}_3)(17e^-)$ ; etc. The later example provides a good example of the role of steric hindrance. When bulky  $\text{PPh}_3$  ligands is replaced by compact CO ligand, a dimer is obtained in the solid state and in solution.

The neutral bis(cyclopentadienyl) complexes of most of the transition metals such as  $\text{CoCp}_2$ ,  $\text{NiCp}_2$  do not obey the 16/18-electron rule. The 18 electron is mostly satisfied by the neutral bis(cyclopentadienyl) complexes of group 8 metals such  $\text{FeCp}_2$ . Complexes which obey 18 electron rule are the most stable. The other complexes are comparatively less stable. The stability of these complexes is suggested by their bond length and their redox reactions. The complex which contain 17 electrons is strong oxidizing agent and is paramagnetic. For example :

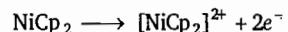


The complex which contains 19 or 20-electrons is strong reducing agent.

For example,  $\text{CoCp}_2$ , a 19 electron complex, is readily oxidized to the 18-electron cation  $\text{CoCp}_2^+$ .

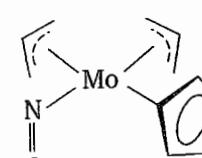
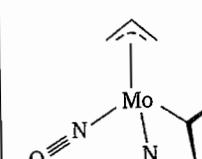


Similarly,  $\text{NiCp}_2$  is a  $20e^-$  complex and is readily oxidized to  $18e^-$  species  $\text{NiCp}_2^{2+}$ .

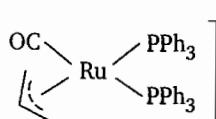


Some examples electron counting are given in Table 1.3.

Table 1.3

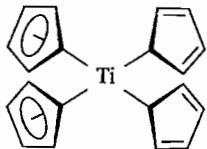
Electron Counting					
S.No	Compound	Oxidation State Method	Neutral Atom Method		
1.	$\text{HMn}(\text{CO})_5$	$\begin{array}{l} \text{Mn}^+ \\   \\ 5\text{CO} \\   \\ \text{H}^- \end{array}$ $5 \times 2 = 10e^-$ $2e^-$ $18e^-$	$\begin{array}{l} \text{Mn} \\   \\ 5\text{CO} \\   \\ \text{H} \end{array}$ $5 \times 2 = 10e^-$ $1$ $18e^-$	$\begin{array}{l} 7e^- \\   \\ 5e^- \\   \\ 1 \end{array}$	
2.	$(\eta^5-\text{C}_5\text{H}_5)_2\text{Fe}$	$\begin{array}{l} \text{Fe}^{2+} \\   \\ 2\text{C}_5\text{H}_5^- \end{array}$ $2 \times 6 = 12e^-$ $18e^-$	$\begin{array}{l} \text{Fe} \\   \\ 2\text{C}_5\text{H}_5 \end{array}$ $2 \times 5 = 10e^-$ $18e^-$	$\begin{array}{l} 8e^- \\   \\ 5e^- \end{array}$	
3.	$(\eta^5-\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$	$\begin{array}{l} \text{Fe}^{2+} \\   \\ \eta^5-\text{C}_5\text{H}_5^- \\   \\ 2\text{CO} \\   \\ \text{Cl}^- \end{array}$ $6e^-$ $6e^-$ $4e^-$ $2e^-$ $18e^-$	$\begin{array}{l} \text{Fe} \\   \\ \eta^5-\text{C}_5\text{H}_5 \\   \\ 2\text{CO} \\   \\ \text{Cl} \end{array}$ $8e^-$ $5e^-$ $4e^-$ $1e^-$ $18e^-$	$\begin{array}{l} 8e^- \\   \\ 5e^- \\   \\ 4e^- \\   \\ 1e^- \end{array}$	
4.	$\text{CH}_3\text{Mn}(\text{CO})_5$	$\begin{array}{l} \text{Mn}^+ \\   \\ \text{CH}_3 \\   \\ 5\text{CO} \end{array}$ $6e^-$ $2e^-$ $10e^-$ $18e^-$	$\begin{array}{l} \text{Mn} \\   \\ \text{CH}_3 \\   \\ 5\text{CO} \end{array}$ $7e^-$ $1e^-$ $10e^-$ $18e^-$	$\begin{array}{l} 7e^- \\   \\ 1e^- \\   \\ 10e^- \end{array}$	
5.		$\begin{array}{l} \text{Mo}^{4+} \\   \\ 2\eta^3-\text{C}_3\text{H}_5^- \\   \\ \eta^5-\text{C}_5\text{H}_5^- \\   \\ \text{NO}^-(\text{b}) \end{array}$ $2e^-$ $8e^-$ $6e^-$ $2e^-$ $18e^-$	$\begin{array}{l} \text{Mo} \\   \\ 2\eta^3-\text{C}_3\text{H}_5 \\   \\ \eta^5-\text{C}_5\text{H}_5 \\   \\ \text{NO}(\text{b}) \end{array}$ $6e^-$ $6e^-$ $5e^-$ $1e^-$ $18e^-$	$\begin{array}{l} 6e^- \\   \\ 6e^- \\   \\ 5e^- \\   \\ 1e^- \end{array}$	
6.		$\begin{array}{l} \text{Mo}^{2+} \\   \\ \eta^3-\text{C}_3\text{H}_5^- \\   \\ \eta^5-\text{C}_5\text{H}_5^- \\   \\ \text{NO}^+(\text{L}) \\   \\ \text{NO}^-(\text{b}) \end{array}$ $4e^-$ $4e^-$ $6e^-$ $2e^-$ $2e^-$ $18e^-$	$\begin{array}{l} \text{Mo} \\   \\ \eta^5-\text{C}_5\text{H}_5 \\   \\ \eta^3-\text{C}_3\text{H}_5 \\   \\ \text{NO}(\text{L}) \\   \\ \text{NO}(\text{b}) \end{array}$ $6e^-$ $5e^-$ $3e^-$ $3e^-$ $1e^-$ $18e^-$	$\begin{array}{l} 6e^- \\   \\ 5e^- \\   \\ 3e^- \\   \\ 3e^- \\   \\ 1e^- \end{array}$	

7.



$\text{Ru}^{2+}$	$6e^-$	$\text{Ru}$	$8e^-$
$2\text{PPh}_3$	$4e^-$	$2\text{PPh}_3$	$4e^-$
$\eta^3\text{-C}_3\text{H}_5^-$	$4e^-$	$\eta^3\text{-C}_3\text{H}_5^-$	$3e^-$
$\text{CO}$	$2e^-$	$\text{CO}$	$2e^-$
	$\underline{16e^-}$	Charge	$-1e^-$
			$\underline{16e^-}$

8.

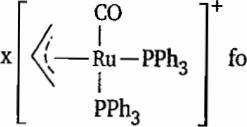


$\text{Ti}^{4+}$	$0e^-$	$\text{Ti}$	$4e^-$
$2\eta^5\text{-C}_5\text{H}_5^-$	$12e^-$	$2\eta^5\text{-C}_5\text{H}_5^-$	$10e^-$
$2\eta^1\text{-C}_5\text{H}_5^-$	$4e^-$	$2\eta^1\text{-C}_5\text{H}_5^-$	$2e^-$
	$\underline{16e^-}$		$\underline{16e^-}$



## Objective Questions

- The complex that does not obey 18 electron rule is :
  - $[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{CO})(\text{PPh}_3)]$
  - $[\text{W}(\text{CO})_3(\text{SiMe}_3)(\text{Cl})(\text{NCMe})_2]$
  - $[\text{IrCl}_3(\text{PPh}_3)_2(\text{AsPh}_2)]^-$
  - $[\text{Os}(\text{N})\text{Br}_2(\text{PMe}_3)(\text{NMe}_2)]^-$
- Among the following, the unstable carbonyl species is :
  - $\text{Mn}(\text{CO})_5\text{Cl}$
  - $[\text{Mn}(\text{CO})_5]^-$
  - $[\text{Mn}(\text{CO})_5]^+$
  - $\text{Mn}(\text{CO})_5$
- In which one of the following complexes is the formal oxidation state and coordination number of Co are -1 and 4 respectively?
  - $\text{Co}_2(\text{CO})_8$
  - $\text{RCo}(\text{CO})_4$
  - $\text{Na}[\text{Co}_4(\text{CO})_{12}]$
  - $\text{Na}[\text{Co}(\text{CO})_4]$
- Identify the 18 e species in the list below :
  - $\text{Ni}(\text{H}_2\text{O})_6^{2+}$
  - $\text{Fe}(\text{CO})_5$
  - $(\eta^6\text{C}_6\text{H}_6)\text{Ru}$
  - $\text{V}(\text{CO})_6$
- The oxidation state of molybdenum in  $[(\eta^7\text{-tropyl})\text{Mo}(\text{Co})_3]^+$  is :
  - +2
  - +1
  - 0
  - 1
- The correct formulation for tetra (cyclopentadienyl) titanium(IV) complex is :
  - $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_4]$
  - $[\text{Ti}(\eta^1\text{-C}_5\text{H}_5)_4]$
  - $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_5)_3]$
  - $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2]$
- Among the complexes (i)  $(\text{C}_6\text{H}_6)_2\text{Cr}$ , (ii)  $[\text{HMn}(\text{CO})_5]$ , (iii)  $[(\text{CH}_3\text{CO})\text{Rh}(\text{CO})\text{I}_3]^-$  and (iv)  $\text{CpFe}(\text{CO})_2(\text{CH}_3)$ , the 18-electron rule is not followed in :
  - (iii) only
  - (ii) and (iii)
  - (i) and (iv)
  - (ii) only
- Oxidation number of Fe in  $[\text{Fe}(\text{NO})(\text{CN})_5]^{2-}$  is :
  - 1
  - 2
  - 3
  - 0
- Oxidation number of Co in  $\text{Co}(\text{NO})(\text{CO})_3$  is :
  - 1
  - 2
  - 3
  - 1

10. The organometallic compound  $W(C_5H_5)_2(CO)_2$  follows the 18-electron rule. The hapticities of the two cyclopentadienyl groups are :
- 5 and 5
  - 3 and 5
  - 3 and 3
  - 1 and 5
11. Which one of the following molecules does not obey the 18-electron rule ?
- $[Mn(CO)_6]^+$
  - $Fe(CO)_5$
  - $[Cr(CO)_5]^{2-}$
  - $[Mn(CO)_4Cl_2]^{2-}$
12. The hapticity of cyclohepta-1,3,5-triene in  $(C_7H_8)Fe(CO)_3$  is :
- 2
  - 4
  - 6
  - 7
13. The complex which obey the 18-electron rule is :
- $Fe(CO)_4$
  - $Ni(CO)_3(PPh_3)$
  - $Cr(CO)_5$
  - $Cr(C_5H_5)_2$
14. To satisfy the 18-electron rule in the complex [cycloheptatriene,  $Mo(CO)_3$ ], the hapticity of the coordinated cycloheptatriene ligand must be :
- 6
  - 5
  - 4
  - 2
15. The oxidation state of Fe in the complex  $[Cp(Fe(CO)_2)_2]$  is :
- +2
  - +1
  - 0
  - 1
16. The complex  follows :
- $18e^-$  rule and stable
  - $16e^-$  rule and unstable
  - $18e^-$  rule and thermodynamically unstable
  - $16e^-$  rule and stable
17. The complex that obeys the 18 electron rule is :
- $[Mn(CO)_5]$
  - $[(\eta^5 - C_5H_5)_2Co]$
  - $[Mo(CO)_3(CH_3CN)_3]$
  - $[(\eta^5 - C_5H_5)_2Ti]$
18. Identify the complex which does not obey the 18 electron rule :
- $[Fe(H_2O)_6]^{2+}$
  - $[Ru(\eta^6 - C_6H_6)(\eta^6 - C_6H_6)]$
  - $Na[Co(CO)_3(PPh_3)]$
  - $[Mn(CO)_5]^-$

19. The hapticity of nitrosyl in  $[Mo(\eta^1 allyl)_3(\eta^3 allyl)_2NO]$  is :

- 1
- 2
- 3
- 0

### ANSWERS

1. (d)
2. (d)
3. (d)
4. (b)
5. (c)
6. (d)
7. (a)
8. (b)
9. (d)
10. (b)
11. (d)
12. (b)
13. (b)
14. (a)
15. (b)
16. (d)
17. (c)
18. (b)
19. (a)



### Subjective Questions

- Show that the metal centres in the following complexes obey the 18-electron rule :
  - $Rh Cl(H)_2(\eta^2 - C_2H_4)(PPh_3)_2$
  - $(\eta^5 - C_5H_5) Ir(\eta^2 - C_2H_4)(PPh_3)$
  - $(\eta^3 - C_3H_5)_2 Rh(\mu - Cl)_2 Rh(\eta^3 - C_3H_5)_2$
  - $(OC_5) Fe$  
  - $[(\eta^5 - C_5H_5) Rh(CH_3)(PPh_3)_2]^+$
- Compute the coordination number, oxidation number of metal, VEC and give the name of the following species. Also select the species which obey the 18-electron rule :
 

(a) $Cp(CO)Ir(\mu - CO)_2Re(CO)Cp$	(b) $[Fe(C_6H_6)(C_5H_5)]^+$
(c) $Ti(\eta^5 - Cp)_2Cl_2$	(d) $[CpFe(CO)(PPh_3)(CF_3)][BF_4]$
(e) $Cp_2^* ZrCl_2$	(f) $[Cr(NO)(CN)_5]^{4-}$
(g) $[Fe(NO)(CN)_5]^{2-}$	(h) $Cr(NO)_4$
(i) $Mn(NO)_3(CO)$	(j) $[Ir(CO)(PPh_3)Cl(NO)]^+$
(k) $Cp_2 CO(\mu - NO)_2$	(l) $[Ir(PPh_3)_3(N_2)_2]^+$
(m) $Np(Cp)_3 Me$	(n) $(\eta^4 - cot) Fe(CO)_3$
(o) $[(\eta^3 - C_3H_5)_2(\mu - Cl)Rh]_2$	(Rh—Rh single bond)
- Following the 18-electron rule determine the unknown quantity in the following complexes:
  - $\{CpFe(CO)_3\}^x$
  - $[CpMn(CO)_x]_2$  (an Mn = Mn double bond)

- (c)  $\text{Ma}_2[\text{Fe}(\text{CO})_x]$   
 (d)  $[\text{CpW}(\text{CO})_x]_2$  (W – W single bond)  
 (e)  $[\text{CpM}(\text{CO})_3]_2$  (a single M – M bond, M is 4d transition metal)

4. A metal complex having a methyl substituted Cp and CO ligand with the formula  $\text{FeC}_9\text{H}_7\text{O}_3^+$ . The complex is highly soluble in polar solvent and obey 18-electron rule of the complex. Determine the structure of the complex.

5. Define organometallic compounds. Which of the following are organometallic compounds ?  
 (i)  $\text{CH}_3\text{MgBr}$  (ii)  $(\text{C}_2\text{H}_5)_2\text{Zn}$   
 (iii)  $\text{Ti}(\text{OEt})_4$  (iv) Zeise's salt  
 (v)  $(\eta^6-\text{C}_6\text{H}_6)_2\text{Cr}$

6. (a) What is meant by the term "Hapticity"? Explain with suitable examples.  
 (b) What hapticities are possible for the interaction of each of the following ligands with a single d-block metal atoms?  
 (i)  $\text{C}_3\text{H}_5^-$ , (ii) butadiene, (iii) cyclobutadiene, (iv) cyclopentadienyl, (v)  $\text{C}_6\text{H}_6$ , (vi) cyclooctatetraene.

7. (a) Give the valence electron count in the following :  
 (i)  $[\text{Mn}(\pi-\text{C}_3\text{H}_3)(\text{CO})_4]$  (ii)  $[\text{HCo}(\text{CO})_4]$   
 (iii)  $\text{Fe}(\pi-\text{C}_5\text{H}_5)_2$  (iv)  $[\text{Mn}(\text{CO})_5\text{Cl}]$   
 (b) Predict whether the following obey E.A.N. rule and explain :  
 (i)  $[\text{Mn}(\text{CO})_5(\text{C}_2\text{H}_4)]^+$   
 (ii)  $[\text{Co}(\pi-\text{C}_3\text{H}_5)(\text{CO})_3]$   
 (iii)  $\text{Cr}(\text{CO})_6$   
 (iv)  $[\text{V}(\text{CO})_6]^-$

8. (a) Using the 18-electron rule, indicate the probable number of  $n$ ,  $m$  and the 3d metal ( $M$ ) in the following :  
 (i)  $[\text{W}(\eta^6-\text{C}_6\text{H}_6)(\text{CO})_n]$   
 (ii)  $[(\eta^6-\text{C}_6\text{H}_6)_n\text{Cr}(\text{CO})_m]$   
 (iii)  $[(\eta^5-\text{C}_5\text{H}_5)\text{M}(\text{C}_2\text{H}_4)_2]$   
 (iv)  $[\text{Rh}(\eta^5-\text{C}_5\text{H}_5)(\text{CO})_n]$   
 (v)  $\text{Ru}_3(\text{CO})_n$

(b) Write the formulae of three organometallic compounds having multicentred bonding.



# Metal Carbonyls

Carbon monoxide is undoubtedly one of the most important and most widely studied ligand in organometallic chemistry. Almost all of the transition metals form metal carbonyls (the complexes containing only CO as ligands) and these homoleptic carbonyls are useful precursors for other organometallic compounds. Though carbon monoxide is not considered a very strong Lewis base, yet it forms strong bonds to the metals in their complexes. In most of the metal carbonyls the metals are always in low oxidation states, most often in an oxidation state of zero but sometimes -1 or +1 and these carbonyls are often quite stable with respect to dissociation, substitution or oxidation. CO may bond to a single metal or it may act as a bridge between two or more metals. The number of CO ligands coordinated to the metal is generally in accordance with the 18-electron rule. The 18-electron rule is followed by almost 99% of metal carbonyls.

## Classification of Metal Carbonyls

**(1) Classification on the Basis of Ligands :** Metal carbonyls can be classified into two categories :

- (i) Homoleptic carbonyl complexes
  - (ii) Heteroleptic carbonyl complexes

**(i) Homoleptic Carbonyl Complexes :** The complexes in which a metal is bound to only CO ligands are known as homoleptic carbonyl complexes. For example,  $\text{Ni}(\text{CO})_4$ ,  $\text{Cr}(\text{CO})_6$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{Co}_2(\text{CO})_8$ ,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Fe}_3(\text{CO})_{12}$ ,  $\text{Ir}_4(\text{CO})_{12}$  etc.

**(ii) Heteroleptic Carbonyl Complexes :** The complexes in which a metal is bound to CO as well as other ligands such as  $PR_3$ ,  $PPh_3$ ,  $PF_3$ ,  $NO$ ,  $RNC$ ,  $PF_3$  etc. For example,  $Ni(CO)_3(PPh_3)$ ,  $Mo(CO)_3(PF_3)_3$ ,  $Cr(CO)_3(NO)_2$  etc.

### (2) Classification on the Basis of Number of Metal Atoms and the Structures of Metal Carbonyls :

**(i) Mononuclear Metal Carbonyls :** These carbonyls contain only one metallic atom and these carbonyls do not contain any bridging CO ligand. For example,  $Ni(CO)_4$ ,  $Cr(CO)_6$ ,  $Fe(CO)_5$  etc.

**(ii) Polynuclear Metal Carbonyls :** Polynuclear carbonyls contain two or more metal atoms. These are classified as :

**(a) Homonuclear Metal Carbonyls :** These contain metal atoms of only one element. For example,  $Fe_2(CO)_9$ ,  $Mn_2(CO)_{10}$ ,  $Co_2(CO)_8$ ,  $Fe_3(CO)_{12}$ ,  $Co_4(CO)_{12}$ ,  $Rh_4(CO)_{12}$ ,  $Ir_4(CO)_{12}$ , etc.

**(b) Heteronuclear Metal Carbonyls :** These carbonyls contain metals of different elements. For example,  $MnCo(CO)_4$ .

The polynuclear metal carbonyls are also classified as :

- (a) Non-bridged metal carbonyls and
- (b) Bridged metal carbonyls.

**(a) Non-bridged Metal Carbonyls :** These carbonyls contain terminal CO ligands and M—M bonds. For example,  $Co_2(CO)_8$  (in solution),  $Mn_2(CO)_{10}$ ,  $Ir_4(CO)_{12}$  etc.

**(b) Bridged Metal Carbonyls :** These carbonyls contain bridged as well as terminal CO ligands and M—M bonds. For example,  $Fe_2(CO)_9$ ,  $Co_2(CO)_8$  (in solid state),  $Fe_3(CO)_{12}$  etc.

### Bonding in Metal Carbonyls

CO is considered to be a good  $\sigma$ -donor as well as a  $\pi$ -acceptor ligand. This property of CO and the other  $\pi$ -acceptor ligands such as  $CN^-$ ,  $NO$ ,  $C_2H_4$  etc. can be explained by the MO diagram of CO (Figure. 2.1). When energy difference between 2s and 2p-orbitals is small there will be mixing of s and  $p_z$  orbitals. Since the energy difference between 2s and 2p-orbitals for carbon is small, therefore, the 2s and  $2p_z$  orbitals on carbon mix to produce two  $sp_z$  mixed atomic orbitals. The higher energy  $sp_z$  orbital on carbon is closer in energy to its pure  $2p_z$  orbital and, therefore, has major contribution from it whereas the lower energy  $sp_z$  orbital of carbon is closer to its pure 2s orbital and, therefore, has major contribution from it.

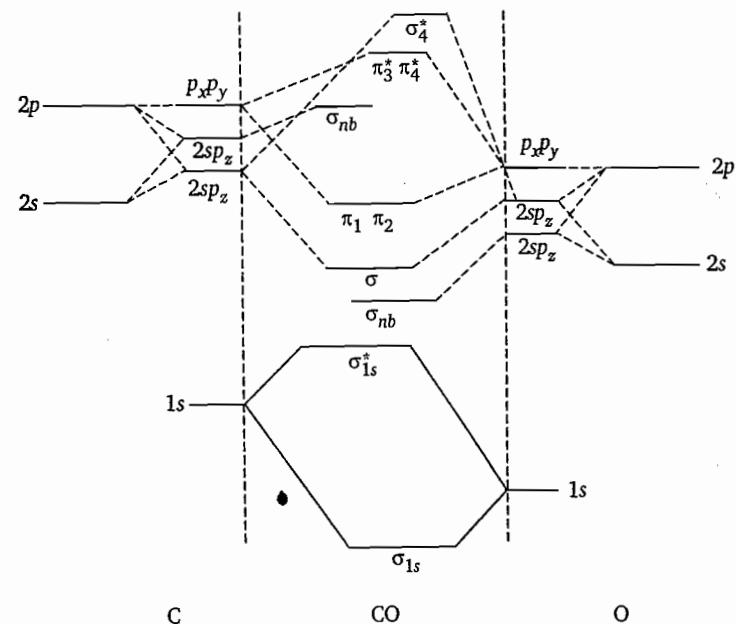


Fig. 2.1 Molecular orbital diagram of CO

Similarly, 2s and  $2p_z$  orbitals of oxygen also mix with one another but not to the same extent to which the orbitals of carbon mix because the energy difference between 2s and  $2p_z$  orbitals on oxygen is higher than that between the same atomic orbitals of carbon and two mixed  $sp_z$  orbitals are formed. The higher energy  $sp_z$  orbital of oxygen is closer to its pure  $2p_z$  orbital and has major contribution from it whereas the lower energy  $sp_z$  orbital of oxygen is closer to its pure 2s orbital and has major contribution from it.

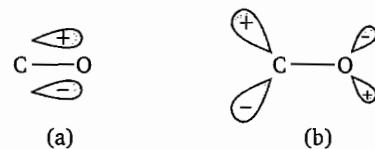
Oxygen is more electronegative than carbon, so the energies of orbitals of oxygen are lower than that of similar orbitals on carbon. The lower energy mixed  $sp_z$  orbital of carbon is comparable in energy with the higher energy mixed  $sp_z$  orbital of oxygen. These two orbitals of same symmetry and comparable energies combine linearly to form  $\sigma$ -bonding and antibonding molecular orbitals. The lower energy  $sp_z$  orbital on oxygen and higher energy  $sp_z$  orbital on carbon are far apart (i.e., large energy difference between them). Though these orbitals have same symmetry, they do not combine and, therefore, these orbitals remain almost non-bonding rather than combining to give MOs, they are localized on oxygen and carbon respectively.

The higher energy  $sp_z$  orbital of carbon is non-bonding but it has some antibonding character. The non-bonding  $sp_z$  orbital on oxygen is close in energy to 2s orbital on oxygen and, therefore, has mostly s-character of 2s-orbital of oxygen.

On the other hand, non-bonding  $sp_z$  orbital on carbon is close in energy to the  $p_z$  orbital of carbon, therefore, it has the characteristics of  $2p_z$ -orbital on carbon. These non-bonding orbitals are

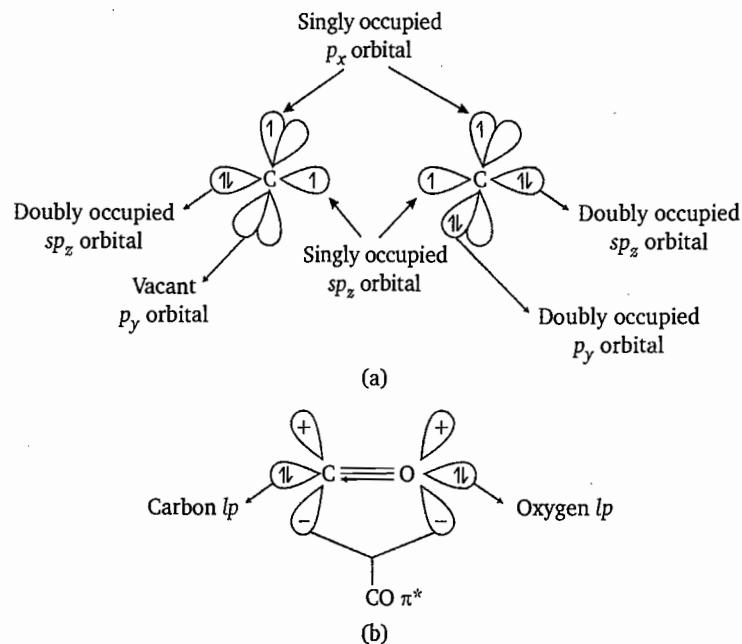
occupied by lone pairs on carbon and oxygen and are directed away from the CO bond. The degenerate  $2p_x$ ,  $2p_y$  orbitals on carbon and same degenerate  $2p_x$ ,  $2p_y$  orbitals on oxygen have  $\pi$ -symmetry. The orbitals on carbon combine with same orbitals on oxygen to give two degenerate  $\pi$ -bonding ( $\pi$ ) and two degenerate  $\pi$ -antibonding ( $\pi^*$ ) orbitals. (Fig. 2.2)

The lower energy atomic orbitals of oxygen contribute more to the bonding molecular orbital and the higher energy atomic orbital of carbon contribute more to antibonding molecular orbitals (Figure. 2.1). Therefore, in CO the bonding molecular orbitals will have the character of orbitals of oxygen and the antibonding molecular orbitals have the character of orbitals of less electronegative carbon. This is due to the conservation of orbitals.



**Fig. 2.2 :** (a) One  $\pi$ -bonding MO (b) One  $\pi$ -antibonding MO

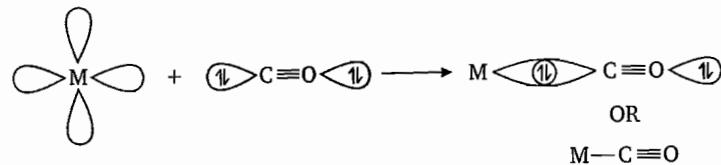
Singly filled  $sp_z$  and  $p_x$  orbitals on each atom form a  $\sigma$  and a  $\pi$ -bond respectively. This leaves the  $p_y$  orbital empty on carbon and the doubly filled  $p_y$  orbital on oxygen (Fig. 2.3). The  $p_y$  orbital on oxygen donates its pair of electrons to the empty  $p_y$  orbital of carbon to form a dative bond or coordinate



**Fig. 2.3**

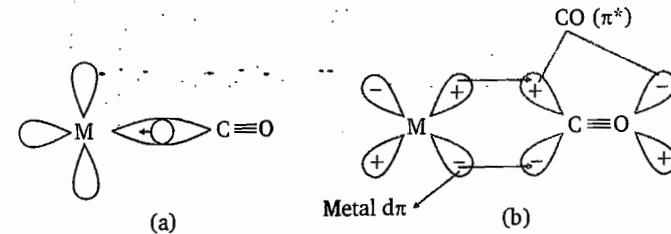
bond [Fig. 2.3(b)]. This dative bond is also a  $\pi$ -bond. This dative bond leads to a  $\bar{C}—O^+$  polarization in CO molecule which is almost exactly cancelled by an opposite polarization  $^+C—O^-$  caused by the higher electronegativity of oxygen. Due to high electronegativity of oxygen the  $\pi$ -bonding electrons are localized on oxygen and cause  $C^+—O^-$  polarization.

The molecular orbitals energy level diagram (Figure. 2.1) shows that the HOMO has a  $\sigma$  symmetry and the HOMO is localized on carbon, not on oxygen because the effective nuclear charge or electronegativity of carbon is less than that of oxygen. The HOMO of CO ligand donates its lone pair of electrons to the empty orbital of suitable symmetry on the metal (e.g., an  $sp_zd_{z^2}$  hybrid orbital) to form a M—CO  $\sigma$ -bond (Figure. 2.4).



**Fig. 2.4**

Carbon monoxide has two LUMO  $\pi^*$  orbitals which are also localized on carbon. These orbitals have correct symmetry to overlap with non-bonding metal  $d$ -orbitals that have  $\pi$  symmetry such as the  $t_{2g}$  ( $d_{xy}$ ,  $d_{yz}$  or  $d_{zx}$ ) orbitals in octahedral complex. A metal atom having electrons in a  $d$ -orbital of suitable symmetry can donate electron density to the LUMO  $\pi^*$  of CO (Fig. 2.5). The  $\pi$  interaction leads to the delocalization of electrons from filled  $d$ -orbitals of suitable symmetry on the metal atom into the empty  $\pi^*$  orbitals on the CO ligands. Because the electron density is flowing from the metal  $d$ -orbitals on to the  $\pi^*$  orbitals on ligands, this donation is known as  $\pi$  back donation or back bonding and the CO ligand is said to be a strong  $\pi$ -acceptor (or  $\pi$ -acid). The  $\sigma$ -donor and  $\pi$ -acceptor interaction are shown in Figure. 2.5.

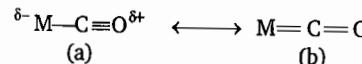


**Fig. 2.5 :** (a)  $\sigma$ -bonding, (b)  $\pi$ -Back-bonding

On the basis of foregoing discussion, the CO ligand is said to be a  $\sigma$ -donor and a  $\pi$ -acceptor and the metal is a  $\sigma$ -acceptor and a  $\pi$ -donor. Some other  $\pi$ -acceptor ligands are  $CN^-$ ,  $NO^+$ ,  $CNR$ ,  $N_2$  etc.

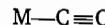
Both the  $\sigma$ - and  $\pi$ -bonding reinforce (*i.e.*, strengthen) each other. The formation of  $\sigma$ -bond results in the increase in electron density on metal and tends to make the CO ligand positive. Both the increase in electron density on the metal, and the positive charge on CO increase the  $\pi$ -accepting ability of CO. The greater electron density on the metal and greater partial positive charge on CO ligand make the effective return of electron density from metal  $d$ -orbital to the  $\pi^*$  orbital of CO ligand. As the electron density delocalized from metal  $d$ -orbital onto  $\pi^*$  orbitals of CO increases, further electron flow from CO to metal  $d$ -orbital results. The result of this two way electron flow is that the metal-ligand bond is stronger than the sum of isolated ligand to metal  $\sigma$ -bonding and metal to ligand  $\pi$ -bonding effects. This kind of mutual strengthening of  $\sigma$ - and  $\pi$ -bonding is called **synergism** and this effect is called **synergistic effect**.

The metal to ligand  $\pi$  back bonding results in the increase in M—C bond strength as the bond order tends to increase. Since the  $\pi$ -back bonding results in occupation of  $\pi^*$  on CO ligand, the bond order of CO ligand itself decreases and, therefore, the C—O bond becomes longer and weaker. Alternatively, increased M—C double bonding leads to decrease C—O multiple bonding as shown by the resonance structures (Fig. 2.6).

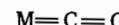


**Fig. 2.6**

If a metal is in high oxidation state, then there will be poor  $\pi$ -back bonding and the bond order of M—C is close to 1 and that of C—O is close to 3.



If the metal is in low oxidation state (*i.e.*, electron rich), then there will be strong  $\pi$  bonding between metal and CO and the bond order of both M—C and C—O is close to 2.



### Evidence for Synergistic Bonding or $\pi$ -Back Bonding

**(I) Infrared Spectroscopy :** Infrared spectroscopy is extensively used to characterize metal carbonyls since the C—O stretching frequencies give very strong sharp bands in a very uncrowded region of the spectrum (*i.e.*, these bands are well separated from stretching frequencies of any other ligands coordinated to metal). Trends in CO bond lengths and their IR stretching frequencies are in general agreement with the  $\pi$ -back bonding model. The vibrational frequency of a bond (Eq. 2.1.) depends on the strength of bond which is measured by the force constant.

$$\bar{v} (\text{in } \text{cm}^{-1}) = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \dots(2.1)$$

where  $k$  = force constant

$\mu$  = reduced mass, for atoms of mass  $m_1$  and  $m_2$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

and  $c$  is the velocity of light ( $3 \times 10^{10}$  cm/sec)

$$(i) \bar{v} \propto \sqrt{k}$$

*i.e.*, as the strength of bond between two atoms increases, stretching frequency of the bond increases and the frequency (or wave number in  $\text{cm}^{-1}$ ) of the corresponding bond will be higher in the infrared spectrum.

$$(ii) \bar{v} \propto \frac{1}{\sqrt{\mu}}$$

*i.e.*, as the reduced mass of the atoms increases, stretching frequency decreases.

The stretching frequency of free CO is  $2143 \text{ cm}^{-1}$ , on the other hand, it is  $2000 \text{ cm}^{-1}$  in  $\text{Cr}(\text{CO})_6$ . The explanation of this is that the back bonding populates the  $\pi^*$  on CO and reduces the bond order of CO towards two and, therefore, resulting in lengthening and weakening of C—O bond.

### Factors Affecting the Magnitude of Stretching Frequency

According to equation 2.1

IR stretching frequency  $\propto$  Bond strength

$\propto$  Bond order

$\propto \frac{1}{\text{Bond length}}$

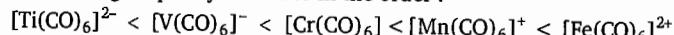
Various factors affecting the stretching frequency are given below :

**(1) Charge on Metal :** A higher electron density on the metal will cause an increase in the extent of back bonding. This leads to an increase in electron density in the  $\pi^*$  orbital on CO, lengthening and weakening of C—O bond and a decrease of the C—O stretching frequency.

A formal negative charge on a metal carbonyl causes the lower ability of metal to attract electrons and a great tendency to back donate electron density to  $\pi^*$  on CO. Higher the formal negative charge on metal carbonyl, more will be the tendency of metal to donate electron density to  $\pi^*$  on CO. Therefore, stretching frequency of C—O decreases. Since the increased extent of back bonding increases the M—C double bond character and, therefore, the stretching frequency of M—C bond increases.

A formal positive charge on a metal carbonyl causes the great ability of metal to attract electrons and lower tendency to back donate electrons to  $\pi^*$  on CO. Higher the formal positive charge on a metal carbonyl, lower will be the tendency of metal to back donate electron density to  $\pi^*$  on CO. Therefore, C—O bond order increases and C—O bond strength increases and hence stretching frequency of C—O bond increases (compare to respective neutral metal carbonyl). On the other hand, M—C bond order is lower and M—C bond is weaker. Therefore, stretching frequency of M—C bond decreases.

For isoelectronic species  $[\text{Ti}(\text{CO})_6]^{2-}$ ,  $[\text{V}(\text{CO})_6]^-$ ,  $[\text{Cr}(\text{CO})_6]$ ,  $[\text{Mn}(\text{CO})_6]^+$  and  $[\text{Fe}(\text{CO})_6]^{2+}$  the C—O stretching frequency increases in the order :



While the M—C bond stretching frequency increases in the reverse direction.

CO stretching frequencies of the these carbonyls ( $\nu_{\text{CO}}$  cm<sup>-1</sup>) are given in Table 2.1.

**Table 2.1**  $\nu_{\text{CO}}$  (in cm<sup>-1</sup>) For Isoelectronic Species

Compound	$\nu_{\text{CO}}$ (in cm <sup>-1</sup> )
$[\text{Ti}(\text{CO})_6]^{2-}$	1750
$[\text{V}(\text{CO})_6]^-$	1860
$[\text{Cr}(\text{CO})_6]$	2000
$[\text{Mn}(\text{CO})_6]^+$	2100
$[\text{Fe}(\text{CO})_6]^{2+}$	2200

For cationic carbonyl complexes such as  $[\text{Fe}(\text{CO})_6]^{2+}$  the C—O stretching frequency is higher than that in CO itself. Due to high positive charge on metal, the ability of metal to back donation of electrons is almost diminished. The HOMO of CO, a  $\sigma$  orbital which is slightly antibonding with respect to the C—O bond, donates its electron pair to metal. Therefore, there is a decrease in the population of HOMO and results in the strengthening of C—O bond.

Alternatively, in free CO, the electrons are polarized towards the more electronegative oxygen. The electron density in the  $\pi$ -orbitals is greater near to the oxygen atom than to the carbon atom. A transition metal cation attracts the bonding electrons and, therefore, reduces the polarization in the C—O bond.



More polarization of C—O bond



Less polarization of C—O bond

Due to the reduction in the polarization of C—O bond, the electrons in the cationic carbonyl complexes are more equally shared between carbon and oxygen, and as a result C—O bond becomes stronger. Hence C—O stretching frequency is high in cationic carbonyl complexes.

**(2) Number of CO Ligands :** As the number of CO ligands attached to a metal increases, the formal negative charge on metal increases. Therefore, the extent of back donation increases and hence C—O stretching frequency decreases as shown Table 2.2.

**Table 2.2**

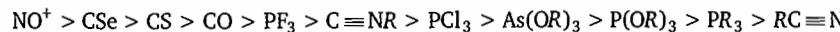
Compound	$\nu_{\text{CO}}$ (in cm <sup>-1</sup> )
$\text{Ni}(\text{CO})_4$	2057
$\text{Fe}(\text{CO})_5$	2034
$\text{Cr}(\text{CO})_6$	1981

**(3) Presence of Other Ligand on Metal :** Carbonyl frequencies are also useful in categorizing the relative  $\sigma$ -donor and  $\pi$ -acceptor properties of other ligand L in the complexes such as  $\text{L}_n\text{M}(\text{CO})_x$ . If a ligand L is a strong  $\sigma$ -donor and weak  $\pi$ -acceptor (such as  $\text{PMe}_3$ ,  $\text{PEt}_3$ ,  $\text{PPh}_3$ ) or only a  $\sigma$ -donor (such as  $\text{NH}_3$ ,  $\text{RNH}_2$  or en) or a  $\sigma$  as well as  $\pi$ -donor (such as  $\text{H}_2\text{O}$ ,  $\text{F}^-$ ), it will supply electron density on metal and this increased electron density on metal will encourage back donation and leads to shorter and stronger M—C bond and longer and weaker C—O bond. Consequently the M—C stretching frequency increases and C—O stretching frequency decreases. Let us consider, for example, two complexes  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_3(\text{NH}_3)_3$ . In both complexes, the Cr has a formal charge of -3 and back donation occurs. However, because  $\text{NH}_3$  has no orbitals available for accepting electron density from the metal, all of the back donation in complex  $\text{Cr}(\text{CO})_3(\text{NH}_3)_3$  goes to three CO ligands. In Complex  $\text{Cr}(\text{CO})_6$ , the back donated electron density is spread among six CO ligands. Because of this difference, the C—O stretching frequency in  $\text{Cr}(\text{CO})_6$  is obtained at 2100 cm<sup>-1</sup> whereas in  $\text{Cr}(\text{CO})_3(\text{NH}_3)_3$  is obtained at 1900 cm<sup>-1</sup>.

If the ligand L is a weak  $\sigma$ -donor but a strong  $\pi$ -acceptor (such as  $\text{PF}_3$ ,  $\text{C}\equiv\text{S}$ ,  $\text{N}\equiv\text{O}^+$ ), it will attract electron density from the metal. This leads to reduction in the extent of back bonding required and, therefore, C—O bond remains shorter and stronger and hence for such carbonyl complexes C—O stretching frequency is high. On the other hand, the M—C bond remains large and weak and, therefore, stretching frequency for M—C bond is low.

The ligands which increase the electron density on the metal will enhance the back  $\pi$ -bonding in metal carbonyls and lead to shorter and stronger M—C bond and longer and weaker C—O bond. Therefore, such ligands lead to increase the M—C bond stretching frequency and to decrease C—O bond stretching frequency.

The ligands which reduces the electron density on the metal will reduce the back  $\pi$ -bonding in metal carbonyls. As a result M—C bond will be longer and weaker and C—O bond will be shorter and stronger. Therefore, M—C bond stretching frequency decreases and the CO stretching frequency increases. The infrared C—O stretching frequencies measurements provide the following order of  $\pi$ -acceptor strength of various ligands :



Some triple bonded ligands which are isoelectronic with CO can also be arranged in order of  $\pi$ -acceptor abilities.



The two charged ligands  $\text{CN}^-$  and  $\text{NO}^+$  of this series differ substantially from other members and are not always good analogs. The electron rich  $\text{CN}^-$  is not only a poor  $\pi$ -acceptor but also a good  $\sigma$ -donor and, therefore, forms many complexes with metal atoms in higher oxidation states. At the other end of this series,  $\text{NO}^+$  is very strongly electron withdrawing. It forms a linearly linked  $\text{M}-\text{NO}$  complexes in which it is considered to be  $\text{NO}^+$ . In such cases NO is considered as the two electron donor  $\text{NO}^+$  on the ionic model and as a three electron donor on the covalent model (Figure. 2.21 and 2.22). When NO takes an additional electron to form  $\text{NO}^-$ , the  $\text{M}-\text{NO}$  link is bent. In such complexes NO is considered as the two electron donor on the ionic model and one electron donor on covalent model (Figure 2.21 and 2.22).

The substituted phosphene ligands show the following order of basicity (*i.e.*,  $\sigma$ -donor ability):



Where R = alkyl and Ar = aryl.

The order of  $\pi$ -acceptor strength of these ligands is :



The  $\sigma$ -donating and  $\pi$ -accepting abilities of substituted phosphines depend upon the nature of the substituents. A highly electronegative atom will attract electron toward itself. Higher the electronegativity of atom attached to phosphorus, more electron density will shift toward it and, therefore,  $\pi$ -accepting ability will be high. Since highly electronegative atom attached to phosphorus is electron withdrawing and will remove electron density from metal. This leads to decrease in the extent of  $\pi$ -back bonding required, weaker  $\text{M}-\text{C}$  bonds and a stronger C—O bond and, therefore, lower  $\text{M}-\text{C}$  and higher C—O stretching frequencies.

$\text{P(OR)}_3$  ligands are somewhat weaker  $\pi$ -acceptors than  $\text{PF}_3$  because F is more electronegative than oxygen of OR group.  $\text{P(OAr)}_3$  is stronger  $\pi$ -acceptor than  $\text{P(OR)}_3$  because Ar group increases the electronegativity of oxygen whereas R group decreases the electronegativity of oxygen (as shown in Figure 2.7) because Ar is an electron withdrawing group and R is an electron releasing group:

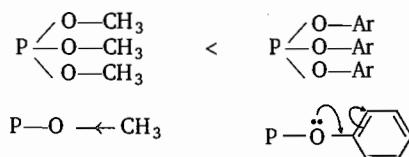
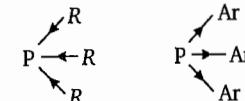


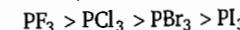
Fig. 2.7

When the attached group is less electronegative as in  $\text{PR}_3$  (where R = H,  $\text{CH}_3-$ ,  $\text{C}_2\text{H}_5-$ ), electron density will be pushed toward the metal. This leads to increase in extent of back bonding, stronger  $\text{M}-\text{C}$  bonds and a weaker C—O bond. Therefore, higher M—C and lower C—O stretching

frequencies result. Therefore, for example, in alkylphosphines, the P-atom becomes a weaker  $\pi$ -acceptor but a stronger  $\sigma$ -donor.  $\text{PAr}_3$  is a stronger  $\pi$ -acceptor than  $\text{PR}_3$  because R group is an electron releasing and Ar is an electron withdrawing group.



For halide phosphines ( $\text{PX}_3$ ) the order of  $\pi$ -accepting ability is :



It is to be noted that in phosphine  $\text{PX}_3$  (where X = H, F, Cl, Br, I, Me, OMe, OAr) vacant 3d orbitals of P as well as  $\sigma^*$  orbitals of P—X act as  $\pi$ -acceptors but the vacant 3d-orbitals play only a minor role.

The effect of other ligands present on  $\nu_{\text{CO}}$  is shown in Table. 2.3.

Table 2.3

Complex	$\nu_{\text{CO}}$ (in $\text{cm}^{-1}$ )
$\text{Ni}(\text{CO})_4$	2131
$\text{Ni}(\text{CO})_3(\text{PF}_3)$	2111
$\text{Ni}(\text{CO})_3[\text{P}(\text{OPh})_3]$	2085
$\text{Ni}(\text{CO})_3\text{PMe}_3$	2064

On moving down the series in Table 2.3, the  $\sigma$ -donor ability of the phosphine ligands increases and the  $\pi$ -acceptor ability decreases.  $\text{PF}_3$  is the strongest  $\pi$ -acceptor and the weakest  $\sigma$ -donor (due to the presence of highly electronegative fluorines). As a result, nickel in  $\text{Ni}(\text{CO})_3(\text{PF}_3)$  carries the lowest electron density and, therefore, it has the lowest ability to donate electron density to  $\pi^*$  orbital of the CO ligands. Therefore, there is less reduction in bond order of free CO. Consequently, the CO ligands in  $\text{Ni}(\text{CO})_3(\text{PF}_3)$  have shorter and stronger C—O bonds and therefore  $\nu_{\text{CO}}$  is larger than the lower complexes in Table 2.3.

On the other hand,  $\text{PMe}_3$  is the strongest  $\sigma$ -donor and weakest  $\pi$ -acceptor. As a result the nickel in  $\text{Ni}(\text{CO})_3\text{PMe}_3$  carries the greatest electron density and it has greatest ability to donate electron density to the  $\pi^*$  orbital of the CO ligands. Consequently, the CO ligands in  $\text{Ni}(\text{CO})_3(\text{PMe}_3)$  have the largest and weakest C—O bonds and hence, lowest C—O stretching frequency.

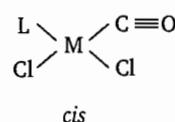
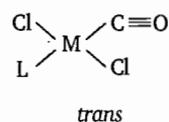
However  $\nu_{\text{CO}}$  in  $\text{Ni}(\text{CO})_4$  is highest because CO ligands are strongest  $\pi$ -acceptors in this series.

Some examples of C—O stretching frequencies of the substituted facial carbonyl complexes of molybdenum are shown in Table 2.4.

Table 2.4

Complex	$\nu_{CO}$ (in $\text{cm}^{-1}$ )
$\text{Mo}(\text{CO})_3(\text{PF}_3)_3$	2090, 2055
$\text{Mo}(\text{CO})_3(\text{PCl}_3)_3$	2040, 1990
$\text{Mo}(\text{CO})_3[\text{P}(\text{OPh})_3]_3$	
$\text{Mo}(\text{CO})_3[\text{P}(\text{OMe})_3]_3$	
$\text{Mo}(\text{CO})_3(\text{PPh}_3)_3$	1934, 1835
$\text{Mo}(\text{CO})_3(\text{Py})_3$	1888, 1746
$\text{Mo}(\text{CO})_3(\text{PMMe}_3)_3$	
$\text{Mo}(\text{CO})_3(\text{NMe}_3)_3$	1945, 1854

If a ligand (L) *trans* to a CO ligand is a  $\sigma$ - and  $\pi$ -donor, it will increase electron density on metal which in turn increases metal to CO back bonding. Consequently, it decreases the C—O bond order and increases the M—C bond order. Thus  $\nu_{CO}$  decreases and M—C stretching frequency increases. If we compare *cis*- and *trans*-isomers of  $[\text{Pt}(\text{CO})\text{LCl}_2]$  the C—O stretching frequency of *trans*- isomer is lower than that of *cis*-isomer.



$\text{Cl}^-$  is  $\sigma$  as well as  $\pi$ -donor.

where L =  $\sigma$ -donor = py,  $\text{NH}_3$ ,  $\text{NMe}_3$

Order of  $\sigma$ -donor ability is :  $\text{NMe}_3 > \text{NH}_3 > \text{Py}$

Order of  $\nu_{C-O}$  → Py >  $\text{NH}_3$  >  $\text{NMe}_3$ .

### Nature of Lewis Acid other than a Metal

The Lewis acid (like  $\text{BH}_3$ ,  $\text{AlCl}_3$ ) other than a metal can not form  $\pi$  back bonding. In case of adduct  $\text{H}_3\text{B} \leftarrow \text{CO}$ , there is no  $\pi$  back bonding and only pure  $\sigma$ -bonding occurs to  $\text{BH}_3$ . Since HOMO in CO is slightly antibonding in character, bond order of CO increases. Thus, CO stretching frequency is raised.

$$\nu_{CO} \text{ for free CO} = 2143 \text{ cm}^{-1}$$

$$\nu_{CO} \text{ for } \text{H}_3\text{B} \leftarrow \text{CO} = 2165$$

### Bonding Modes of CO

The carbonyl ligand may bond to transition metals in an end-on fashion through carbon atom in several ways. It may bond as a terminal ligand as in simple carbonyl complexes such as  $\text{Cr}(\text{CO})_6$ , in which it acts as a two electron donor. The  $\nu_{CO}$  for these complexes is usually in the range of 2120-1850  $\text{cm}^{-1}$ .

The carbonyl ligand may also bridge two or more metals. (In this case, the  $\nu_{CO}$  is in the range of 1860-1600  $\text{cm}^{-1}$ ). When the carbonyl ligand bridges two metals, the  $\nu_{CO}$  is in the range of 1860-1750  $\text{cm}^{-1}$ . A carbonyl that bridges two metals is represented by the prefix  $\mu^2$  (and for convenient by the prefix  $\mu$ ) and donates one electron to each metal. An example of a carbonyl complexes with  $\mu^2\text{-CO}$  bridging is  $\text{Co}_2(\text{CO})_8$ .

When the carbonyl ligand bridges three metals, the  $\nu_{CO}$  lies in the range of 1730-1600  $\text{cm}^{-1}$ . A carbonyl that bridges three metals is represented by the prefix  $\mu^3$ . These most often occur in cluster compounds such as  $\text{Rh}_6(\text{CO})_6$ .

The terminal and bridging modes of bonding and their C—O stretching frequencies are shown in Table 2.5.

Table 2.5

Bonding Modes of CO	$\nu_{CO}$ (in $\text{cm}^{-1}$ )
Free CO	2143
Free $\text{CO}^+$	2184
Terminal M—CO	2120-1850
*Symmetric $\mu^2\text{-CO}$	1860-1750
Symmetric $\mu^3\text{-CO}$	1730-1600

\*Asymmetric  $\mu^2$  and  $\mu^3\text{-CO}$  are also known.

When CO ligand bridges two metals, both metals contribute electron density into  $\pi^*$  orbitals of CO resulting in the lower bond order of bridging CO than for terminal CO ligands. Therefore, C—O bond becomes larger and weaker and hence the  $\nu_{CO}$  for doubly bridging CO is much more lower than for terminal CO ligands. For example,  $\nu_{CO}$  for bridging and terminal CO ligands in  $Fe_2(CO)_9$  (Figure 2.8) are  $1829\text{ cm}^{-1}$  and  $2082, 2019\text{ cm}^{-1}$  respectively.

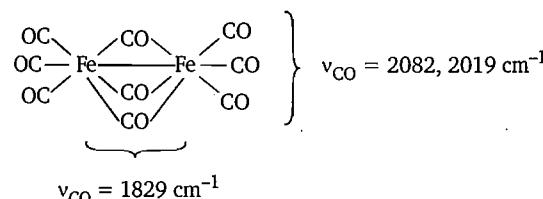
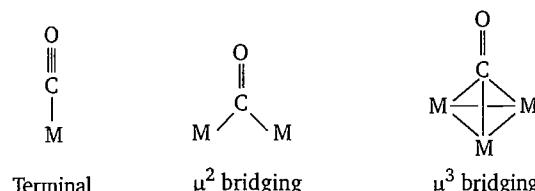
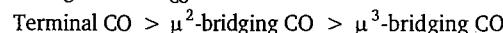


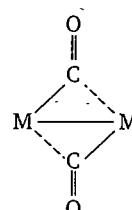
Fig. 2.8

When CO ligand bridges three metals, three metals contribute electron density into  $\pi^*$  orbitals of CO and further decreases the bond order of CO and, therefore, C—O bond length of a triply bridging CO further increases and becomes weaker. Hence the  $\nu_{CO}$  is still lower than in doubly bridging CO. The decreasing order of  $\nu_{CO}$  is :



Asymmetrically bridging CO is also known : Semibridging,  $\sigma/\pi$  asymmetric bridging and isocarbonyl bridging.

In the semibridging carbonyl, the M—CO—M bond is asymmetric rather than symmetric. The semibridging carbonyls are considered to be part way between terminal and bridging carbonyls (Figure 2.9).



Example :

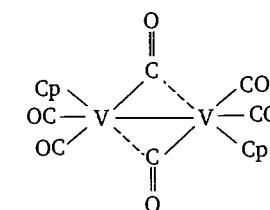


Fig. 2.9

In  $\sigma/\pi$  bridging carbonyl, CO acts as a four or six electron donor and CO ligand donates its  $\sigma$  as well as  $\pi$ -electrons to the two metals (Figure 2.10).

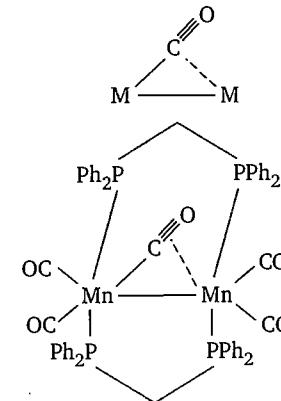


Fig. 2.10

Isocarbonyl bridging occurs via the oxygen atom of a coordinated CO electron deficient early transition metals such as titanium (Figure 2.11), but it is very rare.

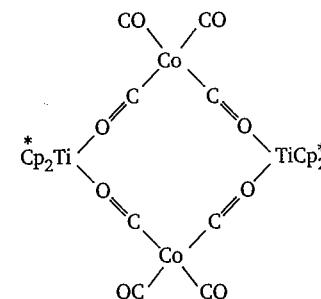
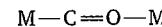


Fig. 2.11

## (II) X-ray Diffraction

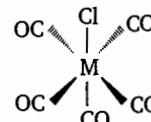
In free CO, the C—O bond length is 112.8 pm. In metal carbonyls, the C—O bond becomes longer and weaker than that of free CO. This is due to  $\pi$ -back bonding. The C—O bond distance values in metal carbonyls for terminal and  $\mu^2$ -CO are 115 and 120 pm respectively.

## Number and Intensity of Infrared Bands

Infrared spectroscopy can be used to determine the structure of carbonyl complexes of transition metals. A molecule is infrared active if a stretching mode results in a change in a dipole moment. For example, in an octahedral complex,  $M(CO)_6$ , a symmetrical stretch of each C—O bond gives no overall change in dipole, therefore, this stretching mode is not seen in the infrared spectrum of the compound.

However for a compound all other possible stretching modes have to be considered. The symmetry of the molecule and group theory are used to calculate the expected number of infrared active stretching modes for a molecule. The number and intensity of infrared stretching bands of C—O depend mainly on the local symmetry about the metal to which the carbonyls are attached. The symmetry of the other ligands and their influence on the true molecular symmetry is usually not important. The calculations of the number of bands are beyond the scope of this book. The number of C—O stretching bands for various geometries are given in Table 2.6. It has been observed that more symmetric is the molecule, the fewer will be the number of infrared bands expected.

For example,  $Cr(CO)_6$  is an octahedral complex with the point group Oh. Table 2.6 shows that one stretching mode of this compound is infrared active and, therefore, only one band is observed in its infrared spectrum.



**Fig. 2.12**

If the symmetry point group of the molecule drops, the number of carbonyl stretching bands will increase (to a limit of one per CO ligand in very low symmetry molecules).

If one CO ligand of  $Cr(CO)_6$  is substituted by a halide (Figure 2.12), the overall molecule is still octahedral but the shape made by the M—CO is a square pyramid with a point group  $C_{4v}$ . Table 2.6 shows that there are three infrared active modes and three infrared bands are observed in its infrared spectrum. If the fourfold array of CO ligands lies in the same plane as the metal atom, two bands will be observed.

**Table 2.6 : Number of C—O Stretching Bands in the Infrared Spectrum**

Complex	Isomer	Structure	Point Group	Number of IR Bands
$M(CO)_6$			Oh	1
$M(CO)_5L$			$C_{4v}$	2 or 3 (If the four old array of CO ligands lies in the same plane as the metal atom two bands will be observed.)
$M(CO)_4L_2$	<i>trans</i>		$D_{4h}$	1
$M(CO)_4L_2$	<i>cis</i>		$C_{2v}$	3 or 4 (If the trans CO ligands are nearly collinear, only three bands will be observed.)
$M(CO)_3L_3$	<i>fac</i>		$C_{3v}$	2
$M(CO)_3L_3$	<i>mer</i>		$C_{2v}$	2 or 3 (If the trans CO ligands are nearly collinear, two bands will be observed.)

Complex	Isomer	Structure	Point Group	Number of IR Bands
$M(CO)_5$			$D_{3h}$	2
$M(CO)_4 L$	axial		$C_{3v}$	2 or 3 (If the three fold array of CO ligands is nearly planar, only two bands will be observed.)
	equatorial			
$M(CO)_3 L_2$	axial-axial		$D_{3h}$	1
	axial-equatorial			
$M(CO)_4$			$T_d$	1
$M(CO)_3 L$			$C_{3v}$	2

If the CO ligands are not related to an inversion centre or a threefold axis of symmetry, a molecule with  $n$ CO ligands will show  $n$ CO IR bands. For example, *cis* isomer of  $M(CO)_2Cl_2$  gives bent arrangement (Figure 2.13) of M—CO bonds and will have two bands in its IR spectrum because both the symmetric [Figure 2.13(a)] and antisymmetric [Figure 2.13(b)] stretches cause the change in dipole moment and are infrared active.

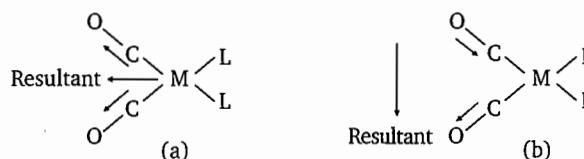


Fig. 2.13 (a) Symmetric stretch (b) Asymmetric stretch of *cis*  $M(CO)_2L_2$

The *trans* isomer of  $M(CO)_2L_2$  gives a linear arrangement of M—CO bonds and only one infrared band is observed because the symmetric stretch does not cause change in dipole moment [Figure 2.14(a)]. Only unsymmetric stretch causes the change in dipole [Figure 2.14(b)].

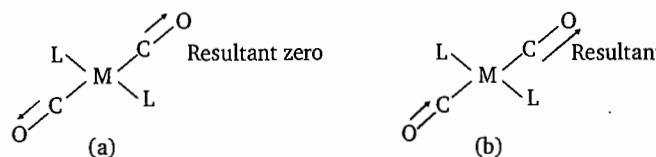


Fig. 2.14 (a) Symmetric stretch (b) Unsymymmetric stretch in *trans*  $M(CO)_2L_2$

Although the number of infrared active bands can be predicted by the symmetry and point groups, fewer bands may sometimes be observed. In some cases bands may overlap and cannot be distinguished; alternatively, one or more bands may be of very low intensity and not readily observed. If isomers are present in a sample, then it may be difficult to determine which infrared absorption bands belong to which compound.

Now let us consider the  $[(\eta^5-Cp)Fe(CO)_2]_2$  complex. In the solid state, this compound exists as a *trans* isomer (Figure 2.15).

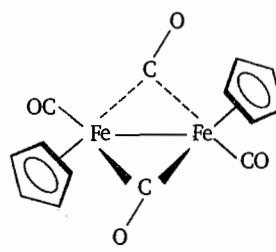


Fig. 2.15

The *trans* isomer exhibits only one high frequency infrared band for terminal CO and a single band for bridging CO ligands, because the two bridging CO ligands are nearly collinear. This indicates that two infrared bands are observed for the *trans* isomer although both are split owing to intermolecular coupling.

In aqueous solution it exists as *cis*-isomer. The *cis* isomer (Figure 2.16) exhibits two high frequency bands for terminal CO and one lower frequency band for bridging CO ligands.

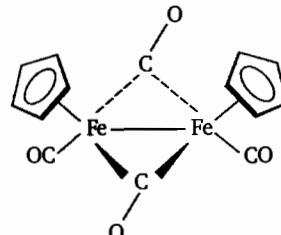
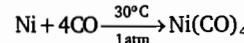


Fig. 2.16.

The intensity of infrared bands depends roughly on the magnitude of the change in dipole moment. The asymmetric vibrations have more intense absorptions whereas the more symmetric vibrations have lesser intensity, (*i.e.*, extinction coefficient).

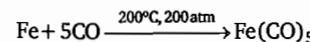
### Synthesis of Metal Carbonyls

**(1) By direct interaction of finely divided metal with carbon monoxide :** This method is usually used to synthesize the carbonyls  $\text{Ni}(\text{CO})_4$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{Co}_2(\text{CO})_8$  only.

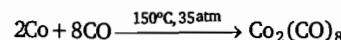


$\text{Ni}(\text{CO})_4$  is toxic, colourless, mp  $-17^\circ\text{C}$ , bp  $43^\circ\text{C}$ .

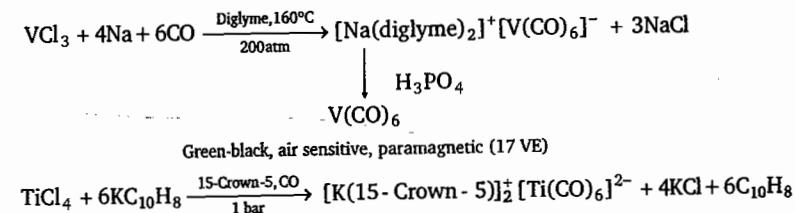
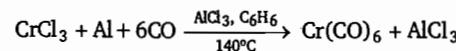
Purification of Ni by the Mond process is based on the decomposition of  $\text{Ni}(\text{CO})_4$ .



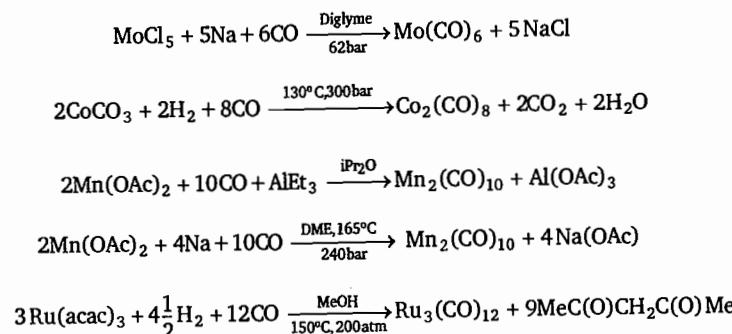
$\text{Fe}(\text{CO})_5$  is an orange and toxic solid, mp  $-20^\circ\text{C}$ , bp  $103^\circ\text{C}$ .



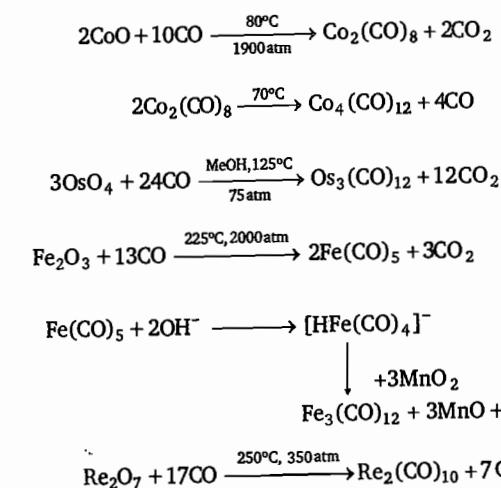
**(2) Reductive carbonylation :** This method is most widely used for the synthesis of binary carbonyls of most of the transition metals. The reducing agents such as Na, Al, Zn, trialkyl aluminium, Grignard reagent or in some cases  $\text{H}_2$  are used in the reaction of a metal halide or acetate or other salt along with carbon monoxide.



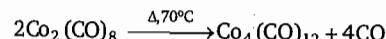
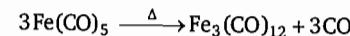
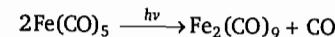
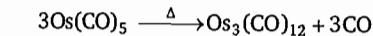
In this reaction potassium and naphthalene react to give the naphthalide radical anion, a powerful reducing agent capable of stabilizing reactive intermediate by coordination to the metal prior to CO coordination.



In the case of reduction of metal oxides, carbon monoxide itself acts as a reducing agent and converts itself into  $\text{CO}_2$ .



(3) Higher carbonyls can be synthesised by thermal or photochemical reaction of lower carbonyls.



### Properties and Reactions of Metal Carbonyls

The mononuclear carbonyls of nickel,  $\text{Ni}(\text{CO})_4$  and iron family  $\text{Fe}(\text{CO})_5$ ,  $\text{Ru}(\text{CO})_5$  and  $\text{Os}(\text{CO})_5$  are liquids at room temperature and pressure but other carbonyls are solids. All of the mononuclear carbonyls are colourless or faintly coloured whereas the polynuclear carbonyls are coloured. The intensity of polynuclear carbonyls increases with increase in number of metal atoms. For example,  $\text{Fe}(\text{CO})_5$  is colourless liquid,  $\text{Fe}_2(\text{CO})_9$  is golden yellow solid and  $\text{Fe}_3(\text{CO})_{12}$  is a very dark green solid. The colours of the polynuclear carbonyls arise from electronic transitions between orbitals that are largely localized on the metal framework. The mononuclear carbonyls are volatile. The high volatility and toxicity of  $\text{Ni}(\text{CO})_4$  requires not to inhaled or allowed to touch the skin.

### Reactions of Metal Carbonyls

The variety of reactions of various carbonyls is so large that only the principal reactions are mentioned here :

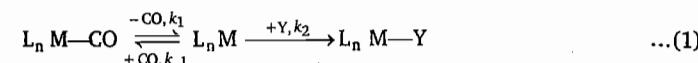
#### (1) Substitution Reactions

The metal carbonyls undergo substitution reactions by either dissociative or associative mechanism depending upon whether these obey 18 electron rule or not. The complexes which obey 18 electron rule undergo substitution reactions by dissociative mechanism because the alternative, associative activation, requires the formation of an energetically unfavourable 20-electron activated complex. The complexes which contain 16 or 17 valence electrons undergo substitution reactions by associative mechanism and its rate is faster than the dissociative reactions of metal carbonyls which obey 18 electron rule. CO ligands can be substituted by other ligands either thermally or photochemically.

Complete removal of all CO ligands either thermally or photochemically is rarely possible. The incoming ligands are generally weaker  $\pi$ -acids than CO and back bonding to the remaining CO ligands increases with each successive removal of CO ligand and increases the M-CO bond strength.

#### Dissociative Substitution

General mechanism of dissociative reactions is given below :



The first step is the slow dissociation of a CO ligand. This step is rate determining and independent of the concentration of incoming ligand Y. The rate law for this reaction is:

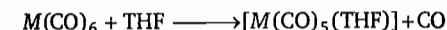
$$\text{Rate} = K_1 [\text{Complex}] \quad \dots(2)$$

In some cases, the back reaction,  $K_{-1}$  becomes important and the intermediate  $\text{L}_n \text{M}$  partitions between the forward and backward reactions. The rate of reaction is affected by increasing the concentration of ligand Y because  $K_2$  now competes with  $K_{-1}$ . The rate of reaction (1) is :

$$\text{Rate} = \frac{k_1 k_2 [\text{Complex}][\text{Y}]}{k_{-1} [\text{CO}] + k_2 [\text{Y}]} \quad \dots(3)$$

If the concentration of CO equation (3) is negligible, the equation (3) reduces to equation (2).

In the dissociative mechanism, an intermediate of reduced coordination number or more probably a solvated intermediate such as  $[\text{Cr}(\text{CO})_5(\text{THF})]$  is formed. This intermediate then combine with the incoming ligand.

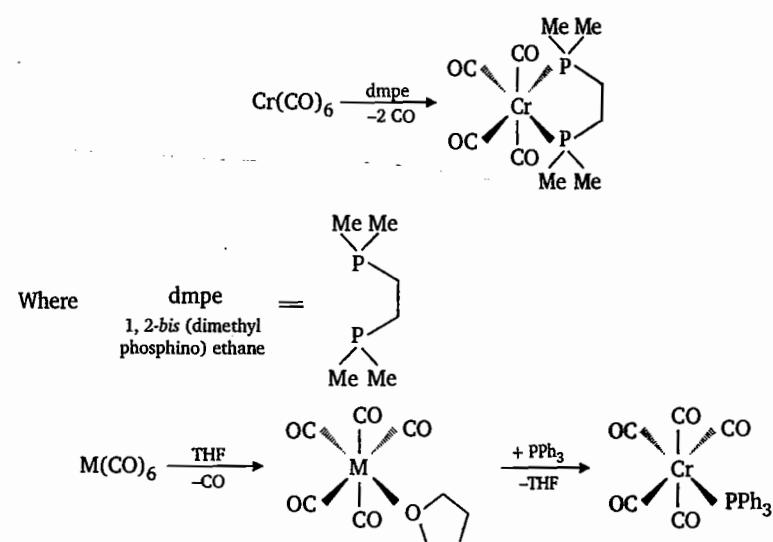
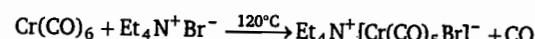
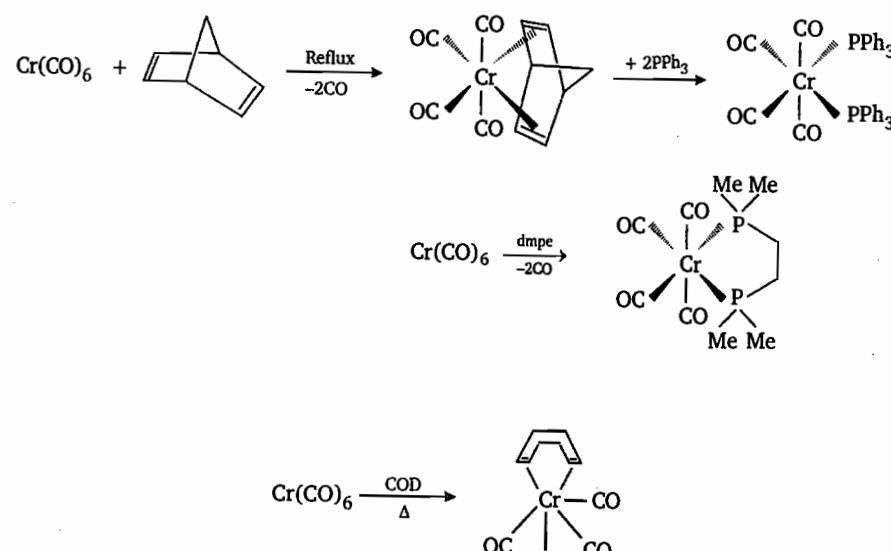
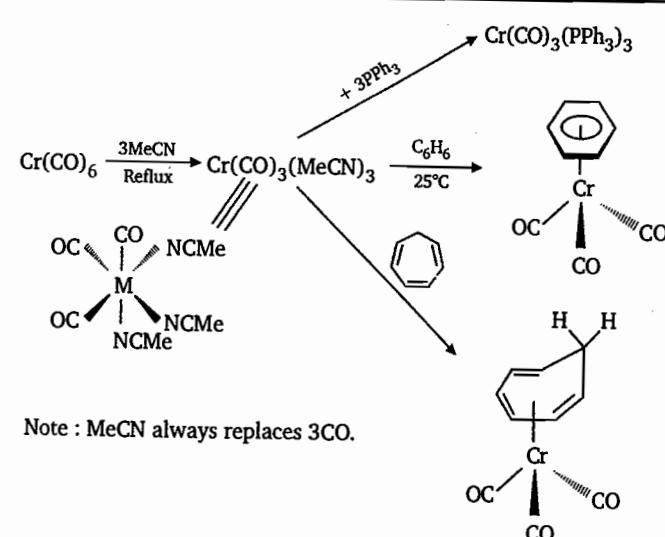


where  $\text{M} = \text{Cr, Mo, W}$

Since tetrahydrofuran (THF) is only a  $\sigma$ -donor ligand, there is no back bonding between metal and THF. In order to minimize electron density on metal, it donates its extra electron to CO by back bonding. This makes M-CO bond strong and M-THF bond breaks. When  $\text{PR}_3$  approaches to metal, it replaces weakly bound THF and gets substituted resulting in the formation of single produced.

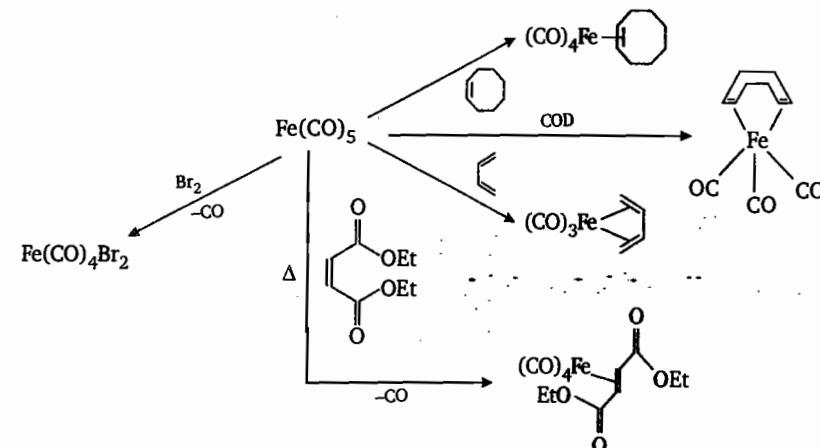
The ligands like Lewis bases, olefins and arenes can thermally be substituted on metal carbonyls. Weakly coordinating ligand, i.e., more labile ligands such as  $\text{CH}_3\text{CN}$ , THF,  $\text{CH}_2\text{Cl}_2$  norborna diene (NBD), cyclooctatetraene (COT) and cyclooctadiene (COD) facilitate removal of CO by stabilizing the coordinatively unsaturated intermediates before they are themselves replaced.





Where  $\text{M} = \text{Cr, Mo}$

Some reactions of  $\text{Fe}(\text{CO})_5$  are shown below:



Subsequent substitutions by the incoming ligands like phosphines,  $\text{PR}_3$  always occur *cis* to the initial ligand. This is because the substitution of any ligand that is a better  $\sigma$  donor but a poorer  $\pi$  acceptor than CO will lead to an increase in the back bonding between metal and the CO ligand *trans* to the incoming ligand. The substitution reaction rarely proceeds further than *fac*-  $\text{M}(\text{CO})_3\text{L}_3$  because the electron density on the metal would be too great.

The facial isomer [Figure 2.17 (a)] in which the incoming  $\text{PR}_3$  ligands occupy a triangular face of the octahedron is preferred to the meridional isomer [Figure 2.17 (b)] in which the ligands occupy a meridian. This is because COs have a higher *trans* effect than that of phosphines. Therefore, substitution continues until there are no COs *trans* to a CO.

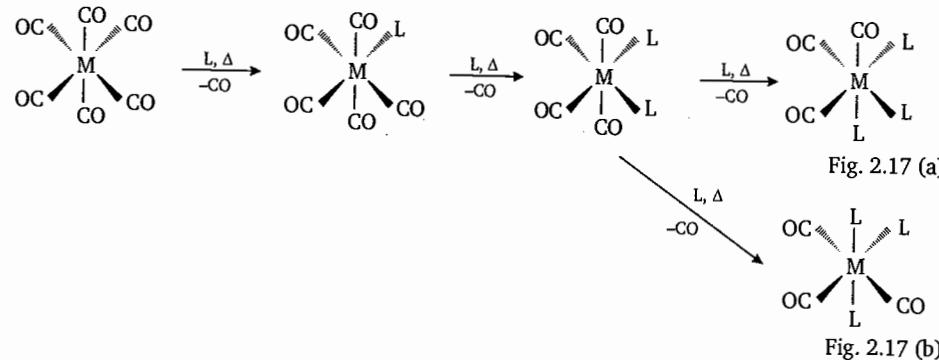


Fig. 2.17

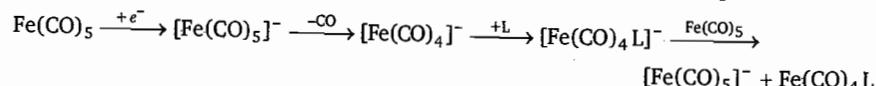
The rate of CO substitution in six-coordinate metal carbonyl,  $\text{M}(\text{CO})_6$  often decreases as more strongly basic ligands like phosphines and phosphites replace CO. With bulky phosphine ligands, further substitution may be thermodynamically unfavourable because of the ligand crowding. When a phosphine ligand (a strong  $\sigma$ -donor and a poorer  $\pi$ -acceptor ligand i.e., a net donor ligand) replaces a CO ligand (i.e., a  $\pi$ -acceptor ligand) electron density increases on the metal and the remaining CO ligands bind more tightly and, therefore, reduce the rate of CO dissociative substitution. The donor ability of the phosphines and phosphites follow the order :



where R is alkyl and Ar is aryl.

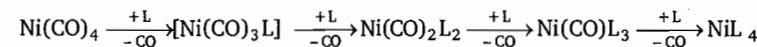
The increased electron density contributed by the phosphine ligand leads to stronger  $\pi$  back bonding to the remaining CO ligands and, therefore, strengthens the M—C bond. Hence this stronger M—C bond leads to decrease the tendency of CO ligand to dissociate from metal and thus decrease the rate of CO dissociative substitution.

In some cases, the substitution of CO ligand can be catalyzed by electron transfer processes. If a small amount of a reducing agent is added to a 18-electron metal carbonyl, the metal carbonyl reduces to a 19-electron metal carbonylate anion radical and a catalytic cycle continues until the metal carbonyl or incoming ligand has been consumed. The 19-electron species with an electron in an M—L  $\sigma^*$  orbital are much more dissociatively labile than their 18-electron counterparts.



Dissociation of a ligand is accelerated for bulky ligands with increased cone angle. For example, the complex  $\text{Ni}(\text{PR}_3)_4$  with cone angle  $118^\circ$  is slightly dissociated whereas the complex  $[\text{Ni}\{\text{P}({}^t\text{Bu})_3\}_4]$  with cone angle  $182^\circ$  is highly dissociated. The ligand  $\text{P}({}^t\text{Bu})_3$  is so bulky that the 14 electron complex  $[\text{Pt}\{\text{P}({}^t\text{Bu})_3\}_2]$  can be isolated.

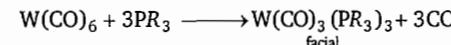
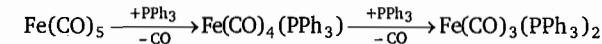
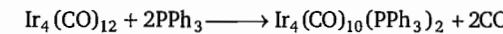
Let us discuss the substitution reactions of  $\text{Ni}(\text{CO})_4$ .



Where L groups are phosphines or phosphites.

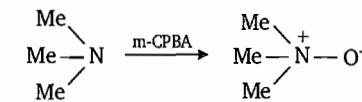
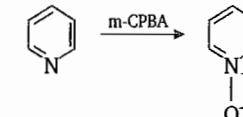
On moving forward to the reaction, the rate of reaction will decrease. The two ligands are readily replaced to form  $\text{Ni}(\text{CO})_2 \text{L}_2$  but the last two are much less reactive. It can be explained in terms of their being only two strong  $\pi$  bonds between Ni and CO ligands and these are largely localized on the remaining two CO ligands and, therefore, produce strong Ni—C bond. Also, since phosphines such as  $\text{PR}_3$  act as strong  $\sigma$ -donor and weak  $\pi$ -acceptor, it is responsible to form strong Ni—C bond which is to be broken during the reaction.

Some dissociative substitution reactions are shown below :

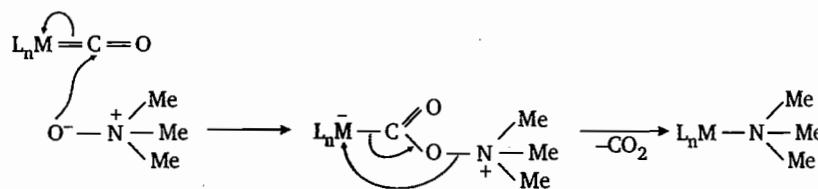


Two NO ligands always replace 3CO ligands.

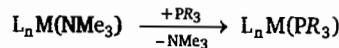
Some dissociative substitution reactions are accelerated by using amine and *m*-chloroperoxybenzoic acid (*m*-CPBA). The *m*-CPBA oxidize the amine into its oxide.



The amine oxide attacks the carbon of CO ligand of  $\text{L}_n\text{MCO}$  to form the  $\text{L}_n\text{M}(\text{NMe}_3)$ .

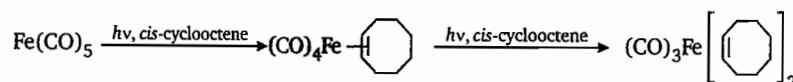
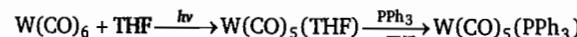
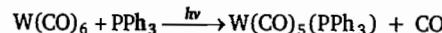


The complex  $L_nM(NMe_3)$  then reacts with the incoming ligand such as  $PR_3$  to form a single product.

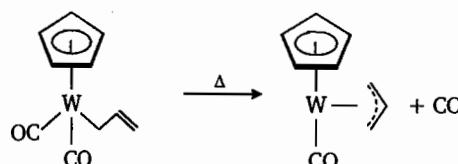
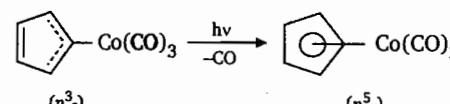
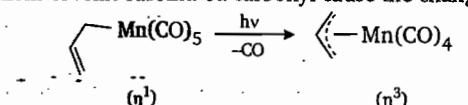


Complexes of 4d-series transition metals react much more faster than those of the 3d- and 5d-series transition metals homologs. This is one of the reasons why Ru, Rh and Pd are much more widely used as most active catalyst than Os, Ir and Pt.

Photochemical substitution of CO usually leads in the formation of monosubstituted product because photochemical excitation of a metal carbonyl with a coordination sphere of mixed substituents causes the dissociation of the ligand which is the most labile (*i.e.*, most weakly bonded) in the ground state. If the ligands of nearly same ligand strength are used, one can replace all the CO ligands. The labile ligands are THF, MeCN, alkenes etc.

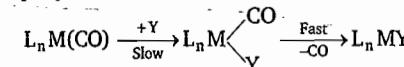


Photochemical reactions of some substituted carbonyl cause the change in hapticity.



### Associative Substitution

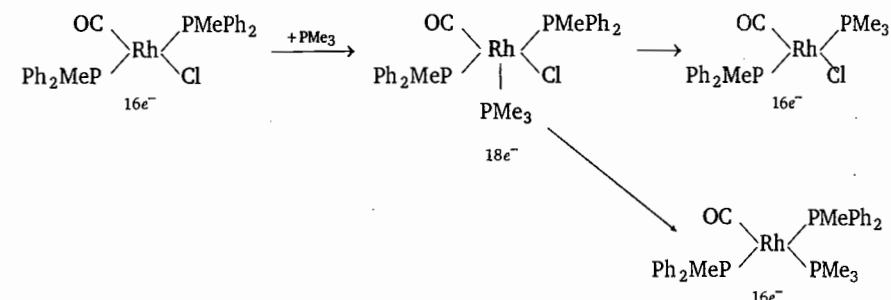
In associative substitution reactions, the incoming ligand first adds to the metal complex to form an intermediate. This is slow and rate determining step. In the next step, the dissociation of one of the original ligands occurs rapidly.



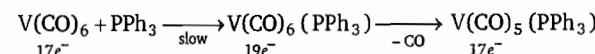
The rate of substitution will be given by the rate equation :

$$\text{Rate} = k [\text{Complex}] [Y]$$

This mechanism is often adopted by an unsaturated 16 electron complexes because the intermediate is 18-electron species and, therefore, provide a lower energy route than the 14-electron intermediate that would be formed in dissociative substitution. For example, associative substitutions on square planar 16 electron complex with  $PR_3$  is shown below :

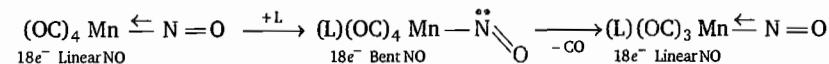


Odd electron complexes (17 or 19  $e^-$ ) react faster than even electron analogs.

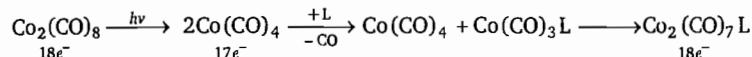


$V(CO)_6$  reacts  $10^{10}$  times faster than  $Cr(CO)_6$ .

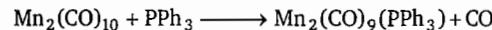
Some 18 electron complexes also undergo associative substitutions. For example, if nitrosyl or allyl ligands are present which can change from a 3- to a 1- electron donor mode.



The binuclear complexes with metal-metal bonds undergo M—M bond homolysis to form electronically unsaturated radicals which then undergo associative substitutions.



The photochemical substitution of CO in  $\text{Mn}_2(\text{CO})_{10}$  by  $\text{PPh}_3$  proceeds via 17 electron intermediate  $\text{Mn}(\text{CO})_5$ .

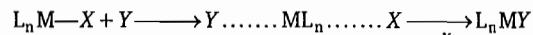


The steric crowding between ligands accelerate dissociative substitutions and decrease the rate of associative substitutions.

### The Interchange Mechanisms (I)

It has been observed that 20 electron intermediates are unlikely but a 20 electron transition state seems to be possible. An intermediate is a species which has to survive as an independent entity. Unlike an intermediate, a transition state has a much shorter life time which is comparable to a molecular vibration (about  $10^{-13}$  s) i.e., a transition state is an unstable entity and 20 electron transition states are common in interchange mechanisms.

In interchange reactions, the leaving and incoming ligands bind simultaneously in one step forming a transition state. The leaving and incoming ligands bind more weakly than they would be in a more stable 18 electron intermediate.

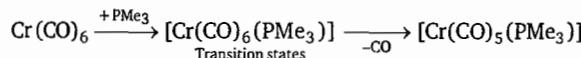


The interchange mechanism is further divided into two following categories :

- (1) Interchange dissociative ( $I_d$ )
- (2) Interchange associative ( $I_a$ )

#### (1) Interchange Dissociative ( $I_d$ )

The  $M-Y$  bond begins to form before the  $M-X$  bond is fully broken but the  $M-X$  bond breaks preferentially and the interchange is more closer to dissociative than to an associative. The evidence for an  $I_d$  mechanism is that certain strong nucleophiles at high concentration with group 6 carbonyls show a second order rate expression.



#### (2) Interchange Associative ( $I_a$ )

The  $M-X$  bond begins to break before the  $M-Y$  bond is fully formed but the  $M-Y$  bond forms preferentially and the interchange is closer to an associative. Experimentally, it is not easy to distinguish an  $I_a$  from associative mechanism because there is no evidence for  $I_a$  mechanism.

### Carbonylate Ions

The reduction of metal carbonyls gives anionic complexes which are called carbonylate ions. Carbonylate ions usually obey the 18 electron rule. The species that form carbonylate ions most readily are odd-electron species particularly 17-electron species and dimers.

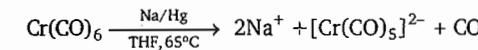
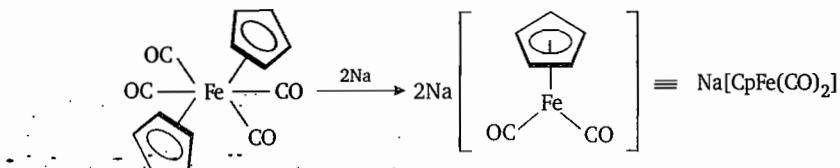
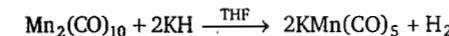
They are often electronically and structurally related to neutral carbonyl complexes. For example,  $[\text{Cr}(\text{CO})_4]^{4-}$ ,  $[\text{Mn}(\text{CO})_4]^{3-}$ ,  $[\text{Fe}(\text{CO})_4]^{2-}$  and  $[\text{Co}(\text{CO})_4]^-$  are isoelectronic and isostructural with  $\text{Ni}(\text{CO})_4$ . Similarly  $[\text{Fe}_2(\text{CO})_8]^{2-}$  is isoelectronic and isostructural with  $\text{Co}_2(\text{CO})_8$  and  $[\text{Cr}_2(\text{CO})_{10}]^{2-}$  is isoelectronic and isostructural with  $\text{Mn}_2(\text{CO})_{10}$ .

The carbonylate ions are thermally stable but in contrast to most neutral metal carbonyls, highly sensitive.

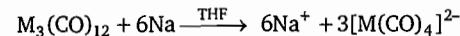
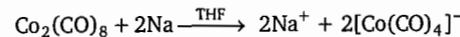
The metal carbonylate ions behave as nucleophiles and are susceptible to attack by electrophiles. They can be oxidized or further reduced and, therefore, they are used in the synthesis of carbonyl derivatives.

### Synthesis of Carbonylate Ions

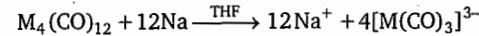
**(1) By Reduction :** A common method of synthesis of carbonylate ions is the reduction of neutral metal carbonyls with strong reducing agents such alkali metals, alkali metal hydrides,  $\text{NaBH}_4$ ,  $\text{Li}[\text{HBET}_3]$ .



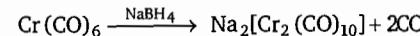
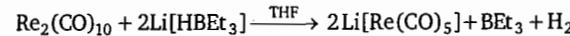
where  $\text{M} = \text{Mn, Tc, Re}$ .



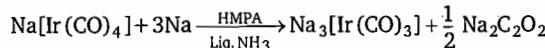
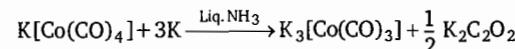
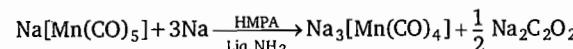
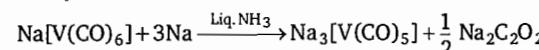
where M = Fe, Ru, Os



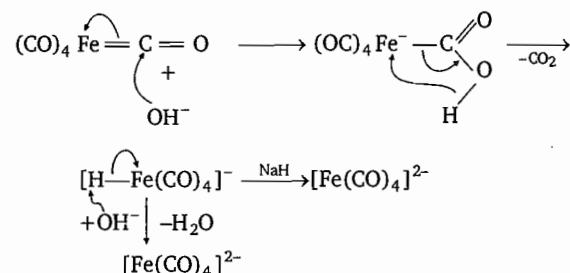
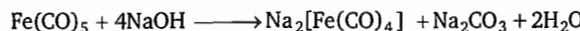
where M = Co, Rh, Ir



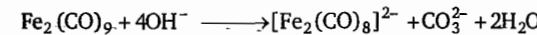
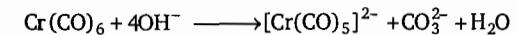
The reduction of metal carbonyls with common reducing agents such as alkali metals leads in the formation of mono or dianionic carbonyls. But reduction with more stronger reducing agent such as Na/liq. NH<sub>3</sub>, Na/HMPA, Li/Naphthalene or alkali metal/crown ether, they are further reduced to form super reduced carbonylates with the formal oxidation state of the metal as low as -4.



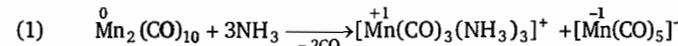
**(2) By Nucleophilic Attack :** The carbonylate ions can also be prepared by the reaction of metal carbonyls with strong bases. These reactions involve the reduction of metal by CO already present in the metal carbonyls.



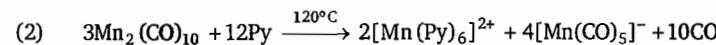
Na<sub>2</sub>[Fe(CO)<sub>4</sub>] or [Fe(CO)<sub>4</sub>]<sup>2-</sup> is called Collman's reagent.



**(3) By Disproportionation :** The binuclear complexes with metal-metal bonds can undergo disproportionation in the presence of non  $\pi$ -acceptor ligands such as NH<sub>3</sub>, py, dppe leading to a carbonyl anions. For example,



In this reaction electron transfer takes place from a 19e Mn(CO)<sub>3</sub>(NH<sub>3</sub>)<sub>3</sub> intermediate to a 17e<sup>-</sup> Mn(CO)<sub>5</sub> fragment to give the disproportionation product.



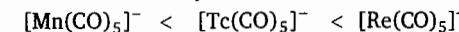
where dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>



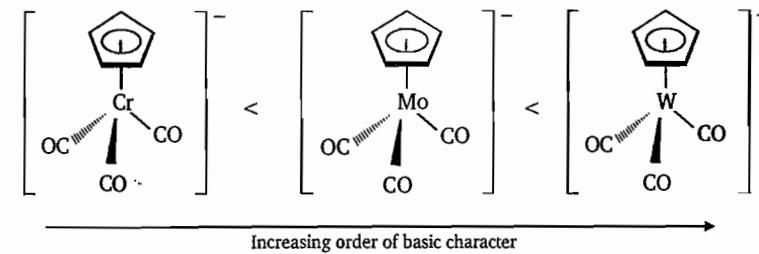
In each of these cases, the disproportionation produces a positive metal ion and a metal in negative oxidation state. The CO ligands bound to the softer metal species, the anion; the nitrogen donor ligands (hard bases) bound to the harder metal species, the cation.

### Properties of Carbonylate Ions

Carbonylate ions behave as nucleophiles and these are basic in nature. The basicity increases on descending the group because on descending the group, electrons become less tightly bound and the carbonylate ions donate electrons readily.



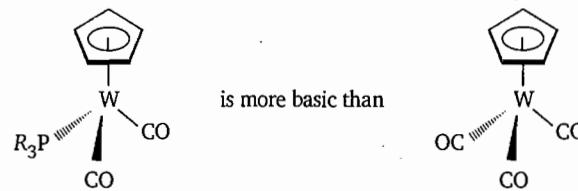
Increasing order of basic character



Higher the negative charge on the carbonylate ion, more will be its basicity.

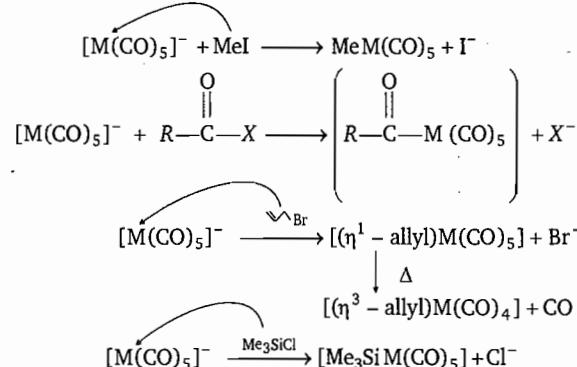
If besides CO other  $\pi$ -acceptor ligands like  $\text{PF}_3$ ,  $\text{N}_2$ ,  $\text{NO}$  etc., are present, then they will withdraw some of the electron density from metal and decrease the electron density on metal and thus will decrease basicity of the carbonylate ion.

If electron donating ligands like  $\text{NH}_3$ ,  $\text{RNH}_2$ , py, Cp,  $\text{R}_3\text{P}$  etc. are present, then they will increase the basicity of the carbonylate ion by donating electron to the metal. For example,

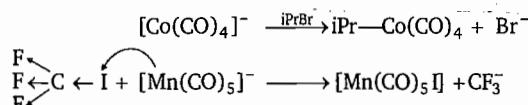


### Reactions and Synthetic Applications of Carbonylate Ions

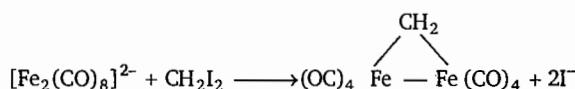
**Nucleophilic Substitutions :** As nucleophiles carbonylate ions attack readily on the positive centre of the organic halogen compounds to give alkyl, aryl or acyl complexes. Alternatively these reactions may be viewed as electrophilic attack on the metal.



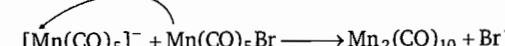
where M = Mn, Te, Re



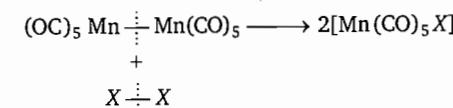
Bridging alkyl complexes can also be prepared by this method.



Nucleophilic attack is also observed on metals.



$\text{Mn}_2(\text{CO})_{10}$  can be used in synthesis of metal carbonyl halides and metal carbonyl hydrides.



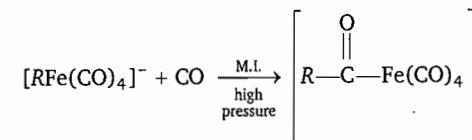
where  $X = \text{Cl}, \text{Br}, \text{I}, \text{H}$ .



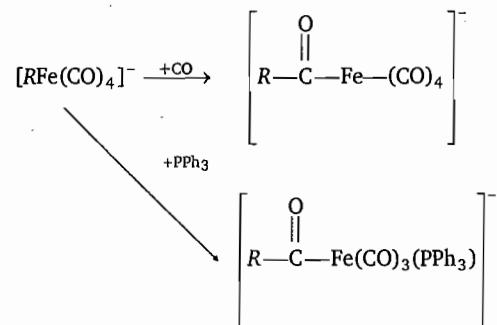
Collman's reagent  $\text{Na}_2[\text{Fe}(\text{CO})_4]$  have found numerous synthetic applications.



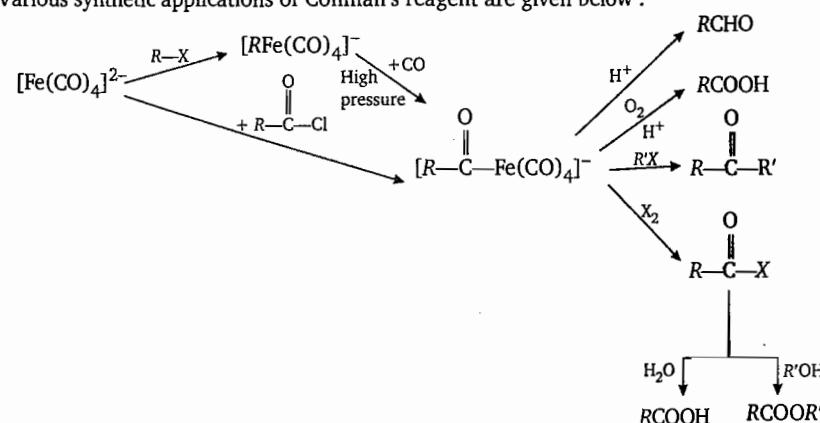
When  $[\text{RFe}(\text{CO})_4]^-$  reacts with CO or  $\text{Ph}_3\text{P}$ , insertion of CO which is already coordinated to metal between metal and alkyl group occurs to give corresponding acyl complexes.



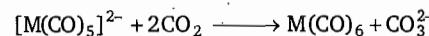
When  $[\text{RFe}(\text{CO})_4]^-$  reacts with CO, alkyl group migrates from M to CO which is already coordinated to metal and create a vacancy and that vacancy has been occupied by the incoming ligand. This phenomenon is called migratory insertion. Migratory insertion occurs in the presence of CO or  $\text{Ph}_3\text{P}$  to give corresponding acyl complexes.



Various synthetic applications of Collman's reagent are given below :



Carbonylate ions are highly reactive and are able to reduce  $\text{CO}_2$ .



Where M = Cr, Mo

**Metal Carbonyl Hydrides :** Carbonyl hydrides are hydrogen derivatives of carbonyl complexes. These are conjugate acids of carbonylate ions.

**Synthesis :**

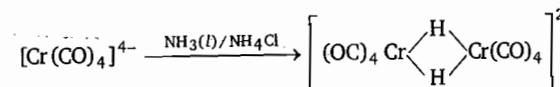
#### (1) By Acidification of Carbonylate Ions :



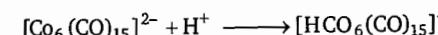
Where M = Mn, Tc, Re.



Carbonylate ions can also be protonated with acids that are even weaker than water.



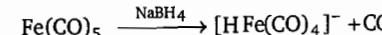
When cluster carbonyls are protonated, a hydride ligand is encapsulated by a framework of metal atoms to form interstitial hydrogen.



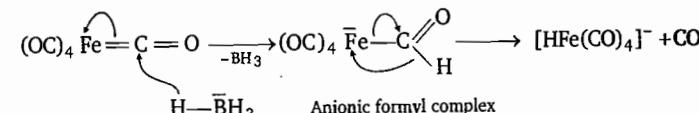
Neutral carbonyl complexes are protonated by strong acids to give cationic hydrides.



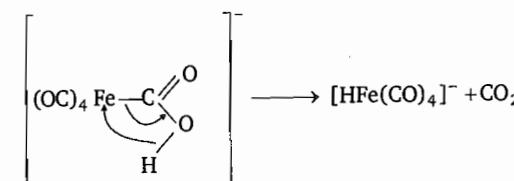
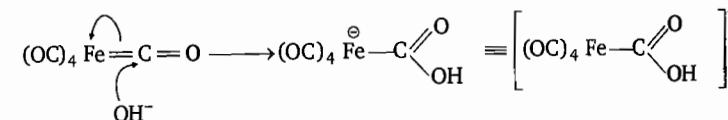
#### (2) By Reduction of Carbonyl Complexes with Hydride Donors :



**Mechanism :**



Hydroxide ion can also serve as the source of hydrogen.

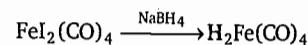
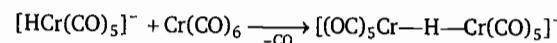
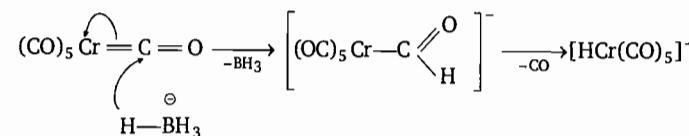


If the hydrogen supplier reagents  $\text{NaBH}_4$  or  $\text{OH}^-$  in these reactions are used in excess, the

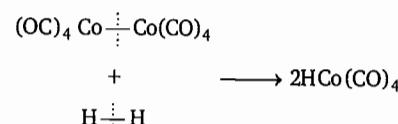
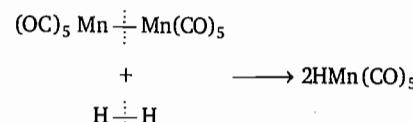
dianionic species will be formed. The intermediates  $\left[ (\text{OC})_4 \text{Fe}-\text{C} \begin{array}{c} \text{O} \\ \diagdown \quad \diagup \\ \text{H} \quad \text{H} \end{array} \right]^-$  and

$\left[ (\text{OC})_4 \text{Fe}-\text{C} \begin{array}{c} \text{O} \\ \diagdown \quad \diagup \\ \text{OH} \quad \text{H} \end{array} \right]^-$  are unstable and decompose to give carbonyl hydride  $[\text{HFe}(\text{CO})_4]^-$  by

eliminating CO and CO<sub>2</sub> respectively. When these reactions are attempted with Cr(CO)<sub>6</sub>, a bridging carbonyl hydride is obtained instead of the [HCr(CO)<sub>5</sub>]<sup>-</sup>.

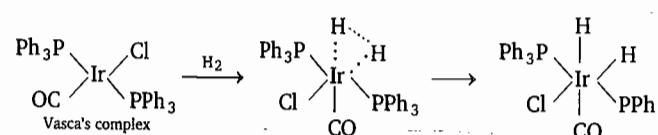


### (3) By Direct Addition of Hydrogen to Carbonyl Complex :



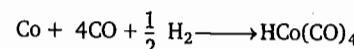
These reactions are known as oxidative cleavage of M—M bond.

Usually the reaction of hydrogen with transition metal carbonyl complexes gives monohydride complexes. But H<sub>2</sub> reacts with coordinatively unsaturated metal centres of 4d- or 5d-series transition metals of the Fe, Co and Ni groups to give a complex with two coordinated H atoms.



In this reaction the oxidation state of Ir increases from +1 and +3 since H is more electronegative than Ir. Therefore, this reaction is called oxidative addition.

### (4) From Elemental Metal, CO and H<sub>2</sub> :



## Properties of Carbonyl Hydrides

The monomeric carbonyl hydrides are usually volatile liquids that are stable under an atmosphere of CO and at low temperature. In the absence of CO they decompose to metal carbonyls with liberation of H<sub>2</sub>. Thermal stability of carbonyl hydrides of transition metals increases on descending the group.



Order of thermal stability

The carbonyl hydrides of transition metals behave as both acid as well as base.

The strong  $\pi$ -acceptor ligands such as CO have strong electron withdrawing character and lead to a polarization of the M—H bond in HM(CO)<sub>n</sub> complexes. As a consequence metal carbonyl hydrides behave as acids in aqueous solution. Both HCo(CO)<sub>4</sub> and HV(CO)<sub>6</sub> are so strong as HCl in water. On the other hand, HRe(CO)<sub>5</sub> is such a weak acid that its conjugate base [Re(CO)<sub>5</sub>]<sup>-</sup> is readily hydrolyzed by water. The hydride H<sub>2</sub>Fe(CO)<sub>4</sub> behaves as a dibasic acid.

The acidic character of metal carbonyl hydrides decreases on descending the group in periodic table. Bridging hydrides are more acidic than complexes with terminal M—H.

The  $\sigma$ -donor ligands such as Cp, phosphines reduce and the  $\pi$ -acceptor ligands acid as CO, NO and PF<sub>3</sub> increase the acidity of M—H bond, therefore, HCo(PR<sub>3</sub>)<sub>4</sub> is an extremely strong base.

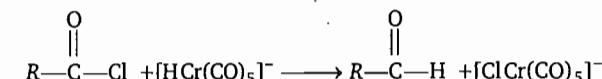


Increasing order of acidity

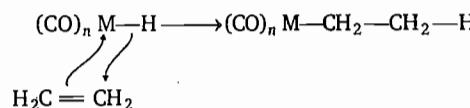
In contrast to the neutral carbonyl hydrides, the anionic carbonyl hydrides are hydride (H<sup>-</sup>) donor but not proton donor. Therefore, anionic carbonyl hydrides find application as reducing agents for alkyl halides or acid chlorides.

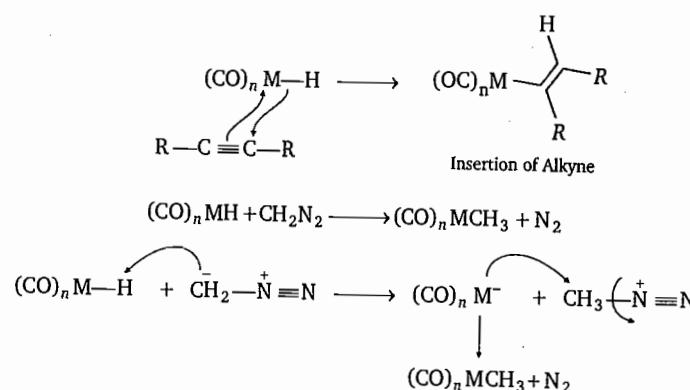


where X = Cl, Br, I

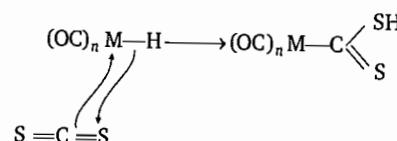
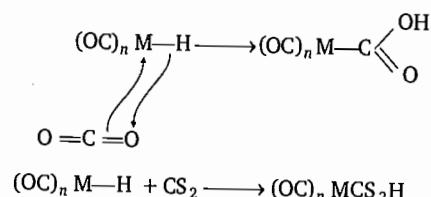
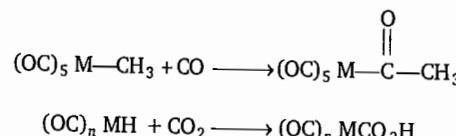


Metal carbonyl hydrides are highly reactive and most reactions involve the insertion of another species into the M—H bond. Some typical reactions of metal carbonyl hydrides are given below :





Metal alkyl give insertion reaction with CO. Insertion of CO occurs between M—CH<sub>3</sub> bond to give metal acyls.



### Bonding Mode of Hydrogen in Hydride Complexes

In multinuclear hydride complexes hydrogen can be bonded as shown in Figure 2.18

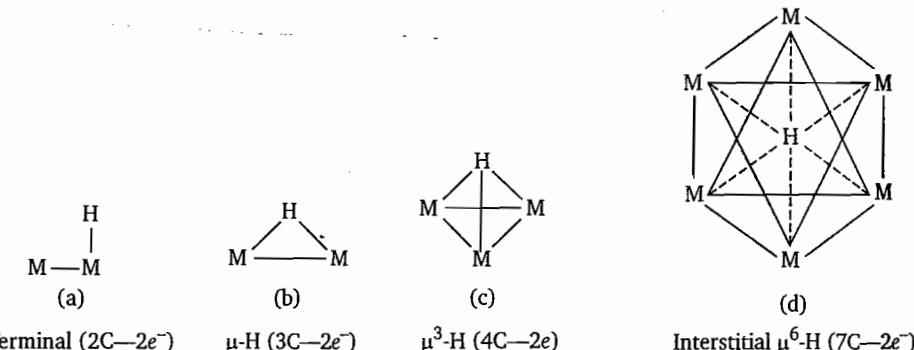


Fig. 2.18

The hydride ligands can adopt terminal, bridging or interstitial (in cluster carbonyls) modes of bonding (Figure 2.20). The terminal M—H bond is  $2C-2e^-$ ,  $\mu$ -H is  $3C-2e^-$ ,  $\mu^3$ -H is  $4C-2e^-$  and interstitial hydride  $\mu^6$ -H in octahedral cage is  $7C-2e^-$  interaction.

### Spectral Properties of M—H Bond

The  $^1H$  NMR spectra of hydride ligands directly attached to metals can provide useful structural information. Protons attached directly to metals in hydride complexes are very strongly shielded and give signals in the approximate range of  $\delta = -7$  to  $-60$  ppm relative to TMS. This seems to suggest a very high electron density on the protons which leads to justify classifying them as organometallic hydrides. For example, chemical shifts for  $HMn(CO)_5$ ,  $H_2Fe(CO)_4$  and  $[HFe(CO)_4]^-$  are  $-7.5$  ppm,  $-11$  ppm and  $-9$  ppm respectively. Whereas typical values of chemical shifts for organic compounds lies in the range of  $0$  to  $+15$  ppm relative to TMS.

Although it is not easy to distinguish between terminal and bridging modes. The chemical shifts of interstitial hydrides are less diagnostic and may occur at chemical shift, e.g.,  $+16.5$  in  $[(\mu_6-H)Ru_6(CO)_{18}]^-$ . Spin-spin coupling with spin active metals of  $I = \frac{1}{2}$  and with *cis* ( $J = 15-30$  Hz) and *trans* ( $J = 90-150$  Hz) phosphines occurs which gives useful structural informations.

Infrared spectroscopy is not reliable for organometallic compounds for characterization of M—H bonds because intensities of absorption in IR spectra due to M—H stretching are often weak. Also, since CO of carbonyl complexes gives signals in the range of  $2120-1600\text{ cm}^{-1}$  and M—H also gives the signal in the range of  $1600-2200\text{ cm}^{-1}$ . Thus, it is not possible to recognize that the signal is either

due to M—CO or M—H stretching. Hydrides which are specially paramagnetic are very difficult to characterize.

Examples of complexes containing hydrogen bridges are shown in Fig 2.19.

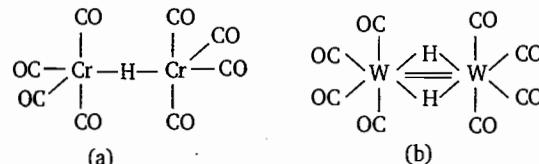


Fig. 2.19

Chemical shift for proton in methyl complexes ( $M-\text{CH}_3$ ) lie between 1 and 4 ppm, similar to their positions in organic compounds. Protons in cyclic  $\pi$ -ligands such as  $\eta^5\text{-C}_5\text{H}_5$  and  $\eta^6\text{-C}_6\text{H}_6$  most commonly have  $^1\text{H}$  chemical shifts between 4 and 7 ppm and because of the relatively large number of protons involved cause themselves to easy identification.

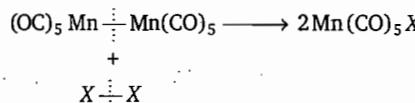
### Metal Carbonyl Halides

Reactions of metal carbonyls with halogens lead to the formation of carbonyl halide complexes by substitution reactions or breaking metal-metal bonds.



where  $X = \text{Br}, \text{I}$

Metal-metal bond in polynuclear carbonyls are often cleaved when these substances are treated with halogens.



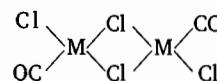
where  $X = \text{Cl}, \text{Br}, \text{I}^-$

As the halogen atom is attached to metal, there is loss in electron density on metal. Consequently the CO stretching frequency of product  $\text{Mn}(\text{CO})_5 X$  becomes significantly higher than  $\text{Mn}_2(\text{CO})_{10}$ .

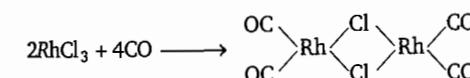
The reaction of CO with some metal halides results in the formation of metal carbonyl halide complexes directly.



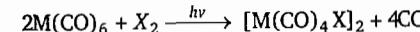
The structure of  $[\text{M}(\text{CO})\text{Cl}_2]_2$  is :



where  $M = \text{Pd or Pt}$



Irradiation of metal hexacarbonyls in the presence of halogens gives seven coordinate dimeric complexes which are halogen bridged (Figure. 2.20)



where  $M = \text{Mo, W}$ ,  $X = \text{Cl, Br, I}$

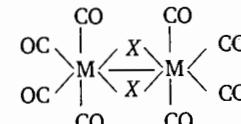
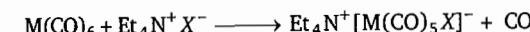


Fig. 2.20 Structure of  $[\text{M}(\text{CO})_4 \text{X}]_2$

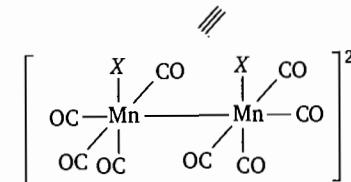
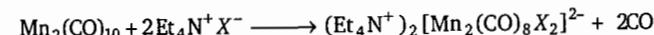
The halogen bridges can be broken by treating the dimers with strong ligand such as pyridine.



Anionic carbonyl halides are obtained when metal carbonyls are treated with ionic halides.

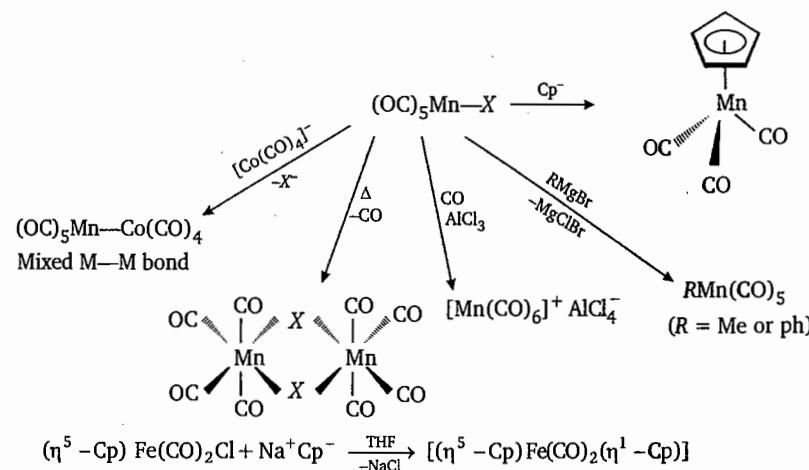


where  $M = \text{Cr, Mo, W}$ .



Pd, Pt, Cu, Ag and Au do not form stable binary carbonyls but give stable carbonyl halides.

The metal carbonyl halides are useful compounds in that the halogen is often easily replaced by other functional groups in substitution reactions.



### Metal Nitrosyls

Free NO molecule has one more electron than CO and this unpaired electron resides in an antibonding  $\pi^*$  molecular orbital and is easily removed to give  $\text{NO}^+$  as in  $\text{NO}^+\text{BF}_4^-$  and  $\text{NO}^+\text{PF}_6^-$  salts.  $\text{NO}^+$  is isoelectronic with CO. When an electron is removed from  $\pi^*$  of NO the bond order increases from 2.5 to 3. Because  $\text{NO}^+$  is nitrosyl ion, the compound containing both NO and CO are called carbonyl nitrosyls. The NO can act as 1- or 3-electron donor on the neutral ligand or covalent model. When NO acts as  $3e^-$  donor, the M—NO unit is linear [Fig 2.21 (a)]. In majority of nitrosyl complexes the MNO unit is linear, consistent with  $sp$ -hybridization on nitrogen. When NO acts as a one electron donor, the MNO unit is bent ( $\text{M}-\ddot{\text{N}}=\text{O}$ ). The bent geometry is due to the presence of a lone pair of

electrons on nitrogen [Figure 2.21 (b)]

In the oxidation counting method or ionic model, NO acts as  $\text{NO}^+$  in linear geometry and as  $\text{NO}^-$  in bent geometry. NO acts as  $2e^-$  donor in both geometries (Figure 2.22).

Although N as well as O atoms in NO are potential donors but the N atom coordinates preferentially avoiding a large formal positive charge on the more electronegative oxygen atom.

In the linear structure, NO transfers one electron to metal resulting in decrease in oxidation state of metal and formation of  $\text{NO}^+$  ion. In bent structure an electron transfer occurs from metal to NO resulting in increase in the oxidation state of metal and formation of  $\text{NO}^-$  ion. Which then coordinates to the negatively charged metal ion (Figure 2.22). The  $\text{NO}^+$  ion is isoelectronic with CO and, therefore, should exhibit the same distribution of electrons in the available molecular orbitals. Accordingly electron density is released from the metal into the  $\pi^*$  orbital of  $\text{NO}^+$  entity, decreasing the N—O bond order (Fig. 2.23):

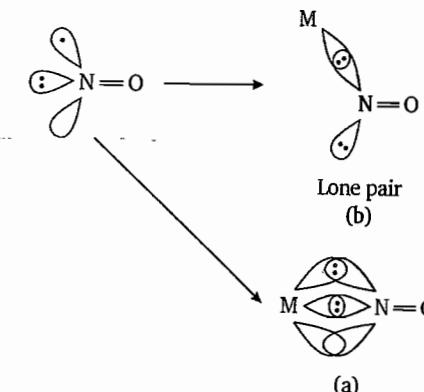


Fig. 2.21 (a) Linear structure (b) Bent structure of M—NO unit on the basis of covalent model

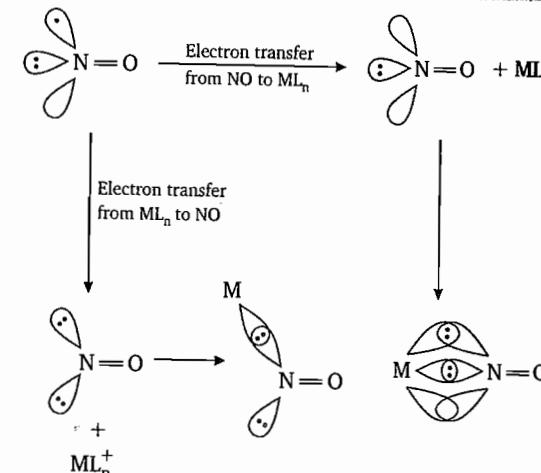


Fig. 2.22



Fig. 2.23

The formal oxidation state of the metal is calculated by considering linear NO as  $\text{NO}^+$  and a bent NO as  $\text{NO}^-$ . When linear NO is converted to bent NO, oxidation state of metal increases by two units.

On covalent model, a linear NO is a  $3e^-$  donor ligand. In this case there is no need of rehybridization on N atom of NO because the metal has a singly occupied  $d\pi$  orbital to overlap with singly occupied  $\pi^*$  orbital of NO to form an M—N  $\pi$  bond and N donates its lone pair of electrons to the empty  $d\sigma$  orbital of metal to form a  $\sigma$  bond. In bent NO, N has to be rehybridized to put this

electron in an  $sp^2$  hybrid orbital pointing towards the metal in order to bind. One of the  $sp^2$ -hybrid orbitals on nitrogen bears a lone pair that causes the nitrosyl group to be bent.

Usually a  $17e^-$   $\text{LnM}$  fragment combines with NO to give only a  $18e^-$  bent nitrosyl complex whereas a  $15e^-$   $\text{LnM}$  fragment gives either an  $18e^-$  linear or  $16e^-$  bent complex.

Some complexes have both linear and bent NO. For examples,  $\text{Cl}(\text{Ph}_3\text{P})_2\text{Ir}(\text{lin-NO})(\text{bent-NO})$  and  $[\text{ClRu}(\text{Ph}_3\text{P})_2(\text{lin-NO})(\text{bent-NO})]^+$  complexes.

It can be expected that M—N bond of the bent nitrosyl would be longer than that of linear nitrosyl because there is only  $\sigma$  M—N bond in bent whereas in linear nitrosyl both  $\sigma$ - as well as  $\pi$  bonding is observed. The M—N bond lengths in  $[\text{ClRu}(\text{Ph}_3\text{P})_2(\text{lin-NO})(\text{bent-NO})]^+$  complex (Figure 2.24) are 173.8 pm and 185.9 pm for linear and bent N—O bonds in this complex are same (117.0 and 116.2 pm respectively). The N—O bond length for  $\text{NO}^+$  (B.O. = 3),  $\text{NO}$  (B.O. = 2.5) and  $\text{NO}^-$  (B.O. = 2) are 106, 115 and 120 pm, respectively. This indicates that NO bond order for both the basal and apical nitrosyls lies between 2 and 3.

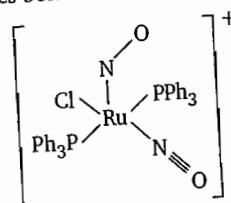


Fig. 2.24 Structure of  $[\text{ClRu}(\text{PPh}_3)_2(\text{lin-NO})(\text{bent-NO})]^+$

Like metal carbonyl complexes, nitrosyls are also characterized using infrared spectroscopy. The N—O stretching frequencies of free  $\text{NO}$ , free  $\text{NO}^+$  and M—NO are  $1876 \text{ cm}^{-1}$ ,  $2250 \text{ cm}^{-1}$  and,  $1900\text{--}1500 \text{ cm}^{-1}$  respectively. Polynuclear nitrosyls are also known in which NO also behaves as bridging ligands. For example,  $\text{CpCr}(\text{NO})_2\text{Cl}$  reacts with  $\text{NaBH}_4$  to give dimer  $[\text{CpCr}(\mu\text{-NO})(\text{NO})]_2$ .

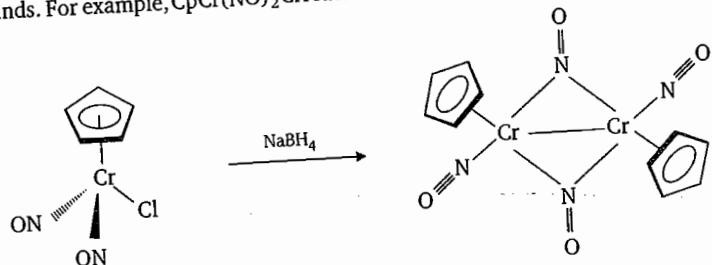
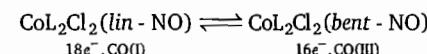


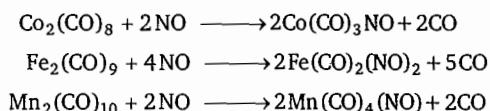
Fig. 2.25

The infrared stretching frequencies are diagnostic for terminal as well as bridging NO ligands. For the product (Fig. 2.25)  $\nu_{\text{NO}}$  (terminal) =  $1672 \text{ cm}^{-1}$  and  $\nu_{\text{NO}}$  (bridging) =  $1505 \text{ cm}^{-1}$ .

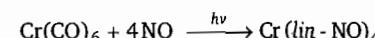
Some nitrosyl complexes are known where the linear and bent forms are in equilibrium. For example,



In this case  $\nu_{\text{NO}}$  (linear) =  $1750 \text{ cm}^{-1}$  and  $\nu_{\text{NO}}$  (bent) =  $1650 \text{ cm}^{-1}$ . The difference between frequencies of  $\nu_{\text{NO}}$  (linear) and  $\nu_{\text{NO}}$  (bent) is small and, therefore, these structural types overlap. Thus the  $\nu_{\text{NO}}$  frequencies are not reliable to characterize the linear and bent structure. Since  $\text{NO}^+$  is stronger  $\pi$ -acceptor than CO ligand, it will cause to increase the C—O stretching frequency. NO can replace CO from some metal carbonyls to form carbonyl nitrosyls. Two linear NO ligands replace three COs, since in electron counting terms,  $3\text{CO} = 2\text{NO}$ .



Depending upon the conditions, it is possible to replace all of the COs in metal carbonyls.



The first bent nitrosyl ligand found in a derivative of Vaska's complex (Fig. 2.26).

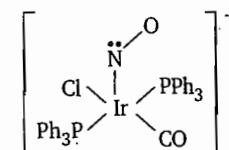
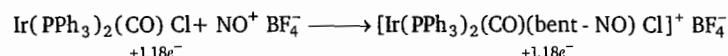
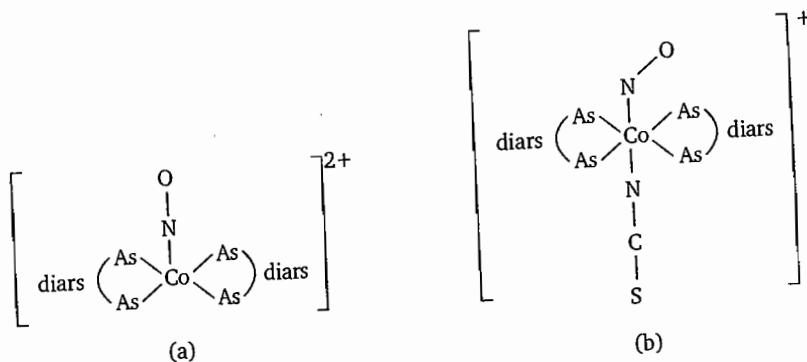


Fig. 2.26 Square pyramidal structure of  $[\text{Ir}(\text{PPh}_3)_2(\text{CO})(\text{bent-NO})\text{Cl}]^+$

When  $[\text{Co}(\text{diars})_2(\text{lin-NO})]^{2+}$  [Figure 2.27(a)] reacts with thiocyanate ion  $\text{SCN}^-$   $[\text{Co}(\text{diars})_2(\text{bent-NO})]^+$  [Figure 2.27 (b)] complex ion is formed.



The  $[\text{Co}^1(\text{diars})_2(\text{lin-NO})]$  obeys 18 electron rule. The reaction of this complex ion with  $\text{SCN}^-$  (a two electron donor) will not give a  $20e^-$  linear nitrosyl complex because it violates the  $18e^-$  rule. In this reaction an electron pair is shifted from a molecular orbital of largely metal character to an orbital of nitrogen. As a result  $3e^-$   $\text{lin-NO}$  changes to  $1e^-$   $\text{bent-NO}$  leaving a coordination site for accepting a pair of electrons.

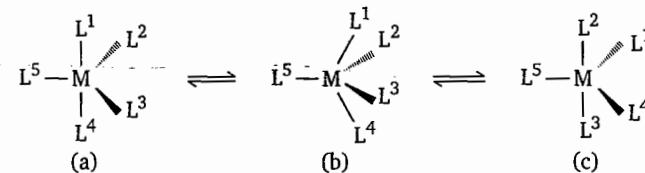


**Fig. 2.27** Structure of : (a)  $[\text{Co}(\text{diars})_2\text{lin}-\text{NO}]^{2+}$  and (b)  $\text{Co}(\text{diars})_2(\text{bent}-\text{NO})(\text{NCS})^+$

### Fluxionality

No molecule is strictly rigid because atoms of any molecule undergo vibrations about their equilibrium positions. The interatomic distances and bond angles are not fixed due to the vibrations (stretching and bending) of atoms. There are many molecules in which molecular vibrations or intramolecular rearrangements cause the atoms or groups to change places with each other. Such rearrangements are found in an enormous variety of compounds such as  $\text{PF}_5$ ,  $\text{Fe}(\text{CO})_5$  and organometallic compounds. Such molecules are said to be stereochemically non-rigid. When two or more conformations are chemically non-equivalent, the molecules are called tautomers and the process is called tautomerisation. If such conformations are equivalent then the molecules are referred to as **fluxional** and the process is called **fluxionality**. Fluxionality is very common for 5-coordinate trigonal bipyramidal complexes, on the other hand, 4- and 6-coordinate complexes are almost rigid.

Among the five coordinate molecules, the trigonal bipyramidal geometry, which has three equatorial ligands and two axial ligands is preferred over square planar geometry but the square planar geometry which has four basal ligands and one axial ligand is not too much different in energy nor in bond angles. Therefore, the strong vibrations can convert trigonal geometry to square pyramidal and back again. The conversion merely requires a bending of four bonds by less than 30° each [Fig. 2.28(a)]. The base of square pyramidal geometry [Fig. 2.28(b)] includes the two axial and two equatorial ligands from TBP geometry. All the four basal ligands in square pyramidal geometry are not equivalent. This square pyramidal geometry being less stable, quickly reverts to the trigonal bipyramidal geometry in such a way that the two axial ligands now become equatorial and the two equatorial ligands become axial [Fig. 2.28(c)]. This mechanism of TBP— $\text{SP}_y$ —TBP interconversion ( $\text{SP}_y \rightarrow$  square pyramid) is called the Berry pseudorotation. The ligands 1-4 become equivalent in the square pyramidal intermediate and 1 and 4, which were axial in TBP become equatorial [Fig. 2.28(c)].



**Fig. 2.28**

The fluxional molecules give fewer NMR resonances than would be predicted from their static geometries. This is due to the reason that the ligands concerned exchanging places more rapidly than the NMR time scale ( $\sim 10^{-1} - 10^{-6}$  s). For example,  $\text{Fe}(\text{CO})_5$  gives only one carbon resonance at 25°C. But its IR spectrum (a technique with the much faster time scale  $\sim 10^{-12}$  s than the ligands exchange) indicates a trigonal bipyramidal geometry with two types of carbonyl ligands (two axial and three equatorial). NMR spectroscopy is used to identify the stereochemical non-rigid and fluxionality in molecules because the energy of activation for both processes (fluxionality and NMR) is in the range of 25-100 kJ mol<sup>-1</sup>.

Four coordinate complexes which are considerably rigid undergo square planar-tetrahedral interconversion in the transition metal complexes. For example, square planar  $\text{Ni}(\text{PR}_3)_2\text{X}_2$  converts to tetrahedral geometry with activation energy of about 45 kJ mol<sup>-1</sup> and at rate of  $\sim 10^5 \text{s}^{-1}$  at room temperature.

The process of fluxionality becomes slower at low temperatures and faster at higher temperatures. At sufficiently low temperature (perhaps if the molecule is in solid state) the rate of exchange of ligands may slow sufficiently that each ligand remains in position during the absorption of the radiowave and the axial and equatorial ligands show distinct NMR peaks and the static spectrum is obtained, this is called the low temperature limit. As the temperature increases, the two sharp peaks broaden. If the temperature of the sample increases continuously, the broadening increases until the two peaks coalesce. On further increasing the temperature, the single peak becomes narrower. This is due to the reason that the rate of exchange of ligands between axial and equatorial positions is too rapid to allow separate radiowave absorption by distinct axial and equatorial ligands (*i.e.*, rate of exchange of ligands is much faster than the NMR time scale) and the fully averaged spectrum is obtained. This is called high temperature limit. The change in NMR spectrum on varying the temperature is shown in Fig. 2.29.

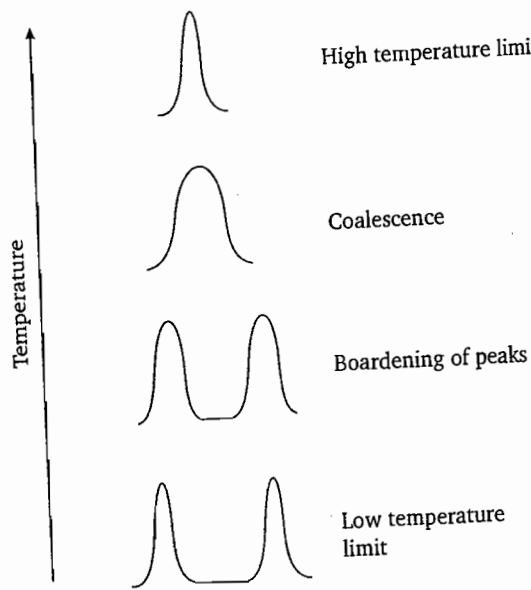


Fig. 2.29

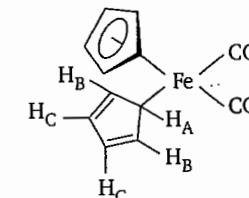
### Fluxionality in Cyclic Polyene Complexes

One of the most remarkable features of many cyclic polyene complexes is their stereochemical non-rigidity. For example, at room temperature, the two cyclopentadienyl rings in ferrocene rotate rapidly relative to each other. This type of fluxionality is called internal rotation.

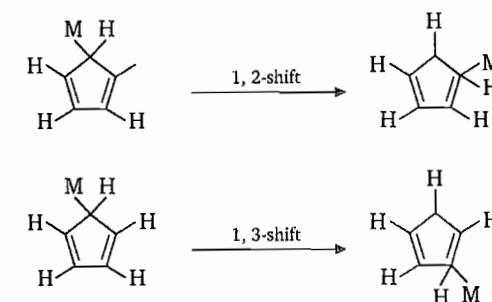
More interesting is the fluxionality that is observed when a conjugate cyclic polyene ligand is attached to the metal atom by some but not all of its carbon atoms. This type of fluxionality is irrespective of the coordination number. A conjugated cyclic polyene ligand, cyclopentadienide ion,  $C_5H_5^-$ , for example, is six  $\pi$ -electron aromatic compound is anionic, since the six  $\pi$ -electrons are delocalized only on five carbon atoms. It gives only one  $^1H$  and one  $^{13}C$  NMR peak at any temperature. It can bind to d-block metal ions in two common modes. It can bind to metal ions using all the five carbon atoms donating three  $\pi$ -electron pairs. In this mode of bonding, it also gives one  $^1H$  and one  $^{13}C$  NMR peak at any temperature. The chemical shifts are different from those observed for free  $C_5H_5^-$  ion. The  $C_5H_5^-$  ion can also bind to metal ions through only one carbon atom donating only one pair of electrons. The compound, for example,  $Ge(\eta^1-C_5H_5)$  gives three  $^1H$  and those  $^{13}C$  NMR peaks in intensity ratio 2 : 2 : 1 at sufficiently low temperatures. But at high temperatures they give peaks in intensity ratio 2 : 2 : 1 at sufficiently low temperatures. But at high temperatures they give peaks in intensity ratio 2 : 2 : 1 at sufficiently low temperatures. This is due to the reason that Ge atom is migrating around the only one of each kind of NMR spectra. This is known as ring whizzing.

Two cyclopentadienide,  $C_5H_5^-$  ligands may bind to a metal ion in two different modes : One with all the five carbon atoms and one through only one carbon atom.

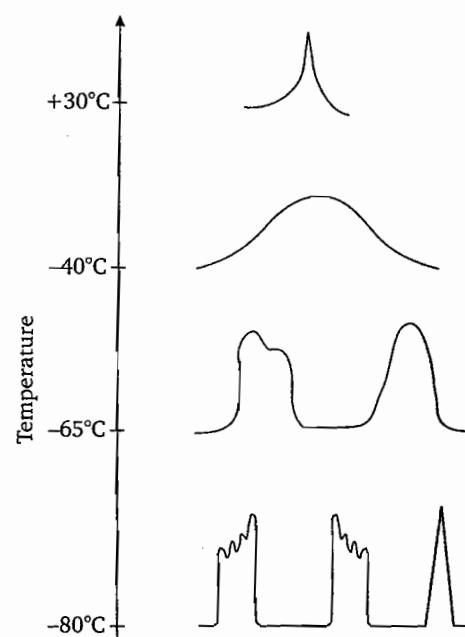
An example is  $Fe(\eta^1-C_5H_5)(\eta^5-C_5H_5)(CO)_2$  in which one Cp ring binds through one carbon atom and the other binds through all the five carbon atoms (Fig. 2.30). This structure is based on 18 electron rule and IR spectroscopy.

Fig. 2.30 Structure of  $Fe(\eta^1-C_5H_5)(\eta^5-C_5H_5)(CO)_2$ 

This compound shows two proton resonances of almost equal intensity at room temperature, one for the  $\eta^5-C_5H_5$  and one for  $\eta^1-C_5H_5$ . This is due to the reason that the iron atom migrates around the  $\eta^1-C_5H_5$  ring at a rate sufficient enough to average all the proton resonances in the  $\eta^1-C_5H_5$  ring. At low temperature (-80°C), three  $^1H$  and three  $^{13}C$  NMR peaks are observed for the three different types of protons of the static  $\eta^1-C_5H_5$  ring. If the temperature of the sample increases from low temperature limit, there will be broadening of the different proton resonances of the  $\eta^1-C_5H_5$  ring. This is due to the reason that the iron undergoes 1, 2 shift (to the adjacent carbon atom) rather than a 1, 3 shift (to the most distant carbon atom) or a random shift (through a pentahedro intermediate).

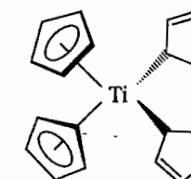


At high temperature limit (+30°C, the room temperature), the ring whizzing occurs too rapidly for the NMR experiment to observe the individual protons, therefore an average signal is observed. At low temperatures, the ring motion is slowed down and therefore the NMR experiment can identify the individual protons. The  $^1H$  NMR spectrum of  $Fe(\eta^1-C_5H_5)(\eta^5-C_5H_5)(CO)_2$  for  $\eta^1-C_5H_5$  group with varying temperature is shown in Fig. 2.31.



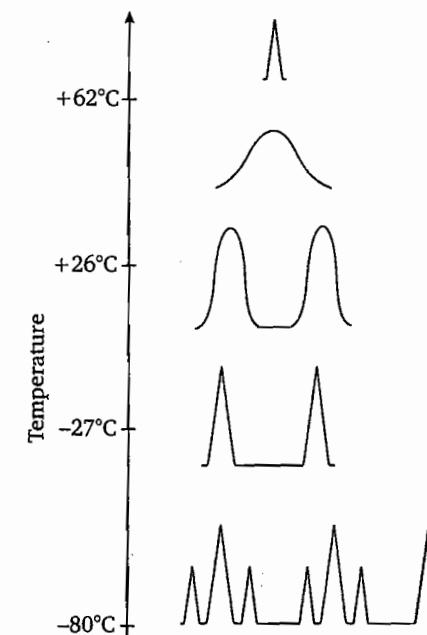
**Fig. 2.31**  $^1\text{H}$  NMR spectrum of  $\text{Fe}(\eta^1-\text{C}_5\text{H}_5)(\eta^5-\text{C}_5\text{H}_5)(\text{CO})_2$  for  $\eta^1-\text{C}_5\text{H}_5$  group with varying temperature

The singlet due to  $\eta^5-\text{C}_5\text{H}_5$  ligand does not change with change in temperature. There are several compounds in which the Cp ligands can exchange their mode of bonding and an interchange between  $\eta^1-\text{Cp}$  and  $\eta^5-\text{Cp}$  ligands has been observed. An example of great interest is  $\text{Ti}(\eta^1-\text{C}_5\text{H}_5)_2(\eta^5-\text{C}_5\text{H}_5)_2$  (Fig. 2.32). At  $-27^\circ\text{C}$  the hydrogen atoms of  $\eta^1-\text{Cp}$  are distinguishable from  $\eta^5-\text{Cp}$  ligands but the ring rotation is not restricted even at  $-27^\circ\text{C}$ . Therefore, the five hydrogen atoms of  $\eta^1-\text{Cp}$  are distinguishable from  $\eta^5-\text{Cp}$  ligands but the ring rotation is not restricted even at  $-27^\circ\text{C}$ . Therefore, the five hydrogen atoms of  $\eta^1-\text{Cp}$  ligands becomes equivalent. There are 10 H of two  $\eta^1-\text{Cp}$  ligands and a singlet is observed. The two  $\eta^5-\text{Cp}$  ligands also have 10 H in identical environment and therefore it also gives a singlet. Thus, this compound shows two sharp singlets at  $\delta$  5.9 ppm and 5.2 ppm at  $-27^\circ\text{C}$  in  $^1\text{H}$  NMR spectrum. As the temperature rises from  $-27^\circ\text{C}$  to  $+26^\circ\text{C}$  the two peaks broaden and at  $+62^\circ\text{C}$  only one sharp singlet is observed. At  $+62^\circ\text{C}$ , the  $\eta^1$  and  $\eta^5$ -Cp rings exchange positions too rapidly that the hydrogen atoms of these rings can not be distinguished by the NMR experiment. Therefore all the 20 H atoms are seen to be equivalent and give only one NMR signal.



**Fig. 2.32** Structure of  $\text{Ti}(\eta^1-\text{C}_5\text{H}_5)_2(\eta^5-\text{C}_5\text{H}_5)_2$

At  $-80^\circ\text{C}$  ring whizzing is restricted. Therefore, NMR can identify all hydrogen atoms of  $\eta^1-\text{Cp}$  ligand and give three peaks of the intensity ratio 2 : 2 : 1. The  $^1\text{H}$  NMR spectrum of  $\eta^1-\text{Cp}$  rings in  $\text{Ti}(\eta^1-\text{Cp})_2(\eta^5-\text{Cp})_2$  at varying temperatures is shown in Fig. 2.33.



**Fig. 2.33**  $^1\text{H}$  NMR spectrum of  $\eta^1-\text{Cp}$  rings in  $\text{Ti}(\eta^1-\text{C}_5\text{H}_5)_2(\eta^5-\text{C}_5\text{H}_5)_2$  at varying temperatures

One of the more complicated forms of stereochemical non-rigidity is exhibited by metal  $\eta^3$ -allyl complexes at room temperature or slightly above. These complexes have characteristic NMR spectrum. The *anti* protons which are closer to the metal are shielded and appear at high field in comparison to the *syn* protons which are far away from the metal. The *syn* and *anti* protons do not couple with each other but these do couple with the proton on the central carbon. Therefore the *syn* and *anti* protons give two doublets and the proton at the central carbon atom gives a multiplet. Since the complex of this type is rigid at lower temperatures, it exhibits a static protons NMR spectrum in

which each of the three types of protons show distinct chemical shift. At higher temperatures this spectrum collapses to a dynamic spectrum in which the two doublets for *syn* and *anti* protons change to a single doublet and the multiplet changes to a quintet. This is due to the rapid (on the NMR time scale) intramolecular rearrangement that causes the *syn* and *anti* protons to have the same chemical shift, i.e., there are two types of protons : four terminal and one on the central carbon atom.

The intramolecular rearrangement causes to lost the distinction between *syn* and *anti* protons.  $^1\text{H}$  NMR spectrum of  $\eta^3$ -allyl complexes at varying temperature is shown in Fig. 2.34.

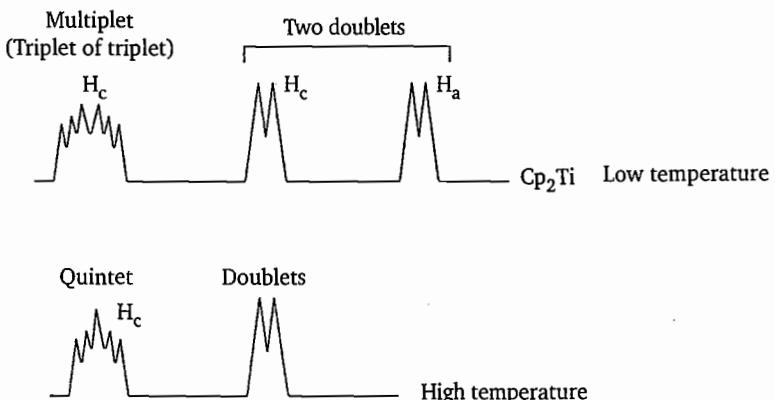


Fig. 2.34  $^1\text{H}$  NMR spectra of  $\eta^3$ -allyl complexes at varying temperature

The intramolecular rearrangement involves a  $\pi - \sigma - \pi$  transformation (Fig. 2.35) followed by rotation around the M—C bond.

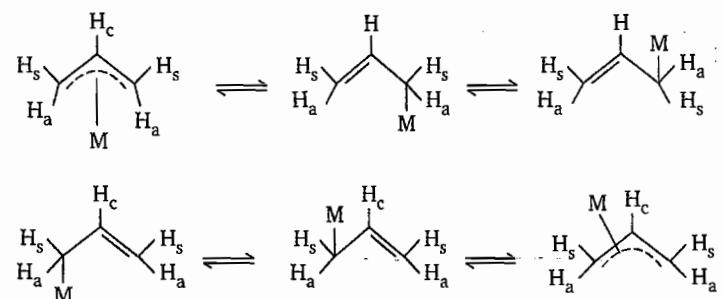


Fig. 2.35

The allene complexes also show stereochemical non-rigidity or fluxionality. An example is tetramethylalleneirontetracarbonyl (Fig. 2.36). The  $^1\text{H}$  NMR spectrum of this complex at  $-60^\circ\text{C}$  in  $\text{CS}_2$  exhibits three peaks in the ratio 1 : 1 : 2 (Fig. 2.37). This indicates that three hydrogens are above the plane and three hydrogens below the plane and six hydrogens in the plane perpendicular to the Fe—C bond.

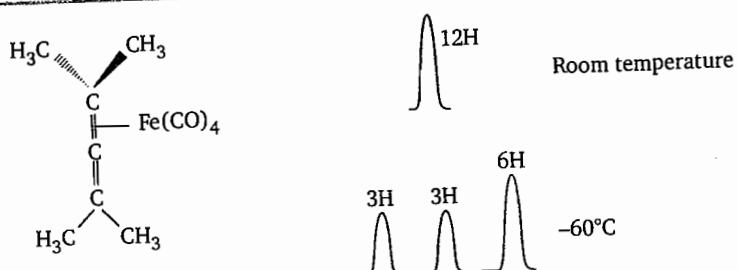


Fig. 2.36

Fig. 2.37

At room temperature, the three peaks collapse at a single peak (Fig. 2.37) representing that all the twelve hydrogens are in the plane and equivalent. This is due to the reason that the iron atom migrates around the allene  $\pi$ -system (Fig. 2.38).

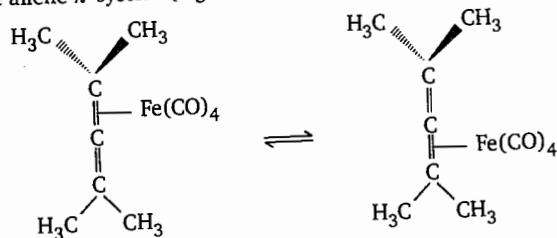


Fig. 2.38 Fluxional behaviour of tetramethylalleneirontetracarbonyl

The binuclear and polynuclear complexes containing bridging as well as terminal ligands also exhibit stereochemical non-rigidity. Such complexes involve interconversion of bridging and terminal ligands and the migration and scrambling of the ligands. The most studied complexes are  $\text{Fe}_2(\text{Cp})_2(\text{CO})_4$  and its derivatives. These processes occur due to extremely low energy ( $< 30 \text{ kJ mol}^{-1}$ ) for these transformation. The complex  $\text{Fe}_2(\text{Cp})_2(\text{CO})_4$  exists in two isomeric forms : *cis* and *trans* (Fig. 2.39).

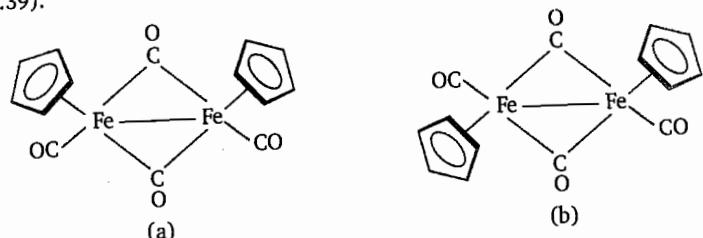
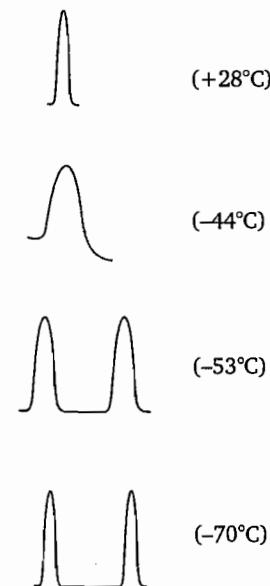


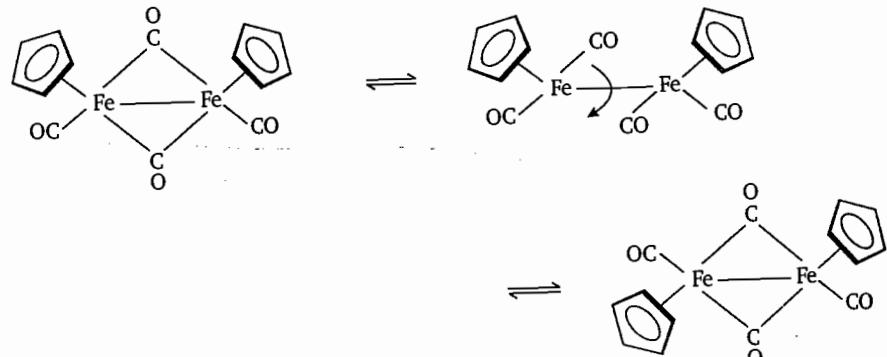
Fig. 2.39 *cis* and *trans* isomers of  $\text{Fe}_2(\text{Cp})_2(\text{CO})_4$

The  $^1\text{H}$  NMR technique shows that two processes occur in solution : (i) *cis* - *trans* isomerization and (ii) scrambling of the terminal and bridged CO ligands. At  $-70^\circ\text{C}$ , two  $^1\text{H}$  NMR signals are observed at different chemical shifts because the *cis*- and *trans*  $\eta^5$ -Cp rings are in different environment. As the temperature increases from low temperature limit the two peaks broaden (at  $-53^\circ\text{C}$ ), on further increase in temperature the broadening increases until the two peaks coalesce ( $-44^\circ\text{C}$ ). On further increasing the temperature, the single narrow peak at  $+28^\circ\text{C}$  (room temperature) is observed (Fig. 2.40). This is due to the reason that *cis*- and *trans* isomerization occurs at much faster rate than the NMR time scale and only an averaged resonance is observed.



**Fig. 2.40**  $^1\text{H}$  NMR spectra of *cis* and *trans*  $\text{Fe}_2(\text{Cp})_2(\text{CO})_4$  with varying temperature

The  $^{13}\text{C}$  NMR technique shows that the *cis* and *trans* transformations is also accompanied by the exchange of terminal and bridging carbonyl groups (Fig. 2.41). The rates of *cis* - *trans* isomerization and bridge-terminal CO scrambling are identical. Therefore, *cis* - *trans* isomerization involves bridge opening, rotation and bridge re-formation to give the other isomer. During the *cis* - *trans* isomerization, the process of bridge-terminal CO scrambling begins and continuation of this process leads to complete bridge-terminal CO scrambling.

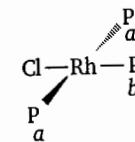


**Fig. 2.41** *cis*- and *trans*-interconversion of  $\text{Fe}_2(\text{Cp})_2(\text{CO})_4$  by scrambling

### $^{31}\text{P}$ NMR Spectroscopy

Except for its lower sensitivity,  $^{31}\text{P}$  ( $I = \frac{1}{2}$ ) shows magnetic properties similar to  $^1\text{H}$  and  $^{19}\text{F}$ .  $^{31}\text{P}$

NMR has been widely used in studying phosphine complexes such as  $\text{RhCl}(\text{PPh}_3)_3$ ,  $\text{IrCl}_3(\text{PPh}_3)_3$  etc. Let us discuss the  $^{31}\text{P}$  NMR spectra of Wilkinson catalyst (Fig. 2.42).



**Fig. 2.42**

It contains two types of phosphorus atoms indicated as  $P_a$  and  $P_b$ . The  $P_a$  atoms are *trans* to each other and  $P_b$  atom is *cis* to  $P_a$ . Each P atom undergo coupling with Rh ( $I = 1/2$ , 100% abundance), give two signals. The  $P_a$  undergoes a *cis* coupling with  $P_b$ , therefore each line resulting from coupling of  $P_a$  with Rh shows a doublet. The  $P_b$  undergoes two *cis* coupling with two  $P'_a$ 's. Therefore, each line resulting from coupling of  $P_b$  with Rh shows a triplet. The proton decoupled  $^{31}\text{P}$  NMR spectrum of Wilkinson catalyst is shown in Fig. 2.43.

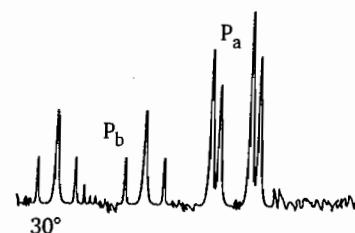


Fig. 2.43

When  $H_2$  is added to the Wilkinson catalyst, the compound shown in Fig. 2.44 is obtained.

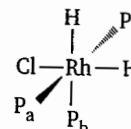


Fig. 2.44

In this compound, only  $P_a$  undergoes coupling with Rh and  $P_b$  becomes a broad hump (Fig. 2.45).

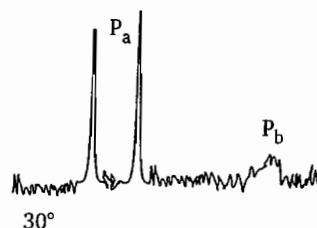


Fig. 2.45

If the compound (Fig. 2.44) is cooled to  $-25^\circ C$ ,  $P_a$  as well as  $P_b$  undergo coupling with Rh as in case of compound shown in Fig. 2.42. The  $^{31}P$  NMR spectrum observed for this compound at  $-25^\circ C$  is shown in figure 2.46. This change in spectrum is due to the reason that the  $P_b$  dissociating rate is slow at  $-25^\circ C$  but comparable with the NMR time scale at room temperature.

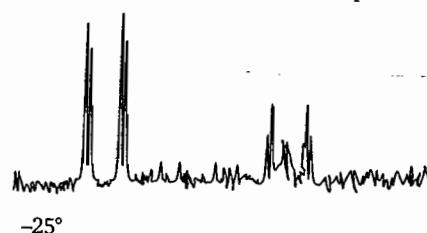


Fig. 2.46

In a fluxional molecule in which two coupled atoms always remain in the same molecule, couplings are retained in the NMR. But when dissociation of a ligand occurs, couplings of that ligands are diminished. In spectrum (Fig. 2.45),  $P_a$  retain full coupling to Rh whereas  $P_b$  does not. This indicates that it is  $P_b$  which undergoes dissociation.

### $^{13}C$ NMR Spectroscopy

$^{12}C$  being non-magnetic (spin number,  $I = 0$ ) is NMR inactive. Like  $^1H$  nucleus,  $^{13}C$  has spin number,  $I = \frac{1}{2}$  therefore principles governing  $^{13}C$  NMR are exactly similar to those of  $^1H$  NMR spectroscopy, but the scale of observed shifts and couplings is greater for  $^{13}C$ . Chemical shifts for  $^{13}C$  are measured (in ppm) from tetramethyl silane (TMS) as reference so that the same sample can be used to study both nuclei. The  $\delta$  scale for TMS is 0.0, for  $^1H$  is 0–15 ppm and for  $^{13}C$  is a 0–250 ppm. Because of the greater range of chemical shifts  $^{13}C$  spectra nearly always contain a separate and distinct resonance for each chemically shifted nucleus in the molecule.

Coupling between  $^{13}C$  and neighbouring protons exhibits in  $^{13}C$  NMR spectra. As in  $^1H$  NMR spectra, the pattern of coupling is also very diagnostic. A C—H fragment gives a doublet,  $CH_2$  gives a triplet and  $CH_3$  gives a quartet in the  $^{13}C$  NMR spectrum. This reveals the number of protons to which the each carbon atom is bound.

The magnetic moment of  $^{13}C$  is about one quarter that of  $^1H$ , therefore, the signals in  $^{13}C$  NMR spectrum are weaker.  $^{13}C$  is 1.6% sensitive as  $^1H$ .

$^{13}C$ — $^{13}C$  coupling is negligible because natural abundance of  $^{13}C$  is only 1.1 per cent. Thus, in one type of  $^{13}C$  NMR spectrum (proton decoupled) each magnetically non-equivalent carbon gives a single sharp peak that does not undergo further splitting. If there are fewer than 100 carbon atoms in a molecule, then there will be, on an average, only one  $^{13}C$  nucleus in the molecule.

It is usually possible to get good proton decoupled  $^{13}C$  NMR spectra from most of the organometallic compounds. Approximate ranges of chemical shifts for  $^{13}C$  NMR spectra of certain groups in organometallic compounds are shown in Table 2.7.

Table 2.7  $^{13}C$  Chemical Shifts Ranges for Organometallic Compounds

Ligand	$^{13}C$ Chemical Shift (in ppm)
Alkyl	-40 to +20
$\pi$ -bonded carbon ligands such as alkenes, Cp, arenes	40 to 120
Carbonyls :	
Terminal ( $M-CO$ )	150-220

Bridging ( $M-C-M$ )		230-290
Carbenes ( $M=C\backslash$ )		200-400

Coupling is transmitted by  $\sigma$ -bonds of a molecule—the higher the *s*-character of a bond, the higher is the coupling. Therefore,  $J_{CH}$  coupling constant values depends upon the hybridization of the C—H bond. Thus,  $J_{CH}$  value for  $\text{C}-\text{H}$  group ( $sp^3$  hybridization) is 125 Hz, for double bonded carbon ( $\text{C}=\text{C}-\text{H}$ )  $sp^2$  hybridization,  $J_{CH} = 170$  Hz and for a triple bonded carbon ( $-\text{C}\equiv\text{C}-\text{H}$ ),  $sp$  hybridization,  $J_{CH} = 250$  Hz.

In polyene and polyenyl complexes, the carbon atoms that are directly attached to the metal tend to be more shielded on binding and a shift relative to the free ligand of  $\sim 25$  ppm to high field is observed. If a metal has a spin,  $I = \frac{1}{2}$ , coupling to the metal is also observed. This is very useful for determination of the hapticity of the ligand.

### Electron Spin Resonance Spectroscopy (ESR)

There are some ions or molecules that contain only paired electrons with no net electron spin, no electronic magnetic moment. Therefore, there is no interaction between the electron spins and applied magnetic field. Thus these ions or molecules are ESR inactive. On the other hand, there are some ions or molecules or atoms that contain one or more electrons with unpaired spins. The electrons in these species will precess in an applied magnetic field with a precise precessional frequency and will undergo transitions between spin states (spin orientations). The measurement of electron spin transition is the basis of electron spin resonance. Since such substances are paramagnetic, ESR spectroscopy is also called electron paramagnetic resonance (EPR) spectroscopy. It can be concluded that the substances with unpaired electrons are ESR active and the substances with only paired electrons are ESR inactive.

The magnetic moment of an unpaired electron is about 700 times that of a proton, therefore, the paramagnetic substances are more ESR sensitive than NMR spectroscopy.

In ESR spectra, two kinds of multiplet structure are observed. The fine structure which occurs only in substance containing more than one unpaired electron spin and the hyperfine structure which occurs due to the presence of an unpaired electrons close to a nucleus with non-zero spin. The number of hyperfine spins is  $(2nl + 1)$ ,  $(2ml + 1)$ ,  $2ll + 1$ . where  $n$ ,  $m$  and  $l$  are the number adjacent atoms with non-zero spins.

Examples :

(1)  $^{13}\text{CF}_2\text{H}^\bullet$  :

$$\begin{aligned} \text{Number of hyperfine lines} &= \left(2 \times 1 \times \frac{1}{2} + 1\right) \left(2 \times 2 \times \frac{1}{2} + 1\right) \left(2 \times 1 \times \frac{1}{2} + 1\right) \\ &= 2 \times 3 \times 2 = 12 \end{aligned}$$

(2)  $[\text{CF}_2\text{D}]^\bullet$  (spin for D is 1) :

$$\begin{aligned} \text{Number of hyperfine lines} &= \left(2 \times 2 \times \frac{1}{2} + 1\right) \left(2 \times 1 \times 1 + 1\right) \\ &= 3 \times 3 = 9 \end{aligned}$$

(3)  $[\text{CClCH}_2]^\bullet$  (I for Cl is  $3/2$ ) :

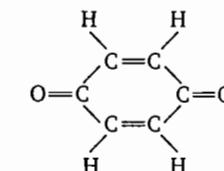
$$\begin{aligned} \text{Number of hyperfine lines} &= \left(2 \times 1 \times \frac{3}{2} + 1\right) \left(2 \times 2 \times \frac{1}{2} + 1\right) \\ &= 4 \times 3 = 12 \end{aligned}$$

(4)  $[\text{C}_6\text{H}_6]^\bullet$  :

$$\text{Number of hyperfine lines} = \left(2 \times 6 \times \frac{1}{2} + 1\right) = 7$$

$^{12}\text{C}$  is non-magnetic, no further splitting occurs.

(5) *p*-benzoquinone radical :



$$\text{Number of hyperfine lines} = 2 \times 4 \times \frac{1}{2} + 1 = 5$$

For systems with more than one unpaired electrons ( $S > \frac{1}{2}$ ), the ground state can be split in the absence of an external field due to the local site symmetry—the zero field splitting. For odd electron systems, this results in pairs of energy levels known as Kramer's doublets. If the system has an even number of unpaired electrons then the zero field splitting within the ground state may result in the ESR transitions being undetectable. Only one ESR signal is observed. For example (1) for a Cr(III) complex, zero field splitting results in the two Kramer's doublets (2). The number of ESR signals observed for Ni(II) octahedral complex is one because Ni(II) contain even number (i.e., two) unpaired electrons.



## Objective Questions

1. The order of CO bond strengths in the following metal hexacarbonyls is likely to be :
  - (a)  $V(CO)_6^- < Cr(CO)_6 < Mn(CO)_6^+$
  - (b)  $Cr(CO)_6 < Mn(CO)_6^+ < V(CO)_6^-$
  - (c)  $Mn(CO)_6^+ < Cr(CO)_6 < V(CO)_6^-$
  - (d)  $V(CO)_6^- < Mn(CO)_6^+ < Cr(CO)_6$
2. The final product in the reaction of  $Cr(CO)_6$  and  $CH_3CN$  is :
  - (a)  $Cr(CO)_4(CH_3CN)_2$
  - (b)  $Cr(CO)_3(CH_3CN)_3$
  - (c)  $Cr(CH_3CN)_6$
  - (d)  $Cr(CO)_3(CH_3CN)_2$
3. The reaction of  $Co_2(CO)_8$  with sodium amalgam followed by methyl iodide leads to formation of :
  - (a)  $Me_3(CO)_3Co$
  - (b)  $(MeCO)_3Co(CO)_3$
  - (c)  $MeCo(CO)_4$
  - (d)  $MeCo(CO)_4I$
4. The correct order of  $\nu_{CO}$  for the compounds  $[Mo(CO)_3(NMe_3)_3]$ ,  $[Mo(CO)_3(P(OPh)_3)_3]$ ,  $[Mo(CO)_3(PMe_3)_3]$ ,  $[Mo(CO)_3(PCl_3)_3]$  in the IR spectrum is :
  - (a)  $[Mo(CO)_3(NMe_3)_3] > [Mo(CO)_3(P(OPh)_3)_3] > [Mo(CO)_3(PMe_3)_3] > [Mo(CO)_3(PCl_3)_3]$
  - (b)  $[Mo(CO)_3(PCl_3)_3] > [Mo(CO)_3(NMe_3)_3] > [Mo(CO)_3(P(OPh)_3)_3] > [Mo(CO)_3(PMe_3)_3]$
  - (c)  $[Mo(CO)_3(PCl_3)_3] > [Mo(CO)_3(P(OPh)_3)_3] > [Mo(CO)_3(PMe_3)_3] > [Mo(CO)_3(NMe_3)_3]$
  - (d)  $[Mo(CO)_3(PMe_3)_3] > [Mo(CO)_3(NMe_3)_3] > [Mo(CO)_3(PCl_3)_3] > [Mo(CO)_3(P(OPh)_3)_3]$
5. In the *trans*- $PtCl_2L(CO)$  complex, the CO stretching frequency for  $L = NH_3$ , pyridine,  $NMe_3$  decreases in the order :
  - (a) Pyridine >  $NH_3$  >  $NMe_3$
  - (b)  $NH_3$  > Pyridine >  $NMe_3$
  - (c)  $NMe_3$  >  $NH_3$  > Pyridine
  - (d) Pyridine >  $NMe_3$  >  $NH_3$
6. Reaction of  $Fe(CO)_5$  with  $OH^-$  leads to complex A which on oxidation with  $MnO_2$  gives B. Compounds A and B respectively are :
  - (a)  $[HFe(CO)_4]^-$  and  $Fe_3(CO)_{12}$
  - (b)  $[Fe(CO)_5(OH)]^-$  and  $Fe_2(CO)_9$
  - (c)  $[Fe(CO)_4]^{2-}$  and  $Mn_2(CO)_{10}$
  - (d)  $[HFe(CO)_4]$  and  $Fe_2O_3$
7. On reducing  $Fe_3(CO)_{12}$  with an excess of sodium, a carbonylate ion is formed. The ion is isoelectronic with :
  - (a)  $[Mn(CO)_5]^-$
  - (b)  $[Ni(CO)_4]$
  - (c)  $[Mn(CO)_5]^+$
  - (d)  $[V(CO)_6]^-$
8. The infra-red stretching frequency  $\nu_{CO}$  of P-S follows the order :
 

(P)  $Mn(CO)_6^+$  (Q) CO (R)  $H_3B \leftarrow CO$  (S)  $[V(CO)_6]^-$

- (a)  $P > R > S > Q$  (b)  $S > P > R > Q$   
(c)  $Q > S > P > R$  (d)  $R > Q > P > S$
9. Which of the following compounds will show the highest C—O stretching frequency in the IR spectrum ?
 

(a)  $[Fe(CO)_4(PPh_3)]$  (b)  $[Fe(CO)_4]^{2-}$   
(c)  $[Fe(CO)_4Br_2]$  (d)  $[Fe(CO)_5]$
10. The value of M—C stretching frequencies of (i)  $[V(CO)_6]^-$ , (ii)  $[Cr(CO)_6]$  and  $[Mn(CO)_6]^+$  follow the trend :
 

(a) (ii) > (i) > (iii) (b) (ii) > (iii) > (i)  
(c) (i) > (ii) > (iii) (d) (iii) > (ii) > (i)
11. Solid  $Co_2(CO)_8$  shows infrared CO stretching bands at 1857, 1886, 2001, 2031, 2044, 2059, 2071 and  $2112\text{ cm}^{-1}$ . When  $Co_2(CO)_8$  is dissolved in hexane, the carbonyl bands at 1857 and  $1886\text{ cm}^{-1}$  disappear. These changes in the infrared spectrum in hexane are due to :
 

(a) loss of terminal CO  
(b) structural change of  $Co_2(CO)_8$  involving conversion of terminal CO to bridging CO  
(c) dissociation of  $Co_2(CO)_8$  to  $Co(CO)_4$   
(d) structural changes of  $Co_2(CO)_8$  involving conversion of bridging CO to terminal CO
12. In linear nitrosyl NO acts as a/an :
 

(a) one electron donor (b) two electron donor  
(c) three electron donor (d) four electron donor
13. Which one of the following is most easily reduced ?
 

(a)  $V(CO)_6$  (b)  $Cr(CO)_6$   
(c)  $Fe(CO)_5$  (d)  $Ni(CO)_4$
14. The oxidation states of manganese in  $NaMn(CO)_5$ ,  $BrMn(CO)_5$  and  $Mn_2(CO)_{10}$  respectively are :
 

(a) 1, -1, 0 (b) -1, 1, 0  
(c) 0, 1, -1 (d) -1, 0, 1
15. The stretching frequency of NO in a 16 electron complex having the following empirical formula  $[Ir(NO)Cl(PPh_3)_2(CO)]^+$  is expected to be :
 

(a)  $1850\text{ cm}^{-1}$  (b)  $1650\text{ cm}^{-1}$   
(c)  $1950\text{ cm}^{-1}$  (d)  $2050\text{ cm}^{-1}$
16. The final product in the reaction :
 
$$[Mn(CO)_6]^+ + MeLi \longrightarrow$$
 is :
 

(a)  $[Mn(CO)_6]^-Me$  (b)  $[Mn(CO)_5Me]$   
(c)  $[Mn(CO)_6]$  (d)  $[(MeCO)Mn(CO)_5]$

17. In the complex,  $[\text{Ni}_2(\eta^5-\text{Cp})_2(\text{CO})_2]$ , the IR stretching frequency appears at  $1857\text{ cm}^{-1}$  (strong) and  $1897\text{ cm}^{-1}$  (weak). The valence electron count and the nature of the M—CO bond respectively are :

- (a)  $16e^-$ , bridging
- (b)  $17e^-$ , bridging
- (c)  $18e^-$ , terminal
- (d)  $18e^-$ , bridging

18. In metal carbonyl complexes, as more electron density moves from the metal *d*-orbitals to the CO  $\pi^*$  orbitals the CO stretching frequency :

- (a) increases
- (b) decreases
- (c) remains same
- (d) disappears

19. The correct order of the CO stretching vibrational frequency is :

- (a)  $[\text{Ti}(\text{CO})_6]^{2-} > [\text{V}(\text{CO})_6]^- > \text{CO} > [\text{Cr}(\text{CO})_6]$
- (b)  $[\text{Cr}(\text{CO})_6] > \text{CO} > [\text{V}(\text{CO})_6]^- > [\text{Ti}(\text{CO})_6]^{2-}$
- (c)  $\text{CO} > [\text{V}(\text{CO})_6]^- > [\text{Ti}(\text{CO})_6]^{2-} > [\text{Cr}(\text{CO})_6]$
- (d)  $\text{CO} > [\text{Cr}(\text{CO})_6] > [\text{V}(\text{CO})_6]^- > [\text{Ti}(\text{CO})_6]^{2-}$

20. The values of CO stretching frequencies of (1)  $\text{Ni}(\text{CO})_4$ , (2)  $\text{Ni}(\text{CO})_3(\text{PMe}_3)$  and (3)  $\text{Ni}(\text{CO})_2(\text{PMe}_3)_2$  follow the trend :

- (a)  $1 > 2 > 3$
- (b)  $3 > 2 > 1$
- (c)  $1 > 3 > 2$
- (d)  $2 > 3 > 1$

21. CO bond order is lowest in :

- (a) Uncoordinated CO
- (b) CO bonded to one metal
- (c) CO bridging two metals
- (d) CO bridging three metals

22. Amongst the following, the metal that does not form homoleptic polynuclear metal carbonyl is :

- (a) Mn
- (b) Fe
- (c) Cr
- (d) Co

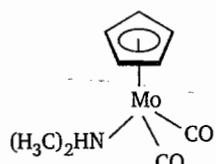
23. Complexes of general formula, *fac*— $[\text{Mo}(\text{CO})_3(\text{Phosphine})_3]$  have the C—O stretching frequency bands as given below,

Phosphines :  $\text{PF}_3$ (A),  $\text{PCl}_3$ (B),  $\text{P}(\text{Cl})\text{Ph}_2$ (C),  $\text{PMe}_3$ (D)  
 $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$       2090(i); 2040(ii); 1977(iii); 1945(iv)

The correct combination of the phosphine and the stretching frequency is :

- (a) A = i, B = ii, C = iii, D = iv
- (b) A = ii, B = i, C = iv, D = iii
- (c) A = iv, B = iii, C = ii, D = i
- (d) A = iii, B = iv, C = i, D = ii

24. For the molecule :



Consider the following statements about its room temperature spectral data :

- A.  ${}^1\text{H NMR}$  has singlets at  $5.48$  and  $3.18\text{ ppm}$
- B.  ${}^1\text{H NMR}$  has multiplet at  $5.48$  and a singlet at  $3.18\text{ ppm}$
- C. IR has CO stretching bands at  $1950$  and  $1860\text{ cm}^{-1}$ .
- D. IR has only one CO stretching band at  $1900\text{ cm}^{-1}$ .

The correct pair of statements is :

- (a) A and C
- (b) B and C
- (c) A and D
- (d) B and D

### ANSWERS

- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (a)  | 2. (b)  | 3. (c)  | 4. (c)  | 5. (a)  | 6. (a)  | 7. (b)  |
| 8. (d)  | 9. (d)  | 10. (c) | 11. (d) | 12. (c) | 13. (a) | 14. (b) |
| 15. (b) | 16. (d) | 17. (c) | 18. (b) | 19. (d) | 20. (a) | 21. (d) |
| 22. (c) | 23. (a) | 24. (a) |         |         |         |         |

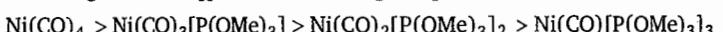


### Subjective Questions

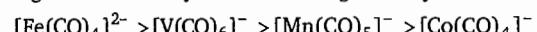
1. What is synergistic effect. How does it relate to metal carbonyl bonding ?

2. Explain the following :

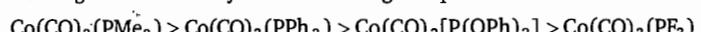
(a) Decreasing order of  $\nu_{\text{CO}}$  for the following complexes is :



(b) Decreasing order of basicity of the following carbonylate ions :



(c) Decreasing order of basicity of the following complexes :



(d) In infrared spectra of  $V(CO)_6$  and  $Cr(CO)_6$   $\nu_{CO}$  is obtained at  $1850\text{ cm}^{-1}$  and  $1980\text{ cm}^{-1}$  respectively and  $\nu_{M-C}$  is obtained at  $460\text{ cm}^{-1}$  and  $440\text{ cm}^{-1}$  respectively.

(e) Decreasing order of stretching frequencies of NO ( $\nu_{NO}$ ) in the following complexes :  
 $[Fe(CN)_5(NO)]^{2-}$ ,  $\nu_{NO} = 1939\text{ cm}^{-1} > [Mn(CN)_5(NO)]^{3-}$ ,  $\nu_{NO} = 1725\text{ cm}^{-1}$   
 $> [Cr(CN)_5(NO)]^{4-}$ ,  $\nu_{NO} = 1515\text{ cm}^{-1}$

(f) The vanadium-carbon bond distance is longer in  $V(CO)_6$  than in  $[V(CO)_6]^-$ .

(g)  $CN^-$ , CO and  $PM_3$  act as  $\sigma$  donors as well as  $\pi$ -acceptors.

(h)  $V(CO)_6$  is easily reduced to  $[V(CO)_6]^-$ .

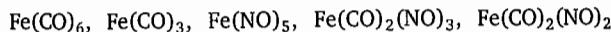
(i)  $[Co(CO)_3(PPh_3)_2]^+$  has only single carbonyl stretching frequency.

3. Match the compounds with the corresponding CO stretching bands in the following tables :

(a)	Compounds	$\nu_{CO}$ (in $\text{cm}^{-1}$ )
	$Cr(NH_3)_3(CO)_3$	1900
	$Cr(CO)_6$	2060
	$Ni(CO)_4$	1980

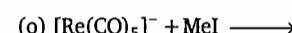
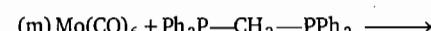
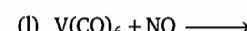
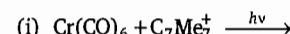
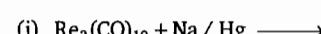
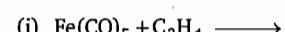
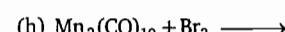
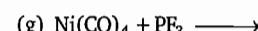
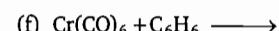
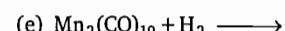
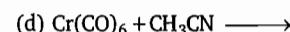
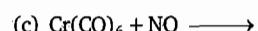
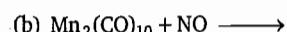
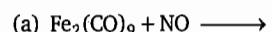
(b)	Compounds	$\nu_{CO}$ (in $\text{cm}^{-1}$ )
	$Ni(CO)_4$	1790
	CO	1890
	$Fe(CO)_4^{2-}$	2143
	$Co(CO)_4^-$	2060

4. Which of the following will be most stable ? Explain.



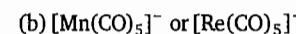
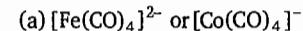
5. When  $Mo(CO)_6$  reacts with an excess of  $CH_3CN$ , a pale yellow product A is formed. When compound A is refluxed with benzene, the pale yellow product B is formed which has the molecular formula  $C_9H_6O_3Mo$  and shows a sharp singlet at  $\delta = 5.5\text{ ppm}$  in the  $^1H$  NMR spectrum. When compound A is refluxed with cyclooctatetraene in hexane, compound C is formed which has the molecular formula  $C_{11}H_8O_3Mo$ . Identify the compound A, B and C.

6. Predict the products from each of the following reactions :



7. The compound  $(C_5H_5)_2Fe(CO)_2$  shows two peaks of equal area in the  $^1H$  NMR spectrum but at lower temperatures it show four resonances of relative intensity 5 : 2 : 2 : 1. Explain

8. Which metal carbonyl should be more basic toward a proton? Explain.



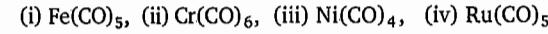
9. Nickel carbonyl,  $Ni(CO)_4$  reacts with cyclopentadiene to give a red diamagnetic compound of formula  $NiC_{10}H_{12}$ . The  $^1H$  NMR spectrum of this compound at room temperature shows four different types of hydrogen, integration give relative areas of 5 : 4 : 2 : 1 with the most intense peak in the aromatic rings. Suggest the structure of  $NiC_{10}H_{12}$  that is consistent with the NMR spectrum.

10. The compound  $Mo(CO)_6$  reacts with LiPh followed by strong carbocation reagent,  $CH_3OSO_2CF_3$  to give a product 'A'. Draw the structure of product 'A'.

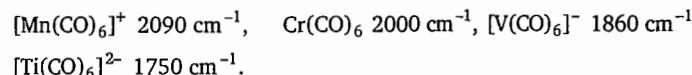
11. (a)  $Ni(CO)_4$  is monomer but the analogous cobalt compound is dimer. Explain.

(b)  $Ni(CO)_4$  is tetrahedral. Explain.

(c) Draw the structures of the following compounds :



12. (a)  $\text{Fe}(\text{CO})_5$  is known while  $\text{Fe}(\text{CO})_6$  is not. Give reason.  
 (b) Why are  $M-\text{CO}$  complexes referred to as  $\pi$ -acid ligand complexes?
13. Using the molecular orbital diagram of carbon monoxide, explain why it acts as an electron donor and acceptor through carbon and not through oxygen.
14. The CO stretching wave numbers in the IR spectra of certain metal carbonyl species are as follows :



The value for  $\text{CO}(g)$  is  $2143 \text{ cm}^{-1}$ . Discuss.

15. The V—C bond lengths in  $\text{V}(\text{CO})_6$  and  $[\text{V}(\text{CO})_6]^-$  are  $200 \text{ pm}$  and  $193 \text{ pm}$  respectively. Explain.
16. (a) Giving reasons arrange the following in order of :

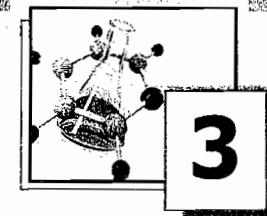
(i) Shortest C—O bond length :



(ii) Lowest C—O stretching frequency :



(b) Manganese does not form a mononuclear carbonyl. Why ?



## Cluster Compounds

Compound in which several metal atoms are bound together directly (*i.e.*, through  $M-M$  bonds) are called metal cluster compounds. The metal atoms in cluster compounds tend to agglomerate to form the maximum number of  $M-M$  bonds in such a way that the  $ML_n$  fragments should be sufficiently sterically unhindered to approach to within  $M-M$  bonding distance of each other. The structures of the clusters resemble the close-packed structures of the elemental metals themselves. This is due to the reason that the clusters contain unsaturated  $L_nM$  fragments. The unsaturated 16-electron fragment  $\text{Os}(\text{CO})_4$  is unstable and forms a stable triangular cluster  $\text{Os}_3(\text{CO})_{12}$  which obeys 18-electron rule. Similarly, the 15-electron fragment  $\text{Rh}(\text{CO})_3$  forms tetrahedral cluster  $\text{Rh}_4(\text{CO})_{12}$  which also obeys 18-electron rule. The tendency to form  $M-M$  bond increases on descending the group in the periodic table.

The stable transition metal clusters can be divided into : (i) organometallic clusters (ii) inorganic clusters.

The most extensive class of organometallic clusters belongs to metal carbonyls because  $M(\text{CO})_n$  fragments are sufficiently unhindered to approach to within metal-metal bonding distance of each other. In these clusters the metals are in low oxidation states (*i.e.*,  $-1, 0, +1, +2$ ).

In inorganic clusters such as  $\text{Re}_2\text{Cl}_8^{2-}$ ,  $\text{Mo}_2\text{Cl}_8^{4-}$ , the metals have higher oxidation states. There are also some naked metal clusters of the posttransition elements such as  $\text{Sn}_9^{2-}$ .

### Metal Carbonyl Clusters

The metal carbonyl-clusters are classified into two categories :

- (1) Low nuclearity carbonyl clusters
- (2) High nuclearity carbonyl clusters.

**(1) Low Nuclearity Carbonyl Clusters (LNCC) :** The first metal carbonyl cluster having M—M bond is  $Mn_2(CO)_{10}$ . The low nuclearity carbonyl clusters contain metal atoms  $\leq 4$ .

**Calculation of number of M—M bonds using 18/16-electron rule in LNCC :** The procedure for calculation of M—M bonds in a compound involves the following steps :

**Step I :** Calculate total valence electrons (TVE) on central metal in the compound (say it is A) which is equal to the number of valence electrons of the metal plus the number of electrons from each ligand and the charge.

**Step II :** Subtract A from  $n \times 18$  (where n is the number metal atoms in the compound), say it is B, i.e.,

$$B = n \times 18 - A$$

**Step III :** The value of  $\frac{B}{2}$  gives the total number of M—M bonds. The value of  $\frac{A}{n}$  gives the number of electrons per metal.

If  $\frac{A}{n} = 18$ , then there will be no M—M bond.

If  $\frac{A}{n} = 17$ , then there will be one M—M bond per metal.

If  $\frac{A}{n} = 16$ , then there will be two M—M bonds per metal.

If  $\frac{A}{n} = 15$ , then there will be three M—M bonds per metal.

If  $\frac{A}{n} = 14$ , then there will be four M—M bonds per metal.

This procedure can not be applied for HNCC.

Calculation of M—M bonds in some multinuclear complex is illustrated below :

**(1)  $M_2(CO)_{10}$  :** Where M = Mn, Tc, Re.

$$A = 2 \times 7 + 2 \times 10 = 34$$

$$B = 2 \times 18 - 34 = 2$$

$$\frac{B}{2} = \frac{2}{2} = 1$$

∴ Total number of M—M bonds = 1

$$\frac{A}{n} = \frac{34}{2} = 17$$

∴ One M—M bond per metal.

**(2)  $Co_2(CO)_8$  :**

$$A = 2 \times 9 + 2 \times 8 = 34$$

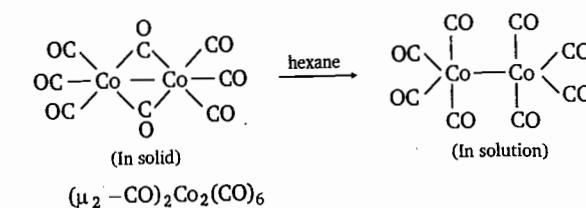
$$B = 2 \times 18 - 34 = 2$$

$$\frac{B}{2} = \frac{2}{2} = 1$$

∴ Total number of M—M bonds = 1

$$\frac{A}{n} = \frac{34}{2} = 17$$

∴ One M—M bond per metal.



**(3)  $Fe_2(CO)_9$  :**

$$A = 8 \times 2 + 2 \times 9 = 34$$

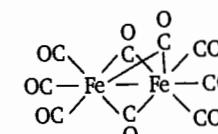
$$B = 2 \times 18 - 34 = 2$$

$$\frac{B}{2} = \frac{2}{2} = 1$$

∴ Total number of M—M bonds = 1

$$\frac{A}{n} = \frac{34}{2} = 17$$

∴ Number of M—M bonds per metal = 1



**(4)  $Fe_3(CO)_{12}$  :**

$$A = 3 \times 8 + 12 \times 2 = 48$$

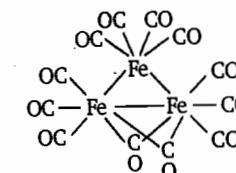
$$B = 3 \times 18 - 48 = 6$$

$$\frac{B}{2} = \frac{6}{2} = 3$$

∴ Total number of M—M bonds = 3

$$\frac{A}{n} = \frac{48}{3} = 16$$

∴ Number of Fe—Fe bonds per Fe atom = 2



(5)  $M_4(CO)_{12}$  : where  $M = Co, Rh$

$$A = 4 \times 9 + 12 \times 2 = 60$$

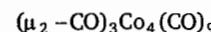
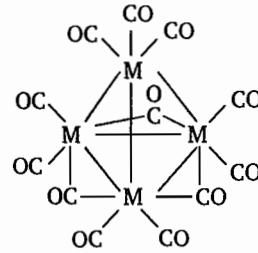
$$B = 4 \times 18 - 60 = 12$$

$$\frac{B}{2} = \frac{12}{2} = 6$$

$\therefore$  Total number of M—M bonds = 6

$$\frac{A}{n} = \frac{60}{2} = 15$$

$\therefore$  Number of Co—Co bonds per Co atom = 3



At high temperature all weakly bridging M—CO bonds are broken. Therefore, all CO ligands become terminal points.

(6)  $M_2(CO)_9$  :

Where  $M = Ru, Os$

$$A = 2 \times 8 + 9 \times 2 = 34$$

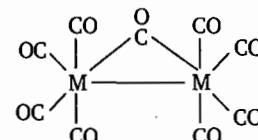
$$B = 2 \times 18 - 34 = 2$$

$$\frac{B}{2} = \frac{2}{2} = 1$$

$\therefore$  Total number of M—M bonds = 1

$$\frac{A}{n} = \frac{34}{2} = 17$$

$\therefore$  Number of M—M bonds per metal = 1



(7)  $M_3(CO)_{12}$  :

Where  $M = Ru, Os$

$$A = 3 \times 8 + 12 \times 2 = 48$$

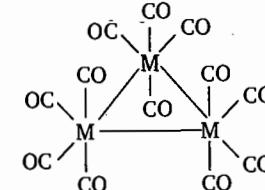
$$B = 3 \times 18 - 48 = 6$$

$$\frac{B}{2} = \frac{6}{2} = 3$$

$\therefore$  Total number of M—M bonds = 3

$$\frac{A}{n} = \frac{48}{3} = 16$$

$\therefore$  Number of M—M bonds per metal = 2



(8)  $Ir_4(CO)_{12}$  :

$$A = 4 \times 9 + 12 \times 2 = 60$$

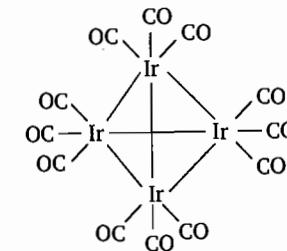
$$B = 4 \times 18 - 60 = 12$$

$$\frac{B}{2} = \frac{12}{2} = 6$$

$\therefore$  Total number of Ir—Ir bonds = 6

$$\frac{A}{n} = \frac{60}{4} = 15$$

$\therefore$  Number of Ir—Ir bonds per Ir atom = 3



The 18-electron rule is of great importance for predicting the number of metal-metal bonds, but it does not play any role to distinguish the bridging and terminal CO ligands, inasmuch as the electron count is the same for either mode of bonding. The factors causing the CO ligands to bridge or not bridge are the steric factors.  $V(CO)_6$  does not dimerize as it would become seven coordinate and increase in steric hindrance. In  $Mn_2(CO)_{10}$ , if bridging occurs, there will be increase in coordination number beyond six and therefore it will be destabilized.

An interesting feature of the structure of binary carbonyl complexes of transition metals is that the ability of CO ligands to bridge transition metals decreases on descending the group in periodic table. For example, in  $Fe_2(CO)_9$ , there are three bridging CO ligands but in  $Ru_2(CO)_9$  and  $Os_2(CO)_9$ , there is only single bridging CO ligand. This is not due to steric hindrance but it is due to the reason that the orbitals of bridging CO ligands are less able to interact effectively with transition metals as the size of the metals increases. As the M—M bond length increases ( $Co < Rh < Ir$ ), the M—C bond length increases or/and the M—C—M bond angle opens up. Either of these changes would

destabilize the compound. For this reason  $\text{Fe}_3(\text{CO})_{12}$  [or  $\text{Fe}_3(\mu_2-\text{CO})_2(\text{CO})_{10}$ ] and  $\text{Co}_4(\text{CO})_{12}$  [or  $\text{Co}_4(\mu_2-\text{CO})_3(\text{CO})_9$ ] are bridged and  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Os}_3(\text{CO})_{12}$  and  $\text{Ir}_4(\text{CO})_{12}$  are unbridged.

**(9)  $[\text{Fe}_4(\text{CO})_{12}(\mu_3-\text{CO})]^{2-}$  :**

$$A = 4 \times 8 + 12 \times 2 + 2 + 2 = 32 + 24 + 4 = 60$$

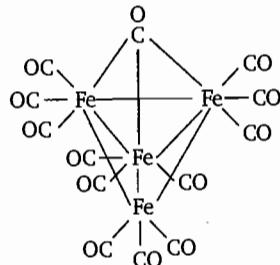
$$B = 4 \times 18 - 60 = 12$$

$$\frac{B}{2} = \frac{12}{2} = 6$$

∴ Total number of Fe—Fe bonds = 6

$$\frac{A}{n} = \frac{60}{4} = 15$$

∴ Number of Fe—Fe bonds per Fe atom = 3



**(10)  $\text{Re}_4\text{H}_4(\text{CO})_{12}$  :**

$$A = 4 \times 7 + 4 + 12 \times 2 = 28 + 4 + 24 = 56$$

$$B = 4 \times 18 - 56 = 72 - 56 = 16$$

$$\frac{B}{2} = \frac{16}{2} = 8$$

∴ Total number of Re—Re bonds = 8

$$\frac{A}{n} = \frac{56}{4} = 14$$

∴ Number of Re—Re bonds per Re atom = 4

This compound requires eight Re—Re bonds rather than the six usually found in tetrahedral arrangement of four metal atoms. The expected distortions for a structure (Fig. 3.1) with two localized Re=Re bonds are not found and the extra Re—Re bonds are considered to be delocalized over the metal framework so that each Re—Re bond becomes shorter.

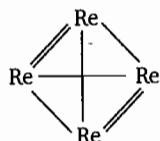


Fig. 3.1

Therefore, the expected structure for Re cluster (Fig. 3.1) would contain two localized Re=Re bonds. This structure shows that the two Re=Re bonds will be shorter and two Re—Re bonds will be

longer. But its structure determination shows that all the four Re—Re bonds are shorter and equal. Therefore, it has been considered that the two extra bonds are delocalized over metal cluster. In this structure each H is found to be  $\mu_3$ —H face bridging (Fig. 3.2). This structure is cubane like.

The two electrons of one M—H bond are donated to two other metals. In this structure, the delocalized Re—Re bonds are included in the  $\mu_3$ —H bridging. Therefore, this compound has six Re—Re bonds (three Re—Re bonds per Re atom) and four bridging  $\mu_3$ —H bonds. In this model, delocalized M—M bonds are included in the  $\mu_3$ —H bridges.

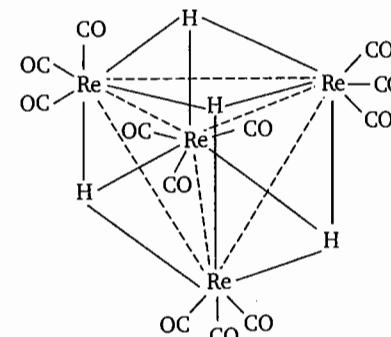


Fig. 3.2

**(11)  $\text{Os}_3\text{H}_2(\text{CO})_{10}$  :**

$$A = 3 \times 8 + 2 \times 1 + 10 \times 2 = 24 + 2 + 20 = 46; \quad B = 3 \times 18 - 46 = 54 - 46 = 8$$

$$\frac{B}{2} = \frac{8}{2} = 4$$

∴ Total number of Os—Os bonds = 4

$$\frac{A}{n} = \frac{46}{3} = 15.33$$

The trinuclear carbonyl clusters which obey 18-electron rule, have TVE = 48. But in this compound TVE = 46, i.e., it lacks 2-electron from TEC of 48. Therefore, it may be considered that this compound contains an Os=Os double bond because the TVE for a system with four M—M bonds in a three metal atoms cluster is 46. By having one Os=Os double bond, each Os atom obeys the 18-electron rule. Due to the presence of Os=Os double bond, like C=C double bond, it behaves as an unsaturated cluster and is much more reactive than  $\text{Os}_3(\text{CO})_{12}$ . Fig. 3.3 shows that one edge of the  $\text{Os}_3$  triangle is shorter than the other and is bridged by two H-atoms.

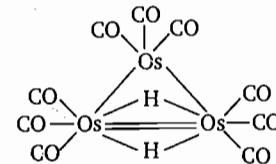


Fig. 3.3

**For square planar complexes :**

**Step I :** Determine TVE (say it is A)

$$\text{Step II : } B = n \times 16 - A$$

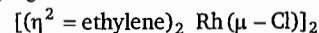
$$\text{Step III : } \frac{B}{2} = \text{Total number of M—M bonds}$$

$$\frac{A}{n} = 16, \quad \text{No M—M bond in the complex}$$

$$= 15, \quad \text{one M—M bond per metal}$$

$$= 14, \quad \text{Two M—M bonds per metal}$$

Some examples illustrating the calculation of number of M—M bonds in square planar complexes obeying 16-electron rule are :



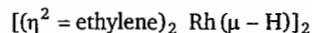
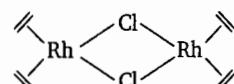
$$A = 4 \times 2 + 2 \times 9 + 2 \times 3 = 8 + 18 + 6 = 32$$

$$B = 2 \times 16 - 32 = 0$$

$$\frac{B}{2} = 0$$

$$\frac{A}{n} = \frac{32}{2} = 16$$

Therefore, number of total M—M bonds and number of M—M bonds per metal is zero.

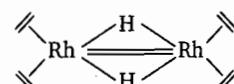


$$A = 4 \times 2 + 2 \times 9 + 2 = 8 + 18 + 2 = 28$$

$$B = 2 \times 16 - 28 = 4$$

$$\frac{B}{2} = \frac{4}{2} = 2 \quad \therefore \text{Total Number of M—M bonds} = 2$$

$$\frac{A}{n} = \frac{28}{2} = 14 \quad \therefore \text{Number of M—M bonds per metal} = 2$$



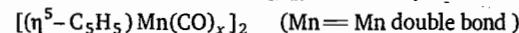
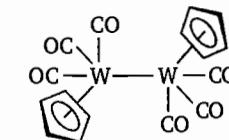
**To Determine the Unknown Quantity Using 18-Electron Rule**



$$2 \times 5 + 2 \times 6 + 2 + 4x = 36$$

$$24 + 4x = 36$$

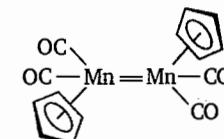
$$x = 3$$



$$2 \times 5 + 2 \times 7 + 4 + 4x = 36$$

$$28 + 4x = 36$$

$$x = 2$$



**To Determine the Expected Charge on the Complex Ions Using 18-Electron Rule**



$$9 + 3 \times 2 + x = 18$$

$$15 + x = 18$$

$$x = 18 - 15 = 3$$

Therefore, charge on the complex ion is = -3



$$3 \times 2 + 10 + 2 + 9 + 3 \times 2 + x = 36$$

$$33 + x = 36$$

$$x = 36 - 33 = 3$$

Therefore, charge on the complex ion = -3



$$15 + 30 + 2 \times 2 + 3 \times 2 + x = 54$$

$$15 + 30 + 4 + 6 + x = 54$$

$$55 + x = 54$$

$$x = 54 - 55 = -1$$

Therefore, charge on the complex ion = +1

### To Identify the Transition Metals in a Complex Using 18-Electron Rule

(i)  $[(\mu^5 -C_5H_5) M (CO)_3]_2$  (M is first row transition metal and one M—M single bond)

$$10 + 2 + 2M + 12 = 36$$

$$2M = 36 - 24$$

$$M = \frac{12}{2} = 6$$

$$M = Cr (3d^5 4s^1)$$

(ii)  $[M (\mu^6 -C_6H_6) (CO)_2]_2$  (M is the second row transition metal and one M=M bond)

$$2M + 4 + 2 \times 6 + 4 \times 2 = 36$$

$$2M = 36 - 24 = 12$$

$$M = 6$$

Therefore, metal is MO ( $4d^5 5s^1$ ).

(iii)  $[M (\mu^3 -C_5H_5) (CO)_5]$  (M is 3d series transition metal)

$$M + 3 + 5 \times 2 = 18$$

$$M = 18 - 13 = 5$$

Therefore, metal is V ( $3d^3 4s^2$ ).

### HIGH NUCLEARITY CARBONYL CLUSTERS (HNCC)

High nuclearity carbonyl clusters have metal atoms  $\geq 5$ , each forming atleast one M—M bond. The first HNCC was discovered to be  $Rh_6(CO)_{16}$ .

### Electron Counting in Carbonyl Clusters

The rules that are applied to LNCC for valence electron count and calculation of number of M—M bonds do not always follow for HNCC. Many carbonyl clusters have structures and are electron deficient similar to higher boranes  $B_nH_n^{2-}$ . Therefore, the approach used to describe the bonding, structure and electron count for higher boranes can be used for carbonyl clusters and other clusters. Wade gave the method for electron counting in HNCC. The structure of the cluster is decided purely by the number of cluster electrons (called skeletal electrons), not by any other factor.

It is a general feature of closo- $B_nH_n^{2-}$  anions that there are no B—H—B or  $BH_2$  group and each B—H bond is a normal  $2e$  bond requiring one electron from B and one electron from H. As boron starts with three electrons, it has two electrons left to contribute to the cluster and these electrons are regarded as skeletal or framework electrons. Thus,  $B_nH_n^{2-}$  anions have  $2n + 2$  skeletal electrons (the  $2n$  electrons from  $nB$  atoms and the 2 electrons from the anionic charge). In borane clusters, each BH unit has an  $sp$  orbital that points directly towards the centre of the cluster and the other two  $p_x$  and  $p_y$  orbitals that point along the surface of the cluster.

The  $nB$  atoms have  $4n$  atomic orbitals which are always distributed as follows :

$n$  in the  $n(B-H_t)$  bonding orbitals,  $(n+1)$  in cluster bonding molecular orbitals,  $(2n-1)$  in non-bonding and antibonding cluster molecular orbitals.

In  $B_nH_n$  cluster, there are  $(n+1)$  cluster bonding molecular orbitals and  $2n$  electrons contributed by  $n$  B—H units, two additional electrons are required for  $B_nH_n^{2-}$  ion. This is the reason why the  $B_nH_n^{2-}$  ions are more stable than  $B_nH_n$  itself.

Since the shape of the cluster depends only on the number of skeletal electrons, it is possible (conceptually) to remove a vertex group,  $BH_t$  from the cluster leaving two skeletal electrons that the vertex  $BH_t$  group was contributing. This is possible only if  $BH^{2+}$  is removed instead of a  $BH_t$  unit leaving one vertex of the cluster empty. If  $BH^{2+}$  unit is removed from  $B_6H_6^{2-}$  then  $B_5H_5^{4-}$  ion is obtained. This will have the same polyhedral structure because the electron count has not changed but one vertex is now unoccupied. The neutral  $B_5H_9$  borane can be obtained by adding the appropriate number of protons (four protons in this case), this does not alter the number of electrons in the system because protons ( $H^+$ ) are the zero electron species. Hence all the bonding molecular orbitals are just filled. The protons bridge the faces of polyhedron which include the missing vertex. In general, the number of skeletal electron pairs in  $B_nH_n^{z-}$  will be equal to  $\frac{1}{2}(2n+z)$  and the number of vertices (V) is  $\left[ \frac{1}{2}(2n+z) - 1 \right]$ .

The boranes are classified as : closo, nido, arachno, hypho and klado boranes.

The boranes in which each corner is occupied by B atoms are called closo boranes. These have the formula  $B_nH_n^{2-}$ . The number of vertices and skeletal electron pairs are respectively  $n$  and  $(n+1)$ . This indicates that the vertices in a closo borane will be one less than the number of skeletal electron pairs.

If one B atom is removed from a vertex of a closo structure, a nido (Latin : nest like) structure will result. The nido boranes have the formula  $B_nH_n^{4-}$  or  $B_nH_{n+4}$ . The number of vertices will be  $(n-1)$  of an  $n$  cornered polyhedron and the number of skeletal electron pairs is  $(n+2)$ .

If two vertex B atoms are removed, an arachno (Greek : spider's web like) borane will result. With two vertices missing, the structure is even more open than in the nido structure. Arachno boranes have the formula  $B_nH_n^{6-}$  or  $B_nH_{n+6}$ . The number of vertices will be  $(n-2)$  of an  $n$  cornered polyhedron and the number of skeletal electron pairs is  $(n+3)$ .

The **hypho** (Greek : net like) boranes have the formula  $B_nH_n^{8-}$  or  $B_nH_{n+8}$ . They have  $(n - 3)$  vertices leaving three vertices unoccupied of an  $n$  cornered polyhedron and the number of skeletal electron pairs is  $(n + 4)$ .

The **klado** (Greek : branched) boranes have the formula  $B_nH_n^{10-}$  or  $B_nH_{n+10}$ . They have  $(n - 4)$  vertices leaving four vertices unoccupied of an  $n$  cornered polyhedron. The number of skeletal electron pairs is  $(n + 5)$ .

The method for calculation of skeletal electron pairs is called the Wade's rule.

Wade has suggested that a BH unit can be replaced by a transition metal equivalent that donate the same number of skeletal electrons. Wade has treated the  $M(CO)_3$  unit as analogous to BH unit. Transition metal with nine valence orbitals (one  $s$ , three  $p$  and five  $d$  orbitals) have five more orbitals than boron which has only four valence orbitals (one  $s$  and three  $p$  orbitals). When these five extra orbitals are filled as a consequence of bonding within the skeleton (or framework) and with surrounding ligands, the number of electron count increases by 10 electrons per skeletal atom. For example, when we replace all the BH units in **closo**  $B_6H_6^{2-}$  with  $Os(CO)_3$  groups, the species  $Os_6(CO)_{18}^{2-}$  is obtained and there is an increase in electron count from 26 to 86.

If the transition metal M is Os, the nine orbitals in  $Os(CO)_3$  are assigned as follows : three orbitals are filled by electron pairs donated by three CO ligands, three more orbitals are filled with six electrons out of the eight electrons of Os, these electrons are used for back bonding to CO ligands. The two electrons are left in the remaining three metal orbitals. These two electrons are available for skeletal bonding similar to a BH unit.

The structures of the HNCC can be determined by skeletal or framework electron counts with the help of Wade's rule.

1. Calculate total electron count (TEC).
2. Add to TEC the valence electrons for interstitial atom, for example, 1 for H, 4 for C, 5 for N, 5 for P and so on.
3. Each metal atom utilizes 12 electrons and each CO ligand utilizes 2 electrons irrespective of its bonding, terminal or bridged for non-skeletal bonding.
4. Calculate polyhedral electron count (PEC) :

$$PEC = TEC - n \times 12$$

where  $n$  is the number of metal atoms.

5. Calculate  $\frac{PEC}{2}$ .

If  $\frac{PEC}{2} = n - 1$ , super closo

- $= n$  hyper closo
- $= n + 1$  closo
- $= n + 2$  nido
- $= n + 3$  arachno
- $= n + 4$  hypho
- $= n + 5$  klado

The valence electron counts corresponding to various structural classifications for main group and transition metal clusters are summarized in Table 3.1.

Table 3.1

Structure Type	Boranes		Transition Metal Clusters	
	TEC	Skeletal Electron Pairs	TEC	PEC/2
closo	$4n + 2$	$n + 1$	$14n + 2$	$n + 1$
nido	$4n + 4$	$n + 2$	$14n + 4$	$n + 2$
arachno	$4n + 6$	$n + 3$	$14n + 6$	$n + 3$
hypho	$4n + 8$	$n + 4$	$14n + 8$	$n + 4$

Some examples of HNCC illustrating their structure type are given below :

1. **Rh<sub>6</sub>(CO)<sub>16</sub>**, here  $n = 6$

$$TEC = 6 \times 9 + 16 \times 2 = 86 = 14 \times 6 + 2 \quad (14n + 2)$$

$$PEC = 86 - 6 \times 12 = 14$$

$$\frac{PEC}{2} = \frac{14}{2} = 7 = 6 + 1 \quad (n + 1)$$

Therefore,  $Rh_6(CO)_{16}$  is a **closo** metal cluster.

2. **Os<sub>5</sub>C(CO)<sub>15</sub>**

$$TEC = 5 \times 8 + 4 + 15 \times 2 = 74 = 14 \times 5 + 4 \quad (14n + 4)$$

$$PEC = 74 - 5 \times 12 = 14$$

$$\frac{PEC}{2} = \frac{14}{2} = 7 = 5 + 2 \quad (n + 2)$$

Therefore,  $Os_5C(CO)_{15}$  is a **nido** metal cluster.

3. **Ni<sub>5</sub>(CO)<sub>12</sub><sup>2-</sup>**

$$TEC = 5 \times 10 + 12 \times 2 + 2 = 76 = 14 \times 5 + 6 \quad (14n + 6)$$

$$PEC = 76 - 5 \times 12 = 16$$

$$\frac{PEC}{2} = \frac{16}{2} = 8 = 5 + 3 \quad (n + 3)$$

Therefore,  $Ni_5(CO)_{12}^{2-}$  is an **arachno** metal cluster.

4. **Co<sub>6</sub>(CO)<sub>16</sub>**

$$TEC = 6 \times 9 + 16 \times 2 = 54 + 32 = 86 = 14 \times 6 + 2 \quad (14n + 2)$$

$$PEC = 86 - 6 \times 12 = 14$$

$$\frac{\text{PEC}}{2} = \frac{14}{2} = 7 = 6 + 1 (n + 1)$$

Therefore,  $\text{Co}_6(\text{CO})_{16}$  is a **closو** metal cluster.

### 5. $\text{Ru}_6\text{C}(\text{CO})_{17}$

$$\text{TEC} = 6 \times 8 + 4 + 17 \times 2 = 48 + 4 + 34 = 86 = 14 \times 6 + 2 (14n + 2)$$

$$\text{PEC} = 86 - 6 \times 12 = 14$$

$$\frac{\text{PEC}}{2} = \frac{14}{2} = 7 = 6 + 1 (n + 1)$$

Therefore,  $\text{Ru}_6\text{C}(\text{CO})_{17}$  is a **closو** metal cluster.

### 6. $\text{Ru}_5\text{N}(\text{CO})_{14}$

$$\text{TEC} = 5 \times 8 + 5 + 14 \times 2 + 1$$

$$= 40 + 5 + 28 + 1 = 74 = 14 \times 5 + 4 (14n + 4)$$

$$\text{PEC} = 74 - 5 \times 12 = 14$$

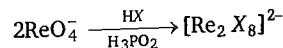
$$\frac{\text{PEC}}{2} = \frac{14}{2} = 7 = 5 + 2 (n + 2)$$

Therefore,  $\text{Ru}_5\text{N}(\text{CO})_{14}$  is a **nido** metal cluster.

## INORGANIC METAL CLUSTERS

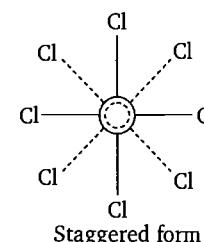
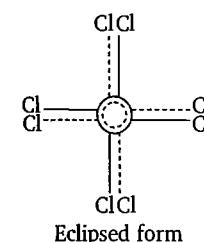
### Binuclear Clusters Containing M—M multiple Bonds

The most widely studied binuclear species are  $[\text{Re}_2\text{X}_8]^{2-}$  ions, (where X is F, Cl, Br, I, NCS,  $\text{CH}_3$  etc.). The  $[\text{Re}_2\text{Cl}_8]^{2-}$  ion was the first inorganic compound containing a metal-metal quadruple bond. It is isostructural with  $[\text{Mo}_2\text{Cl}_8]^{4-}$ .  $[\text{Re}_2\text{X}_8]^{2-}$  ions can be prepared by reduction of  $\text{ReO}_4^-$  with  $\text{H}_2$ ,  $\text{H}_3\text{PO}_2$  or  $\text{PhCOCl}$  in the presence of  $\text{X}^-$  ions.



In lower halide clusters, the metal oxidation state are usually +2, +3 or +4.

In  $[\text{Re}_2\text{X}_8]^{2-}$  ions, the Re—Re distance (224 pm) is extremely short compared with an average Re—Re bond distance of 275 pm in rhenium metal and 248 pm in  $\text{Re}_3\text{Cl}_9$ . Re—Cl bonds may either have eclipsed or staggered conformation. But the structural analysis has shown that the Cl atoms are eclipsed rather than staggered (Fig. 3.4).

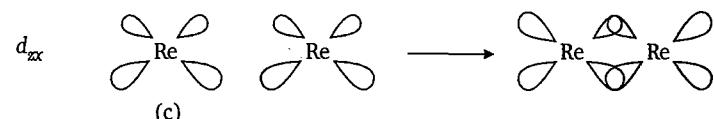
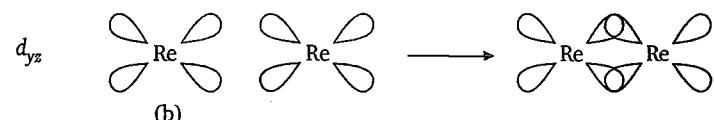
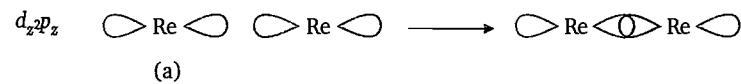


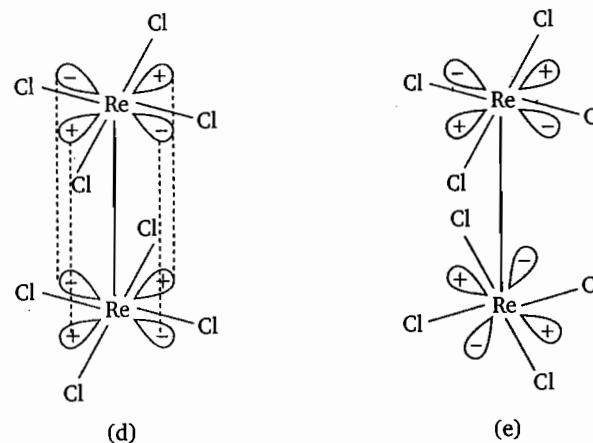
○ Front Re  
○ Rear Re

**Fig. 3.4**

Both of these features can be recognized due to quadruple M—M bonds. Each rhenium atom is bonded to four chlorine atoms that are almost in a square planar array. The  $d_{x^2-y^2}$  orbitals of the two metals are used for bonding to  $\text{Cl}^-$  ligands. The Re—Cl bonds are formed by using  $dsp^2$ -hybrid orbitals on both metals utilizing  $d_{x^2-y^2}$  orbitals. This leaves four orbitals  $d_{z^2}$ ,  $d_{yz}$ ,  $d_{zx}$  and  $d_{xy}$  and the four electrons on each  $\text{Re}^{3+}$  ion ( $d^4$ ). The metal  $d_{z^2}$  and  $p_z$  orbitals may hybridize to form two  $dp$  hybrid orbitals: one orbital directed towards the other rhenium atom and a second orbital directed in the opposite direction. The former hybrid orbital overlaps with the similar on the second Re atom to form a Re—Re  $\sigma$ -bond [Fig. 3.5(a)] whereas the second orbital forms a non-bonding orbital.

The  $d_{xz}$  and  $d_{yz}$  orbitals of each metal atom overlap to form two  $\pi$ -bonds [Figure 3.5(b) and (c)] in  $xz$  and  $yz$  planes respectively. Finally, sideways overlap of  $d_{xy}$  orbitals of the two metals form a  $\delta$  bond. The formation of the  $\delta$  bond causes the eclipsed conformation because overlap of the  $d_{xy}$  orbitals is possible only in this geometry [Fig. 3.5(d)]. If the chlorine atoms are staggered the two  $d_{xy}$  orbitals will likewise be staggered which results in zero overlap [Fig. 3.5(e)].





**Fig. 3.5** (a) Formation of  $\sigma$ -bond by the overlapping of  $d_{z^2}p_z$  hybrid orbitals on each Re atom, (b) Formation of a  $\pi$ -bond by overlap of  $d_{yz}$  orbitals on each Re atom, (c) Formation of another  $\pi$ -bond by overlap of  $d_{zx}$  orbitals on each Re atoms, (d) Formation of a  $\delta$ -bond by overlap of  $d_x^2$  orbitals in eclipsed conformation and (e) Zero overlap in staggered conformation.

The binuclear metal clusters with quadruple bond are possible only when each metal has  $d^0$  configuration.

A qualitative molecular orbital diagram for the formation of M—M bonds is shown in Fig. 3.6. The Re—Cl bonds are regarded as coordinate bonds between  $\text{Re}^{3+}$  ions and the  $\text{Cl}^-$  ligands. The eight  $d$ -electrons from two  $\text{Re}^{3+}$  ions (four electrons from each  $\text{Re}^{3+}$  ion) occupy a  $\sigma$ -bonding, two  $\pi$ -bonding and one  $\delta$ -bonding molecular orbitals to form the quadruple bond. Therefore, the electronic configuration in  $[\text{Re}_2\text{Cl}_8]^{2-}$  ion (Fig. 3.6) will be  $\sigma^2\pi^4\delta^2$ . Which indicates how many electrons are present in each bonding molecular orbital. The complex is, therefore, diamagnetic.

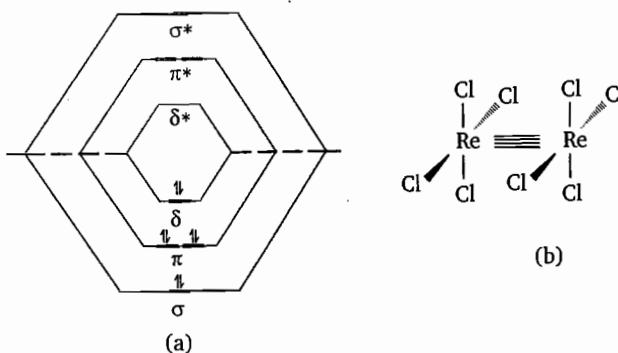


Fig. 3.6

The species  $[\text{Re}_2\text{Cl}_8]^{2-}$  [Fig. 3.6 (b)] and  $[\text{Mo}_2\text{Cl}_8]^{4-}$  are isostructural. In both the cases the Cl atoms are eclipsed and both have considerably shorter M—M bond distance (Re—Re = 224 pm, Mo—Mo = 214 pm) than in the metals themselves (Re—Re = 275 pm, Mo—Mo = 273 pm) this is due to the formation of M—M quadruple bond.

The strength of bonds follows the order :  $\sigma > \pi > \delta$ . The  $\delta$ -bond is the weakest bond but it is strong enough to maintain  $[Re_2 X_8]^{2-}$  in the eclipsed conformation. This  $\delta$  bond strength is comparable to that of a hydrogen bond. The  $Re \equiv Re$  bond energy is  $\sim 85$  kcal/mol, of which  $\sim 6$  kcal/mol is assigned to the  $\delta$  bond. Both  $\delta$  and  $\delta^*$  molecular orbitals are almost non-bonding. If electron is added to  $\delta^*$  or removed from  $\delta$  orbital, there will be no too much loss in stability. The compounds, for example, which occupied  $\delta^*$  orbital are  $[Re_2Cl_4(PMe_2Ph)_4]$ ,  $[Re_2Cl_4(PMe_2Ph)_4]^+$ ,  $[Re_2Cl_4(PMe_2Ph)_4]^{2+}$ . These compounds are stable and have been synthesized. Some examples of cluster compounds are given below :

$[\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4] \approx$

Let the oxidation state of Re =  $x$

$$2x - 4 + 0 = 0$$

$$2x = +4$$

$$x = +2$$

$$\text{Re}^{2+} \rightarrow 4d^5$$

Therefore number of  $d$ -electrons on two  $\text{Re}^{2+}$  ions = 10, Electronic configuration in this compounds is  $\sigma^2 \pi^4 \delta^2 \delta^{*2}$ .

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(8 - 2) = 3.0$$

All electrons are paired, therefore, it is diamagnetic.

$$[\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]^+$$

Let the oxidation states of two Re atoms are  $x$  and  $y$ .

$$x + y - 4 = +1$$

$$x + y = +5$$

$$x = +2, y = +3$$

$$\text{Re}^{2+} = 4d^5, \text{Re}^{3+} = 4d^4$$

Therefore, number of  $d$ -electrons on  $\text{Re}^{2+}$  and  $\text{Re}^{3+}$  ions  
 $= 5 + 4 = 9$

Electronic configuration in this cluster ion is

$$\sigma^2 \pi^4 \delta^2 \delta^*$$

$$\text{Bond order} = \frac{1}{2}(8 - 1) = 3.5$$

There is one unpaired electron, therefore, it is paramagnetic.

**[Re<sub>2</sub>Cl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>4</sub>]<sup>2+</sup>** :

Let the oxidation states of two Re atoms are  $x$  and  $y$ .

$$x + y - 4 + 0 = +2$$

$$x + y = +6$$

$$x = +3, y = +3$$

$$\text{Re}^{3+} = 4d^4$$

Number of electrons on two Re<sup>3+</sup> ions = 8

Electronic configuration in this cluster ion is  $\sigma^2\pi^4\delta^2$ .

$$\text{Bond order} = \frac{8 - 0}{2} = 4$$

All electrons are paired, therefore, it is diamagnetic.

The compounds, for example, which have less than full occupation of the  $\delta$ -bonding orbital are :

[Mo<sub>2</sub>(HPO<sub>4</sub>)<sub>4</sub>]<sup>2-</sup>, [Mo<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>]<sup>2-</sup>, [Mo<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>]<sup>3-</sup> and [Mo<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>]<sup>4-</sup>. These compounds are also stable and have been synthesized.

**[Mo<sub>2</sub>(HPO<sub>4</sub>)<sub>4</sub>]<sup>2-</sup>** :

Let the oxidation states of Mo atoms are  $x$  and  $y$ .

$$x + y - 8 = -2$$

$$x + y = +6$$

$$x = +3, y = +3$$

$$\text{Mo}^{3+} \rightarrow 4d^3$$

Number of electrons in two M<sup>3+</sup> ions = 6

Electronic configuration in this cluster ion is :  $\sigma^2\pi^4$

$$\text{Bond order} = \frac{6 - 0}{2} = 3.0$$

Since all electrons are paired, therefore, this cluster ion is diamagnetic.

**[Mo<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>]<sup>2-</sup>** :

$$x + y - 8 = -2$$

$$x + y = +6$$

$$x = +3, y = +3$$

$$\text{Mo}^{3+} \rightarrow 4d^3$$

Number of valence electrons on two Mo<sup>3+</sup> ions = 6

Electronic configuration in this cluster ion is :  $\sigma^2\pi^4$

$$\text{Bond order} = \frac{6 - 0}{2} = 3.0$$

Since all electrons are paired, therefore, this cluster ion is diamagnetic.

**[Mo<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>]<sup>3-</sup>** :

$$x + y - 8 = -3$$

$$x + y = +5$$

$$x = +2, y = +3$$

$$\text{Mo}^{2+} \rightarrow 4d^4, \text{Mo}^{3+} \rightarrow 4d^3$$

Number of valence electrons on Mo<sup>2+</sup> and Mo<sup>3+</sup> ions is = 7

Electronic configuration in this cluster ion is :  $\sigma^2\pi^4\delta^1$

$$\text{Bond order} = \frac{7 - 0}{2} = 3.5$$

Since there is one unpaired electron, therefore, this ion is paramagnetic.

**[Mo<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>]<sup>4-</sup>** :

$$x + y - 8 = -4$$

$$x + y = +4$$

$$x = +2, y = +2$$

$$\text{Mo}^{2+} = 4d^4$$

Number of valence electrons on two Mo<sup>2+</sup> ions = 8

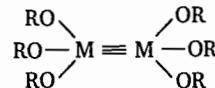
Electronic configuration in this cluster ion is :  $\sigma^2\pi^4\delta^2$

$$\text{Bond order} = \frac{8 - 0}{2} = 4$$

Since all electrons are paired, therefore, this ion is diamagnetic.

The energy difference between  $\delta$  and  $\delta^*$  orbitals lie in the visible region of the electromagnetic radiations. Therefore, most of the complexes with quadruple bond are of intense colour. For example, [Re<sub>2</sub>Cl<sub>8</sub>]<sup>2-</sup> and [Mo<sub>2</sub>Cl<sub>8</sub>]<sup>4-</sup> are royal blue and dark yellow respectively. The colour of compounds containing M—M quadruple bonds is due to  $\delta - \delta^*$  transition.

The compound  $[M_2(OR)_6]$ , where  $M = Mo, W$  has an  $M—M$  triple bond and an electronic configuration  $\sigma^2\pi^4$ . In these compounds good overlap is possible in the staggered geometry as the  $d_{xy}$  orbital is not participating in bonding.



If the two metals have no electrons in  $d$ -orbitals, then no metal-metal bond is formed. In general if each metal has 1, 2, 3 and 4 electrons in  $d$ -orbitals then single, double, triple and quadruple bonds are formed respectively and if each metal has 5, 6 or 7 electrons in  $d$ -orbitals then triple, double and single bond are formed respectively. To form a  $M—M$  bond of bond order  $n$ , the number of  $d$ -electrons being shared between two metals should be equal to or greater than  $n$  because it needs a minimum of  $n$  electrons.

### Binuclear Compounds Containing Quintuple Bond

A quintuple bond in chemistry is an unusual type of chemical bond reported by Philip Power et al in 2005 for an aryl substituted dichromium compound. (Figure 3.7).

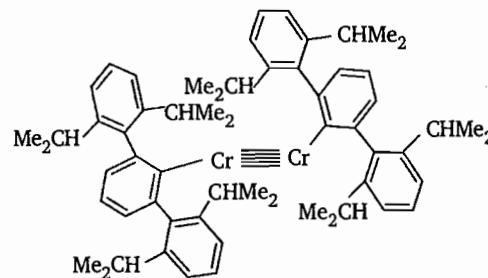


Fig. 3.7

The bulky aryl group [2, 6 {((2,6-diisopropyl)phenyl) phenyl] stabilizes the chromium dimer having low coordination number. This red colour compound is stable upto 200°C. Each of the chromium atoms has six electrons. One of the electrons of each chromium atom is used for bonding with substituted aryl group. The remaining ten electrons of the two chromium atoms are distributed in molecular orbitals with the electronic configuration  $\sigma^2\pi^4\delta^4$  (Fig. 3.8).

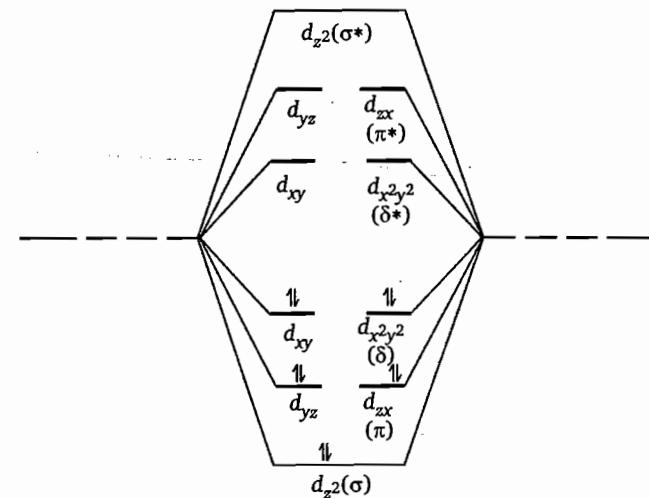


Fig. 3.8 Molecular orbital diagram for metal-metal quintuple bond

The  $\delta$  - orbitals are highest occupied molecular orbitals (HOMO) and  $\delta^*$  are the lowest unoccupied molecular orbitals (LUMO). Bond order according to this MO diagram is  $(10 - 0) / 2 = 5$ .

In 2009, a dimolybdenum compound with quintuple bond and two diimido bridging ligands has been synthesised (Fig. 3.9).

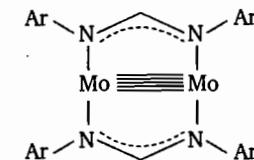


Fig. 3.9

### The Isolobal Analogy

The isolobal analogy was developed by Roald Hoffmann in 1982. According to Hoffmann two fragments are isolobal if the number, symmetry properties, approximate energy and shape of their frontier molecular orbitals and the number of electrons in them are similar not identical but similar.

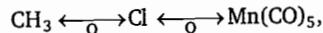
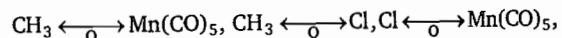
Some of the reactions of the metal carbonyls are parallel with main group non-metals and compounds. For example, chlorine atom and methyl ( $CH_3^+$ ) free radical both have 7 valence electrons, one short of a noble gas configuration. Three of  $sp^3$  orbitals of carbon are involved in the formation of  $\sigma$  - bonds with the hydrogens. The fourth  $sp^3$  orbital is singly occupied and has higher energy than the bonding ones. The  $Mn(CO)_5$  fragment has 17 valence electrons, one short of the 18-electron. The  $\sigma$  - bonding between Mn and CO ligands in this fragment may be considered to involve the five of  $d^2sp^3$  hybrid orbitals of Mn. The sixth hybrid orbital is singly occupied and has higher energy than the five

$\sigma$ - bonding orbitals. Hoffmann points out that any fragment with a singly occupied orbital of a  $\sigma$ -type is a free radical and may be able to form structures similar to those found for methyl radical. Halogen atom and methyl radical exhibit chemical similarities with 17-electron organometallic fragments like  $\text{Mn}(\text{CO})_5$ . (Table 3.2).

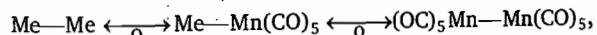
Table 3.2 Properties of  $\text{CH}_3$ ,  $\text{Cl}$  and  $\text{Mn}(\text{CO})_5$  fragment

Properties	$\text{Mn}(\text{CO})_5$	$\text{CH}_3$ and $\text{Cl}$
1. Exist as dimer.	$\text{Mn}_2(\text{CO})_{10}$	$\text{CH}_3-\text{CH}_3, \text{Cl}_2$
2. Reduced to anion.	$[\text{Mn}(\text{CO})_5]^-$	$\text{CH}_3, \text{Cl}^-$ (as in $\text{CH}_3\text{MgCl}$ )
3. Conjugate base of an acid.	$[\text{Mn}(\text{CO})_5]^-$ conjugate base of $\text{HMn}(\text{CO})_5$	$\text{CH}_3$ conjugate base of $\text{CH}_4$ and $\text{Cl}^-$ conjugate base of $\text{HCl}$
4. Combine with one another	$\text{RMn}(\text{CO})_5, \text{Mn}(\text{CO})_5\text{I}$	$\text{RCl}, \text{RCH}_3, \text{ICl}, \text{CH}_3\text{I}$

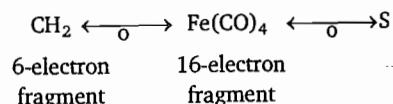
Therefore, these three fragments are isolobal or electronically equivalent with each other. It is to be noted that if two fragments are both isolobal with a third, they are also isolobal with each other. The isolobal analogy is expressed by a double headed twirly arrow ( $\longleftrightarrow$ ).



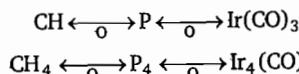
The two fragments say  $\text{CH}_3$  and  $\text{Mn}(\text{CO})_5$  are not isoelectronic because  $\text{Mn}(\text{CO})_5$  has more electron than  $\text{CH}_3$  but the orbital by which the two fragments form bonds to other fragments are the same in symmetry and occupancy.



A 16-electron fragment such as  $\text{Fe}(\text{CO})_4$  and a 6-electron fragment  $\text{CH}_2$  and group 16 element such as S are isolobal as each of these  $\text{CH}_2$  and S is 2-electron short of a noble gas configuration and  $\text{Fe}(\text{CO})_4$  is 2-electron short of 18-electron configuration.



A 15-electron fragment such as  $\text{Ir}(\text{CO})_3$  is isolobal with a 5-electron  $\text{CH}$  fragment and with group 15 elements such as phosphorus. Each of these is three electron short of a closed shell and each has three vacant sites and form tetrahedral structures.



Structures of  $\text{P}_4$  and  $\text{Ir}_4(\text{CO})_{12}$  are shown in Fig. 3.10.

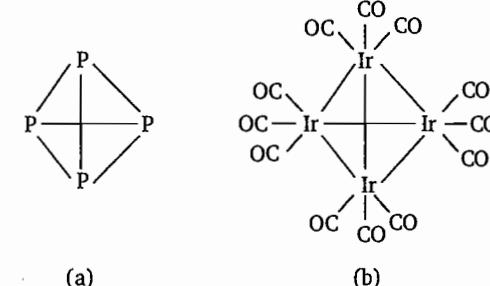


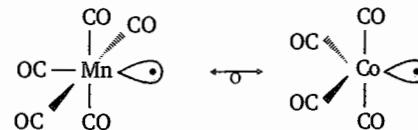
Fig. 3.10 Structure of: (a)  $\text{P}_4$ ; (b)  $\text{Ir}_4(\text{CO})_{12}$

Correlation between transition metal fragments and main group elements/fragments according to electron count is given in Table 3.3.

Table 3.3 Correlation between Transition Metal and Main Group Elements/Fragments

S.No	Transition Metal	Main Group Elements/Fragments
1.	18	8
2.	17	7
3.	16	6
4.	15	5
5.	14	4

The fragments of polyhedra with same number of valence electrons and with same or different coordination numbers are also isolobal with one another. For example, 17-electron fragments  $\text{Mn}(\text{CO})_5$  and  $\text{Co}(\text{CO})_4$  of an octahedron and trigonal bipyramidal respectively are isolobal.

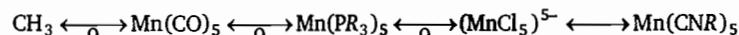


Some examples of isolobal fragments of polyhedra with same number of electrons and different coordination numbers are given in Table 3.4.

**Table 3.4**

Main Group Fragment	Valence electrons	Fragments of Transition Metal Polyhedra	Valence Electrons of Fragments
CH <sub>3</sub>	7	$d^9 - ML_4$ $d^7 - ML_5$ $d^5 - ML_6$ $d^3 - ML_7$ $d^1 - ML_8$	17
CH <sub>2</sub>	6	$d^{10} - ML_3$ $d^8 - ML_4$ $d^6 - ML_5$ $d^4 - ML_6$ $d^2 - ML_7$	16
CH	5	— $d^9 - ML_3$ $d^7 - ML_4$ $d^5 - ML_5$ $d^3 - ML_6$	15

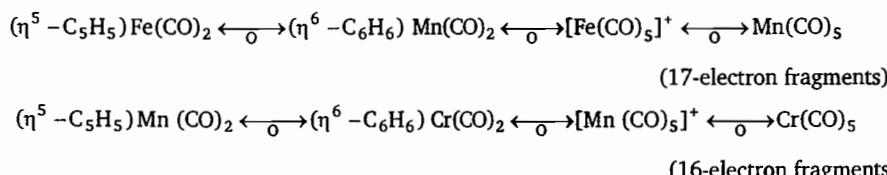
The two electron donor ligands are treated similar to CO. For example,



## 7-electron fragment

### 17-electron fragment

$\eta^5$ -C<sub>5</sub>H<sub>5</sub> and  $\eta^6$ -C<sub>6</sub>H<sub>6</sub> are treated to occupy three coordination sites and to be 5 and 6-electron donors. For example,



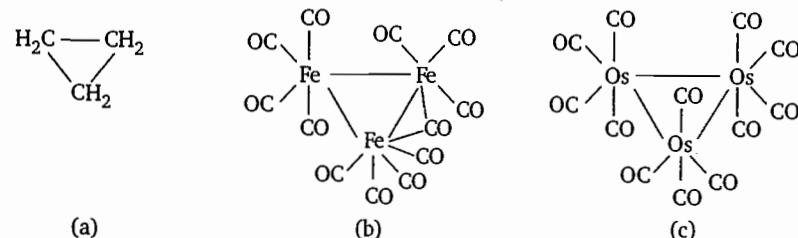
Some examples of transition metal fragments which are isolobal with main group fragments are given in Table 3.5.

**Table 3.5** Some Isolobal Fragments of Transition Metals and Main Group Elements

<b>CH<sub>4</sub></b>	<b>CH<sub>3</sub></b>	<b>CH<sub>2</sub></b>	<b>CH</b>	<b>C</b>
Cr(CO) <sub>6</sub>	Mn(CO) <sub>5</sub>	Fe(CO) <sub>4</sub>	Mn(CO) <sub>4</sub>	Fe(CO) <sub>3</sub>
[Mn(CO) <sub>6</sub> ] <sup>+</sup>	[Fe(CO) <sub>5</sub> ] <sup>+</sup>	Cr(CO) <sub>5</sub>	Co(CO) <sub>3</sub>	Ni(CO) <sub>2</sub>
	[Cr(CO) <sub>5</sub> ] <sup>-</sup>	Ni(CO) <sub>3</sub>		
Fe(CO) <sub>5</sub>	Co(CO) <sub>4</sub>	CpCo(CO)	CpCr(CO) <sub>2</sub>	Cr(CO) <sub>4</sub>
Ni(CO) <sub>4</sub>	CpFe(CO) <sub>2</sub>	[Co(CO) <sub>4</sub> ] <sup>+</sup>	CpNi	CpCo
CpMn(CO) <sub>3</sub>	Co(CO) <sub>4</sub> , V(CO) <sub>6</sub>	CH <sub>3</sub> <sup>+</sup>	CH <sub>2</sub> <sup>+</sup>	CH <sup>+</sup>
CH <sub>3</sub> <sup>-</sup>	CH <sub>2</sub> <sup>-</sup>	CH <sup>-</sup> S	P	

Since a 6-electron  $\text{CH}_2$  fragment is isolobal with 16-electron  $\text{Fe}(\text{CO})_4$  fragment. The two  $\text{CH}_2$  fragments combine together to form stable  $\text{CH}_2=\text{CH}_2$ , whereas the dimer of  $\text{Fe}(\text{CO})_4$  is not nearly as

stable. Also, both  $\text{CH}_2$  and  $\text{Fe}(\text{CO})_4$  form three membered cyclic structures, cyclopropane and  $\text{Fe}_3(\text{CO})_{12}$  respectively. Cyclopropane is a trimer of  $\text{CH}_2$  fragments but  $\text{Fe}_3(\text{CO})_{12}$  has two bridging CO ligands (Fig. 3.11) and therefore, is not a perfect trimer.  $\text{Os}_3(\text{CO})_{12}$  is isoelectronic with  $\text{Fe}_3(\text{CO})_{12}$  and is perfect trimer formed by combination of three  $\text{Os}(\text{CO})_4$  fragments which are isolobal with  $\text{Fe}(\text{CO})_4$  and  $\text{CH}_2$ .



**Fig. 3.11** Structure of (a) cyclopropane, (b)  $\text{Fe}_3(\text{CO})_{12}$ , (c)  $\text{Os}_3(\text{CO})_{12}$

Similarly  $\text{Co}(\text{CO})_3$ ,  $\text{Rh}(\text{CO})_3$ ,  $\text{Ir}(\text{CO})_3$ , CR and P fragments are isolobal with each other. The 15-electron fragment  $\text{Ir}(\text{CO})_3$  forms a  $\text{Ir}_4(\text{CO})_{12}$  that has a tetrahedral symmetry P and CR fragments also form tetrahedral symmetries of  $\text{P}_4$  and  $(\text{CR})_4$  respectively. The  $\text{Co}(\text{CO})_3$  and  $\text{Rh}(\text{CO})_3$  fragments form isoelectronic  $\text{Co}_4(\text{CO})_{12}$  and  $\text{Rh}_4(\text{CO})_4$  complexes respectively and they have nearly tetrahedral array of Co and Rh atoms but have three bridging CO ligands (Fig. 3.12). If one or more  $\text{Co}(\text{CO})_3$  fragments of  $\text{Co}_4(\text{CO})_{12}$  are replaced by CR fragment (Fig. 3.12), the tetrahedral structures now, do not have bridging CO ligands. This is similar to the replacement of P atoms in the  $\text{P}_4$  tetrahedron by  $\text{Co}(\text{CO})_3$  fragments.

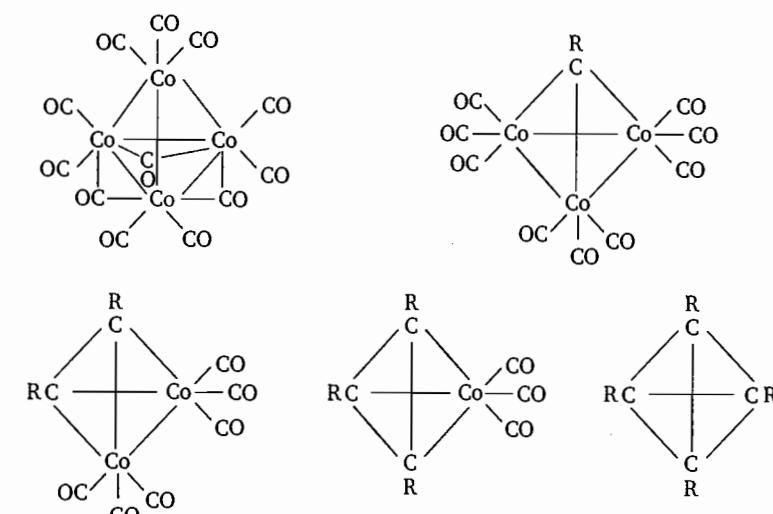


Fig. 3.12

Isolobal analogy in boranes and carbonyl clusters can be determined using electron counts and geometries of the clusters.

Superhyper closo boranes ( $B_nH_n$ )<sup>2+</sup> with  $(n - 1)$  skeletal electron pairs are isolobal with the superhyper closo carbonyl clusters with  $\frac{PEC}{2} = (n - 1)$ .

**For Example :**

$Os_8(CO)_{23}$  or  $[Os_8(CO)_{24}]^{2+}$  :

$$TEC = 8 \times 8 + 23 \times 2 = 64 + 46 = 110$$

$$PEC = 110 - 8 \times 12 = 110 - 96 = 14$$

$$\frac{PEC}{2} = \frac{14}{2} = 7 = 8 - 1 (n - 1) \quad \text{superhyper closo}$$

$[B_8H_8]^{2+}$  :

$$\text{Number of skeletal electron pairs} = \frac{(8 \times 2 - 2)}{2} = \frac{14}{2} = 7$$

$$= 8 - 1 (n - 1) \quad \text{super hyper closo}$$

$$\text{Therefore, } Os_8(CO)_{23} \longleftrightarrow [Os_8(CO)_{24}]^{2+} \longleftrightarrow [B_8H_8]^{2+}$$

Similarly, hypercloso boranes  $B_nH_n$  are isolobal with hypercloso (i.e., polyhedron with one face metal capped), closo boranes are isolobal with closo (i.e., regular polyhedron like tbp, oh), nido boranes are isolobal with nido (i.e., polyhedron with one vertex unoccupied), arachno boranes are isolobal with arachno (i.e., polyhedron with two vertices unoccupied) and hypho boranes are isolobal with hypho (i.e., polyhedron with three vertices unoccupied) metal clusters. A transition metal cluster and a borane are isolobal if both have same number of vertices. Some examples are given below :

**(1)  $Os_6(CO)_{18}$  :**

$$TEC = 6 \times 8 + 18 \times 2 = 48 + 36 = 84$$

$$PEC = 84 - 6 \times 12 = 84 - 72 = 12$$

$$\frac{PEC}{2} = \frac{12}{2} = 6 (= n) \quad \text{hypercloso}$$

**$B_6H_6$  :**

$$\text{Number of skeletal electron pairs} = \frac{6 \times 2}{2} = 6 (= n) \quad (\text{hypercloso})$$

$$\text{Therefore, } Os_6(CO)_{18} \longleftrightarrow [B_6H_6]$$

**(2)  $[Os_6(CO)_{18}]^{2-}$  :**

$$TEC = 6 \times 8 + 18 \times 2 + 2 = 48 + 36 + 2 = 86$$

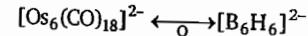
$$PEC = 86 - 6 \times 12 = 86 - 72 = 14$$

$$\frac{PEC}{2} = \frac{14}{2} = 7 = 6 + 1 (n + 1) \quad \text{closo (regular octahedron)}$$

$[B_6H_6]^{2-}$  (regular octahedron)

$$\text{Number of skeletal electron pairs} = \frac{(6 \times 2 + 2)}{2} = \frac{14}{2} = 7 (n + 1) \quad \text{closo}$$

Therefore,



**(3)  $[Os_5(CO)_{15}]^{2-}$  :**

$$TEC = 5 \times 8 + 15 \times 2 + 2 = 40 + 30 + 2 = 72$$

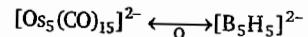
$$PEC = 72 - 5 \times 12 = 12$$

$$\frac{PEC}{2} = \frac{12}{2} = 6 (n + 1) \quad \text{closo}$$

$[B_5H_5]^{2-}$

$$\text{Number of skeletal electron pairs} = \frac{5 \times 2 + 2}{2} = 6 (n + 1) \quad (\text{closo})$$

Therefore,



**(4)  $Fe_4C(CO)_{13}$  :**

$$TEC = 4 \times 8 + 4 + 13 \times 2 = 32 + 4 + 26 = 62$$

$$PEC = 62 - 4 \times 12 = 62 - 48 = 14$$

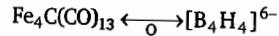
$$\frac{PEC}{2} = \frac{14}{2} = 7 (n + 4) \quad \text{Arachno}$$

$[B_4H_4]^{6-}$

$$\text{Number of skeletal electron pairs} = \frac{4 \times 2 + 6}{2}$$

$$= \frac{14}{2} = 7 (n + 4) \quad \text{arachno}$$

Therefore,



**(5)  $Fe_5C(CO)_{15}$  :**

$$TEC = 5 \times 8 + 4 + 15 \times 2 = 40 + 4 + 30 = 74$$

$$PEC = 74 - 5 \times 12 = 14$$

$$\frac{PEC}{2} = \frac{14}{2} = 7 (n + 2) \quad \text{nido}$$

$[\text{Fe}_5(\text{CO})_{15}]^{4-}$ :

$$\text{TEC} = 5 \times 8 + 15 \times 2 + 4 = 40 + 30 + 4 = 74$$

$$\text{PEC} = 74 - 5 \times 12 = 14$$

$$\frac{\text{PEC}}{2} = \frac{14}{2} = 7(n+2) \quad \text{nido}$$

 $[\text{B}_5\text{H}_5]^{4-}$ :

$$\begin{aligned} \text{Number of skeletal electron pairs} &= \frac{5 \times 2 + 4}{2} = \frac{14}{2} \\ &= 7(n+2) \quad \text{nido} \end{aligned}$$

Therefore,  $\text{Fe}_5(\text{CO})_{15} \longleftrightarrow_{\text{O}} [\text{Fe}_5(\text{CO})_{15}]^{4-} \longleftrightarrow_{\text{O}} [\text{B}_5\text{H}_5]^{4-}$

 $[\text{HCo}_6(\text{CO})_{15}]^{-}$ :

$$\text{TEC} = 1 + 6 \times 9 + 15 \times 2 + 1 = 1 + 54 + 30 + 1 = 86$$

$$\text{PEC} = 86 - 6 \times 12 = 86 - 72 = 14$$

$$\frac{\text{PEC}}{2} = \frac{14}{2} = 7(n+1) \quad \text{closo}$$

 $[\text{Co}_6(\text{CO})_{15}]^{2-}$ :

$$\text{TEC} = 6 \times 9 + 15 \times 2 + 2 = 54 + 30 + 2 = 86$$

$$\text{PEC} = 86 - 6 \times 12 = 14$$

$$\frac{\text{PEC}}{2} = \frac{14}{2} = 7(n+1) \quad \text{closo}$$

 $[\text{Fe}_6(\text{CO})_{18}]^{2-}$ :

$$\text{TEC} = 6 \times 8 + 18 \times 2 + 2 = 48 + 36 + 2 = 86$$

$$\text{PEC} = 86 - 6 \times 12 = 14$$

$$\frac{\text{PEC}}{2} = \frac{14}{2} = 7(n+1) \quad \text{closo}$$

 $[\text{B}_6\text{H}_6]^{2-}$ :

$$\text{Number of skeletal electron pairs} = \frac{6 \times 2 + 2}{2} = \frac{14}{2} = 7(n+1) \quad \text{closo}$$

Therefore,  $[\text{HCo}_6(\text{CO})_{15}]^- \longleftrightarrow_{\text{O}} [\text{Co}_6(\text{CO})_{15}]^{2-} \longleftrightarrow_{\text{O}} [\text{Fe}_6(\text{CO})_{18}]^{2-} \longleftrightarrow [\text{B}_6\text{H}_6]^{2-}$

 $(7) [\text{CpNi}]_6$ :

$$\text{TEC} = 6 \times 5 + 6 \times 10 = 30 + 60 = 90$$

$$\text{PEC} = 90 - 6 \times 12 = 90 - 72 = 18$$

$$\frac{\text{PEC}}{2} = \frac{18}{2} = 9(n+3) \quad \text{Arachno}$$

 $[\text{B}_6\text{H}_6]^{6-}$ :

$$\text{Number of electron pairs} = \frac{6 \times 2 + 6}{2} = \frac{18}{2} = 9(n+3) \quad \text{arachno}$$

Therefore,  $[\text{CpNi}]_6 \longleftrightarrow_{\text{O}} [\text{B}_6\text{H}_6]^{6-}$

**Zintl Ions**

The ionic clusters of main group elements are called Zintl ions. Since these ions have no ligand, these are also known as naked clusters. Some examples of Zintl ions are :  $\text{Pb}_5^{2-}$ ,  $\text{Sn}_9^{4-}$ ,  $\text{Sb}_4^{2-}$ ,  $\text{Sn}_4^{2-}$ ,  $\text{Ge}_4^{2-}$ ,  $\text{Bi}_3^{3+}$ ,  $\text{Sn}_5^{2-}$ ,  $\text{Bi}_5^{3+}$ ,  $\text{Te}_6^{2+}$ ,  $\text{Sb}_7^{3-}$  etc.

Zintl ions are also classified into closo, nido, arachno and hypho clusters.

If  $\text{TEC} = 4n + 2$  (closo)

$\text{TEC} = 4n + 4$  (nido)

$\text{TEC} = 4n + 6$  (arachno)

$\text{TEC} = 4n + 8$  (hypho)

where  $n$  = number of metal atoms in the Zintl ion.

**Examples:**

(1)  $\text{Pb}_5^{2-}$ , TVE =  $5 \times 4 + 2 = 22(4n+2)$

Because  $n = 5$ , the total electron count =  $4n + 2$ . Therefore,  $\text{Pb}_5^{2-}$  has closo structure.

(2)  $\text{Sn}_9^{4-}$ , TVE =  $9 \times 4 + 4 = 40$

Because  $n = 9$ , the total electron count =  $4n + 4$ . Therefore,  $\text{Sn}_9^{4-}$  has nido structure.

(3)  $\text{Bi}_5^{3+}$ , TVE =  $5 \times 5 - 3 = 22 = 4n + 2$

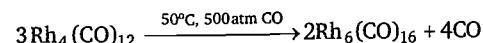
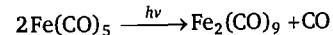
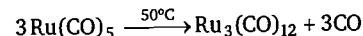
Therefore,  $\text{Bi}_5^{3+}$  is a closo.

(4)  $\text{Sb}_4^{2-}$ , TVE =  $4 \times 5 + 2 = 22 = 4n + 6$

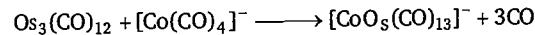
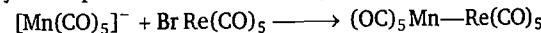
Therefore,  $\text{Sb}_4^{2-}$  is arachno.

### Synthesis of Carbonyl Clusters :

(1) By pyrolysis of mono-, di- and trinuclear carbonyls:



(2) By nucleophilic attack of a carbonyl anion :



## **Objective Questions**

- 1.** Intense band at  $15000\text{ cm}^{-1}$  in the UV-visible spectrum of  $[\text{Bu}_4\text{N}]_2\text{Re}_2\text{Cl}_8$  is due to the transition :

  - (a)  $\pi \rightarrow \pi^*$
  - (b)  $\delta \rightarrow \delta^*$
  - (c)  $\delta \rightarrow \pi^*$
  - (d)  $\pi \rightarrow \delta^*$

**2.** The number of metal-metal bonds in  $[\text{W}_2(\text{OPh})_6]$  is :

  - (a) 1
  - (b) 2
  - (c) 3
  - (d) 4

**3.** The bond order of the metal-metal bonds in  $[\text{Re}_2\text{Cl}_8]^{2-}$ ,  $[\text{Re}_2\text{Cl}_6(\text{P}(\text{C}_2\text{H}_5)_3)_2]$  and  $[\text{Re}_2\text{Cl}_4(\text{P}(\text{C}_2\text{H}_5)_2\text{Ph}_2)_4]$  respectively are :

  - (a) 4, 4 and 3
  - (b) 3, 4 and 4
  - (c) 4, 2 and 3
  - (d) 2, 3 and 4

**4.** Among the following, the correct statement is :

  - (a)  $\text{CH}$  is isolobal to  $\text{Co}(\text{CO})_3$
  - (b)  $\text{CH}_2$  is isolobal to  $\text{Ni}(\text{CO})_2$
  - (c)  $\text{CH}$  is isolobal to  $\text{Fe}(\text{CO})_4$
  - (d)  $\text{CH}_2$  is isolobal to  $\text{Mn}(\text{CO})_4$

**5.** The correct statement regarding the terminal/bridging CO groups in solid  $\text{Co}_4(\text{CO})_{12}$  and  $\text{Ir}_4(\text{CO})_{12}$  is :

  - (a) both have equal number of bridging CO groups
  - (b) number of bridging CO groups in  $\text{Co}_4(\text{CO})_{12}$  is 4
  - (c) the number of terminal CO groups in  $\text{Co}_4(\text{CO})_{12}$  is 8
  - (d) the number of bridging CO groups in  $\text{Ir}_4(\text{CO})_{12}$  is zero

**6.** Which of the following metal fragments,  $d^9 - \text{ML}_n$  is isolobal with  $\text{CH}$  ?

  - (a)  $d^7 - \text{ML}_5$
  - (b)  $d^8 - \text{ML}_4$
  - (c)  $d^9 - \text{ML}_3$
  - (d)  $d^5 - \text{ML}_6$

**7.** Among the following clusters :

$A = [(\text{H})\text{Co}_6(\text{CO})_{15}]^-$ ,  $B = [(\text{H})_2\text{Os}_6(\text{CO})_{18}]$ ,  $C = [(\text{H})_2\text{Os}_5(\text{CO})_{16}]$

H is encapsulated in :

  - (a) A only
  - (b) B only
  - (c) B and C only
  - (d) A and B only

**8.** The correct statement regarding the terminal/bridging CO groups in solid  $\text{Co}_4(\text{CO})_{12}$  and  $\text{Ir}_4(\text{CO})_{12}$  is :

  - (a) both have equal number of bridging CO groups
  - (b) number of bridging CO groups in  $\text{Co}_4(\text{CO})_{12}$  is 4





## Subjective Questions

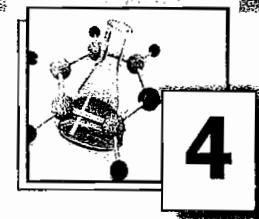
- $[\text{Re}_2\text{Cl}_8]^{2-}$  adopts an eclipsed conformation whereas  $\text{Re}_2(\text{CO})_{10}$  adopts a staggered conformation in the solid state. Explain
  - Calculate total number of M—M bonds and number of M—M bonds per metal in the following species using 18-electron rule. Also draw the structures of each species:
 

(a) $\text{Ir}_4(\text{CO})_{12}$	(b) $\text{Fe}_3(\text{CO})_{12}$
(c) $[\text{CpMo}(\text{CO})_2]_2$	(d) $[(\mu_3 - \text{CO})\text{Fe}_4(\text{Co})_{12}]^{2-}$
(e) $[(\mu - \text{H})_2\text{Cp}(\text{NO})\text{WH}]_2$	(f) $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$
  - Predict the M—M bond order for the following species:
 

(a) $[(\text{OC})_4\text{Cr}(\mu - \text{PPh}_2)_2\text{Cr}(\text{CO})_4]$
(b) $[(\text{OC})_4\text{Mn}(\mu - \text{PPh}_2)_2\text{Cr}(\text{CO})_4]$
  - Calculate the total valence electron counts of the following clusters. Also classify them as close, nido, arachno and hypho:
 

(a) $[\text{B}_6\text{H}_6]^{4-}$	(b) $[\text{Co}_8(\text{CO})_{18}\text{C}]^{2-}$
(c) $\text{Fe}_5(\text{CO})_{15}\text{C}$	(d) $\text{Os}_6(\text{CO})_{18}$
(e) $\text{Rh}_7(\text{CO})_{16}$	
  - Classify the following species as closo, nido, arachno or hypho:
 

(a) $\text{B}_4\text{H}_6(\text{CoCp})_2$	(b) $\text{B}_3\text{H}_7[\text{Fe}(\text{CO})_3]_2$
(c) $\text{Pb}_5^{2-}$	(d) $\text{Sn}_9^{4-}$
(e) $[\text{Re}_7\text{C}(\text{CO})_2]^{3-}$	(f) $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$
- 

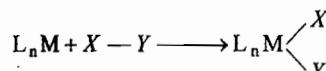


## Reactions of Organometallic Compounds

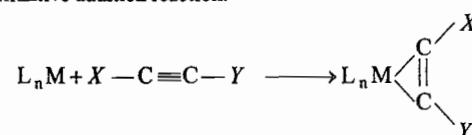
### Oxidative Addition

Oxidative addition reactions are among the most important reactions in organometallic chemistry. An Oxidative addition reaction involves :

- The addition of a molecule  $X - Y$  with cleavage of  $X - Y$  single bond to a coordinatively unsaturated compound in a relatively low oxidation state.
- Formal oxidation of metal by two units and at the same time increase in metal coordination number by 2.



Addition of a multiply bonded species with reduction in the bond order to form a metallacycle is also an oxidative addition reaction.

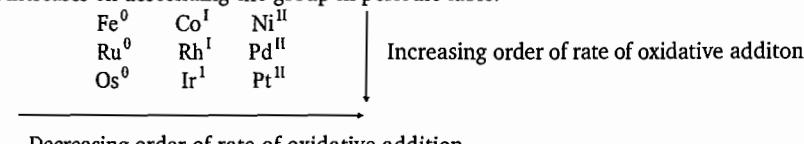


Addition of a C—H bond in an ortho-metallation step is also an oxidative addition reaction.



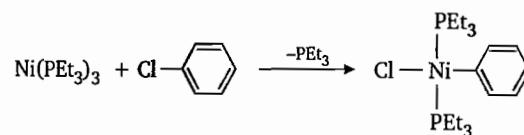
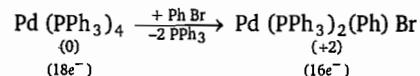
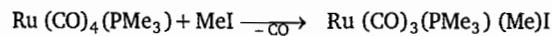
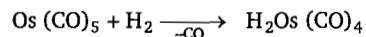
The important feature of oxidative addition reactions are :

1. The metal should be in low oxidation state (0, +1 or sometimes +2), i.e., there should be non-bonding electron density on metal.
2. The complex must have two vacant sites, i.e., the complex must be coordinatively unsaturated.
3. The rate of oxidative addition reaction decreases with increase in oxidation state of metal and increases on descending the group in periodic table.



Decreasing order of rate of oxidative addition

4. Most commonly the metal in the complexes in their low oxidation states have  $d^8$  or  $d^{10}$  configuration. For example,  $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$ ,  $d^8[\text{Pd}(\text{PPh}_3)_4]$ ,  $d^{10}[\text{Ni}(\text{P}(\text{OEt})_3)_4]$ ,  $d^{10}$ .
5. The metal must have stable higher oxidation state separated by 2 units because during oxidative addition oxidation state of metal increases by 2 units.
6. In general, it is seen that during oxidative addition square planar complex converts into octahedral complex and a 16-electron complex changes to a 18-electron complex.
7. The complexes with metals of oxidation state higher than +2 rarely give oxidative addition reactions.
8. The complexes with metals in their highest oxidation state do not give oxidative addition reactions. For example,  $\text{Cr}^{6+}$ ,  $\text{Mn}^{7+}$ ,  $\text{Ta}^{5+}$  can not undergo oxidative addition to give  $\text{Cr}^{8+}$ ,  $\text{Mn}^{9+}$  and  $\text{Ta}^{7+}$  respectively.
9. Complexes with  $d^0$  metals do not undergo oxidative addition.
10. An electron rich  $\sigma$ -donor ligand coordinated to the metal increases the rate of oxidative addition reaction whereas a  $\pi$ -acceptor ligand decreases the rate of oxidative addition reaction.
11. In general steric hindrance decreases the rate of oxidative addition reaction.
12. The complexes with 18-electrons can not undergo oxidative addition without loss of a 2-electron ligand because a  $2e^-$  site must be present on metal for the reaction to occur. For example,



If the number of ligands that can be accommodated within the coordination sphere of metal is restricted, ionic complex may result.

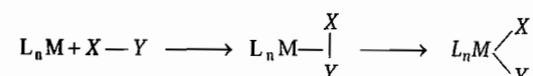


The 18-electron complex such as  $[\text{Fe}(\text{CO})_4]^{2-}$  has only four ligands but addition of  $X-Y$  would require the use of antibonding molecular orbitals which is energetically not favourable.

### Mechanisms for Oxidative Addition Reactions

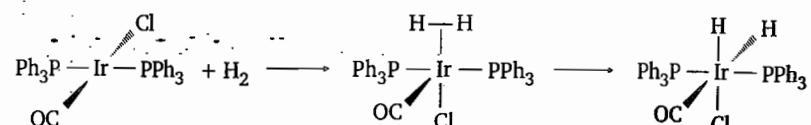
Depending upon the nature of  $X-Y$ , oxidative addition reactions may undergo by the following mechanisms:

**(1) Concerted Reaction :** If  $X-Y$  is non-polar such as  $\text{H}_2$ ,  $\text{O}_2$  then it undergoes oxidative addition reaction through concerted or three centred transition state. Concerted oxidative addition reaction is an associative reaction in which the incoming ligand  $X-Y$  first binds as a  $\sigma$  complex and then undergoes  $X-Y$  bond breaking resulting in strong back donation of two electrons from the metal into the  $\sigma$ -antibonding molecular orbital of  $X-Y$  ligand.

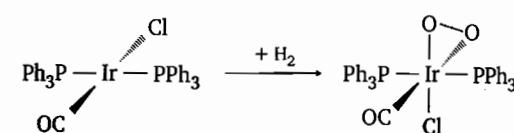


The second step really involves the oxidation of metal because two electrons are formally transferred to  $\sigma$ -antibonding of  $X-Y$ . Some examples of concerted reaction of Vaska's complexes are :

**(i) Oxidative addition of  $\text{H}_2$  on Vaska's complex :**

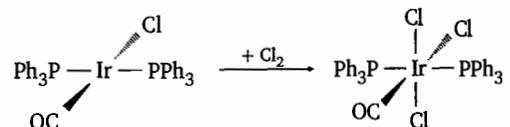


**(ii) Oxidative addition of  $\text{O}_2$  on Vaska's complex :**

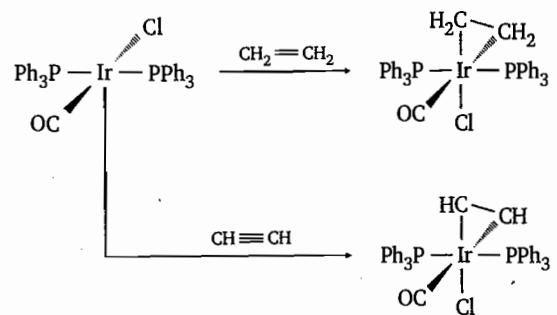


In this reaction  $\text{O}-\text{O}$  bond is not completely broken but the bond order of  $\text{O}_2$  is reduced from 2 to 1.

(iii) Oxidative addition of halogen ( $X_2$ ) on Vaska's complex :

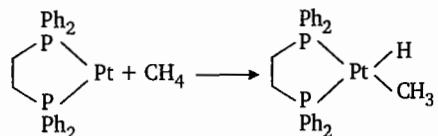


(iv) Oxidative addition of alkenes and alkynes on Vaska's complex :

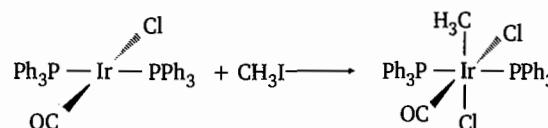
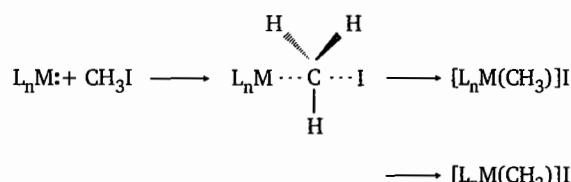


In these reactions, the *trans* (CO)Cl set of ligands become *cis* in the product. In the TBP transition state the strong  $\pi$ -acceptor CO ligand occupies the equatorial position.

(v) Oxidative addition of methane :



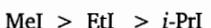
(2)  $S_{N}2$  and Radical Reactions : If  $X-Y$  is an electrophilic polar molecule such as alkyl halides ( $CH_3Cl$ ,  $CH_3Br$ ,  $CH_3I$ ), oxidative addition reactions proceed by  $S_{N}2$  mechanism involving two electron transfer or via radical, one electron transfer mechanism. In  $S_{N}2$  mechanism, the electron pair of metal of  $L_nM$  directly attacks at the least electronegative atom of  $X-Y$  molecule and provides an electron pair to  $\sigma$ -antibonding molecular orbital formally to break  $X-Y$  molecule into  $X^-$  and  $Y^-$  ions. The  $L_nM$  compound itself oxidized to  $L_nM^{2+}$ .



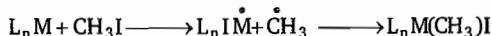
Like concerted reactions, these reactions are also second order reactions but they are accelerated in polar solvents.  $R$  and  $X$  may be *cis* or *trans* to one another in the final product as expected for the recombination of the ion pair formed in the first step. In the reaction (1) the product is *trans*, because the *trans* effect of  $CH_3$  group is high and therefore, it prefers the position *trans* to the vacant site in the 16 electron square pyramidal intermediate. It is to be noted that in polar solvents, the molecules that dissociate are not restricted to occupy the *cis* position.

The radical mechanism may proceed in two ways—the non-chain and the chain mechanisms.

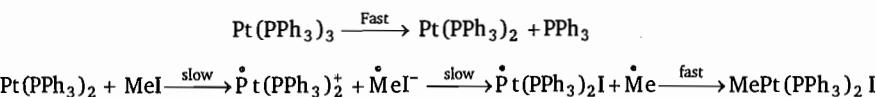
The more nucleophilic the metal (higher electron density on metal, low oxidation state of metal), greater will be its reactivity in  $S_{N}2$  oxidative addition. For example,  $Ni(PR_3)_4$  undergoes oxidative addition more faster than  $Ni(PAr_3)_4$ . Increase in steric hindrance on carbon leads to decrease in the rate of oxidative addition. Therefore reactivity of alkyl halides follow the order :



The non-chain reaction involves the addition of alkyl halides,  $RX$  to  $Pt(PPh_3)_3$  (where  $R = Me, Et$  and  $X = I, R = PhCH_2, X = Br$ ). In non-chain oxidative addition, one electron from  $M$  is transferred to the  $\sigma$ -antibonding orbital of  $RX$  to form  $M^+$  and  $RX^-$ . First  $X^-$  is coordinated to  $M^+$  forming  $MX$  and  $R$  radicals. These radicals readily recombine to give the product.



For example,



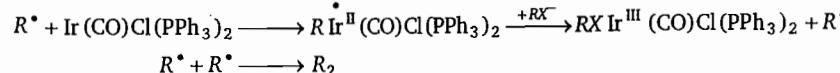
For a given alkyl halide, rate of oxidative addition reaction increases with increasing basic character of metal and the order of reactivity of alkyl halide is :



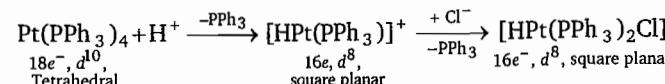
The rate of oxidative addition reaction increases with increasing stability of alkyl radical :



The radical chain reaction occurs mainly between EtBr or PhCH<sub>2</sub>Br and Vaska's complex as shown below :

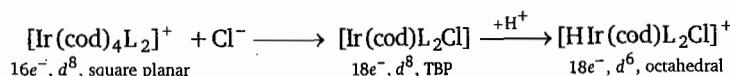


**(3) Ionic Mechanisms :** Hydrogen halides are dissociated in polar solvents to give proton ( $\text{H}^+$ ) and halide ions ( $X^-$ ) which add to metal complexes in separate steps. Usually the complex in which the metal is in low oxidation state and the ligands are basic enough, gets protonated followed by the addition of halide ion to form the final product.



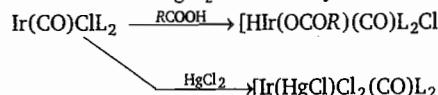
$$\text{Rate of reaction} = k[\text{complex}][\text{H}^+]$$

There are some rare cases in which the halide ion binds first followed by protonation of the intermediate. These reactions are accelerated by electron acceptor ligands and by the net positive charge on the complex ion.



$$\text{Rate} = k[\text{complex}][\text{Cl}^-]$$

Lewis acids such as  $\text{RCOOH}$  and  $\text{HgCl}_2$  also react by same mechanism.

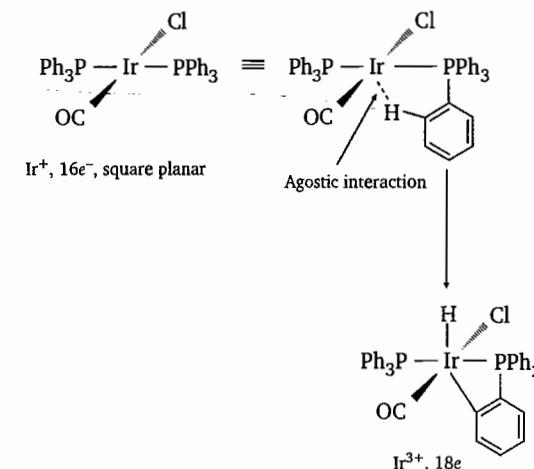


### Intramolecular Oxidative Addition : C—H Activation or Orthometallation or Cyclometallation

There are some reactions which involve the transfer of hydrogen atom from a coordinated ligand to the metal atom followed by (or simultaneous with) a change in bonding mode to the ligand from which the hydrogen atom came. These reactions are referred to as cyclometallation reactions or intramolecular oxidative addition reactions.

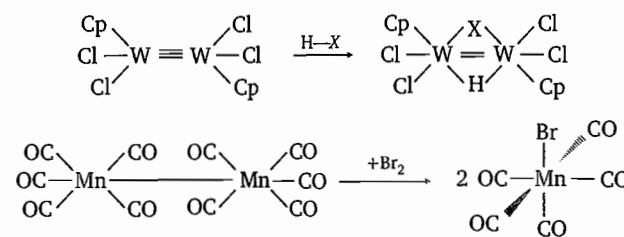
In Vaska's complex,  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  the coordinated triphenylphosphine can undergo intramolecular cyclometallation. This cyclometallation occurs due to agostic interaction between the

metal and hydrogen atom *ortho* to the phosphorus bound carbon. This reaction is also called orthometallation because the *ortho* carbon of the phenyl group participates in cyclometallation.



### Oxidative addition to M—M multiple Bond

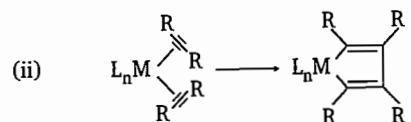
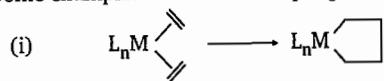
Addition of a ligand may occur across the M—M multiple bond. In this reaction oxidation state of each metal increases by one unit but the coordination number of each metal increases by two units. The M—M bond order also decreases by one unit.



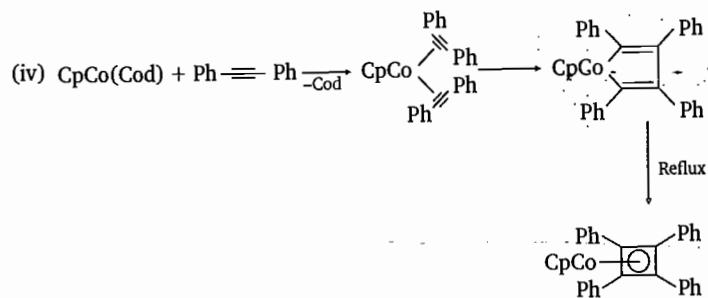
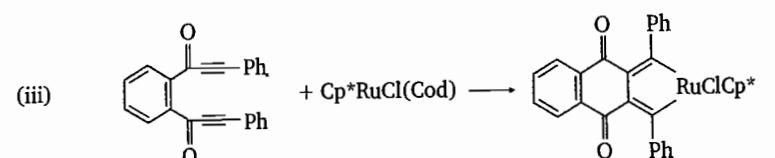
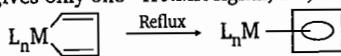
### Oxidative Coupling

The reaction in which a metal induces a coupling between two unsaturated ligands such as alkene or alkyne to give a metalacycle is called an oxidative coupling reaction. The formal oxidation state of the metal increases by two units, the electron count decreases by two units but the coordination number remains unchanged. The original two neutral ligands form new bonds between them.

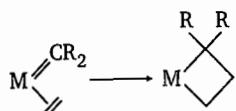
Some examples of oxidative coupling reactions are :



If  $R = H$ , two NMR signals with equal intensity should be obtained. But it has been observed that on refluxing it gives only one  $^1\text{H-NMR}$  signal, i.e., all the 4-H atoms are in same environment.

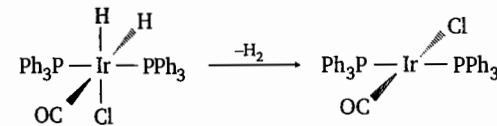
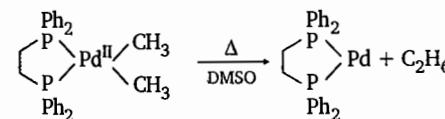
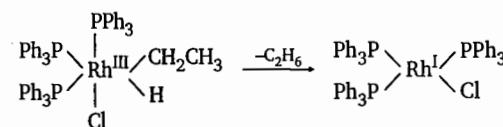
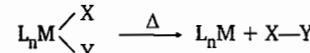


Coupling is not only limited to alkene but also carbenes and alkenes undergo oxidative coupling.

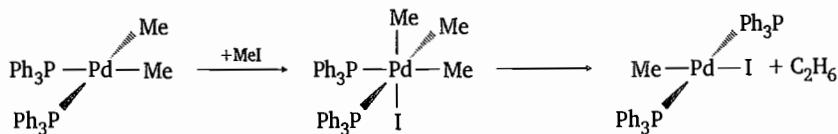


### Reductive Elimination

The reaction in which two *cis* ligands bound to metal couple together and leave the metal and the formal oxidation of the metal is reduced by two units is called a reductive elimination reaction. The reductive elimination reaction is the reverse of the oxidative addition reactions. Some examples are :



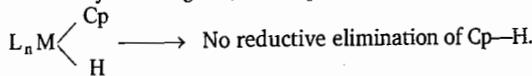
Some times the molecule eliminated is different from the one added oxidatively. For example,



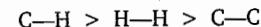
### Salient Features of Reductive Eliminations are :

1. Since the reductive elimination involves transfer of an electron pair back onto the metal from two anionic ligands, the metal, therefore, should be in high oxidation state. It means that the electron deficient metal facilitates the reductive elimination.
2. The ligands which are to be eliminated should be *cis* to each other. The ligands which are *trans* to each other will not eliminate.
3. The  $\pi$ -acceptor ligands attached to metal will enhance the rate of reductive elimination.
4. The low valent product formed after reductive elimination must be stable.

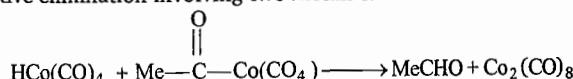
5. The presence of bulky groups or steric crowding facilitate the reductive elimination.  
 6. If Cp is present *cis* to any other ligand, then Cp will never eliminate.



7. The rate of reductive elimination follow the order :



8. The reductive elimination involving two metals is also known to occur. For example,

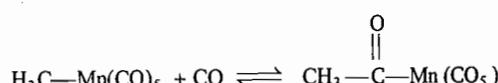
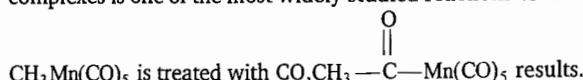


9. In reductive elimination reactions entropy increases.

10. The reductive elimination is most common for intermediate oxidation states such as the  $d^8$  metals Ni<sup>II</sup>, Pd<sup>II</sup> and Au<sup>III</sup> and the  $d^6$  metals Pt(IV), Pd(IV), Ir(III) and Rh(III).

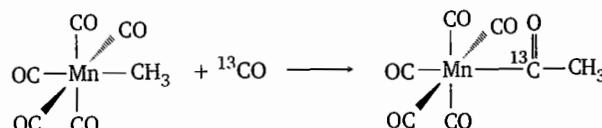
### Migratory Insertion

The introduction of an unsaturated ligand such as CO,  $\text{CH}_2=\text{CH}_2$  between two other atoms initially bound together is called as insertion. The insertion of CO into M—CH<sub>3</sub> bond to give acyl complexes is one of the most widely studied reactions of transition metal alkyls. For example, when

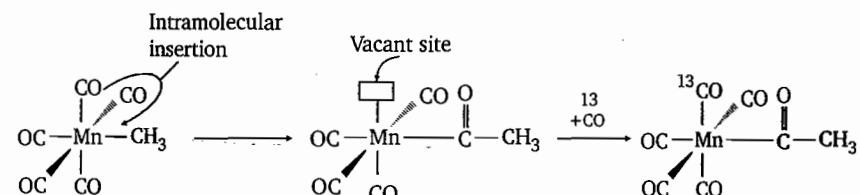


Three expected mechanisms are possible for this reaction. The mechanisms become apparent if <sup>13</sup>C labelled CO is used as incoming ligand.

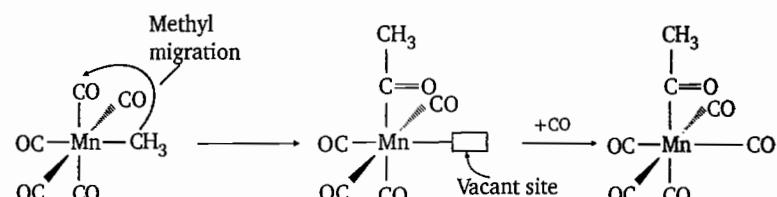
**Mechanism-1 :** Direct insertion of incoming CO ligand into metal-alkyl bond.



**Mechanism-2 :** In this mechanism the CO ligand *cis* to alkyl group migrates and inserts into the metal-alkyl bond resulting in a 5-coordinate intermediate with a vacant site available for attachment of an incoming CO ligand.



**Mechanism-3 :** In this mechanism the alkyl (CH<sub>3</sub>) group would migrate rather than the CO ligand and attach itself to a CO ligand *cis* to the alkyl group resulting in a 5-coordinate intermediate with a vacant site available for an incoming CO ligand.



The reverse of this reaction is called decarbonylation or deinsertion or elimination.

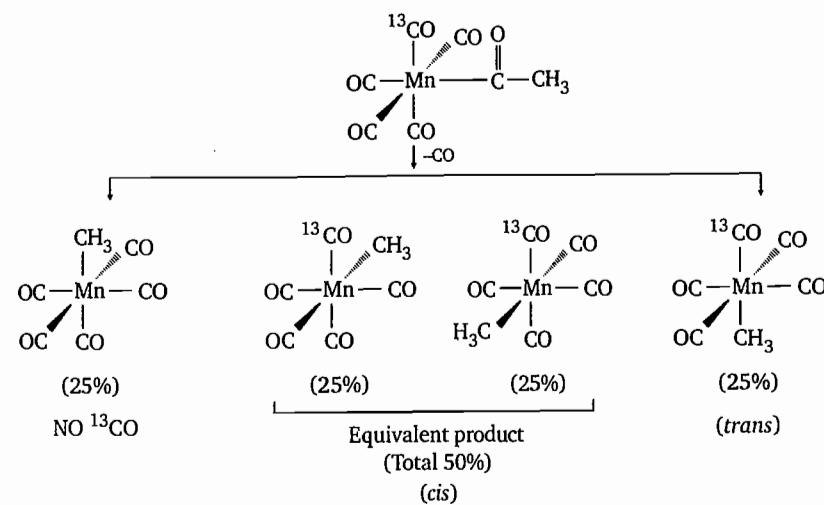
### Evidence in Favour of Migratory Insertion

These three mechanisms are seen to be indistinguishable as product in each mechanism is seen to be identical. The reaction of <sup>13</sup>CO with CH<sub>3</sub>Mn(CO)<sub>5</sub> gives a product *cis*-(CH<sub>3</sub>CO)Mn(<sup>13</sup>CO)(CO)<sub>4</sub> which have no <sup>13</sup>CO in the acyl group. Furthermore, none of the incoming <sup>13</sup>CO ends up *trans* to the acyl group. This indicates that the reaction would not proceed through mechanism, 1, i.e., no reaction occurs between incoming gaseous CO and the M—CH<sub>3</sub> bond.

The infrared studies of <sup>13</sup>CO has revealed that the reaction of CO with CH<sub>3</sub>Mn(CO)<sub>5</sub> proceeds by the migration of alkyl group rather than by insertion of CO ligand.

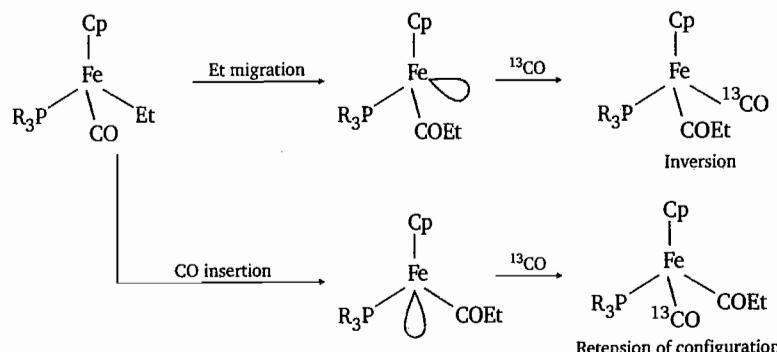
The CO of the acyl group of mechanism 2 has the choice of four *cis* positions to which it may migrate by replacing the CO ligand that is initially present. One of these sites is occupied by <sup>13</sup>CO. As a result, 25% of the product would have no <sup>13</sup>CO and 75% would have <sup>13</sup>CO *cis* to the alkyl.

Experimentally it has been observed that 25% of the product has no <sup>13</sup>CO, 25% has <sup>13</sup>CO *trans* to the alkyl group and 50% has <sup>13</sup>CO *cis* to the alkyl group. A methyl migration is consistent with these experimental results. As the alkyl group migrates, it may displace the <sup>13</sup>CO ligand to give a product containing no <sup>13</sup>CO (25%), it may displace either of the two CO ligands *cis* to the <sup>13</sup>CO ligands (but not the CO ligand that is *trans* to acyl group) to give the product with CH<sub>3</sub> *cis* to <sup>13</sup>CO (50%) or it may displace the CO ligands *trans* to <sup>13</sup>CO to give *trans* product (25%).



Since the alkyl migration is consistent with these experimental results, therefore, when the term CO insertion is used, it often means that there is alkyl migration.

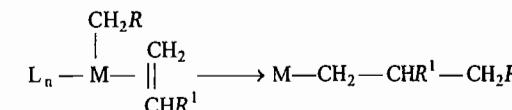
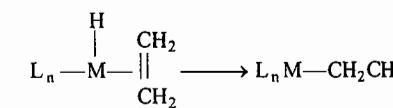
An another important evidence in favour of the migratory insertion is the stereochemical evidence.



When the reaction is carried out in  $\text{CH}_3\text{NO}_2$ , the product with inversion centre is formed which is consistent with Et migration.

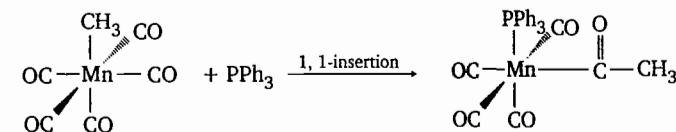
### Insertion of Alkenes

The migratory insertion of an alkene into  $\text{M}-\text{H}$  or  $\text{M}-\text{R}$  bond results in the conversion of a coordinated alkene to a  $\sigma$ -bonded alkyl group. This reaction involves migration of an H or alkyl group and results in carbon chain growth.



The H or alkyl group is migrated to the  $\beta$ -carbon of the alkene to form the metal alkyl complex. It is to be noted that CO insertion occurs into  $\text{M}-\text{R}$  bond but not in  $\text{M}-\text{H}$  bond. The insertion reactions can be classified into (1) 1,1-insertion (2) 1,2-insertion.

In 1,1-insertion reactions, the metal and the migrated ligand make the bonds to the same atom of the unsaturated ligand such as CO.



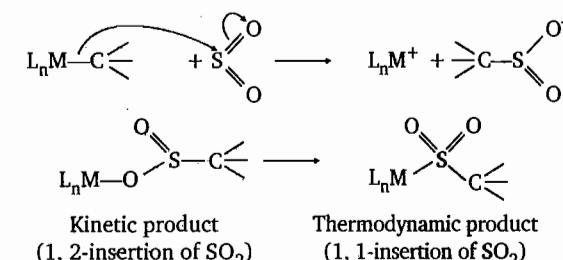
The insertion of CO into metal-alkyl bond of  $\text{CH}_3\text{Mn}(\text{CO})_5$  is also an example of 1,1-insertion.

In 1,2-insertion reactions, the metal and the migrated ligand make bonds to the adjacent atoms of the unsaturated ligand. Insertion of an alkene into  $\text{M}-\text{H}$  or  $\text{M}-\text{R}$  bond is an example of 1,2-insertion.

In general,  $\eta^1$ -ligands tend to favour 1,1-insertion whereas the  $\eta^2$ -ligands tend to favour 1,2-insertion.

$\text{SO}_2$  is an example which can undergo both 1,1- and 1,2-insertions. It is a strong electrophile with a vacant orbital on sulphur and therefore, it can attack even 18e complexes.

As an electrophile it can attack at the  $\alpha$ -carbon of the alkyl group from the side-opposite of the metal and forms an alkyl sulfinate ion,  $\text{RSO}_2^-$  with inversion at carbon. Since the negative charge is present on oxygen, kinetically oxygen of this ion can bound to the metal to form O-bound sulfinate complex. Since S is softer than O, therefore, the thermodynamic product is usually the S-bound sulfinate with soft metal. It can be concluded that in this reaction sequence  $\text{SO}_2$  first undergoes 1,2 insertion and then 1,1 insertion.



**Salient Features of the Migratory Insertions are given below :**

- During migratory insertion there is no change in the formal oxidation state of metal.
- The migratory insertion creates vacant site which is being occupied by the incoming ligand.
- The two ligands undergoing migratory insertion must be *cis* to each other.
- The two ligands which are *trans* to each other never undergo migratory insertion.
- Migratory insertions are usually favoured on more electron deficient metals.
- If there are two different alkyl groups coordinated to the metal (Fig. 4.1) the alkyl group which is more electron rich will be better nucleophile for migrating to the electron deficient CO ligand.

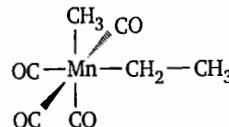
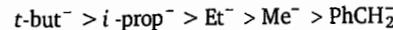


Fig. 4.1

- Migratory insertion is also possible for the ligands other than CO such as  $\text{PMe}_3$ ,  $\text{PPh}_3$ . The ligands which are better donors, have greater tendency for displacing the alkyl group for migratory insertion (for example,  $\text{PMe}_3 > \text{PPh}_3$ ).
- If a migratory ligand is chiral (Fig. 4.2) then the reaction usually proceeds with retention of configuration at that chiral carbon.

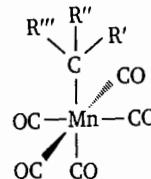


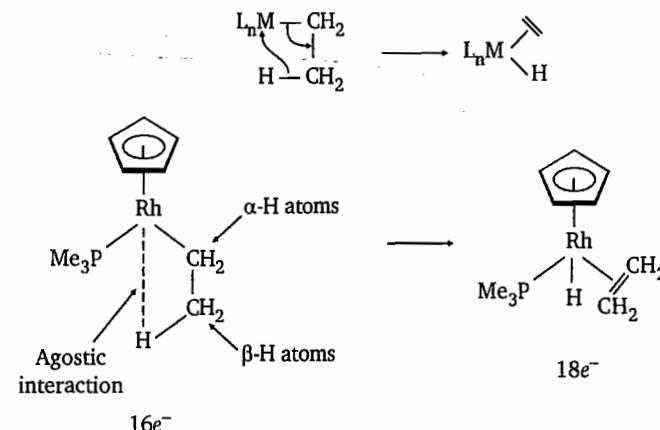
Fig. 4.2

- The bulky ligands coordinated to the metal will enhance the rate of migratory insertion.
- The Lewis acid such as  $\text{AlCl}_3$  enhance the rate of migratory insertion.
- The insertion reactions are reversible but usually one direction is observed.
- CO insertion usually takes place into  $\text{M}-\text{R}$  but not into  $\text{M}-\text{H}$  bond. Whereas alkene insertion is more common for  $\text{M}-\text{H}$  bond but much less common for  $\text{M}-\text{R}$  bond. The repeated alkene insertion into an  $\text{M}-\text{R}$  bond produces alkene polymer and the reaction is called alkene polymerization.

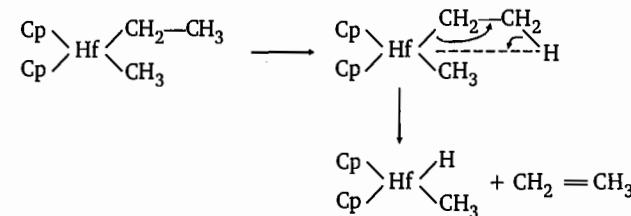
 **$\beta$ -H Elimination**

$\beta$  - hydrogen elimination is the reverse of the alkene insertion. It involves the transfer of  $\beta$ -hydrogen atom from the alkyl group to the metal and the conversion of the  $\sigma$ -alkyl group to the  $\pi$ -bonded alkene, *i.e.*,  $\text{C}-\text{H}$  bond is activated. The first step involves a cyclic intermediate with an

agostic  $\text{M}-\text{H}-\text{C}$  interaction. The agostic interaction is a three centred two electron ( $3c-2e$ ) interaction between the metal M and a C—H bond in a ligand attached to metal.



$\beta$  -elimination is responsible for the decomposition of some metal alkyl complexes.

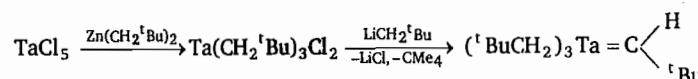
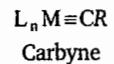
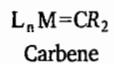

**Some Important Features of the  $\beta$  -Hydrogen Elimination Reactions are given below :**

- These reactions are usually given by 16-electron complexes because there is a  $2e$  site available for accommodation of hydride ion, except for Pd(II) and Pt(II) which tend to avoid the  $18e$  configuration.
- $\beta$  -H transfer to metal leads to removal of alkene.
- There is no change in formal oxidation state of the metal.
- An  $18e$  complex may give  $\beta$ -hydrogen elimination reaction after removing a ligand so that there would be a vacant site.
- Electron count increases by two units.
- The alkyl complexes that have  $\beta$ -hydrogen in alkyl group undergo  $\beta$ -elimination reactions.
- The alkyl complexes that lack  $\beta$ -hydrogen tend to be more stable thermally than those have  $\beta$ -hydrogen and therefore they can not undergo  $\beta$  -elimination. This does not mean that methyl complexes are necessarily stable, they may undergo other types of reactions. Some examples of alkyl groups that have no  $\beta$  -hydrogens are Me,  $\text{CH}_2\text{CMe}_3$ ,  $\text{CH}_2\text{SiMe}_3$ ,  $\text{CH}_2\text{Ph}$ .

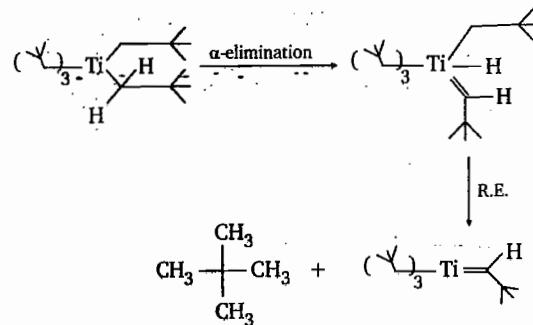
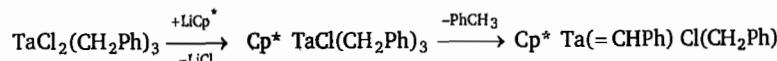
8. The coordinatively saturated complexes (the complexes in which all the coordination sites are occupied) containing  $\beta$ -hydrogens as in  $(\eta^5\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Et}$  are generally more thermally stable than complexes having vacant coordination sites.
9. Steric hindrance also prevent  $\beta$ -H-elimination.
10. The  $\beta$ -elimination is much more faster for  $d^2$  or higher transition metals than for  $d^0$  and main group elements alkyl complexes.

### $\alpha$ -H Abstraction

The alkyl complexes of early transition metals containing one or two  $\alpha$ -hydrogens but not  $\beta$ -hydrogens in alkyl groups may undergo  $\alpha$ -hydrogen abstraction to give carbene or carbyne complexes.



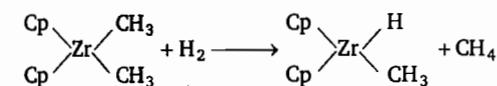
Abstraction of a two  $\alpha$ -H atoms gives a carbyne complex.



The  $\beta$ -elimination gives an alkene, a stable compound that dissociates from the metal. Whereas the methylene ligand formed from the  $\alpha$ -elimination is very unstable in the free state and therefore does not dissociate from the metal.

### Hydrogenolysis

Substitution reactions of hydrogen with transition metal complex are called hydrogenolysis reactions.



The metal centre has 16 electrons and there is no change in the oxidation state.

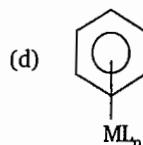
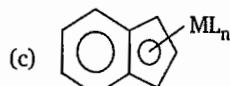
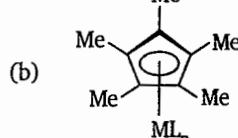
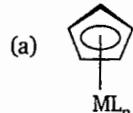


## Objective Questions

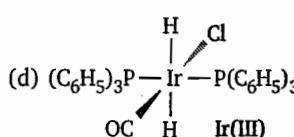
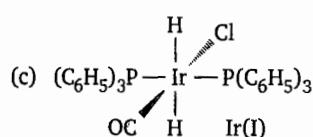
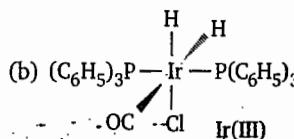
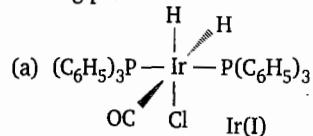
1. The reaction

- $[(CO)_5Mn(Me)] + CO \rightarrow [(CO)_5Mn(C(O)Me)]$  is an example for :
- (a) oxidative addition
  - (b) electrophilic substitution
  - (c) nucleophilic substitution
  - (d) migratory insertion

2. Substitution of L with other ligand will be easiest for the species :



3.  $IrCl(CO)[P(C_6H_5)_3]_2$  (*trans*-chlorocarbonylbis(triphenylphosphine)iridium(I)) also known as Vaska's complex can undergo oxidative addition with dihydrogen. Which of the following structures is a correct depiction of the geometry and oxidation state of the ensuing product:



4. The reaction :



is an example for :

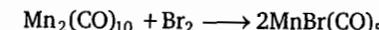
- (a) oxidative addition
- (b) electrophilic substitution
- (c) nucleophilic substitution
- (d) migratory insertion

5. The following reaction :



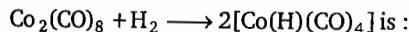
- (a) oxidative addition
- (b) reductive elimination
- (c) migratory insertion
- (d) addition

6. The following reaction is :



- (a) reductive elimination
- (b) addition
- (c) insertion
- (d) oxidative addition

7. The following reaction :



- (a) oxidative addition
- (b) reductive elimination
- (c) insertion
- (d) addition

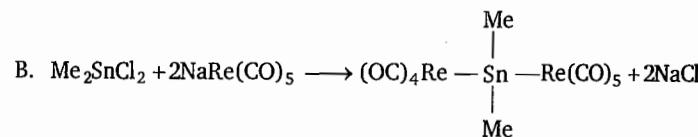
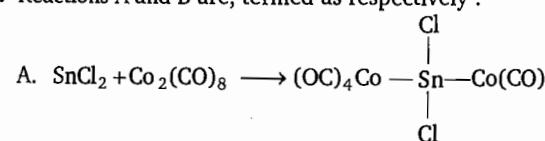
8. The oxidative addition and reductive elimination steps are favoured by :

- (a) electron rich metal centres
- (b) electron deficient metal centres
- (c) electron deficient and electron rich metal centres respectively
- (d) electron rich and electron deficient metal centres respectively

9. Oxidative addition of  $O_2$  to  $Ir(CO)Cl(PPh_3)_2$ , the oxidation state and coordination number of Ir changes respectively by :

- (a) 1 and 3
- (b) 2 and 2
- (c) 3 and 1
- (d) 2 and 3

10. Reactions A and B are, termed as respectively :



- (a) insertion, metathesis

- (b) metathesis, insertion

- (c) oxidative addition, metathesis

- (d) oxidative addition, insertion

11.  $[\text{Ru}(\text{C}_2\text{H}_5)\text{Cl}(\text{PPh}_3)_3]$  is stable only under a pressure of ethene because :

- (a) it is a 16-electron complex
- (b) it forms an 18-electron adduct with ethene
- (c) one of the decomposition products is ethene
- (d) it prevent  $\alpha$ -elimination of ethene



## Subjective Questions

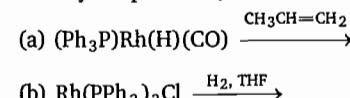
1. Discuss the following with suitable example :

- (a) Oxidative addition
- (b) Reductive elimination
- (c) Migratory insertion
- (d)  $\beta$ -hydrogen elimination
- (e)  $\alpha$ -hydrogen abstraction
- (f) Orthometallation
- (g) oxidative coupling
- (h) Agostic interaction

2. Which of the following compounds undergoes oxidative addition reaction faster ? Give explanation.

- (a)  $\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{Cl}$  or  $\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}$
- (b)  $\text{Ir}(\text{dmpe})(\text{CO})\text{Cl}$  or  $\text{Ir}(\text{dppe})(\text{CO})\text{Cl}$
- (c)  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  or  $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}$

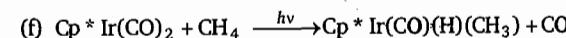
3. Identify the product (draw structure) of the following reaction :



4. How is  $\text{Mn}_2(\text{CO})_{10}$  is converted into  $(\text{CH}_3)_2\text{Mn}(\text{CO})_5$

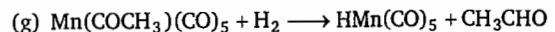
5. Classify the following reactions as oxidative addition, reductive elimination, migratory insertion,  $\beta$ -hydrogen elimination, oxidative coupling, simple addition or ligand coordination change :

- (a)  $[\text{Ni}(\text{PPh}_3)_4] \longrightarrow [\text{Ni}(\text{PPh}_3)_3] + \text{PPh}_3$
- (b)  $[\text{Ni}(\text{CO})_4\text{I}_2] \longrightarrow \text{Ni}(\text{CO})_4 + \text{I}_2$
- (c)  $[\text{Ni}(\text{CNR})_4] + \text{Cl}_2 \longrightarrow [\text{Ni}(\text{CNR})_4\text{Cl}_2]$
- (d)  $[\text{Fe}(\text{CO})_5] + \text{I}_2 \longrightarrow [\text{Fe}(\text{CO})_4\text{I}_2] + \text{CO}$
- (e)  $\text{Co}_2(\text{CO})_8 + \text{H}_2 \longrightarrow 2\text{HCo}(\text{CO})_4$

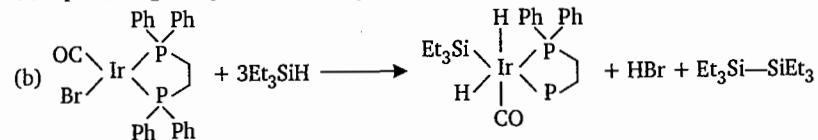
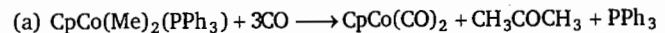


### ANSWERS

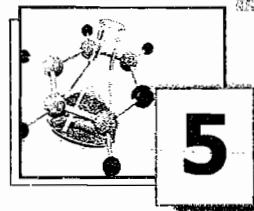
- |        |        |         |         |        |        |        |
|--------|--------|---------|---------|--------|--------|--------|
| 1. (d) | 2. (c) | 3. (b)  | 4. (d)  | 5. (c) | 6. (d) | 7. (a) |
| 8. (c) | 9. (b) | 10. (a) | 11. (c) |        |        |        |



6. Write the mechanism in the following reaction :



□□□



## Alkyl, Carbene, Carbyne, Alkene, Alkyne, Allyl and Buta-1,3-diene complexes

### Metal Alkyl Complexes

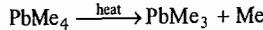
An alkyl ligand acts as a one electron donor monohapto ligand and, therefore, forms an M—C single bond. The earliest complexes are well known for *s*- and *p*-block element such as Grignard reagents and methyl lithium. The alkyl complexes of transition elements are less common than the *s*-and *p*-block elements. The transition metal complex containing only alkyl ligands are relatively rare. Some examples containing alkyl ligand only include  $\text{TiMe}_4$ ,  $\text{WMe}_6$  etc. The M—C bond dissociation enthalpy (or bond strength) decreases on descending the group in periodic table for main group metals whereas increases on descending the group for transition metals (Table. 5.1)

The bond dissociation energies of transition metal alkyls are greater than that of  $\text{PbMe}_4$  (Table. 5.1). Therefore, the transition metal alkyls should be much more stable than, for example, lead alkyls. But this is in sharp contrast to the observed decomposition temperatures of transition metal alkyls, for examples,  $\text{TiMe}_4$  (decomposition temperature =  $-50^\circ\text{C}$ ) and lead alkyls, for examples,  $\text{PbMe}_4$  (decomposition temperature  $> 200^\circ\text{C}$ ) and  $\text{PbEt}_4$  (decomposition temperature  $> 100^\circ\text{C}$ ). Therefore, the difference in stability between the tetraalkyls of Ti and Pb is not thermodynamic but kinetic.

Table. 5.1

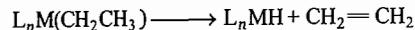
Main group metal alkyls	Bond dissociation enthalpy (kJ mol <sup>-1</sup> )
$\text{SnMe}_4$	217
$\text{PbMe}_4$	152
<b>Transition metal alkyls</b>	
$\text{Ti}(\text{CH}_2\text{CMe}_3)_4$	198
$\text{Zr}(\text{CH}_2\text{CMe}_3)_4$	250
$\text{Hf}(\text{CH}_2\text{CMe}_3)_4$	266

In the tetralkyls of Pb, all available orbitals are occupied: The four  $\sigma$ -bonds to alkyls supply an octet of electrons, the  $5d$ -orbitals are filled, the  $6d$  and  $\sigma^*$ -orbitals are energetically not accessible. Consequently tetraalkyls of Pb decomposes by M—C bond homolysis gain a comparatively high energy.

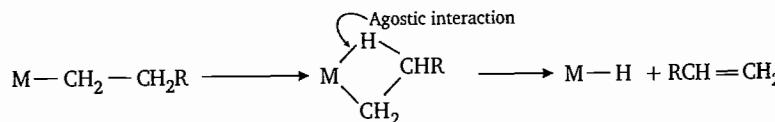


In contrast to the *s*-and *p*-block metals, transition metals possess vacant *d*-orbitals which kinetically facile reactions such as  $\beta$ -H elimination, alkene insertion, CO insertion and reductive elimination which lead to the transformation of the alkyl ligand into other groups.

In a  $\beta$ -hydrogen elimination reaction, an H-atom on the  $\beta$ -carbon atom of an alkyl group is transferred to the metal atom and an alkene is eliminated.



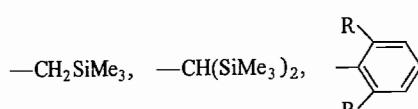
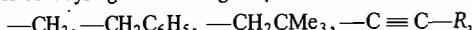
The reverse of this reaction is an alkene insertion into the M—H bond. Both reaction are proceed through a cyclic intermediate involving a 3c-2e M—H—C bond which is called an agostic interaction.



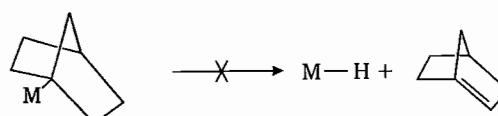
The driving force for  $\beta$ -hydride elimination reaction is the formation of a stronger M—H bond than M-alkyl bond and the elimination of an alkene ligand that reduces the unsaturation of the metal complex.

If there are no hydrogen atoms on  $\beta$ -carbon or if there is no  $\beta$ -carbon atom in the alkyl complex,  $\beta$ -H elimination is blocked. Since methyl ligands have no  $\beta$ -H atoms, the complex containing methyl ligands are more stable than that of ethyl ligands.  $\beta$ -H elimination is also blocked if the  $\beta$ -H on the alkyl is unable to approach the metal such as  $-\text{C}\equiv\text{CH}$ ,  $-\text{CMe}_3$ ,  $-\text{CHMe}_2$  and if the metal has  $d^0$  configuration.

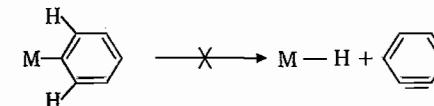
Some examples of alkyl ligands having no  $\beta$ -H atoms are:



$\beta$ -H elimination reaction is energetically unfavourable in bridgehead alkyl, yet they have  $\beta$ -H.



The  $\sigma$ -bonded  $\eta^1$ -aryl ligands, similar to the alkyl ligands, are relatively strong anionic ligands. Though they have  $\beta$ -H atoms but do not undergo  $\beta$ -elimination reactions.



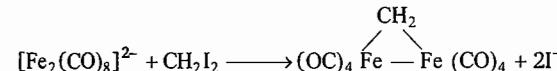
Therefore, aryl complexes are more stable than alkyl complexes having  $\beta$ -H atoms.

The alkyl ligands are very strong anionic  $\sigma$ -donors and are second only to hydrides in donor strength. The  $\sigma$ -donor strength of alkyl ligands increases as the substitution on the alkyl carbon replacing hydrogens with electron releasing groups such as other alkyl groups increases, but the steric hindrance can weaken the M—C bond.

### Synthesis of Metal Alkyl Complexes

#### 1. By the Reaction of Metal Carbonylate Anions with Alkyl Halides :

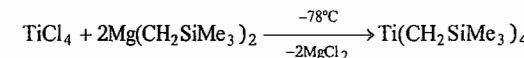
The metal carbonylate ions are strong nucleophiles and react readily with electrophiles such as alkyl halides. For example,



#### 2. By Oxidative Addition :



#### 3. By Alkylation of Metal Halides:



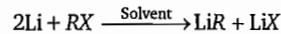
#### 4. By the reaction of transition metal halide with organolithium, organomagnesium or organoaluminium (a nucleophilic attack on metal).



## METAL ALKYLS OF MAIN GROUP ELEMENTS

### Alkyl Lithium

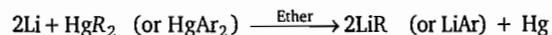
Lithium alkyls and aryls are most important group 1 organometallic compounds. Lithium alkyls can be prepared by the reaction of lithium metal with alkyl halides in ether, cyclohexane, or benzene.



Lithium aryls are best prepared by the reaction of *n*-butyl lithium, *n*-BuLi with an aryl halide.



Lithium alkyls or aryls can also be prepared by the reaction of metal with dialkyl mercury or diaryl mercury.



The crystal structure of methylolithium is body centred cubic with the  $\text{Li}_4(\text{CH}_3)_4$  units at each lattice site. Each unit is a tetramer in which the four lithium reside at the corner of a tetrahedron and the triply bridging methyl groups are located above the centres of the triangular faces (Fig. 5.1). Each carbon atom is essentially a six coordinate (three hydrogens of the methyl and three lithium atoms). The carbon atoms of the methyl groups are bound to the three lithium atoms at the corners of the tetrahedron.

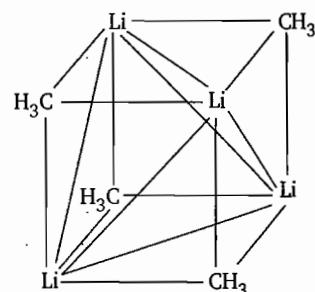


Fig. 5.1.

Each face contains three vacant 2s orbitals or hybrids of 2s and 2p orbitals of lithium and one  $sp^3$  hybrid orbital of  $\text{CH}_3^-$  containing a pair of electrons at the centre of a face. Bonding of the methyl group to three lithium atoms involves an  $sp^3$  orbital on the methyl group simultaneously overlapping three orbitals on the Li atoms (Fig. 5.2). Therefore, the bridging bond is a four centre-two-electron ( $4c-2e$ ) bond. Since carbon is more electronegative than lithium, the lowest energy orbital (containing the bonding pair of electrons) has more contribution from  $sp^3$  orbital of carbon. Thus LiC bond is mainly ionic.

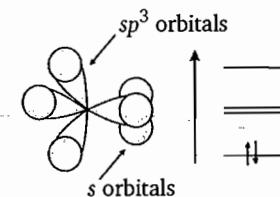


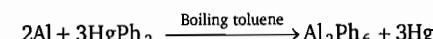
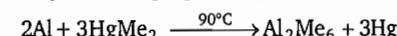
Fig. 5.2. The orbital overlap leading to the formation of four centre two electron bond

### Aluminium Trialkyls

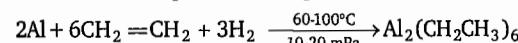
Organometallic chemistry of aluminium is much more important than that of other members of group 13. Boron trialkyls and gallium trialkyls do not undergo dimerization. On the other hand aluminium trialkyls and triaryls are often dimeric. Steric hindrance inhibits the dimerization, i.e., the tendency of formation of dimers decreases with increase in the size of alkyl groups. Therefore, dimerization of aluminium alkyls occurs for aluminium trimethyl, aluminium triethyl and aluminium triphenyl. The tendency of dimerization with branched chain alkyls such as *t*Pr, *t*Bu, Me<sub>3</sub>CCH<sub>2</sub> and mesityl (= 2, 4, 5-trimethylphenyl, 2, 4, 6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) is less marked and these are usually monomeric with planar 3-coordinate.

Aluminium trialkyls and triaryls are colourless, highly reactive, volatile liquids or low melting solids which ignite spontaneously in air and react violently with water. Therefore, they should be handled carefully.

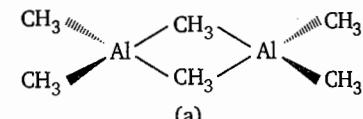
Aluminium alkyls and aryls can be prepared by the reaction of Al with HgMe<sub>2</sub> or HgPh<sub>2</sub>



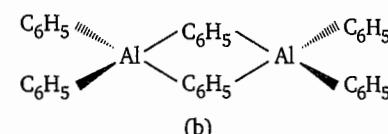
Aluminium triethyl and higher alkyl compounds are prepared by reaction of Al with appropriate alkene and H<sub>2</sub> gas at elevated temperature and pressure.



**Structure :** The structures of Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub> and Al<sub>2</sub>Ph<sub>6</sub> are shown in Fig. 5.3.



(a)



(b)

Fig. 5.3. Structure of (a) Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub>, (b) Al<sub>2</sub>Ph<sub>6</sub>

These dimers are similar in structure of the  $\text{Al}_2\text{Cl}_6$  (Fig. 5.4) but the bonding is different. In  $\text{Al}_2\text{Cl}_6$ , the bridging Al—Cl—Al bonds are 2 centre-2-electron ( $2c-2e$ ) bonds, i.e., each Al—Cl bond involves an electron pair.

In aluminium alkyls, the Al—C—Al bond is three-centre two-electron bond which is formed by overlap of an orbital on the alkyl group with orbitals on two aluminium atoms. In the aluminium alkyls, the Al—C—Al bonds are longer than the terminal Al—C bonds.

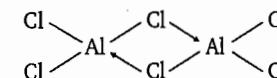


Fig. 5.4 Structure of  $\text{Al}_2\text{Cl}_6$

It is to be noted that the alkyls of elements of groups 1st, 2nd and 13th are electron deficient, therefore, they are commonly found as dimers or polymers. Alkyls of group 14, for example,  $\text{R}_4\text{Si}$  are monomeric because they have complete octet and do not coordinate extra ligands.

### Metal Carbenes

Carbenes (or methylidene groups) : $\text{CH}_2$ , : $\text{CHR}$ , : $\text{CR}_2$  are rarely stable in free state. They are both thermodynamically and kinetically unstable and this instability contributes to the very strong binding of carbenes to metal atoms. A free carbene has two spin states: singlet ( $\downarrow\uparrow$ ) and triplet ( $\uparrow\uparrow$ ). Singlet carbenes have an electron pair in  $sp^2$ -hybrid orbital whereas the triplet carbenes have one unpaired electron in one  $sp^2$ -hybrid orbital and one  $p$ -orbital. (Figure. 5.5)

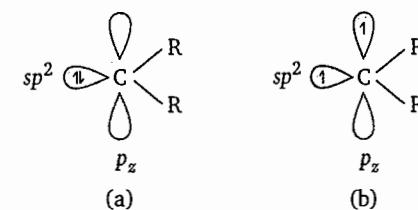
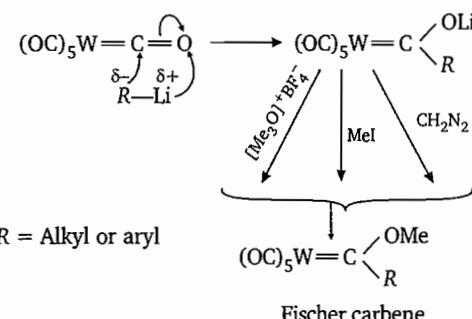


Fig. 5.5 (a) Singlet carbene (b) Triplet carbene

These carbenes are distinct spin isomers with different H—C—H bond angles but not resonance forms which always have the same spin. The non-bonding electrons on either of the singlet or triplet carbenes can participate in bond formation with metal atoms. Both the singlet and triplet carbenes are monohapto, two-electron ligands that form  $\text{M}=\text{C}$  double bonds. The compounds containing  $\text{M}=\text{C}$  double bonds are called metal carbenes. The metal carbenes are classified into two categories: 1. Fischer and 2. Schrock carbenes.

### 1. Fischer Carbenes

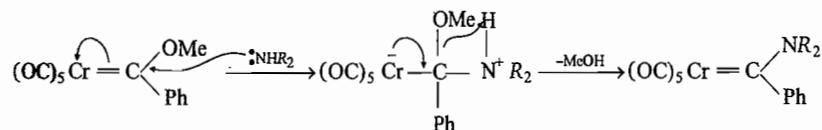
The first carbene complex was made by Fischer and Massbol in 1964. It was prepared by nucleophilic attack of alkyl lithium on a carbon atom of hexacarbonyltungsten,  $\text{W}(\text{CO})_6$  followed by alkylation.



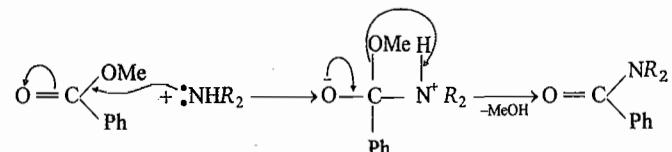
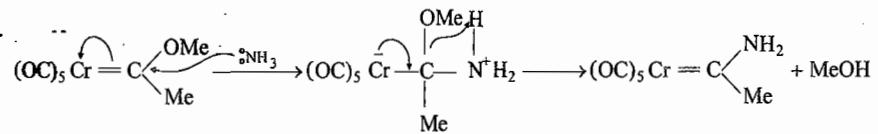
$R = \text{Alkyl or aryl}$

Fischer carbene

The carbon atom in Fischer carbenes is electron deficient, therefore, it is attacked by nucleophiles. For examples, the attack of an amine on the electrophilic carbon atom of a Fischer carbene results in the displacement of the —OR group to give a new carbene ligand.

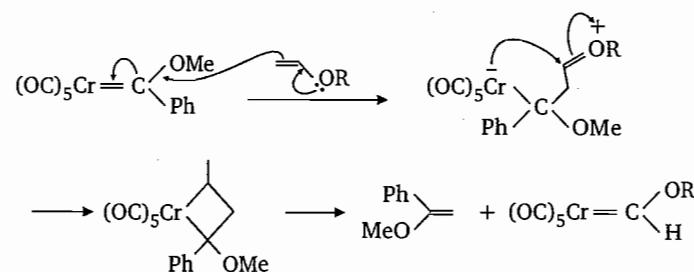


If  $(\text{OC})_5\text{Cr}$  group is replaced with the oxygen atom, this reaction is seen to be aminolysis of esters to give amides.



This reaction is favourable because nitrogen is not as electronegative as oxygen and its  $\pi$  donating ability exceeds that of oxygen.

The addition of carbon nucleophiles or alkenes forms metallacycles which can break down to a carbene and an alkene.



In a Fischer carbene a singlet carbene [Figure. 5.6 (a)] containing a heteroatom such as O, N donates its lone pair of electrons from  $sp^2$ -hybrid orbital to the metal to form a  $\sigma$ -bond and an empty  $p_z$  orbital on carbene accepts electron density from filled metal  $d\pi$  orbital to form metal-carbon double bond [Figure. 5.6 (b)]. The Fischer carbenes are characterized by middle to late transition metals in low oxidation states having  $\pi$  acceptor ligands such as CO and  $\pi$  donor ligands such as  $-OMe$  or  $-NMe_2$  on the carbene carbon. The electrophilicity of the carbon atom bound to the metal in these carbons can be explained as:

The significant electronegative late transition metals have  $d\pi$ -orbitals at lower energy than the carbon  $p$  orbitals. As a result the electron density of  $\pi$ -orbital is largely localized on the metal atom. Conversely the vacant  $\pi$ -orbital is mainly located on carbon atom which is, therefore, attacked by the nucleophiles because direct  $M \leftarrow C$  donation is only partly compensated by  $M \rightarrow C$  back donation.

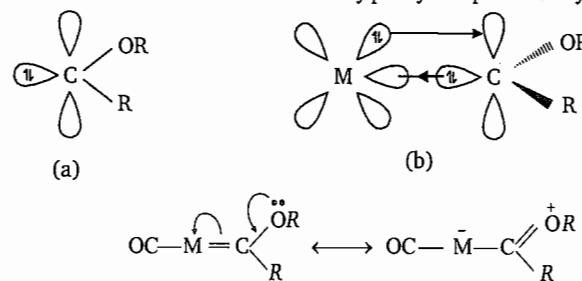


Fig. 5.6 (a) Singlet carbene (b) Fischer carbene

The electron deficient Fischer carbene is affected by the presence of the lone pair(s) of electrons on its  $\pi$ -donor substituents such as  $-OR$  because electron pair from filled  $p$ -orbitals of oxygen atom may also be donated to empty carbon  $p$ -orbital of carbene to form carbon-oxygen double bond. This indicates that the metal  $d\pi$  and filled  $p$  orbital of  $OR$  compete for  $\pi$ -bonding to carbene carbon as shown in figure 5.7.

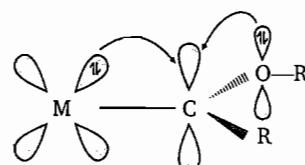


Fig. 5.7

The competition between the  $M-C$  and  $C-O$   $\pi$ -bonds may lead to the resonance structures (Figure. 5.8)

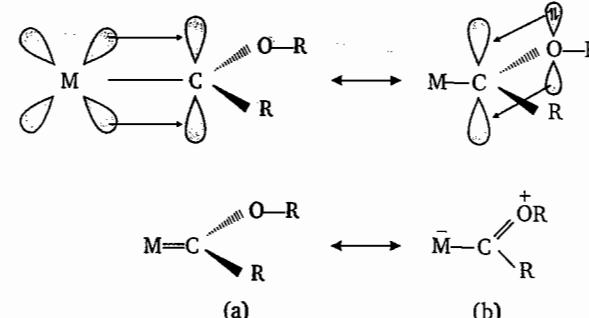
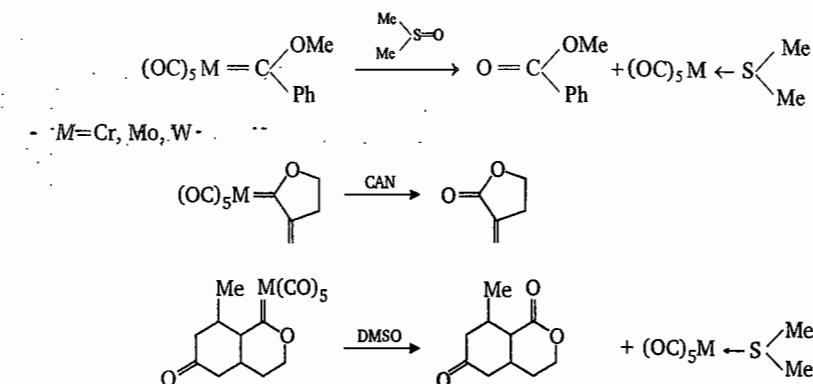


Fig. 5.8

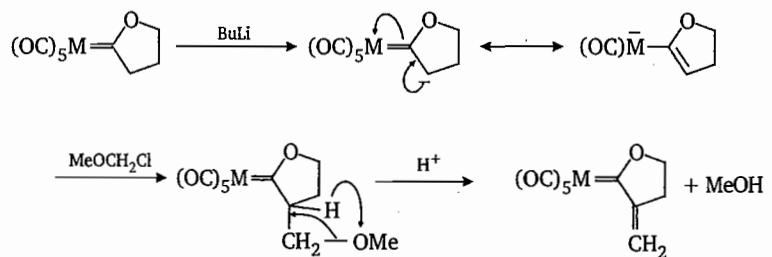
The  $p\pi-p\pi$  bond between C and O atoms is stronger than the  $d\pi-p\pi$  bond between metal and carbon of carbene because symmetry and size of combining  $p$ -orbitals are same.

The X-ray studies has shown that  $M-C$  bond is long and  $C-O$  bond is short. The  $M-C$  bond is shorter than expected for single  $M-C$  bond and it is longer than the expected  $M-C$  double bond. This indicates that the  $M-C$  bond order is between 1 and 2. This supports the structure shown in Figure 5.4 (b).

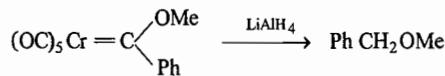
A carbene ligand of Fischer carbene can undergo oxidative cleavage with reagents such as ceric ammonium nitrate (CAN), dimethyl sulphoxide (DMSO) or pyridine N-oxide or even with air to give ketone.



In a Fischer carbene, abstraction of a proton  $\beta$  to the metal atom may occur by a base such as an organolithium,  $BuLi$ . The resulting negative charge can be delocalized on to the metal. The anion then can be alkylated by carbon electrophiles.

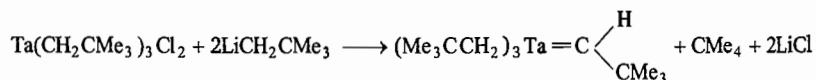
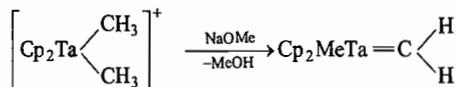


The carbene ligand can also be removed by reducing the carbene carbon using reducing agent such as  $\text{LiAlH}_4$ .



## 2. Schrock Carbenes

Just ten years later the discovery of Fischer carbenes, Schrock discovered the nucleophilic carbenes.



Schrock carbenes contain early transition metals in high oxidation states, non  $\pi$ -acceptor ligands coordinated to the metal and non- $\pi$ -donating substituents on carbon. Resonance pair (Fig. 5.9) describes a schrock type carbene.

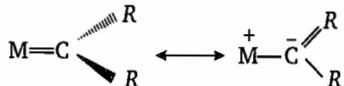


Fig. 5.9 Schrock carbene

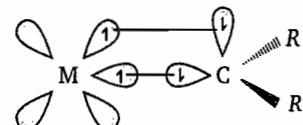
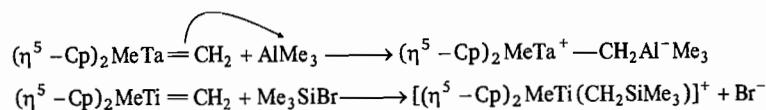
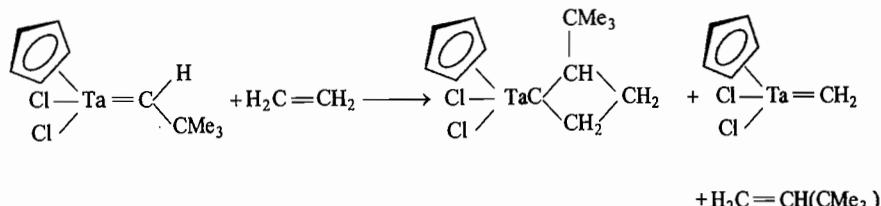


Fig. 5.10

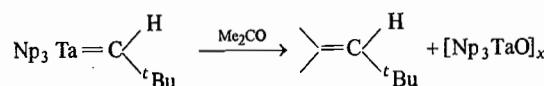
In a Schrock carbene the two orbitals (one  $sp^2$  and one  $p$ -orbital) on triplet carbene each containing one electron overlap with two metal  $d$ -orbitals each containing one electron to form two covalent bonds as shown in Fig. 5.10. Each  $\text{M}-\text{C}$  carbene bond is polarized so as to put negative ( $\delta^-$ ) charge on carbon atom bound to metal because carbon atom is more electronegative than metal leading to a nucleophilic character (i.e., susceptible to attack by electrophile carbene carbon). The nucleophilic character of a Schrock carbene is shown in the following reaction:



Alkene metathesis reaction is also an important reaction of Schrock Carbenes.



This reaction proceeds through a four membered ring including the metal atom. A Schrock carbene also reacts with ketones like Wittig ( $\text{Ph}_3\text{P}=\text{CH}_2$ ) reagent.



## Tebbe's Reagent

The Schrock carbene  $\text{Cp}_2\text{Ti}=\text{CH}_2$  is a highly nucleophilic carbene complex. The protected form of this carbene is called the Tebbe's reagent (Figure 5.11) Tebbe's reagent is formed by the reaction of  $\text{Cp}_2\text{TiCl}_2$  with  $\text{AlMe}_3$  as shown below:

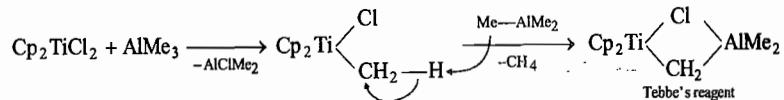
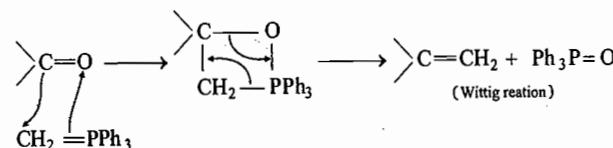
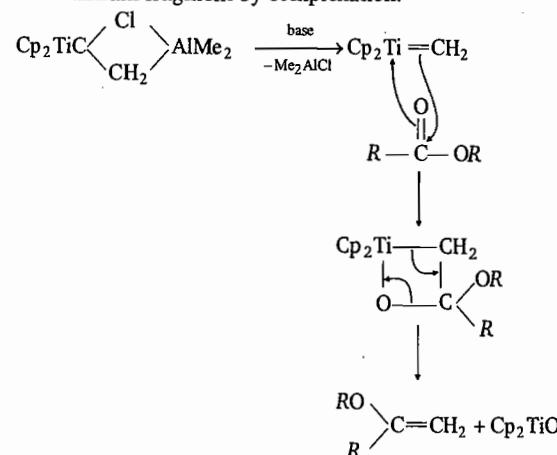


Fig. 5.11

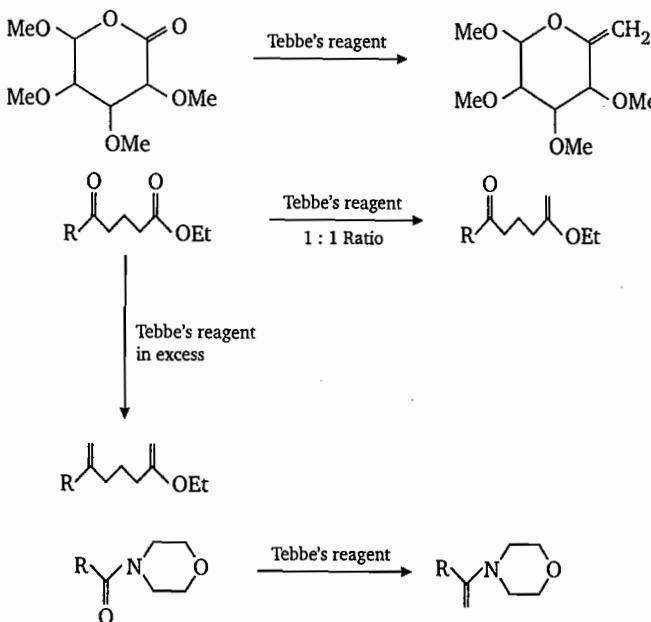
Tebbe's reagent is an example of a bridging carbene. This reagent gives products similar to given by the Wittig reagent. Wittig reagent  $\text{Ph}_3\text{P}=\text{CH}_2$  converts only the keto and aldehyde groups to  $>\text{CH}_2$  group. But the Tebbe's reagent converts  $>\text{C}=\text{O}$  group of aldehydes, ketones as well as  $\text{R}-\text{C}(=\text{O})-\text{OR}, \text{R}-\text{C}(=\text{O})-\text{NR}_2, \text{R}-\text{C}(=\text{O})-\text{OH}$  to  $>\text{CH}_2$  group.



Tebbe's reagent first loses  $\text{Me}_2\text{AlCl}$  to form  $\text{Cp}_2\text{Ti} = \text{CH}_2$ , a 16e complex, a base is sometimes required to remove the aluminium fragment by complexation.

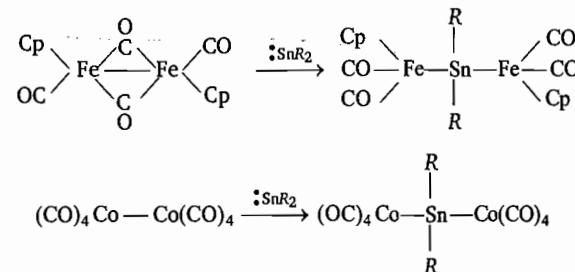


Some other reactions of Tebbe's reagent are:



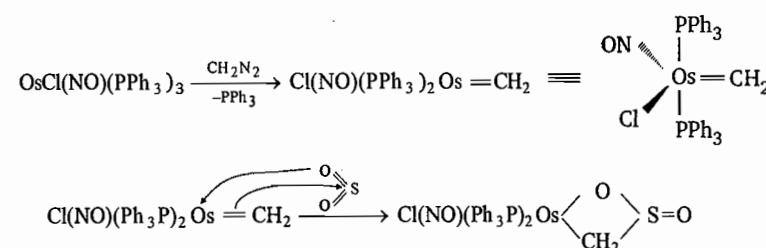
### Insertion Reaction

Similar to carbene :  $\text{CR}_2$ ,  $\text{:SnR}_2$  also behaves as carbene and shows insertion reactions. For examples.



### Carbenes Intermediate Between Fischer and Schrock Types

These are the carbenes which have properties intermediate between that of the Fischer and Schrock carbenes, because they react both with electrophiles such as  $\text{SO}_2$  or  $\text{H}^+$  and with nucleophiles such as  $\text{CO}$  or  $\text{CNR}$ . One of the most studied carbene is an osmium complex  $\text{Cl}(\text{NO})(\text{Ph}_3\text{P})\text{Os} = \text{CH}_2$  which can be synthesised as shown in the following reaction:



### Comparison between Fischer and Schrock Carbenes

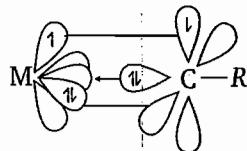
1. In Fischer carbenes the middle to late transition metals in low oxidation states are present whereas in Schrock carbenes the early transition metals in high oxidation states are present.
2. In Fischer carbenes the carbene is electron deficient, attacked by nucleophiles and stabilized by heteroatom or phenyl group whereas in Schrock carbenes, the carbene carbon is electron rich, attacked by electrophile and destabilized by hetero atoms.
3. Fischer carbenes usually obey 18e rule whereas Schrock carbenes do not.
4. In Fischer carbenes the free carbene is singlet whereas in Schrock carbenes the free carbene is triplet.

5. In Fischer carbenes the M—C bond is relatively weak and has low rotational barrier ( $10\text{--}15\text{ kJ mol}^{-1}$ ) whereas in Schrock carbenes M—C bond is relatively strong and has high rotational barrier ( $60\text{--}100\text{ kJ mol}^{-1}$ ).

### Metal Carbynes

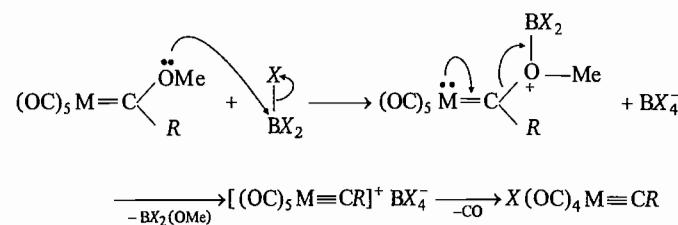
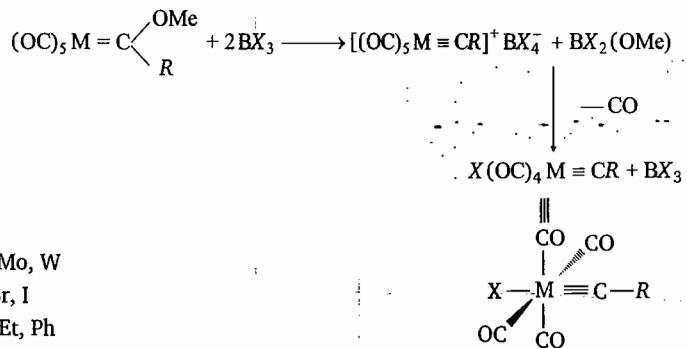
The carbyne or alkylidyne ligands have the general formula CH or CR. The metal carbynes are also classified as : 1. Fischer and 2. Schrock carbynes.

In Fischer carbenes, the carbyne ligands are monohapto three electron donor ligands, similar to the nitrosyl ligand with a pair of electrons in an  $sp_z$  hybrid orbital and single electron in a  $p$  orbital (either  $p_x$  or  $p_y$  orbital) and are bound to the metal by an  $M \equiv C$  triple bond. The carbyne ligand in a Fischer carbyne is doublet. An electron pair from  $sp$ -hybrid orbital of the doublet carbyne is donated to an empty  $d$ -orbital of the metal to form a  $\sigma$ -bond. A single electron in a  $p$ -orbital overlaps with a  $d$ -orbital having a single electron to form a  $\pi$ -bond. The second  $\pi$ -bond between the metal and the carbyne carbon results from donation of an electron pair from a filled  $d$ -orbital of metal atom to an empty  $p$ -orbital of carbyne carbon Fig. 5.12.



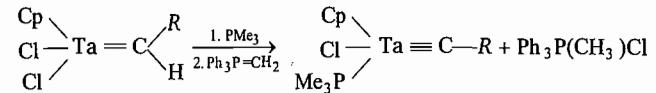
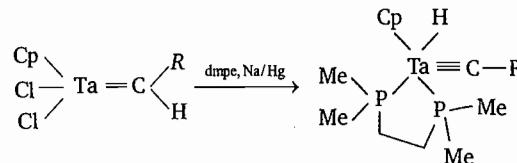
**Fig. 5.12 Fischer Carbyne.**

Fischer carbyne was first synthesised by Fischer from the reaction of Fischer carbene with boron trihalide  $BX_3$ .

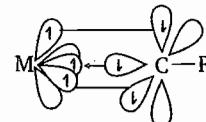


In this reaction, first the Lewis acid attacks the oxygen, the basic site of the carbene.

Subsequently, the intermediate loses a CO ligand followed by a halogen coordination in a position *trans* to the carbyne ligand. After Fischer, Schrock also synthesised a carbyne with an early transition metal in high oxidation states.

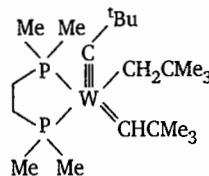


In the Schrock carbynes, the carbyne ligand is a quartet (i.e., it contains three unpaired electrons). The quartet carbyne ligand forms three covalent bonds (one  $\sigma$  and two  $\pi$ -bonds) to metal via three unpaired electrons as shown in Figure 5.13.



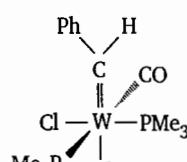
**Fig. 5.13.**

The complexes containing the three alkyl, carbene and carbyne ligands are also known. For example.

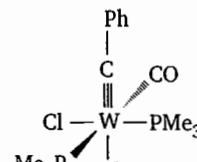


The X-ray spectroscopy shows that the metal-carbon single, double and triple bond distances are 225 pm, 194 pm and 178 pm respectively. These data suggest that the M—C bond length of carbyne is shorter than the analogous single and double bonds. These bond lengths are consistent with the W—C bond orders of 1, 2 and 3 respectively.

The infrared stretching frequency of CO ligand coordinated to metal in a carbyne complex is lower than that of CO coordinated to the metal in a corresponding carbene complex.



$$\nu_{\text{CO}} = 1938 \text{ cm}^{-1}$$



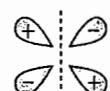
$$\nu_{\text{CO}} = 1870 \text{ cm}^{-1}$$

This indicates that carbyne ligand is a better electron donor than carbene and helps in  $\pi$ -back bonding from M to CO as the electron density increases on the metal and, therefore, reduces CO infrared stretching frequency.

## Metal Alkene Complexes

Ethylene is one of the simplest linear  $\pi$ -electron organic compound which has a single  $\pi$  bond resulting from the interactions of two  $2p$  orbitals on its carbon atoms. Interaction of the two  $p$  orbitals results in the formation of one bonding and one antibonding  $\pi$  molecular orbitals.

### Molecular orbitals of $\text{CH}_2 = \text{CH}_2$



### Relative Energy

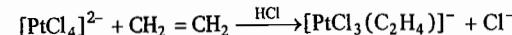
$\pi^*$  (antibonding)



$\pi$  (bonding)

The antibonding  $\pi$ -molecular orbital has one nodal plane perpendicular to the internuclear axis whereas the bonding  $\pi$ -molecular orbital has no nodal plane. The  $\pi$ -bonding orbital is completely filled which is the HOMO and  $\pi^*$  antibonding orbital is unoccupied, which is the LUMO.

Probably the first and most well known alkene complex is Zeise's salt,  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$  that was discovered in 1827. Zeise isolated stable yellow crystals after refluxing alcoholic solution of  $\text{K}_2[\text{PtCl}_4]$ . Zeise's salt is really  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$  containing a water of crystallization. Zeise's salt is now made from the reaction of  $\text{K}_2[\text{PtCl}_4]$  with ethylene.



The ethylene molecule occupies the fourth coordination site of the square planar complex with the C—C bond axis perpendicular to the square plane. The four C—H bonds in the ethylene complex are slightly bent away from the metal as shown in Fig. 5.14.

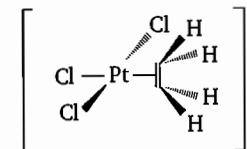


Fig. 5.14:

The C—C and C—H  $\sigma$ -bonding orbitals are of very low energy and the  $\sigma$ -antibonding orbitals are of very high energy as compared to the metal  $d$ -orbitals. But the C—C  $\pi$  bonding and  $\pi$ -antibonding orbitals (HOMO and LUMO respectively) have energies similar to those of the metal  $d$ -orbitals. For Zeise's salt, the best bonding picture is given by the Dewar-Chatt model. According to this model, the filled  $\pi$ -orbitals (HOMO) projects toward the metal and donates electrons to an empty  $d$  orbital of  $\sigma$ -symmetry of metal to form  $\sigma$ -bond. At the same time, the empty  $\pi^*$  orbitals in ethylene accept electron density back donated by metal (Figure 5.15). This is another example of synergistic effect of  $\sigma$  donation and  $\pi$ -acceptance encountered with the CO ligand.

Consequently, the ethylene molecule interacts with metal both as a  $\sigma$ -donor through C—C  $\pi$  orbital and as a  $\pi$  acceptor through the C—C  $\pi^*$  orbital. Due to steric interaction with the adjacent ligands, there is  $\pi$  interaction between the metal  $d_{zx}$  and the C—C  $\pi^*$  orbital.

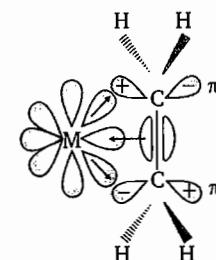


Fig. 5.15 Orbital overlap according to Dewar-Chatt Model in Zeise's salt

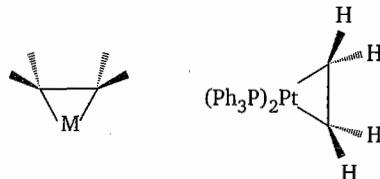
As the back donation from the metal is important to stabilize the complex, only the metals in low oxidation states favours the interaction with soft  $\pi$  electron donors. The C—C distance in Zeise's salt is 137.5 pm in comparison with 133.7 pm in free ethylene. The lengthening of C—C bond in Zeise's salt can be explained as follows :

(1) Donation of  $\pi$ -electron density to the metal to form  $\sigma$ -bond reduces the  $\pi$ -bonding electron density within the ethylene molecule and results in the weakening and lengthening of C—C bond.

(2) The back donation of electron density from the metal to the  $\pi^*$  orbital of ethylene reduces its bond order and hence results in the weakening and lengthening of C—C bond.

This bonding picture is supported by infrared spectroscopy. The vibrational frequencies of C—C bond of coordinated ethylene are lower than in free ethylene molecule. For example, the stretching frequency of C=C bond (i.e.,  $\nu_{C-C}$ ) in Zeise's salt is observed at 1516 cm<sup>-1</sup> in comparison with 1623 cm<sup>-1</sup> in free ethylene. The extent of  $\pi$ -back bonding depends upon the nature of metal, the substituents on ethylene and the other ligands.

Metal in high oxidation state behaves as weak  $\pi$ -base i.e., has less electron density and, therefore, results in poor  $\pi$ -back bonding and hence M—C bond becomes longer and C—C bond length becomes shorter. A metal in low oxidation state (i.e., metal is much more strongly  $\pi$ -basic), has more electron density and, therefore, results in strong  $\pi$ -back bonding. Hence M—C bond becomes shorter and the C—C bond becomes longer as the more electron density shifts into the  $\pi^*$  orbital of ethylene. For example, in the Zeise's salt itself M—L  $\sigma$  bonding predominates because the Pt(II) is weak  $\pi$ -basic and C—C bond length in coordinated ethylene (C—C bond length = 137.5 pm) resembles the free ethylene (C—C bond length = 133.7 pm). Pt(0), in contrast, is much more strong  $\pi$  base as in  $Pt(PPh_3)_2 C_2H_4$ . Therefore, in this complex, the C—C bond length becomes much more longer (=143 pm). In such a case the metal ethylene system has the metalacyclopropane structure (Fig. 5.16). In metalacyclopropane complex the carbons are rehybridized from  $sp^2$  to  $sp^3$ .



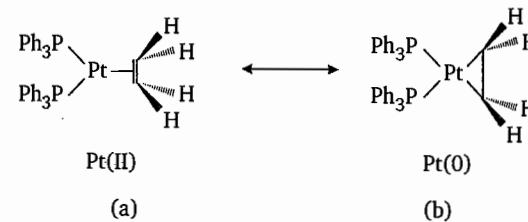
**Fig. 5.16.** Metalacyclopropane structures

In this complex, the hydrogen atoms are bent considerably out of the plane and the ethylene molecule lies in the same plane as the other ligands unlike the case of Zeise's salt where the planarity is sterically prevented. If the ligands other than ethylene coordinated to the metal are electron releasing (i.e.,  $\sigma$ -donor or strong  $\sigma$ -donor and weak  $\pi$ -acceptor) then they increase electron density on metal which inturn increases  $\pi$ -back bonding and hence decreases M—C bond length and increases C—C bond length. If the ligands other than ethylene are  $\pi$ -acceptor or weak  $\sigma$ -donor and strong  $\pi$ -acceptor (i.e., electron withdrawing ligand) decrease electron density on metal as a result  $\pi$ -back bonding decreases. Hence, M—C bond length increases and C—C bond length increases.

The substituent present on ethylene also affect the  $\pi$ -back bonding. If the electron releasing substituents are present on alkene, they increase electron density on alkene and 'therefore' increases the  $\pi$ -donation ability of alkene to the metal. As a result  $\pi$ -back bonding decreases.

The presence of electron withdrawing groups on the alkene such as  $C_2F_4$  and  $C_2(CN)_4$  enhances the  $\pi$ -back bonding and makes the alkene to bind more strongly to the metal. The presence of electron withdrawing groups on alkene encourages the  $\pi$ -accepting ability of the alkene. A shorter M—C bond results than does the unsubstituted ethylene. For example,  $Pt(PPh_3)_2 C_2(CN)_4$  has an even longer C—C bond length (149 pm) than the unsubstituted ethylene complex.

If the ability of donation of electron density from the metal atom to alkene ligand is small (metal in high oxidation state), substituent on the alkene bent only slightly away from the metal and the C—C bond length is slightly longer than in the free alkene. This suggests the Figure. 5.17 (a) On the other hand, with electron rich metal or electron withdrawing groups on the ethylene, the back donation is encouraged. The groups or substituents on the ethylene are then bent away from the metal and the C—C bond length approaches that of a single C—C bond. This suggest the Figure 5.17(b) The two structures Figure 5.17(a) and Figure 5.17(b) may exist as resonance structure.

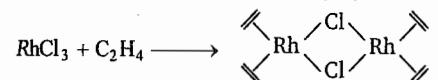


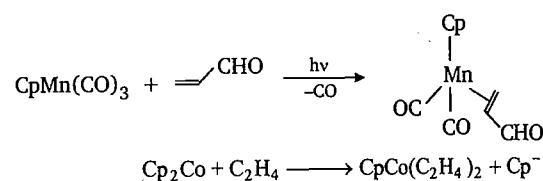
**Fig. 5.17.**

Because alkenes are soft electron donors and strong  $\pi$ -acceptors, they exhibit a strong *trans* effect. Therefore, in Zeise's salt Pt—Cl bond *trans* to ethylene is longer (about 234 pm) whereas there in *cis* positions are shorter (230 pm).

### Synthesis of Metal Alkene Complexes :

Methods of Synthesis of some metal alkene complexes are given below:





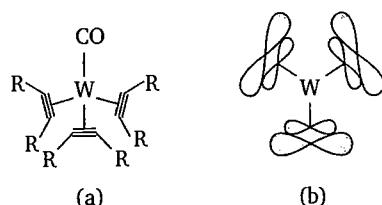
### Alkyne Complexes

Though alkynes are very similar to alkenes in their coordination behaviour but they have additional perpendicular  $\pi$ -electron pair. The alkynes have two  $\pi$ -bonds, therefore, they can act as neutral 2 or 4e donors. Alkynes are more electronegative than alkenes, and, therefore, are more better  $\pi$ -acceptors, hence they encourage  $\pi$ -back donation and bind more strongly. The substituents of the carbon of acetylene bent away from the metal by  $30^\circ$ – $40^\circ$  in the complexes. The M—C bond distances are slightly shorter and stronger than in the corresponding alkene complexes because of stronger  $\pi$ -accepting ability and less crowding than alkenes.

When alkynes act as 2e donor, the metallacyclopropene model is most appreciated as shown below:



Alkynes can form complexes which are coordinatively unsaturated. The complex, for example, Figure 5.18(a) is a 14e species, when alkyne acts as conventional 2e donor. In such cases the alkyne can also donate its second  $\pi$  electron pair from C=C  $\pi$ bonding orbital which lies at right angle to the first and the alkyne is now becomes a 4e donor and this compound might be seem to be 20e complex but one combination of second  $\pi$ -orbital of an alkyne ligand finds no match among the d-orbitals of metals Figure 5.18 (b). Therefore, this compound is an 18e species.

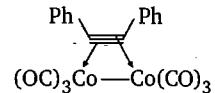


**Fig. 5.18**

An alkyne has two  $\pi$  and two  $\pi^*$  orbitals that can interact with metal orbitals. When an alkyne behaves as a 4e donor, the both  $\pi$ -orbitals can donate electron density to metal (to form two bonds) and both the  $\pi^*$  orbitals can accept electron density from metal d-orbitals.

Substituted alkynes readily bridge an M—M bond in which the alkyne donates its both pairs of  $\pi$ -electrons (one pair to each metal) and, therefore, regarded as a 4e donor. For example, in

$\eta^2$ -diphenylethyne hexacarbonylcobalt(0) in which one  $\pi$ -orbitals donates electron density to one of the Co and the second  $\pi$ -orbital donates electron density to other Co atom. (Figure 5.19)



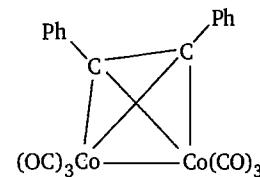
**Fig. 5.19**

When acetylene reacts with  $\text{Co}_2(\text{CO})_8$ , two moles of CO are eliminated.



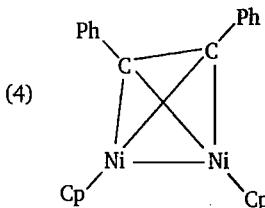
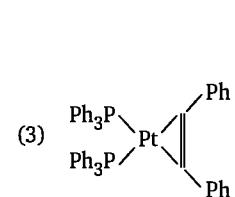
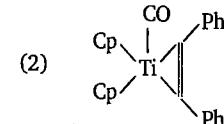
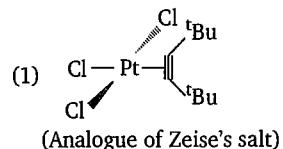
The elimination of two moles of CO and the 18 electron rule predicts that the acetylene ligand is acting as 4e donor.

The telrahedrane form (Figure 5.19) is equivalent of the structure (Figure 5.20) based on the metallacyclop propane model.



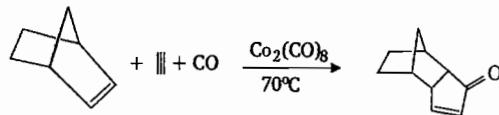
**Fig. 5.20**

Some examples of complexes having the different modes of bonding of metal to alkynes are shown below:



### The Pauson-Khand Reaction

The addition of an alkene, alkyne and CO molecules in the presence of  $\text{Co}_2(\text{CO})_8$  as catalyst to form a substituted cyclopentanones is called the Pauson-Khand reaction.



### Allyl Complexes

An allyl ligand can function as a monohapto  $\eta^1$  (one electron donor) as Me ligand or a trihapto  $\eta^3$  (three electron donor) as enyl ligand. As a monohapto  $\eta^1$  ligand it binds the metal with a  $\sigma$  bond with a free  $\text{C}=\text{C}$  bond as shown in Fig. 5.21 (a). Intermediate cases between Figure 5.21 (a) and 5.21 (b) are also known :

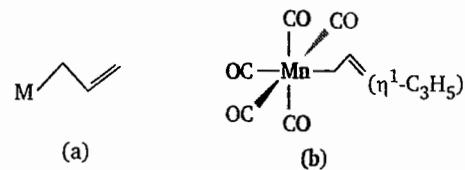


Fig. 5.21.

As a trihapto  $\eta^3$ -ligand, it has delocalized  $\pi$ -electrons over the three  $\pi$ -orbitals and has all the three carbon atoms at the same bonding distance from the metal (Figure 5.22)

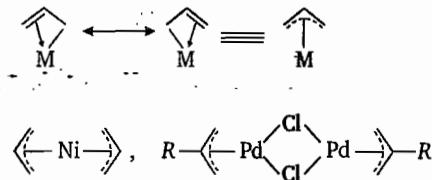


Fig. 5.22

Bonding between metal and  $\eta^3 - \text{C}_3\text{H}_5$  ligand is shown in Figure 5.23. The three  $\pi$ -molecular orbitals of the allyl radical can overlap with  $\sigma$  and  $\pi$  orbitals of the metal. The lowest energy  $\pi$  orbital of  $\eta^3$ -allyl ligand can donate its electron density to a suitable orbital on the metal to form a  $\sigma$ -bond.

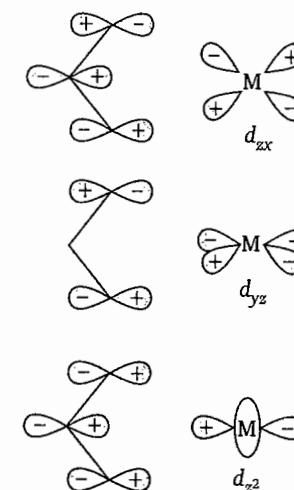
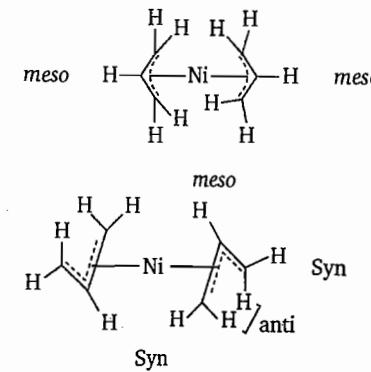


Fig. 5.23 Bonding interactions between metal  $d$ -orbitals and the  $\pi$ -orbitals of an allyl ligand

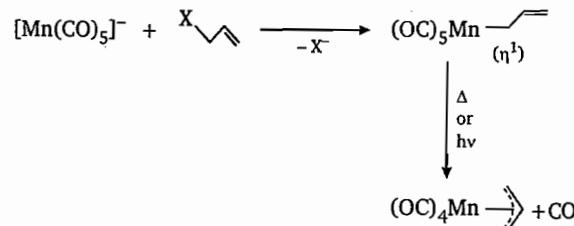
The next  $\pi$ -orbital, non-bonding in free allyl can act as a  $\pi$ -donor or  $\pi$ -acceptor depending upon the electron distribution between the metal and the  $\eta^3$ -allyl ligand. The highest energy empty  $\pi$ -orbital acts as a  $\pi$ -acceptor. Therefore, these can be synergistic  $\sigma$ -and  $\pi$ -interactions between metal and  $\eta^3$ -allyl ligand. The  $\text{C}-\text{C}-\text{C}$  bond angle within the  $\eta^3$ -allyl ligand is about  $120^\circ$  which is consistent with  $sp^2$ -hybridization. The  $\pi$ -interaction between a  $\pi$ -orbital of allyl ligand and the metal  $d_{zx}$  orbital is not very significant.

The anti (*trans* to *meso*) hydrogen atoms bent away from the metal and the syn (*cis* to *meso*) and *meso* hydrogen atoms bent towards the metal.



## Synthesis of Allyl complexes

### 1. By the reaction of organometallic anion and allyl halides.

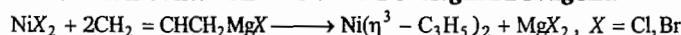


where  $X = \text{Cl}, \text{Br}$

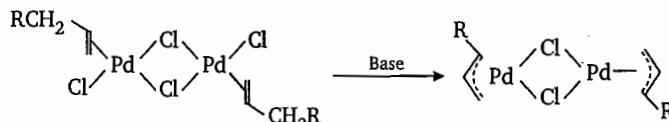
In this reaction loss of one CO ligand results in conversion of  $\eta^1$ - to  $\eta^3$ -allyl.

The  $[\text{Mn}(\text{CO})_5]^-$  ion displace  $X^-$  from allyl halide to give an 18-electron product containing  $\eta^1$ -allyl ligand. The allyl ligand switches to  $\eta^3$ -allyl when a CO ligand is lost.

### 2. By the reaction of metal halide with the Grignard reagent.



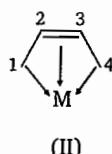
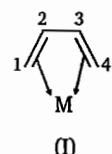
### 3. From alkenes



The coordinated allyl group is susceptible to nucleophilic attack and very useful in organic synthesis.

## Buta-1,3-diene complexes

Buta-1,3-diene usually acts as a  $4e$  donor in its *cisoid* conformation. The two possible bonding interactions between metal and butadiene ligand are shown below:



The structure I is analogous to the Chatt-Dewar extreme for alkenes in which two independent alkenes-metal interactions take place. But the type I structure is rarely seen where the  $\text{C}_1-\text{C}_2$  and  $\text{C}_3-\text{C}_4$  bond lengths are shorter than  $\text{C}_2-\text{C}_3$ . In the type II structure  $\text{C}_1$  and  $\text{C}_4$ , form two  $\sigma$ -bonds

and  $\text{C}_2-\text{C}_3$  forms one  $\pi$ -bond with metal. In this type  $\text{C}_1-\text{C}_2$  and  $\text{C}_3-\text{C}_4$  (146 pm) bond lengths are seen to be longer (40 pm) than  $\text{C}_2-\text{C}_3$  as in (butadiene)  $\text{Fe}(\text{CO})_5$  which has intermediate character with the  $\text{C}_1-\text{C}_2$ ,  $\text{C}_2-\text{C}_3$  and  $\text{C}_3-\text{C}_4$  bond lengths about equal (146 pm).

In majority of complexes, the substituents at  $\text{C}_1$  and  $\text{C}_4$  twist  $\sim 20^\circ-30^\circ$  out of the plane of the ligand and bent away from the metal so that the corresponding  $p$ -orbitals on  $\text{C}_1$  and  $\text{C}_2$  can overlap better with metal (Fig 5.24). This supports the type II structure for butadiene complexes.

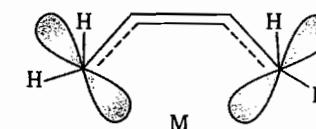


Fig. 5.24

The most important molecular orbitals of the butadiene which involve in bonding with metal are  $\psi_2$  (HOMO) and  $\psi_3$  (LUMO). The molecular orbital diagram (Fig. 5.25) shows that both the depletion of electron density in  $\psi_2$  by a  $\sigma$  donation to the metal and population of  $\psi_3$  by back donation from the metal causes the lengthening the  $\text{C}_1-\text{C}_2$  and shortening the  $\text{C}_2-\text{C}_3$  bonds, because the  $\psi_2$  is  $\text{C}_1-\text{C}_2$  bonding and  $\text{C}_2-\text{C}_3$  antibonding and  $\psi_3$  is  $\text{C}_1-\text{C}_2$  antibonding and  $\text{C}_2-\text{C}_3$  bonding in character.

The structure of the bound form of the ligand like butadiene ligand is often similar to that of first excited state of the free ligand. This is due to the reason that, in order to reach the first excited state, an electron is promoted from HOMO to the LUMO depleting the HOMO and populating the LUMO.

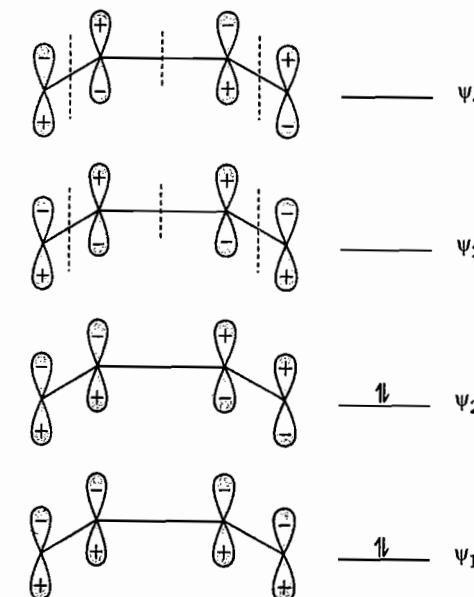
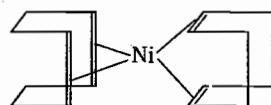


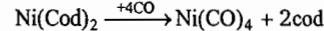
Fig. 5.25 Molecular orbitals of non-bonded 1,3-butadiene

The complexes formed by butadiene or other polyene ligands are similar to chelates and are, therefore, usually more stable than the equivalent complex with individual ligands such as alkenes because the entropy of dissociation of the complex is lower than when the liberated ligands move independently. For example, bis ( $\eta^4$ -cycloocta-1,5-diene) nickel(0) (Fig 5.26) is more stable than the corresponding complex containing four alkene ligands.

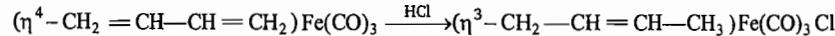


**Fig. 5.26** Structure of  $\text{Ni}(\text{Cod})_2$

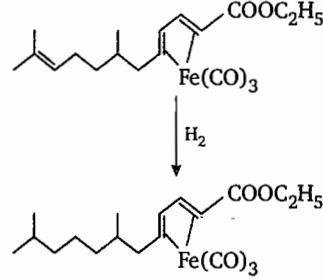
Metal complexes of cod are often used as starting substances in synthesis because they often have intermediate stability. The cod ligand can be displaced by the stronger ligands.



The butadiene ligand in its complexes undergoes protonation at  $\text{C}_1$  because the HOMO  $\psi_2$  has highest electron density there.



The organic fragment  $\text{Fe}(\text{CO})_3$  in the iron tricarbonyl-1,3-diene acts as a protecting group for the diene and prevents additions to the double bonds and allows the reactions to occur on the other parts of the molecule. For example (shown below), the  $\text{Fe}(\text{CO})_3$  fragment is used to protect two  $\text{C}=\text{C}$  bonds against hydrogenation while it takes place readily at the third  $\text{C}=\text{C}$  bond.



### Davies-Green-Mingos (DGM) Rule

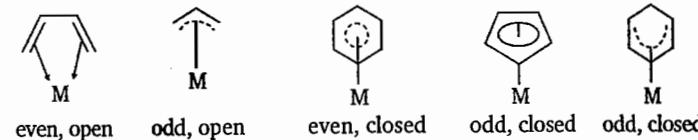
This rule provides the site of nucleophilic attack at 18 electron complexes having several polyene or polyenyl ligands. According to this rule :

(2) Nucleophilic attack occurs at open coordinated polyenes before closed polyenes.

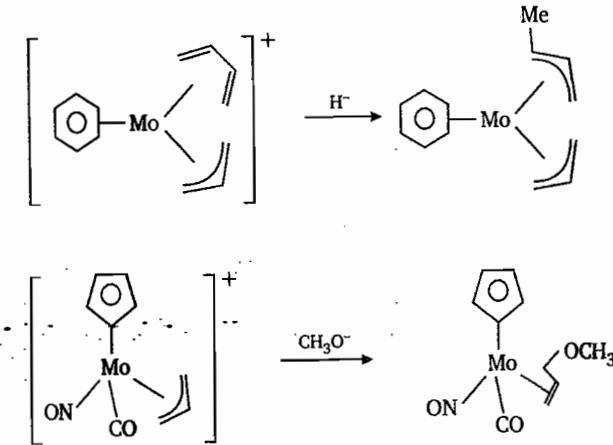
(3) In case of open polyenes (even ligands), nucleophilic attack occurs at terminal carbon atom. In case of open polyenyls (odd ligands), nucleophile usually attacks at terminal carbon but at nonterminal if  $\text{LnM}$  is electron donating.

Polyenes or even ligands are those which have even electron count or even donor carbon atoms on the covalent model (e.g.,  $\eta^2-\text{C}_2\text{H}_4$ ,  $\eta^4-\text{C}_4\text{H}_8$ ). Odd ligands are those which have an odd electron count on covalent model (e.g.,  $\eta^3-\text{C}_3\text{H}_5$ ,  $\eta^5-\text{C}_5\text{H}_5$ ). The closed ligands are those which have conjugated  $\pi$ -system of the polyene or polyenyl in a ring (e.g.,  $\eta^5-\text{Cp}$ ).

Some ligands and their classification according to DGM rule are :



The following examples illustrate the DGM rule :



- (1) Nucleophilic attack occurs at polyenes (even) before polyenyls (odd).



## Objective Questions

1. Schrock carbenes are :
  - (a) triplets and nucleophilic
  - (b) triplets and electrophilic
  - (c) singlets and nucleophilic
  - (d) singlets and electrophilic
2. The incorrect statement regarding the Fischer-type metal carbene complexes is that :
  - (a) carbene acts as a  $\sigma$ - donor and  $\pi$ -acceptor
  - (b) all atoms directly connected to carbene C atom are coplanar
  - (c) the bond between the metal and the carbene C atom has partial double bond character
  - (d) the carbene C atom is nucleophilic
3. How many carbene unit in the given complex have ?
 

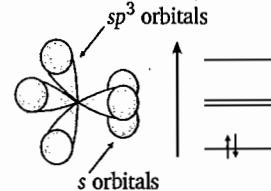
[PCY3]Ru(Cl)(Ph)[N+Mes2]2

  - (a) 1
  - (b) 2
  - (c) 4
  - (d) 0
4. Which one of the following statements is true for  $[ML_n(CR_2)_2]$  complex, in which,  $M$  = transition metal,  $L$  = ligand;  $CR_2$  = Fischer carbene ?
  - (a)  $L$  is non- $\pi$ -acceptor type
  - (b)  $R$  group is non- $\pi$ -donor type
  - (c) Carbon center is electrophilic in its reactivity
  - (d) Metal atom is in its high formal oxidation state
5. For the metal-olefin complexes (i)  $[PtCl_3(C_2H_4)]^-$  and (ii)  $[PtCl_3(C_2F_4)]^-$ , the correct statement is that :
  - (a) carbon-carbon bond length is same both in (i) and (ii)
  - (b) carbon-carbon bond length in (i) is smaller compared to that of (ii)
  - (c) carbon-carbon bond length in (i) is larger compared to that of (ii)
  - (d) a metallacycle is formed in each complex
6. Identify the order according to increasing stability of the following organometallic compounds,  $TiMe_4$ ,  $Ti(CH_2Ph)_4$ ,  $Ti(i-Pr)_4$  and  $TiEt_4$  ( $Me$  = methyl,  $Ph$  = phenyl,  $i-Pr$  = isopropyl,  $Et$  = ethyl)
  - (a)  $Ti(CH_2Ph)_4 < Ti(i-Pr)_4 < TiEt_4 < TiMe_4$
  - (b)  $TiEt_4 < TiMe_4 < Ti(i-Pr)_4 < Ti(CH_2Ph)_4$

- (c)  $Ti(i-Pr)_4 < TiEt_4 < TiMe_4 < Ti(CH_2Ph)_4$
- (d)  $TiMe_4 < TiEt_4 < Ti(i-Pr)_4 < Ti(CH_2Ph)_4$
7. The incorrect statement about Zeise's salt is :
  - (a) Zeise salt is diamagnetic
  - (b) the oxidation state of Pt in Zeise's salt is +2
  - (c) All the Pt—Cl bond lengths in Zeise's salt are equal
  - (d) C—C bond length of ethylene moiety in Zeise's salt is longer than that of free ethylene molecule
8. In metal-olefin interaction, the extent of increase in metal  $\rightarrow$  olefin  $\pi$ -back donation would :
  - (a) lead to decrease in  $C=C$  bond length
  - (b) change the formal oxidation state of the metal
  - (c) change the hybridization of the olefin carbon from  $sp^2$  to  $sp^3$
  - (d) increase with the presence of electron donating substituents on the olefin
9. Identify the order representing increasing  $\pi$ -acidity of the following ligands :
  - $C_2F_4$ ,  $NET_3$ ,  $CO$  and  $C_2H_4$
  - (a)  $CO < C_2F_4 < C_2H_4 < NET_3$
  - (b)  $C_2F_4 < C_2H_4 < NET_3 < CO$
  - (c)  $C_2H_4 < NET_3 < CO < C_2F_4$
  - (d)  $NET_3 < C_2H_4 < C_2F_4 < CO$
10. Which one of the following molecules exists as a monomer under ambient conditions ?
  - (a) Trimethylaluminium
  - (b) Triethylaluminium
  - (c) Triphenylaluminium
  - (d) Trimesitylaluminium
11. The reaction of  $[Cp_2TaMe_2]I$  ( $Cp = C_5H_5^-$ ) with  $NaOMe$  yields :
  - (a)  $[Cp_2Ta(OMe)_2]I$
  - (b)  $[Cp_2Ta(Me)OMe]I$
  - (c)  $Cp_2TaMe=CH_2$
  - (d)  $Cp_2Ta(OMe)=CH_2$
12. The reaction between  $[PdCl_4]^{2-}$  and  $C_2H_4$  produces a new compound. Compared to free  $C_2H_4$ , the C—C bond order of the product is :
  - (a) between 1 and 2
  - (b) less than 1
  - (c) unaltered
  - (d) greater than 2
13. The molecule :
 

(OC)5M=C\OCH3

 obeys  $18e^-$  rule. The two 'M' satisfying the conditions are :
  - (a)  $Cr, Re^+$
  - (b)  $Mo, V$
  - (c)  $V, Re^-$
  - (d)  $Cr, V$
14. Though cyclobutadiene ( $C_4H_4$ ) is highly unstable and readily polymerizes in its free state, its transition metal complexes could be isolated because :



- (a) CH<sub>3</sub>—Al interactions in Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub>
  - (b) B—H interactions in B<sub>2</sub>H<sub>6</sub>
  - (c) CH<sub>3</sub>—Li interactions in Li<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>
  - (d) CH<sub>3</sub>CH<sub>2</sub>—Mg interactions in EtMgBr(OEt<sub>2</sub>)<sub>2</sub>

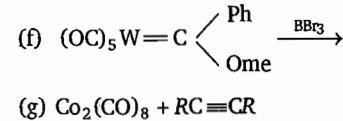
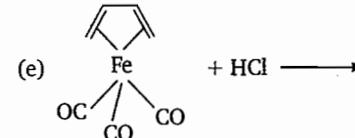
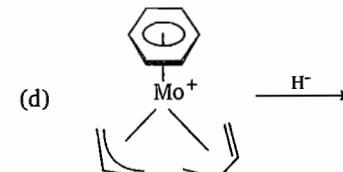
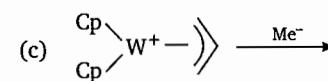
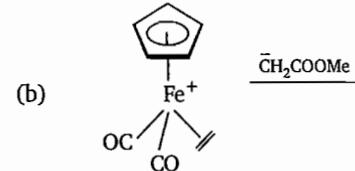
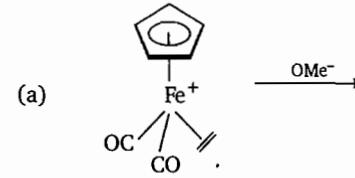
ANSWERS

- 1.** (a)      **2.** (b)      **3.** (a)      **4.** (c)      **5.** (b)      **6.** (c)      **7.** (c)  
**8.** (c)      **9.** (d)      **10.** (d)      **11.** (c)      **12.** (a)      **13.** (a)      **14.** (b)  
**15.** (c)      **16.** (a)      **17.** (b)      **18.** (c)

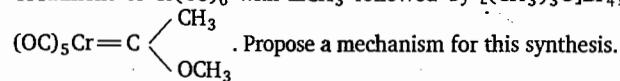


## **Subjective Questions**

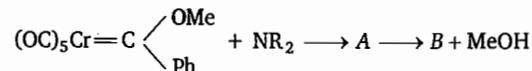
1. Discuss the structure and bonding of Zeise's salt.
  2. What are the Fischer type and Schrock type carbenes. Give two examples of each. How Fischer type carbene differs from Schrock type carbene?
  3. Write the product(s) in the following reactions :



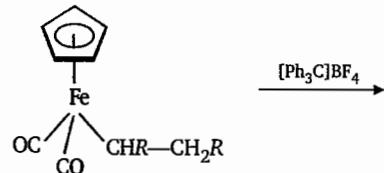
4. Treatment of  $\text{Cr}(\text{CO})_6$  with  $\text{LiCH}_3$  followed by  $[(\text{CH}_3)_3\text{O}] \text{BF}_4^-$ , gives the carbene complex



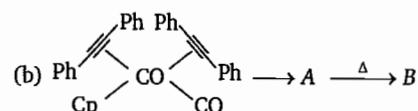
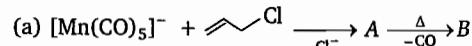
5. Write the products A and B in the following reaction :



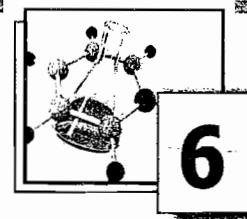
6. Write the product in the following reaction :



7. Write the products A and B in the following reaction :



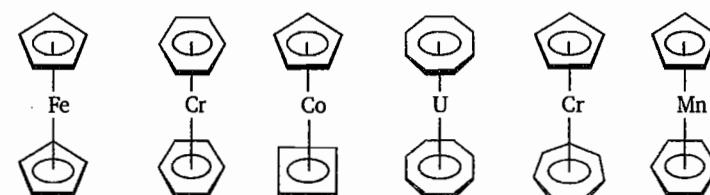
□□□



## Cyclic Polyene Complexes

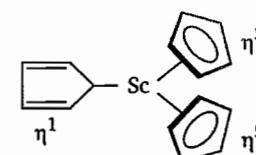
The cyclic polyene ligands ranging from cyclobutadiene to cyclooctatetraene have delocalized  $\pi$ -electrons. These ligands are bonded to metal by donation of  $\pi$ -electrons from their filled  $\pi$ -orbitals to the metal and by back donation of electrons from the metal into empty  $\pi^*$ -orbitals of the ligands. Cyclobutadienyl ( $\text{C}_4\text{H}_4^{2-}$ ), cyclopentadienyl ( $\text{C}_5\text{H}_5^-$ ), benzene and cycloheptatrienyl ( $\text{C}_7\text{H}_7^+$ ) behave as six electron donors and cyclooctatetraenyl ( $\text{C}_8\text{H}_8^{2-}$ ) behaves as a ten electron donor.

The organometallic compounds in which a metal lie between two planar polyhapto rings are known as sandwich compounds or metallocenes. Some sandwich compounds are shown in figure 6.1.



**Fig. 6.1** Structures of some Sandwich compounds

Some cyclic polyenes are known to form complexes in which they are bound to a metal atom through some but not all of their carbon atoms. In these cases the ring is non-planar (Fig. 6.2).

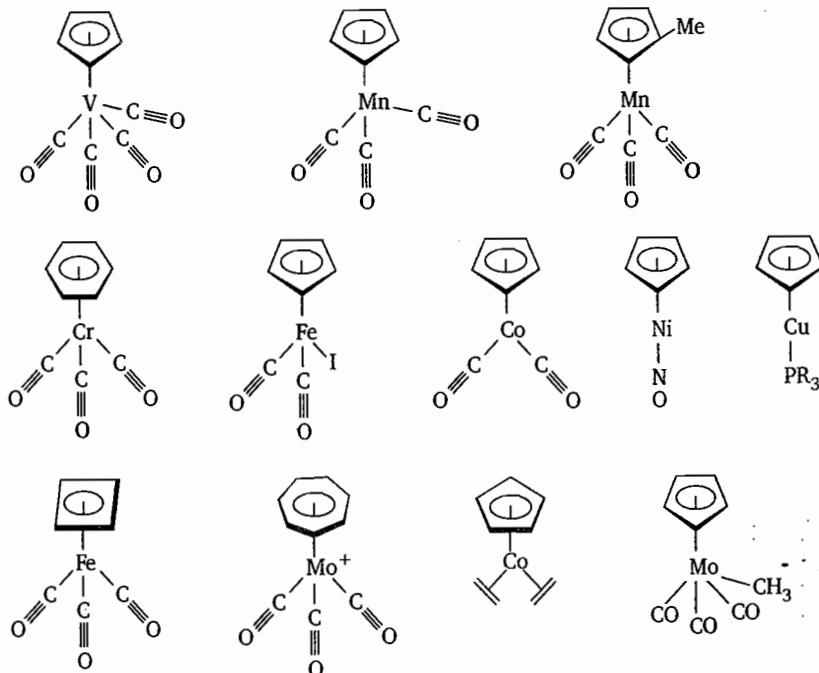


**Fig. 6.2**

Besides the homoleptic cyclopolyene complexes (complexes having only one type of cyclic ligands) there are so many other organometallic compounds in which other cyclic ligands are also coordinated to metal.

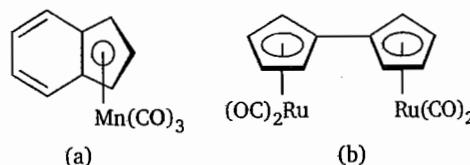
### Half Sandwich Compounds

Some organometallic compounds contain in addition to one cyclic polyene ligand other ligands such as CO, NO,  $R_3P$ , RNC or  $X^-$  ( $Cl^-$ ,  $Br^-$ ,  $I^-$ ). These compounds are called half sandwich compounds. Half sandwich compounds may be either monomers or dimers, with and without metal-metal bonds as necessary to follow 18 electron rule. To obey the 18 electron rule, number of ligands other than cyclic ligands varies one complex to other. Some examples are shown in figure 6.3.



**Fig. 6.3** Structures of some half sandwich compounds

Substituted Cp rings, such as indenyl and coupled rings as in fullerenes also form metal complexes (Fig. 6.4).

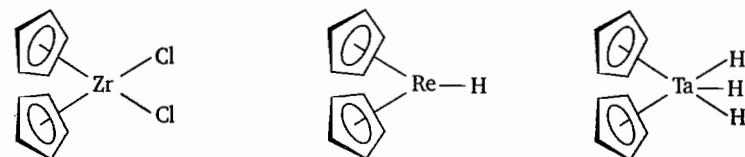


**Fig. 6.4**

Aromatic heterocyclic compounds such as pyridine, thiophene and pyrrole also form sandwich or half sandwich compounds with metals, for example,  $(\eta^5-C_4H_4N)(\eta^5-C_5H_5)Fe$ ,  $(\eta^5-C_4H_4S)Cr(CO)_3$  and  $(\eta^6-C_5H_5N)W(CO)_3$ .

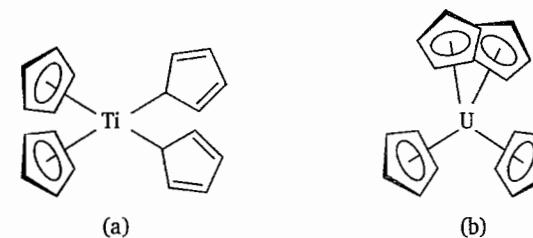
### Bent Sandwich Compounds

These compounds contain two cyclopentadienyl rings and other additional ligands like CO,  $CH_3$ ,  $CH_2=CH_2$ ,  $PMe_3$ , H, Cl, etc. In these compounds the rings are tilted with respect to one another because the steric requirement of additional ligands prevent parallel rings. Bent sandwich compounds are generally formed by transition metals on the left side of the periodic table because in these compounds the additional ligands prevent the cyclopentadienyl rings from existing in a parallel arrangement. Some examples of bent sandwich compounds are shown in figure 6.5.



**Fig. 6.5** Structures of Bent Sandwich compounds

There are some bent sandwich compounds which contain more than two cyclopentadienyl rings. The increasing number of cyclopentadienyl rings increases steric hindrance and causes the rings to be tilted. Examples of such compounds are  $(\eta^5-Cp)_2(\eta^1-Cp)_2Ti$  and  $(\eta^5-Cp)_4U$  (Fig. 6.6).



**Fig. 6.6** Structures of (a)  $(\eta^5-Cp)_2(\eta^1-Cp)_2Ti$ ; (b)  $(\eta^5-Cp)_4U$

The presence of lone pair of electrons on Pb(II) and Sn(II) results in similar tilting of the rings in  $Cp_2Sn$  and  $Cp_2Pb$ .

### Triple Deckers

These are the compounds in which two metals are sandwiched alternately between cyclic ligands. In these compounds a cyclic ligand bridges two metals. Some examples of triple deckers are shown in figure 6.7.

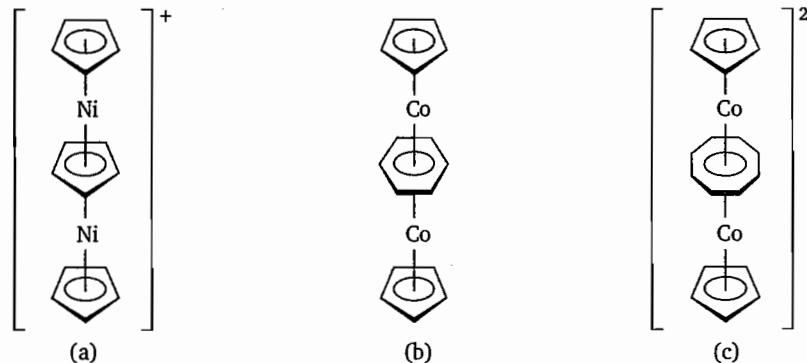


Fig. 6.7 : Some triple deckers containing cyclic ligands

The  $C_5H_5$  group is commonly abbreviated as Cp, the alkyl substituted,  $Me_5C_5^-$  as  $Cp^*$ .  $Cp^*$  is stronger  $\sigma$ -donor but a weaker  $\pi$ -acceptor than Cp because the methyl groups attached to Cp ring are electron releasing and increases electron density on Cp ring. The alkyl groups attached to Cp ring increase the steric hindrance and, therefore, increases the kinetic stability. There are no hydrogen atoms directly attached to carbons of the ring, therefore, prototropic rearrangement involving C—H activation and agostic interactions become least. Agostic interaction is the interaction of H-atom simultaneously to both carbon and the metal ion in the same complex. Complexes containing  $Cp^*$  groups are more soluble in non-polar solvents than the complexes which contain Cp rings.

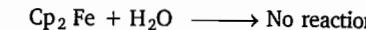
The 18 electron rule is not obeyed as consistently by the sandwich compounds as by the carbonyl and nitrosyl complexes and their derivatives. Some examples of the sandwich compounds which do not obey 18 electron rule are :  $(\eta^5-C_5H_5)_2V$ ,  $(\eta^5-C_5H_5)_2Cr$ ,  $(\eta^5-C_5H_5)_2Mn$ ,  $(\eta^5-C_5H_5)_2Co$ ,  $(\eta^5-C_5H_5)_2Ni$  etc. Ferrocene,  $(\eta^5-C_5H_5)_2Fe$  shows exceptionally thermal stability (stable to 500°C) and is not oxidized by air. On the other hand, cobaltocene which is a 19-electron species, is readily oxidized to the 18 electron species, cobaltocenium ion  $[(\eta^5-C_5H_5)_2Co]^+$ . This indicates that ferrocene is much more stable than cobaltocene.

The neutral sandwich compounds of the type  $Cp_2M$  are formed, when metals are in +2 oxidation state. Some examples are  $Cp_2V$ ,  $Cp_2Cr$ ,  $Cp_2Fe$ ,  $Cp_2Co$  etc. If the metals are in higher oxidation states, i.e., in +3, +4 and +5, the bent sandwich compounds of  $Cp_2MX_{n-2}$  type are formed, where  $n$  is the oxidation state of metal and  $X$  is a uninegative monodentate ligand. The examples of this type of complexes are  $Cp_2Co^+$ ,  $Cp_2TiCl_2$ ,  $Cp_2ReH$ ,  $Cp_2TaH_3$ ,  $Cp_2NbBr_3$  etc.

The 4d- and 5d-series transition metals do not form stable isolable  $Cp_2M$  compounds,  $Cp_2Ru$  and  $Cp_2Os$  be the exceptions. They form hydrides such as  $Cp_2ReH$ ,  $Cp_2WH_2$  by H abstraction. A

rhenocene exists as a dimer with a Re—Re bond and obey 18 electron rule. The compound  $Cp_2W$  exists as intermediate that has carbene like behaviour.

Metallocenes may be either ionic or covalent. Metallocenes such as  $Cp_2V$ ,  $Cp_2Cr$ ,  $Cp_2Fe$  and  $Cp_2Co$  are covalent and have strong covalent bonding between the metal and the rings. But all of these metallocenes are not stable with respect to oxidation etc., though they have strong bonding with respect to dissociation of the rings from the metal ions. The bonds between the metal ion and the rings have some polar character, however these do not react with polar compounds like water.



In contrast some compounds like  $NaCp$ ,  $MgCp_2$ ,  $Cp_2Mn$  and  $SmCp_3$  are ionic and have very reactive  $C_5H_5$  group. They react with polar compounds like water.



These compounds have salt like nature and are usually referred to as metal cyclopentadienides rather than cyclopentadienyl complexes.

In  $NaCp$ ,  $TiCp$ ,  $Cp_2Be$  and  $Cp_2Mg$ , no  $d$ -orbitals are available and so the bonding is likely to be ionic.  $Cp_2Be$  and  $Cp_2Mg$  have a sandwich structure but in  $Cp_2Be$ , one of the rings is considerably closer to Be than the other.  $NaCp$  and  $TiCp$  exhibit open face sandwich structure with planar Cp rings.

Manganocene,  $Cp_2Mn$  unlike the other metallocenes, is dimorphic. It is polymeric in solid state and consists of infinite chains of  $CpMn$  fragments bridged by cyclopentadienyl rings as shown in figure 6.8. At high temperature it is isomorphous with ferrocene. It is ionic, high spin  $d^5$  and formulated as  $Mn^{2+} 2Cp^-$ .

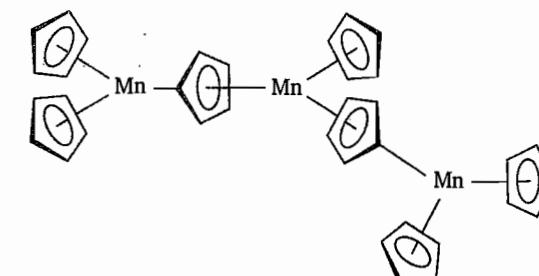


Fig. 6.8 : Solid state structure of  $Mn^{2+} 2Cp^-$

### Bonding in Metallocenes (Cyclopentadienyl Complexes)

The bonding in ferrocene and other metallocenes containing cyclic polyenes is best explained by molecular orbital theory which is based on linear combination of atomic orbitals (LCAO-MO) approximation.  $C_5H_5$  group is a regular pentagon and each carbon of  $C_5H_5$  group is  $sp^2$ -hybridized. Each carbon atom uses these  $sp^2$ -hybrid orbitals in forming  $\sigma$ -bonds to hydrogen and neighbouring carbons. So each carbon atom has a  $p_z$  or  $p\pi$  orbital perpendicular to the plane giving  $5p_z$  orbitals (Fig.6.9).

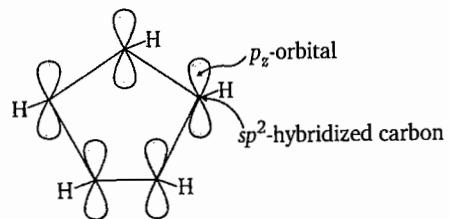


Fig. 6.9.

The C—C  $\sigma$ -bonds are formed by overlapping of  $sp^2-sp^2$  orbitals and C—H bond is formed by overlapping of  $sp^2-1s$  orbitals.

The  $p_z$  or  $p\pi$ -orbitals on each carbon of the planar  $C_5H_5$  group are combined linearly to form five  $\pi$ -molecular orbitals. These  $\pi$ -MOs have the following symmetries:

One molecular orbital with no nodal plane—a symmetry. This orbital is strongly bonding. This orbital has unbroken i.e., doughnut electron density above and below the plane of ring. Two doubly degenerate molecular orbitals with one nodal planes perpendicular to the plane of the ring— $e_1$  symmetry. These two orbitals are weakly bonding. Two doubly degenerate MOs with two nodal planes— $e_2$  symmetry. These two orbitals are markedly anti-bonding.

The energy of  $\pi$ -molecular orbitals increase with increase in number of nodal planes. Thus, order of energy of  $\pi$ -orbitals of different symmetries is :

$$a < e_1 < e_2$$

This pattern continues with doubly degenerate  $\pi$ -MOs of increasing number of nodal planes and increasing energy until the number of  $\pi$ -MOs becomes equal to the number of  $p\pi$  or  $p_z$  orbitals in the ring. If the number of MOs is odd, the highest energy anti-bonding molecular orbital is doubly degenerate and if the number is even, the highest energy anti-bonding molecular orbital is non-degenerate.

The five  $\pi$ -MOs of one  $C_5H_5$  group (or ring) having same symmetry linearly combined (i.e., added or subtracted) with five MOs of the other ring to give ten ligand group orbital (LGOs) of gerade (*g*) or ungerade (*u*) symmetries, which in turn can be combined with atomic orbitals of matching symmetry on the metal to form MOs. The metal atomic orbitals have  $a_{1g}$ ,  $a_{2u}$ ,  $e_{1u}$ ,  $e_{1g}$  and  $e_{2u}$  symmetries. The subscript *g* and *u* refers to the parity of the orbitals: *g* (German gerade, even)

indicates that the orbital is symmetric with respect to inversion, whereas the subscript *u* (ungerade, odd) indicates that the orbital is anti-symmetric with respect to inversion.

The LGOs for a pair of  $C_5H_5$  rings are formed, when the  $\pi$ -MOs of same energy and same number of nodal planes are combined linearly. For example, consider the lowest energy  $\pi$ -MO with no nodal plane of the ring. If the wave functions for this orbital on the two rings are added, a gerade (*g*) LGO of the same symmetry ( $a_{1g}$ ) as an  $s$  or  $d_{z^2}$  orbital is produced. On the other hand, if the two wave functions are subtracted, an ungerade LGO of the same symmetry as an  $p$  orbital ( $a_{2u}$ ) is obtained. Similarly, other LGOs can be constructed by either adding or subtracting the molecular orbitals of higher energies of the two rings.

The  $+z$  direction of the upper ring is taken to be pointing downward while the  $+z$  direction of the lower ring is taken to be pointing upward. It means that the  $+z$  direction of both rings point towards the centre of the ring system (Fig. 6.10).

The ten LGOs of two  $C_5H_5$  rings combine with nine orbitals (the five  $3d$ , one  $4s$  and the three  $4p$  orbitals) of similar symmetries giving a total nineteen molecular orbitals. If both rings have the positive lobes of lowest energy  $\pi$  MOs towards the metal, the  $s$  and  $d_{z^2}$  orbitals have correct symmetry. If one ring has the positive lobe towards the metal and the other the negative lobe towards the metal, the  $p_z$  orbital has the correct symmetry. There are some LGOs which remain non-bonding, there is no suitable metal orbital available to overlap them. It is not only necessary to use correct symmetry orbitals for appreciable bonding interaction but also the same energies.

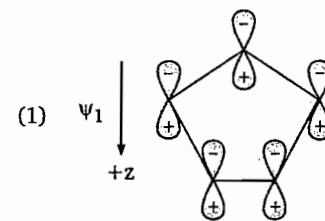
The metal orbitals which interact with the appropriate LGOs are shown in Table 6.1 :

Table 6.1

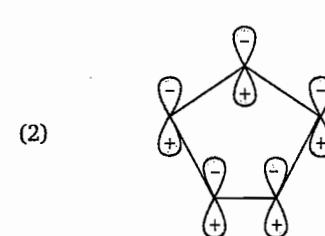
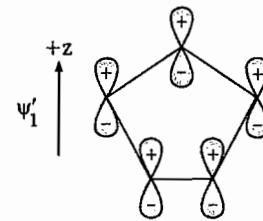
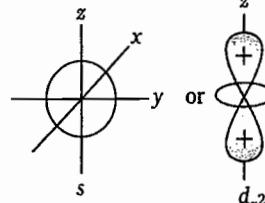
LGOs	Metal Orbitals
$a_{1g}$	$s$ and $d_{z^2}$
$2e_{1g}$	$d_{xz}$ and $d_{yz}$
$2e_{1u}$	$p_x$ and $p_y$
$2e_{2g}$	$d_{xy}$ and $d_{x^2-y^2}$
$2e_{2u}$	No suitable orbital on metal
$a_{2u}$	$p_z$

The symmetries of LGOs along with the metal orbitals with which they can overlap, are shown in figure 6.10.

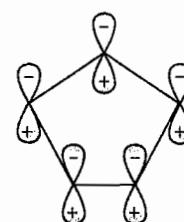
The interaction of LGOs with metal orbitals of appropriate symmetries produces bonding, non-bonding and anti-bonding molecular orbitals. The formation of bonding and anti-bonding molecular orbitals by the interaction, for example, between the  $d_{yz}$  orbital of metal and its appropriate group orbital (one of the one nodal plane group orbital) is shown in figure 6.11.



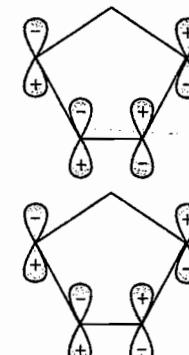
$$\psi_{a_{1g}} = \frac{1}{\sqrt{2}} (\psi_1 + \psi'_1)$$



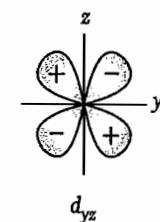
$$\psi_{a_{2u}} = \frac{1}{\sqrt{2}} (\psi_1 - \psi'_1)$$



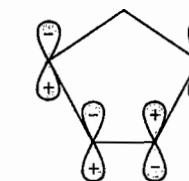
(3)



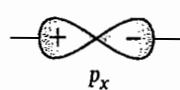
$$\psi_{e_{1g}} = \frac{1}{\sqrt{2}} (\psi_1 + \psi'_1)$$



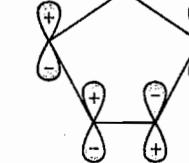
(4)



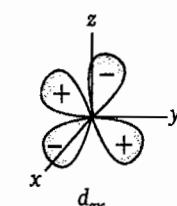
$$\psi_{e_{1u}} = \frac{1}{\sqrt{2}} (\psi_1 - \psi'_1)$$

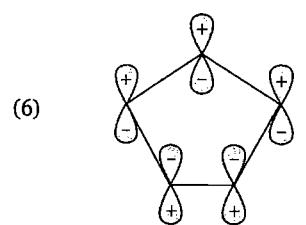


(5)

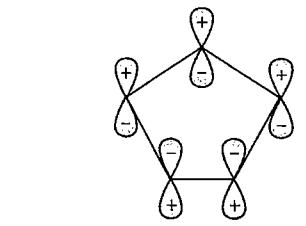
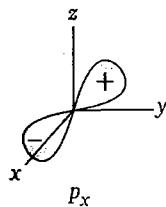


$$\psi_{e_{1g}} = \frac{1}{\sqrt{2}} (\psi_3 + \psi'_3)$$

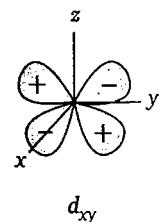




$$\Psi_{e_{1u}} = \frac{1}{\sqrt{2}} (\psi_3 - \psi'_3)$$

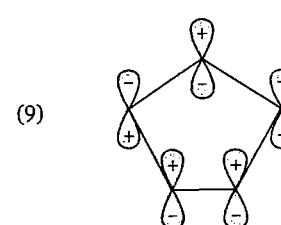


$$\Psi_{e_{2g}} = \frac{1}{\sqrt{2}} (\psi_4 + \psi'_4)$$

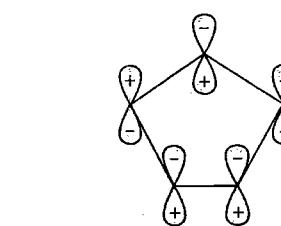
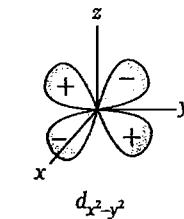


$$\Psi_{e_{2u}} = \frac{1}{\sqrt{2}} (\psi_4 - \psi'_4)$$

No suitable orbital  
on metal



$$\Psi_{e_{2g}} = \frac{1}{\sqrt{2}} (\psi_5 + \psi'_5)$$



$$\Psi_{e_{2u}} = \frac{1}{\sqrt{2}} (\psi_5 - \psi'_5)$$

No suitable orbital  
on metal

Fig. 6.10

The molecular orbital energy diagram supported by photoelectron spectroscopy studies in conjunction with ligand field theory for ferrocene is shown in figure 6.12.

The energy of  $a_{1g}$  orbital of cyclopentadiene is too much less than  $a_{1g}$  ( $4s$  or  $3d_{z^2}$ ) orbitals, therefore,  $a_{1g}$  orbital of the ring interacts slightly with  $a_{1g}$  orbitals of iron. Thus,  $a_{1g}$  bonding molecular orbital is mainly ligand based and  $a_{1g}$  ( $3d_{z^2}$ ) orbital is non-bonding and localized on the metal. Similarly, the  $a_{2u}$  orbital has little interaction with even higher energy  $Fe\ 4p_z$  orbital with which it is formally able to combine. The pair of  $e_{1g}$  MOs arises from the bonding combination of the ligand  $e_{1g}$  orbitals with  $e_{1g}$  ( $d_{zx}$  and  $d_{yz}$ ) orbitals on metal and form two strong  $\pi$ -bonds. This is due

to the reason that energy difference between  $e_{1g}$  orbitals of ligand and  $e_{1g}$  orbitals of metal and their symmetries are well-matched. This is the main contribution to the stability of the complex. The corresponding anti-bonding  $e_{1g}^*$  orbitals are unoccupied but involve in electronic transitions. Although the interaction of ligand  $e_{1u}$  orbitals with metal  $e_{1u}$  ( $p_x, p_y$ ) orbitals is favourable, but due to large energy difference they interact very little and the  $e_{1u}$  molecular orbitals are again mainly ligand based but with some contribution from metal  $4p_x$  and  $4p_y$  orbitals. Since the energy of ligand  $e_{2g}$  orbitals is higher than those of  $e_{2g}$  ( $d_{xy}$  and  $d_{x^2-y^2}$ ) orbitals of same symmetry of the metal, they do not interact very effectively and, therefore, the  $e_{2g}$  molecular orbitals are metal based and are non-bonding. Also the metal  $a_{1g}$  (i.e.,  $d_{z^2}$ ) orbital does not interact very effectively with  $a_{1g}$  orbitals of the ligand, therefore, is localized on metal and is non-bonding.

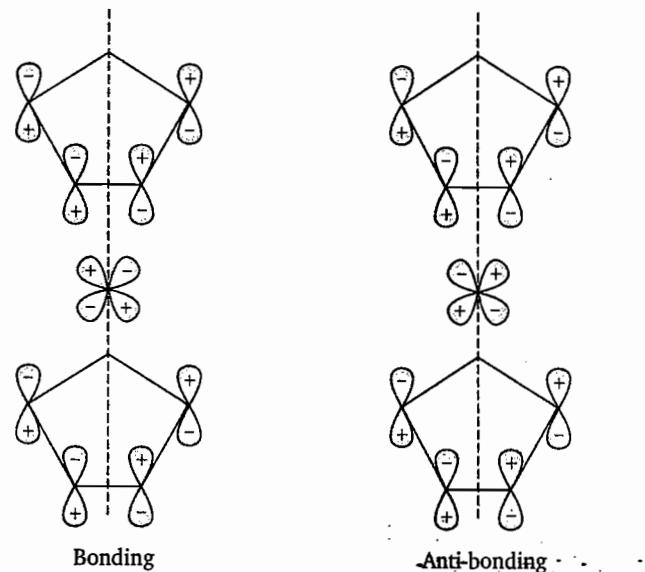


Fig. 6.11

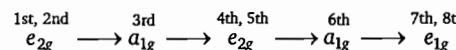
The orbitals of metallocenes that are of most interest are those having the greatest  $d$ -orbital character. These orbitals are the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO respectively).

The electron-electron repulsion between the  $\pi$ -electron density of the ligand  $e_{2g}$  orbitals and the metal  $e_{2g}$  ( $d_{x^2-y^2}$  and  $d_{xy}$ ) orbitals is minimum as the lobes of the  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals are not directed towards the cyclopentadiene ring. The  $a_{1g}$  ( $d_{z^2}$ ) orbital has one lobe and  $e_{1g}$  ( $d_{yz}$  and  $d_{zx}$ ) orbitals have two lobes directed towards the cyclopentadiene ring and, therefore, repulsion between  $a_{1g}$  of metal and that of Cp ring lower than between  $e_{1g}$  of metal and  $e_{1g}$  of Cp ring.

Therefore, the order of energy molecular orbitals ( $e_{2g}, a_{1g}$ , and  $e_{1g}$ ) which are localized on metal is  $e_{2g} < a_{1g} < e_{1g}$ .

It can be seen from molecular orbital energy level diagram (Fig. 6.12) that ferrocene contain 18 valence electrons in bonding and non-bonding MOs and the anti-bonding MOs are unoccupied. Since the bonding MOs are localized on Cp rings, therefore, 12 electrons supplied by two Cp ring ( $2 \times 6e$ ) are filled in bonding MOs ( $a_{1g}, a_{2u}$  and  $e_{1g}$ ) and 6 electrons supplied by  $Fe^{2+}$  ion are filled in non-bonding  $e_{2g}$  and  $a_{1g}$  orbitals. Thus, the distribution of six  $Fe^{2+}$  ion electrons in frontier molecular orbital is  $e_{2g}^4 a_{1g}^2 e_{1g}^0$ . The  $a_{1g}$  is HOMO and  $e_{1g}$  is LUMO in ferrocene. Ferrocene obeys the 18-electron rule. According to ligand field theory, the energy difference between  $e_{2g}$  and  $a_{1g}$  MOs is less than the pairing energy, therefore, these orbitals are first singly filled and then pairing occurs.

The electron distribution of the metal electrons in the frontier molecular orbitals in metallocenes is as follows :

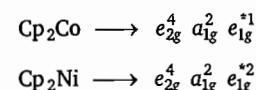


The metallocenes like cobaltocene  $Cp_2Co$ , nickelocene  $Cp_2Ni$ , chromocene  $Cp_2Cr$  and  $Cp_2V$  etc. have similar structures and are 19, 20, 16 and 15 electron species respectively.

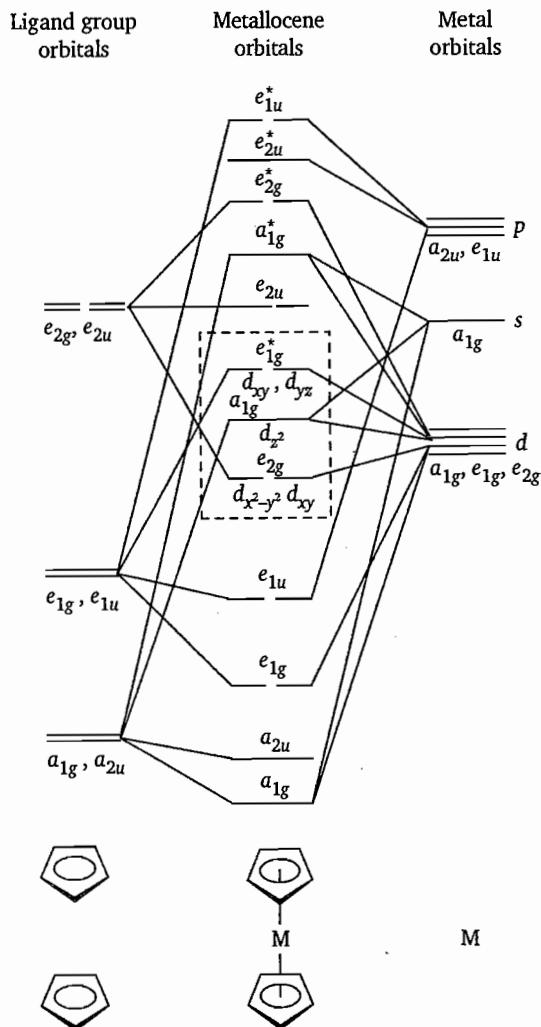
The frontier molecular orbitals  $e_{2g}, a_{1g}$  and  $e_{1g}$  are regarded as bonding, non-bonding and slightly anti-bonding respectively. Since these frontier molecular orbitals are neither strongly bonding nor anti-bonding, no significant change in the metal-ligand bond length is observed when ferrocene is oxidized to the ferrocenium ion and, therefore, the complex is not destabilized strongly. This characteristic also permits the possibility of existence of metallocenes that diverge from 18 electron rule such as  $Cp_2Co$  ( $19e^-$ ),  $Cp_2Ni$  ( $20e^-$ ) and  $Cp_2Fe^+$  ( $17e^-$ ) species.

The  $Cp_2Co$  and  $Cp_2Ni$  species have 1 and 2 easily oxidizable electrons in the anti-bonding  $e_{1g}^*$  orbitals. As a consequence  $M-C$  bond length increases and  $\Delta H$  for metal-ligand dissociation decreases.

The  $Cp_2Fe$  is fairly readily oxidized to ferrocenium ion,  $Cp_2Fe^+$  on removal of an electron from non-bonding  $a_{1g}$  orbital. The 19 and 20 electron species ( $Cp_2Co$  and  $Cp_2Ni$  respectively) are much less stable and much more readily oxidized than ferrocene because the electrons are lost from the anti-bonding  $e_{1g}$  orbitals to give 18 electron  $Cp_2Co^+$  and  $Cp_2Ni^{2+}$  ions. The electronic configurations of  $Cp_2Co$  and  $Cp_2Ni$  are :



$Cp_2V(15e^-)$ ,  $Cp_2Cr(16e^-)$  have unfilled bonding MOs and are highly reactive and bond to additional groups readily to confirm to 18 electron rule.



**Fig. 6.12.** Qualitative molecular orbital diagram for a metallocene.

The cyclopentadienyl metallocenes of the elements of transition metals of 3d-series are isomorphous and have almost same melting points in the range of 167-174°C (Table 6.2). Except ferrocene, all other metallocenes are paramagnetic. Physical properties of some metallocenes of the transition metals of 3d-series are given in Table 6.2.

**Table 6.2 : Physical Properties of Some Metallocenes of the Transition Metals of 3d-series.**

Compound	Valence Electrons	Electronic Configuration	No. of Unpaired Electrons	Magnetic Moment (in B.M.)	Melting Point (in °C)	Frontier Molecular Orbitals	Colour	M—C Bond Length (in pm)
Cp <sub>2</sub> V	15	$e_{2g}^2 a_{1g}^1$	3 (paramagnetic)	3.84	167	HOMO $a_{1g}$ LUMO $e_{1g}^*$	Purple	228
Cp <sub>2</sub> Cr	16	$e_{2g}^3 a_{1g}^1$	2 (paramagnetic)	3.20	173	HOMO $a_{1g}$ LUMO $e_{1g}^*$	Scarlet red	217
Cp <sub>2</sub> Mn	17	$e_{2g}^2 a_{1g}^1 e_{1g}^{*2}$	5 (paramagnetic)	5.86	173	HOMO $e_{1g}^*$ LUMO $e_{2u}$	Brown	238
Cp <sub>2</sub> Fe	18	$e_{2g}^4 a_{1g}^2$	0 (Diamagnetic)	0	174	HOMO $a_{1g}$ LUMO $e_{1g}^*$	Orange	206
Cp <sub>2</sub> Co	19	$e_{2g}^4 a_{1g}^2 e_{1g}^{*1}$	1 (paramagnetic)	1.73	173	HOMO $e_{1g}^*$ LUMO $e_{2u}$	Purple	212
Cp <sub>2</sub> Ni	20	$e_{2g}^4 a_{1g}^2 e_{1g}^{*2}$	2 (paramagnetic)	2.86	173	HOMO $e_{1g}^*$ LUMO $e_{2u}$	Green	220

The  $e_{1g}^*$  orbitals of a metallocene are analogous to the  $e_g$  orbitals and the  $a_{1g}$  in combination with the  $e_{2g}$  orbitals are analogous to the  $t_{2g}$  orbitals of an octahedral complex. Thus, similar to the octahedral complexes, metallocenes may either be high spin or low spin complexes.

Cp<sub>2</sub>Mn has a high spin configuration  $e_{2g}^2 a_{1g}^1 e_{1g}^{*2}$  which corresponds to the five unpaired electrons and hence an anomalously long M—C bond length (238 pm).

If one or more methyl substituted two cyclopentadienyl groups are joined to the Mn<sup>2+</sup> ion substituents, for example, one or more methyl groups on the ring, increases the energy difference between MOs and spin pairing occurs and electronic configuration becomes  $a_{1g}^2 e_{2g}^3$  suggesting that  $e_{2g}$  and  $a_{1g}$  orbitals have crossed one another.

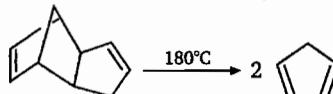
## FERROCENE

### [Bis (cyclopentadienyl)iron(II)]

Ferrocene is the first sandwich compound and was first synthesised by P. L. Pauson and T. J. Kealy in 1951. Its structure was determined a few years later by G. Wilkinson and E. O. Fisher.

## Synthesis

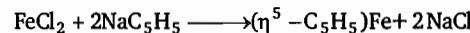
1. The general synthesis of metallocenes begins with the preparation of parent molecule, cyclopentadiene  $C_5H_6$  which is obtained by thermal cracking of dicyclopentadiene.



Hydrogen atoms on the cyclopentadiene are slightly acidic, therefore, metallic sodium reacts with a solution of cyclopentadiene in tetrahydrofuran (THF) to form sodium cyclopentadienide and liberate hydrogen.

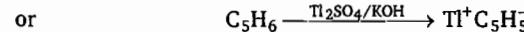


The reaction of sodium cyclopentadienide with  $\text{FeCl}_2$  in ethereal solvent, especially THF gives ferrocene.

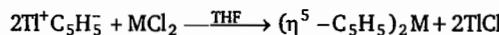


The other metallocenes can also be prepared by this reaction.

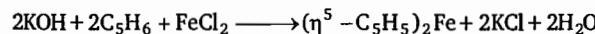
Ferrocene and other metallocenes can also be prepared by the reaction of thallium cyclopentadienide and  $\text{MCl}_2$  in THF solvent.



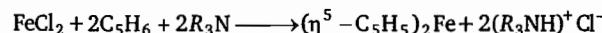
Since hydrogen atoms of cyclopentadiene are slightly acidic, therefore, TlOH facilitates the removal of  $H^+$  ions leaving  $C_5H_5^-$ .



2. By the reaction of aqueous solution of  $\text{FeCl}_2$  with alkaline solution of cyclopentadiene.

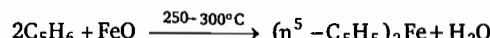
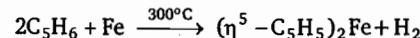


3. By the reaction of  $\text{MCl}_2$  with cyclopentadiene in the presence of amine.

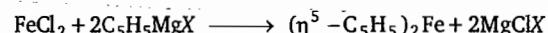
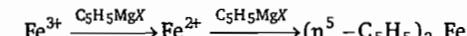


Use of amines facilitates the removal of the acidic hydrogen of cyclopentadiene allowing the synthesis to be accomplished at lower temperature.

4. By the reaction of Fe or  $\text{FeO}$  with cyclopentadiene at high temperatures.



5. By the reaction of Grignard's reagent (cyclopentadienyl magnesium bromide) with  $\text{FeCl}_3$  in which  $\text{Fe(III)}$  is reduced to  $\text{FeCl}_2$  which then reacts to form ferrocene.



## Physical Properties

1. Ferrocene is a diamagnetic crystalline solid with an odour like camphor and has a m.p.  $174^\circ\text{C}$ , boiling point  $249^\circ\text{C}$  and it sublimes at  $100^\circ\text{C}$ .
2. Ferrocene is the most stable of all the metallocenes and it is exceptionally stable and does not decompose upto  $500^\circ\text{C}$ .
3. It is insoluble in water but dissolves in most organic solvents.
4. It is unaffected by air i.e., not easily oxidized by air. It is also stable towards hydrolysis due to absence of ionic bonding.
5. It is readily oxidized by, for example, aqueous silver ion or  $I_2$  or  $\text{FeCl}_3$  or dil.  $\text{HNO}_3$  to give paramagnetic blue ferrocenium ion,  $\text{Cp}_2\text{Fe}^+$ . This large size cation is precipitated by large size anions like  $I_3^-$ ,  $\text{Br}_3^-$ ,  $\text{SbCl}_6^-$ ,  $\text{BF}_4^-$  etc.
6. In the solid state ferrocene has the two parallel cyclopentadienyl rings, originally, were thought to be staggered ( $D_{5d}$ ) as shown in Fig. 6.13. Electron diffraction studies of gas phase ferrocene, on the other hand, suggests that the cyclopentadienyl rings are eclipsed ( $D_{5h}$ ) as shown in figure 6.14 rather than staggered with a quite small energy barrier to internal rotation of the two rings of  $4 \pm 1 \text{ kJ mol}^{-1}$  allowing the two rings rotate freely. X-rays and neutron diffraction studies support the eclipsed structure of gas phase ferrocene. The rotation angle between the two ring is  $9^\circ$ .

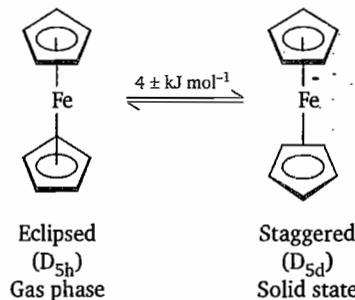


Fig. 6.13

Since the energy of barrier to internal rotation is very small and the rotational angle between two rings is  $\sim 9^\circ$  rather than  $0^\circ$  for precisely eclipsed, therefore, ferrocene exists as nearly eclipsed in the solid state.

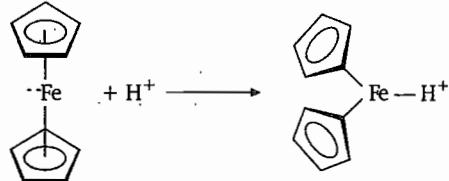
It has also been observed that at 298 K, there is rotation of rings even in the solid state. All the C—C bond length are equal and the iron is at equidistant from all carbons of Cp rings. The ruthenocene and osmocene have eclipsed rings similar to ferrocene in gas phase.

In the derivatives of ferrocene with the substituents on Cp rings, like decamethyl ferrocene, ( $\eta^5\text{-C}_5\text{Me}_5$ )Fe, the two rings are staggered, the energy barrier to rotation between two rings is higher and the two Cp<sup>\*</sup> rings are staggered in both the gas and solid states. The methyl groups are tilted away from Fe because the methyl groups on one ring repel the methyl groups on the other ring as they have larger size than hydrogens.

7. Ferrocene gives one  ${}^1\text{H}$ NMR signal because all hydrogens are in the same environment and are equivalent. Ferrocene is not a fluxional molecule.



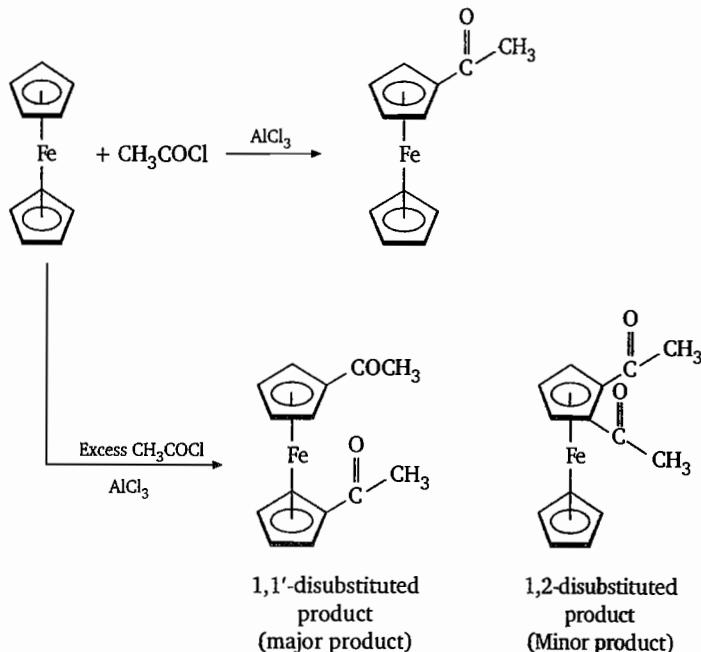
8. Ferrocene behaves a Lewis base and, therefore, on placing in strong acid, Fe(II) centre of ferrocene gets protonated. The singal in  ${}^1\text{H}$ NMR spectrum of the solution at  $\delta=2.1$ -ppm shows the presence of a metal hydride  $\text{Cp}_2\text{FeH}^+$ . The Fe(II) centre of ferrocene is oxidized in strong acid medium to Fe(III).



### (1) Friedal-Craft Acylation

Ferrocene undergoes Friedal-Craft acylation  $3.0 \times 10^6$  times faster than benzene. It undergoes Friedal-Craft acylation using acetyl chloride and  $\text{AlCl}_3$  very readily on one ring and only slightly less readily on both the rings to give mono acetyl and only one isomer of 1, 1'-diacetyl ferrocene. The formation of only one isomer of 1, 1'-diacetyl ferrocene indicates the free rotation of the two rings. In the absence of rotation of rings, three 1, 1'-disubstituted isomers could be formed but only one isomer has been isolated.

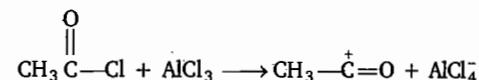
When excess of acetyl chloride is used 1, 1'- and 1, 2-disubstituted (same ring substitution) compounds are formed in the ratio of 60 : 1.



### Reactions of Ferrocene

Like benzene, the rings in ferrocene are aromatic and undergo electrophilic substitution reactions. Ferrocene undergoes electrophilic substitution reactions more faster than benzene indicating that electrons of Cp ring are more readily available. Some electrophilic substitution reactions of ferrocene are given ahead :

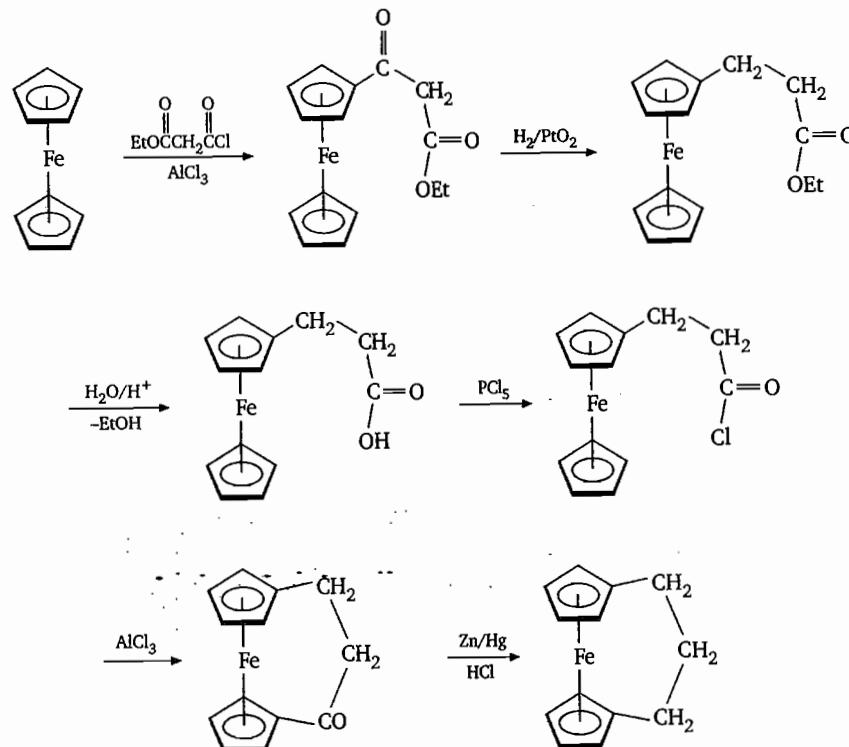
The  $\text{AlCl}_3$  catalyst react with  $\text{CH}_3\text{COCl}$  to produce the electrophile  $\text{CH}_3-\overset{\ddagger}{\text{C}}=\text{O}$ .



Because of the entry of electron withdrawing acetyl group, the first ring becomes deactivated towards further electrophilic substitution. Therefore, the second acetyl group attacks the unsubstituted ring. Thus, 1, 1'-disubstituted isomer is major product rather than the 1, 2-product.

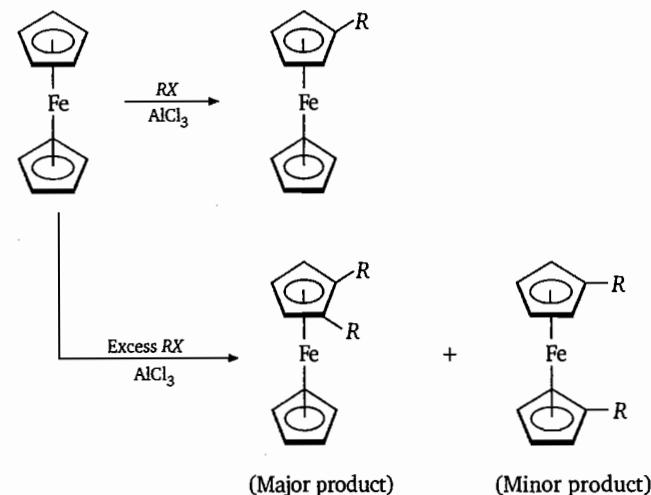
It is also possible to introduce the acetyl group by the reaction of acetic anhydride with phosphoric acid as a catalyst. In this reaction only mono acetyl product is formed, because acylation of first ring deactivates the second and the concentration of  $\text{CH}_3-\overset{+}{\text{C}}=\text{O}$  using  $\text{H}_3\text{PO}_4$  is too small to produce the diacetyl product.

By the sequence of reactions, the two Cp rings of ferrocene can be connected using  $\text{EtOCOCH}_2\text{COCl}$  as the starting acid chloride as shown below:



## (2) Friedel-Crafts Alkylation

Ferrocene undergoes Friedel-Crafts alkylation using alkyl halide ( $RX$ ) and  $\text{AlCl}_3$  on one ring to give mono alkyl derivative of ferrocene. The entry of the alkyl group which is the electron releasing group, activates the ring for further electrophilic substitution. Thus, the further electrophilic substitution occurs on the mono substituted ring.



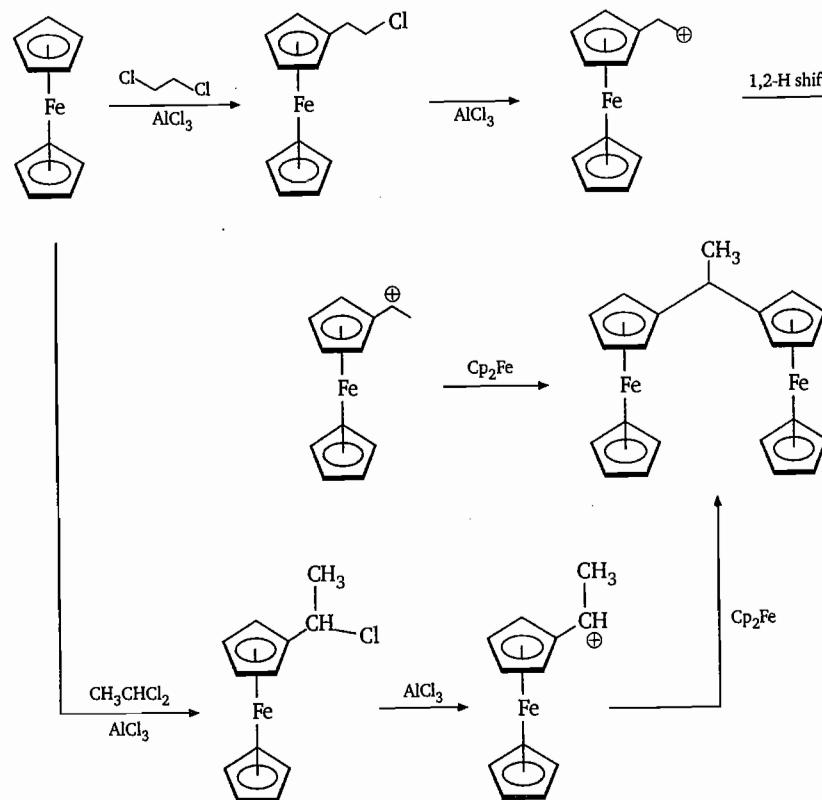
The  $\text{AlCl}_3$  catalyst reacts with  $RX$  to generate the electrophile  $R^+$ .



Where ever possible, the carbocation will rearrange to form the most stable one in the order of  $3^\circ > 2^\circ > 1^\circ$ .

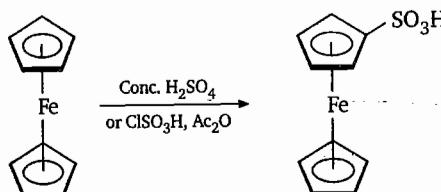
By a sequence of reactions, the two cyclopentadienyl rings of ferrocene can be connected.

For example :



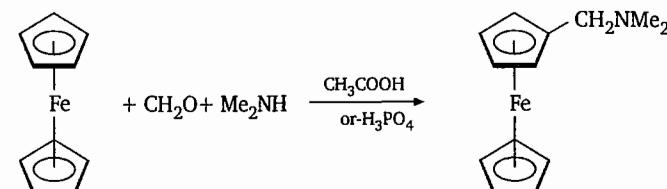
### Sulphonation

Sulphonation of ferrocene can be achieved as follows :



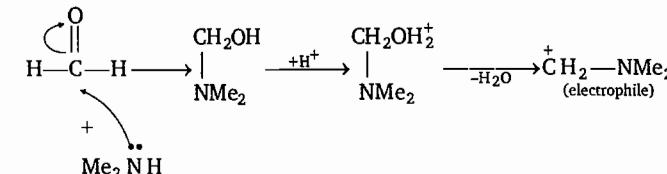
### Mannich Reaction

Dimethylamine and formaldehyde undergo a Mannich reaction with ferrocene to give dimethylaminomethylferrocene.



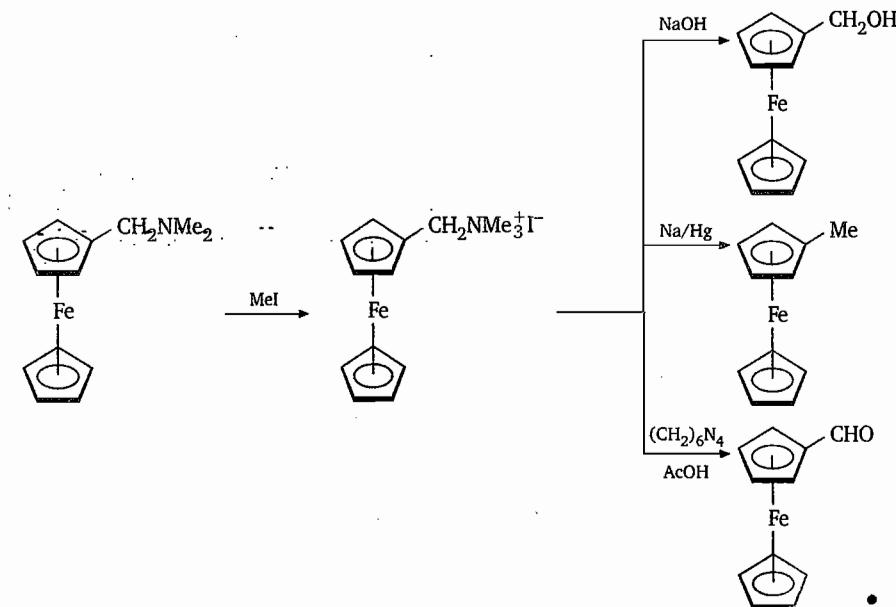
This product is used for the preparation of many other derivatives.

### Mechanism :



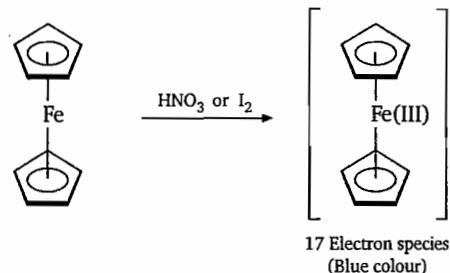
This electrophile attacks on the Cp ring to give product.

This product is used for the preparation of many other derivatives.



### Nitration and Halogenation

The direct introduction of  $-\text{NO}_2$  or  $-X$  group into ferrocene is not possible because ferrocene is readily oxidized to ferrocenium ion by the oxidizing electrophile and makes it inactive.

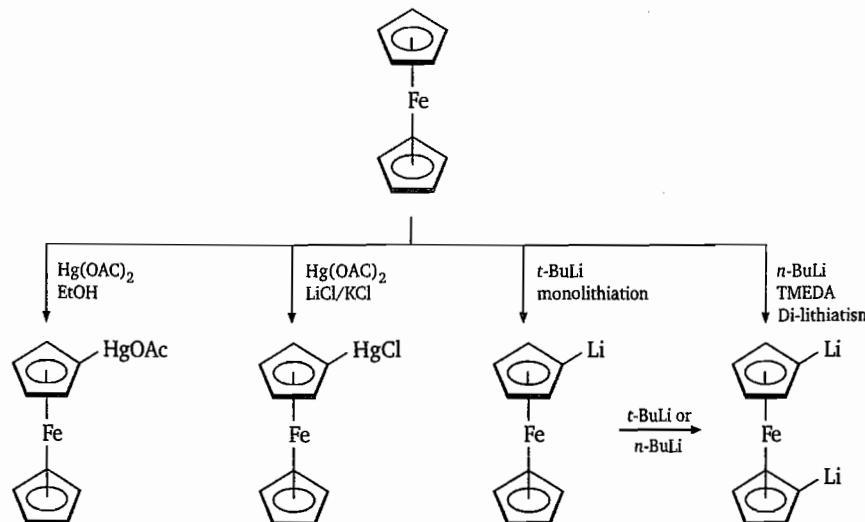


The ferrocenium ion is stabilized with larger size anion like  $\text{I}_3^-$ ,  $\text{Br}_3^-$ ,  $\text{SbCl}_6^-$ ,  $\text{BF}_4^-$  etc.

Both nitro and halo derivatives of ferrocene are prepared indirectly from the metallated derivatives.

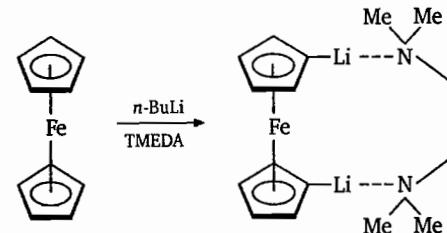
### Metallation

The introduction of a metal into the ring is called a metallation reaction. Metallation reactions of ferrocene are useful for synthesising another derivatives. Some metallation reactions are given below :

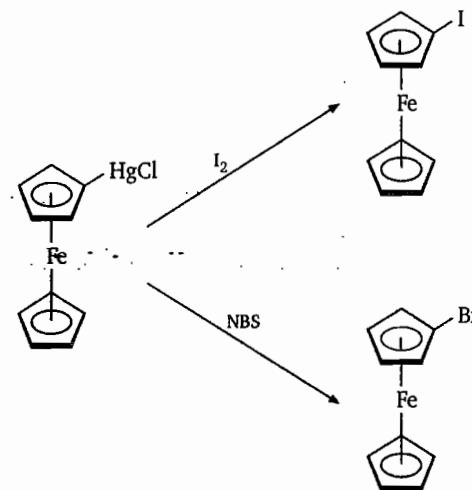


Mono lithiated ferrocene is formed by the reaction of ferrocene with *t*-butyllithium. The use of *t*-BuLi increases the yield of monolithiated product substantially, but some dilithiation also takes place. Mono substituted ferrocene derivatives have been prepared by the reaction of monolithiated ferrocene with a variety of reagents. Some important reactions of monolithiated ferrocene are given in scheme Fig. 6.14.

Dilithiated ferrocene can be prepared by the reaction of *n*-BuLi with ferrocene in the presence of tetramethyl ethylene diamine (TMEDA). The use of the solvent TMEDA stabilizes the dilithiated ferrocene by forming an ion-dipole interaction. This TMEDA adduct of dilithiated ferrocene is used for further electrophilic substitution reactions to form 1, 1'-disubstituted ferrocene derivatives. Some important reactions of dilithiated ferrocene are given in the Fig. 6.15.



The mercury derivative of ferrocene is used for other monosubstituted ferrocene derivatives as given below :



The important reactions of halogen derivatives of ferrocene are given in Fig. 6.16.

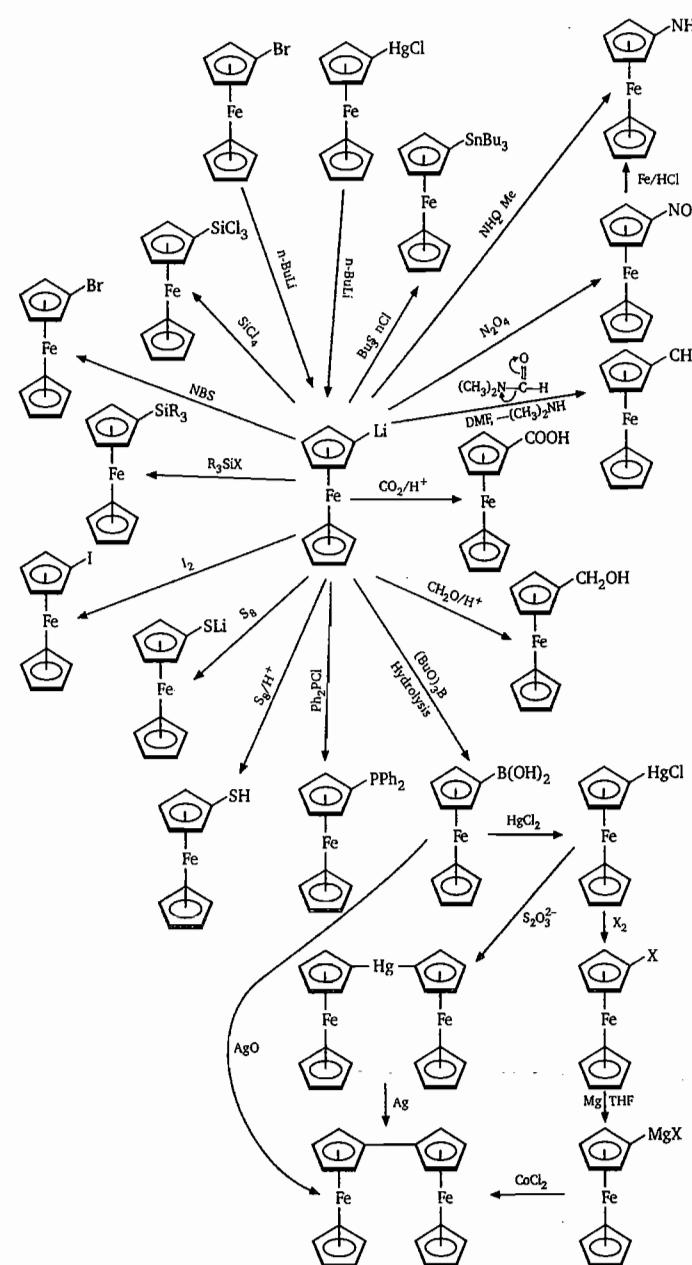


Fig. 6.14 Synthesis and reaction of mono-lithiated ferrocene

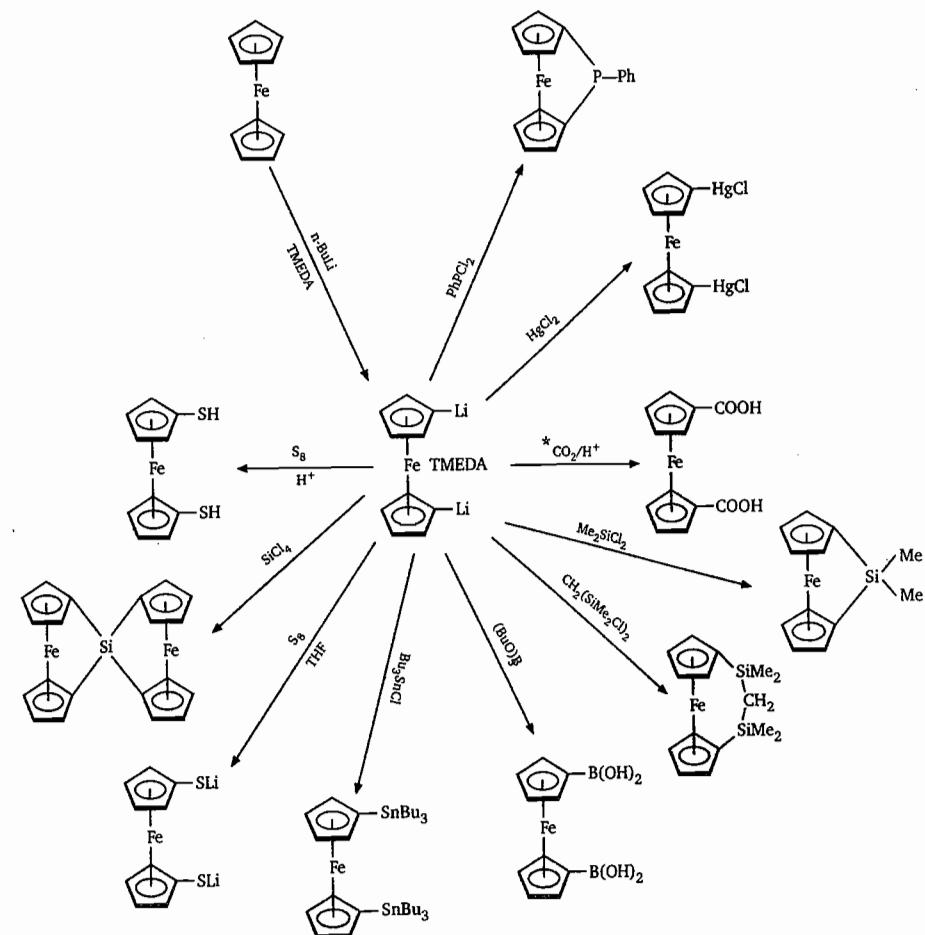
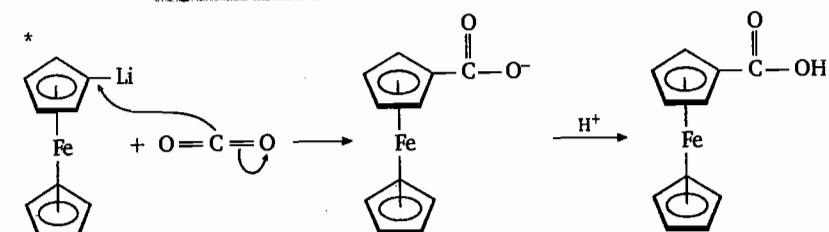
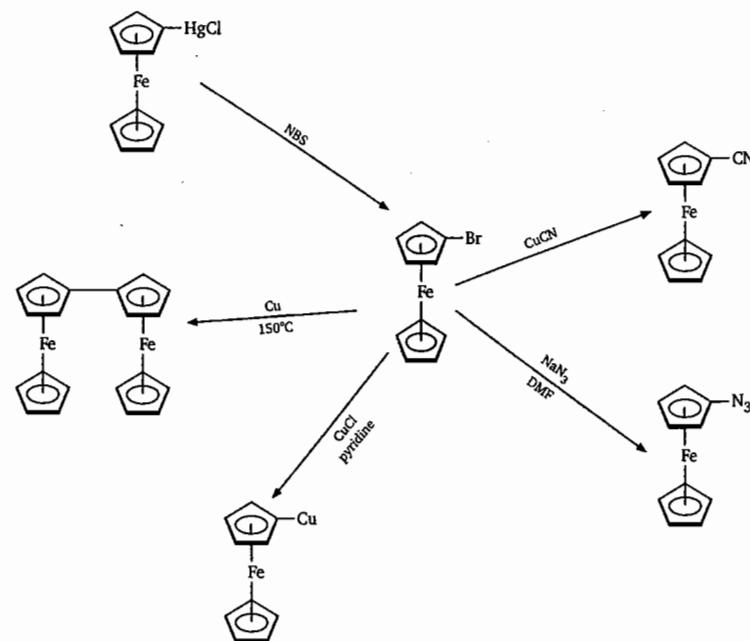


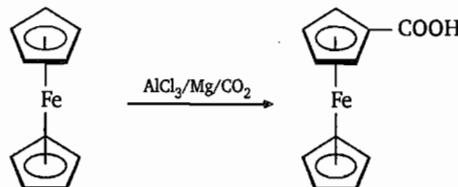
Fig. 6.15 Synthesis and Reaction of 1,1'-dilithio ferrocene





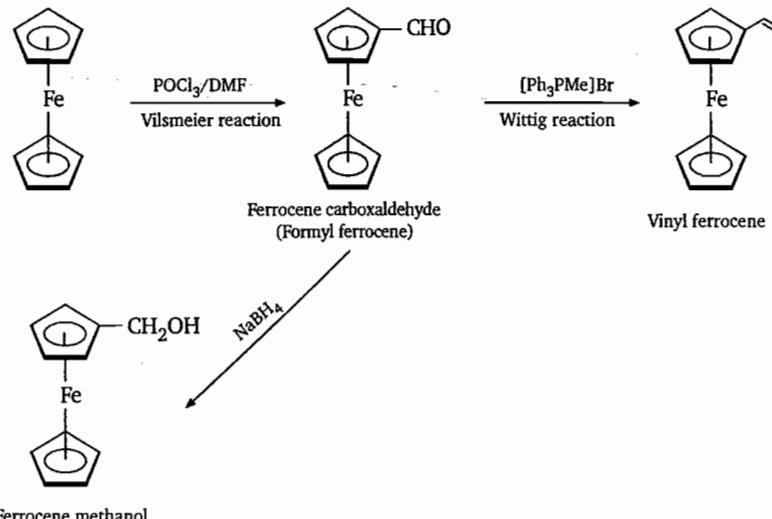
**Fig. 6.16** Synthesis and reactions of bromoferrrocene

### Synthesis of Ferrocene Carboxylic Acid

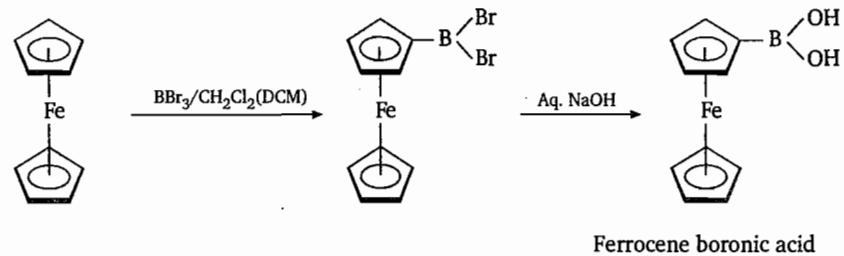


**Vilsmeier Reaction :** Ferrocene reacts with POCl<sub>3</sub> in presence of DMF to give ferrocene carboxaldehyde (Vilsmeier reaction) which on reaction with [Ph<sub>3</sub>MeP]Br gives Vinyl ferrocene (Wittig reaction).

Ferrocene carboxaldehyde on reduction with NaBH<sub>4</sub> gives ferrocene methanol.



### Synthesis of Ferrocene Boronic Acid



Ferrocene boronic acid is also an important precursor for the synthesis of various derivatives of ferrocene (Fig. 6.17).

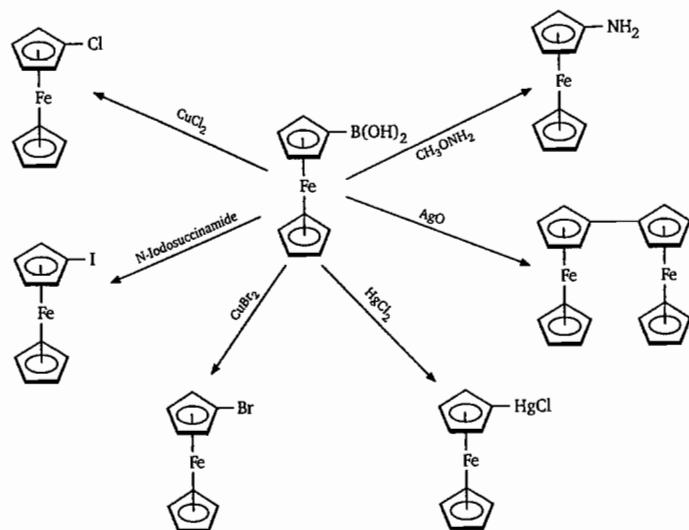
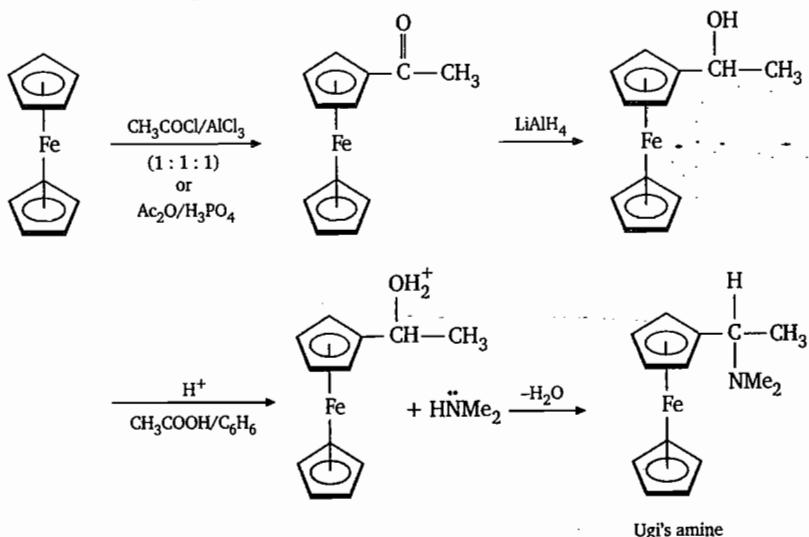


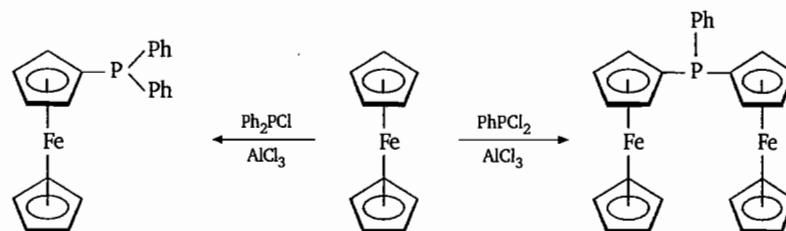
Fig. 6.17

### Synthesis of Ugi's Amine

*N,N*-dimethyl-1-ferrocenyl ethylamine (i.e., Ugi's amine) can be prepared by the following sequence of reactions using acetyl ferrocene as starting precursor.



### Synthesis of Mono- and Diferrocenyl Phenyl Phosphines



### Applications of Ferrocene

Ferrocene and its derivatives have many applications because of the redox properties of the iron and the fact that the Cp rings can be derivatized. Some important applications of ferrocene and its derivatives are :

1. as a liquid hydrocarbon fuel additive. Its addition to diesel fuel reduces smoke emissions and increases fuel economy.
2. as electron transfer catalysts.
3. as biosensor.
4. as UV absorber.

### CHEMISTRY OF OTHER METALLOCENES

Unlike ferrocene, most of the other metallocenes are air sensitive or pyrophoric since they are not 18 electron species.

$\text{Cp}_2\text{Ti}$ , a 14 e complex is a highly reactive and paramagnetic complex with  $e_{2g}^2$  configuration. When two molecules of titanocene are combined together, one C—H bond is broken of each Cp ring and the two hydrogens are oxidatively added to titanium atoms making bridges (Fig 6.18). The two Cp rings are coupled together through C—C  $\sigma$ -bond. This dimer is a dark green solid.

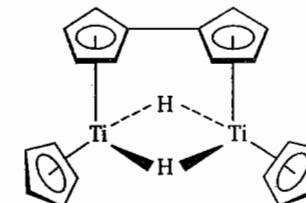
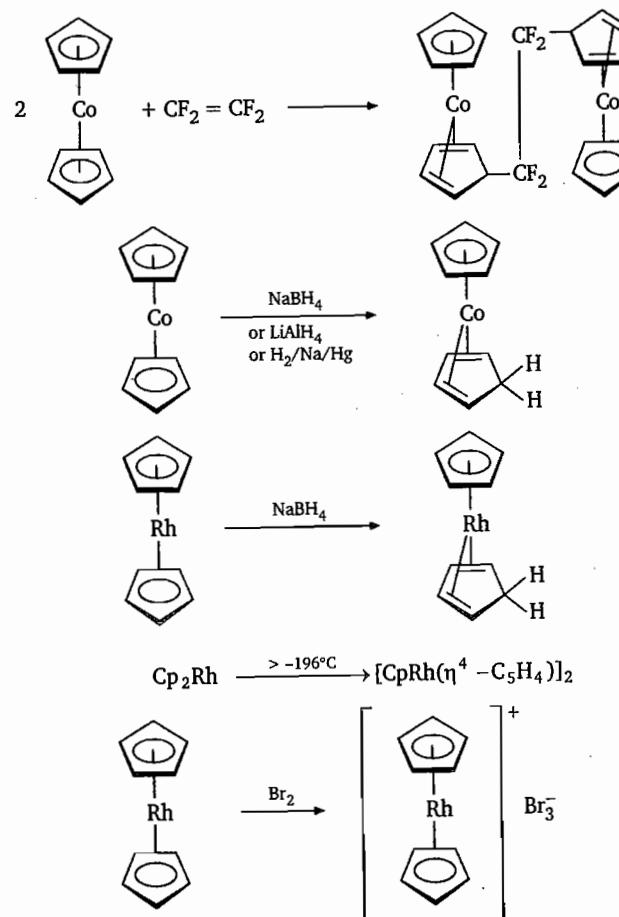


Fig. 6.18

If pentamethylcyclopentadienyl ( $\text{Me}_5\text{C}_5$ ) is used instead of cyclopentadienyl ligand, there will be no C—H cleavage as the ligand has no H-atoms on the ring carbons. It is also more electron rich than Cp and, therefore, forms some what stronger metal-ligand bonds. Due to steric hindrance of  $\text{Cp}^*$ , associative reactions are hindered.

$\text{Cp}_2\text{V}$  is an air sensitive violet solid.  $\text{Cp}_2\text{Cr}$  is an air sensitive red solid.  $\text{Cp}_2\text{Mn}$  is a pyrophoric brown solid. At room temperature  $\text{Cp}_2\text{Mn}$  is a polymeric solid and consists of infinite chains of  $\text{CpMn}$  fragments bridged by cyclopentadienyl rings. At temperature above  $159^\circ\text{C}$  it has orange colour and its structure is similar to ferrocene. It is ionic, high spin  $d^6$  complex and formulated as  $\text{Mn}^{2+} 2\text{Cp}^-$ . In contrast to other metallocenes,  $\text{Cp}_2\text{Mn}$  is hydrolyzed easily and reacts with  $\text{CO}_2$  to give carboxylic acid salt.

$\text{Cp}_2\text{Co}$ ,  $\text{Cp}_2\text{Rh}$ ,  $\text{Cp}_2\text{Ir}$  (19 electron species) and  $\text{Cp}_2\text{Ni}$  (20 electron species) complexes contain electrons in anti-bonding  $e_{1g}^*$  orbitals. Hence, these complexes undergo reactions leading to 18 electron species.



Some important reactions of  $\text{Cp}_2\text{Ni}$  are shown in Fig. 6.19.

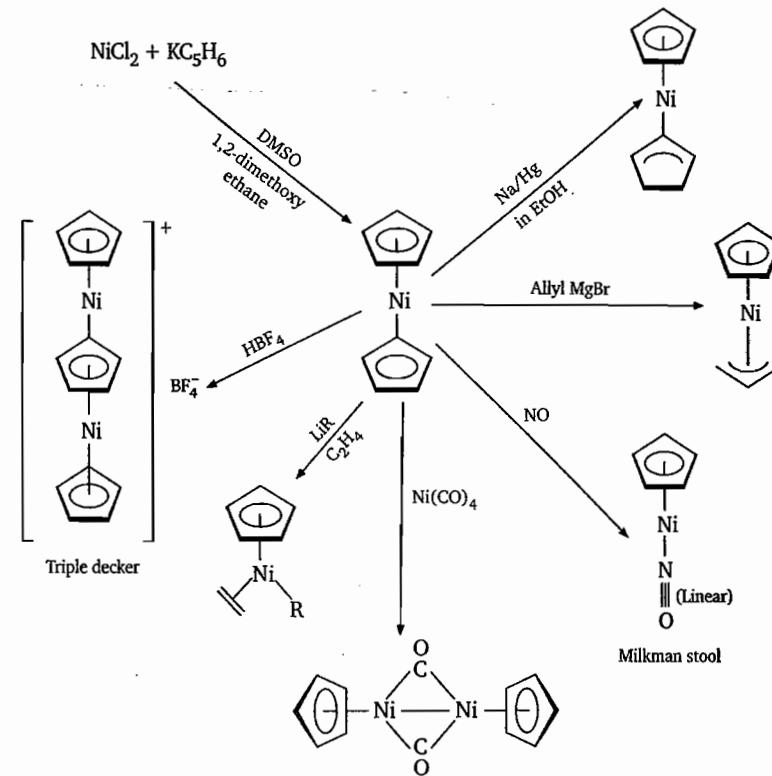
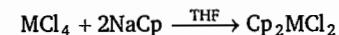


Fig. 6.19. Synthesis and reactions of  $\text{Cp}_2\text{Ni}$

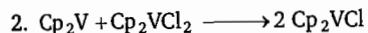
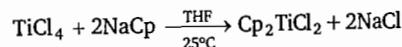
### Bent Sandwich Compounds

Bent sandwich compounds play a major role in the organometallic chemistry of the transition metals of the left side and the middle of the periodic table because in these compounds the steric requirements of the additional ligands prevent the cyclopentadienyl rings from existing in a parallel arrangement. Some of the compounds are used as catalyst for olefin polymerization. The general methods of synthesis of bent sandwich compounds are given below :

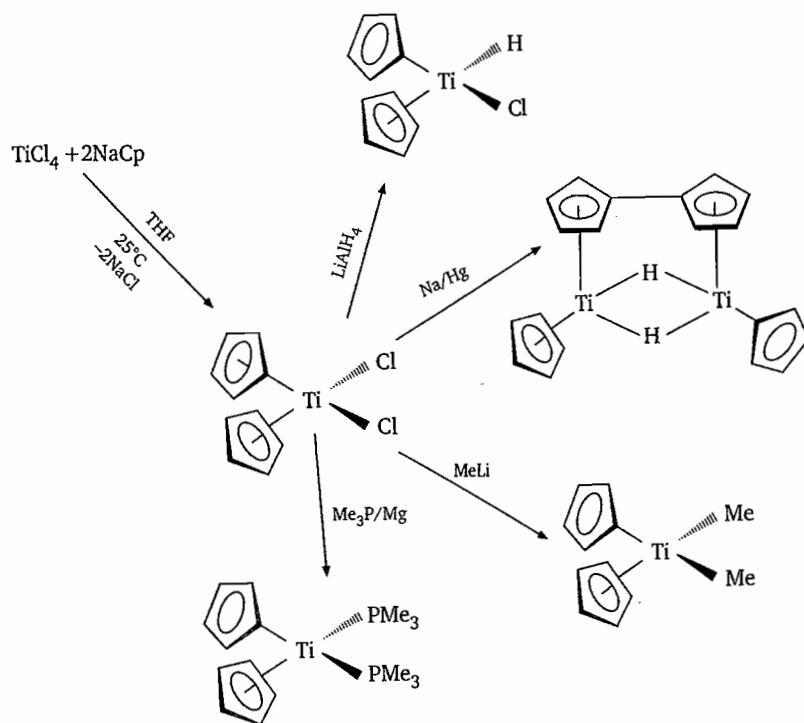
#### 1. By the action of $\text{NaCp}$ on $\text{MCl}_4$ :



where  $\text{M} = \text{Ti, Zr, Hf, V, Nb, Ta, Mo, W, etc.}$



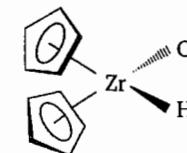
Some important reactions of titanocene dichloride are given in the scheme (Fig. 6.20).



**Fig. 6.20** Reactions and synthesis of  $\text{Cp}_2\text{TiCl}_2$ .

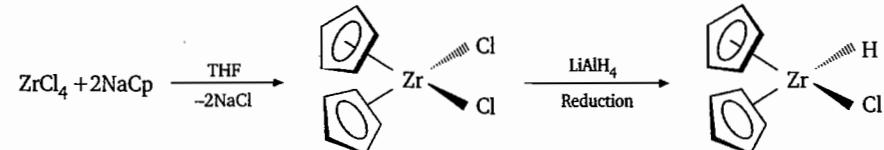
### Schwartz's Reagent

It is also a bent sandwich compound of formula  $\text{Cp}_2\text{Zr}(\text{Cl})(\text{H})$  and it has the structure shown in figure 6.21.

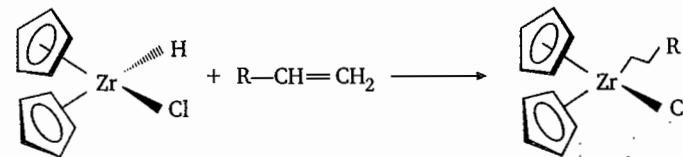
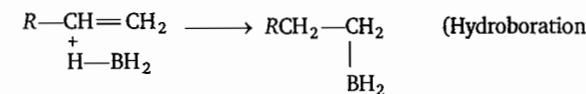


**Fig. 6.21** Structure of Schwartz's reagent

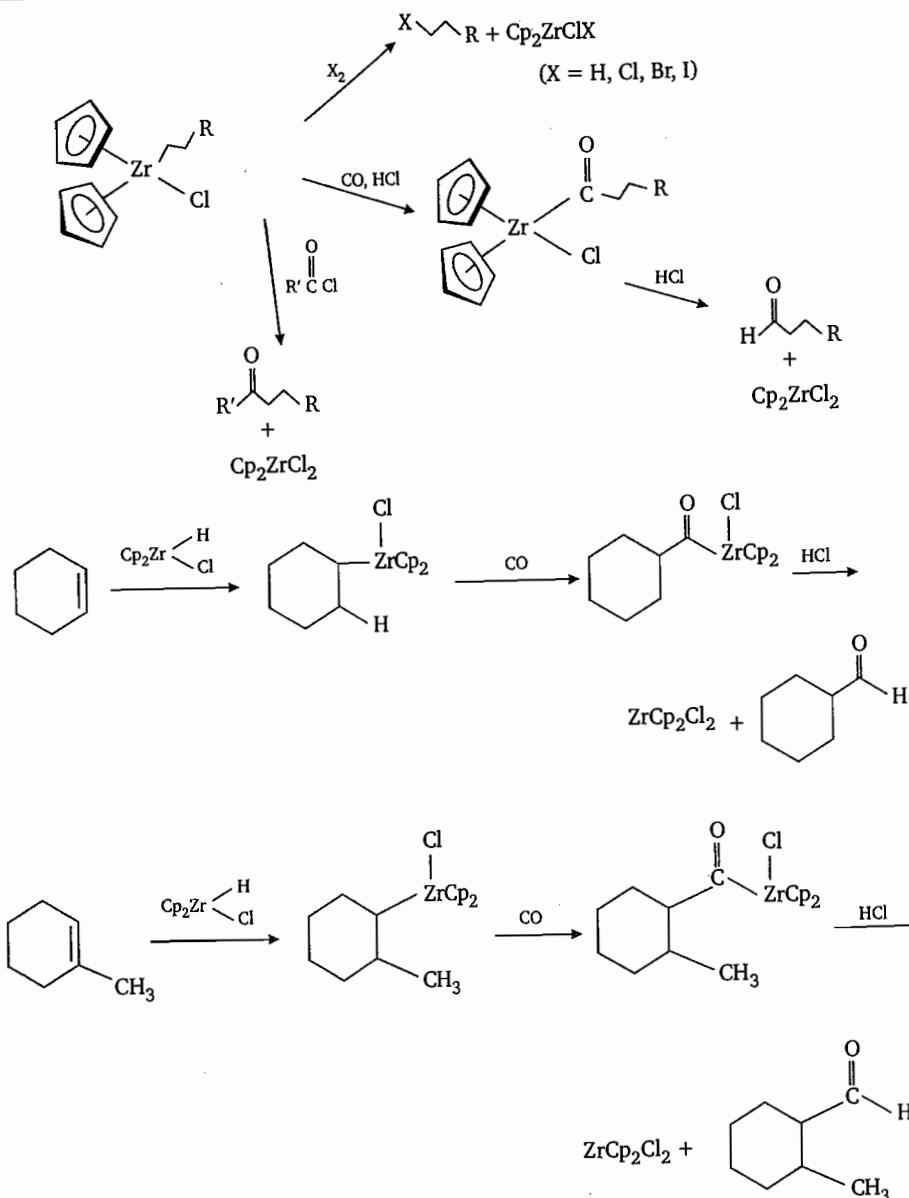
It is prepared by the following reaction :



Schwartz's reagent is an important sandwich compound and used for hydrozirconation reaction similar to hydroboration. This reaction involves the insertion of terminal or internal olefin into Zr—H bond of the reagent.



The reaction is used for synthesis of terminal substituted compounds.



### Arene Complexes

Arenes (benzene and its derivatives such as toluene) usually act as neutral hexahapto ( $\eta^6$ ) six electron donors (Figure 6.22), although tetrahapto ( $\eta^4$ ) and dihapto ( $\eta^2$ ) complexes are also known. In the  $\eta^4$ -complexes, the ring is usually strongly folded whereas in  $\eta^6$ -arene complex, benzene ring remains flat.

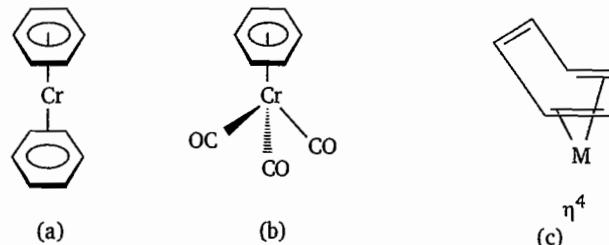


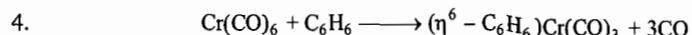
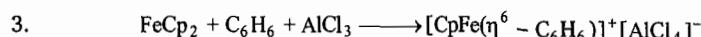
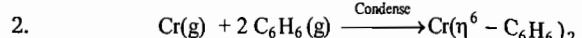
Fig. 6.22. (a)  $Cr(\eta^6 - C_6H_6)_2$ , (b)  $Cr(\eta^6 - C_6H_6)(CO)_3$ , (c)  $\eta^4$ -complex of benzene

### Synthesis of Arene Complexes

#### 1. Fischer-Hafner Synthesis



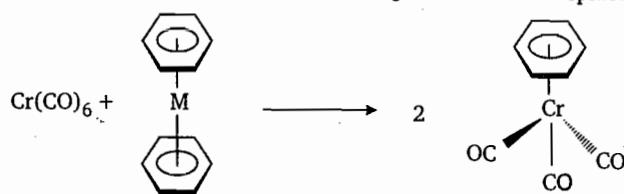
The cation can be reduced to  $Cr(\eta^6 - C_6H_6)_2$  with sodium dithionite in the presence of a base.



Compounds of this type with just one ring system are usually referred as half sandwich compounds.

The rings of the dibenzene complexes of Group 6 metals (Cr, Mo, W) are eclipsed and have a small rotational barrier.

**Properties :** The C—C bond lengths are usually equal but slightly longer than in the free arenes. Arenes are much more reactive than cyclopentadienyl groups and are more easily lost from the metal complex. Therefore, arenes are usually considered to be actor rather than spectator ligands. Unlike, ferrocene these complexes have labile rings which can be displaced.



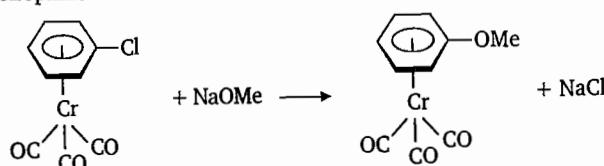
where M = Cr, Mo, W

The benzene rings can be completely displaced by more active ligand

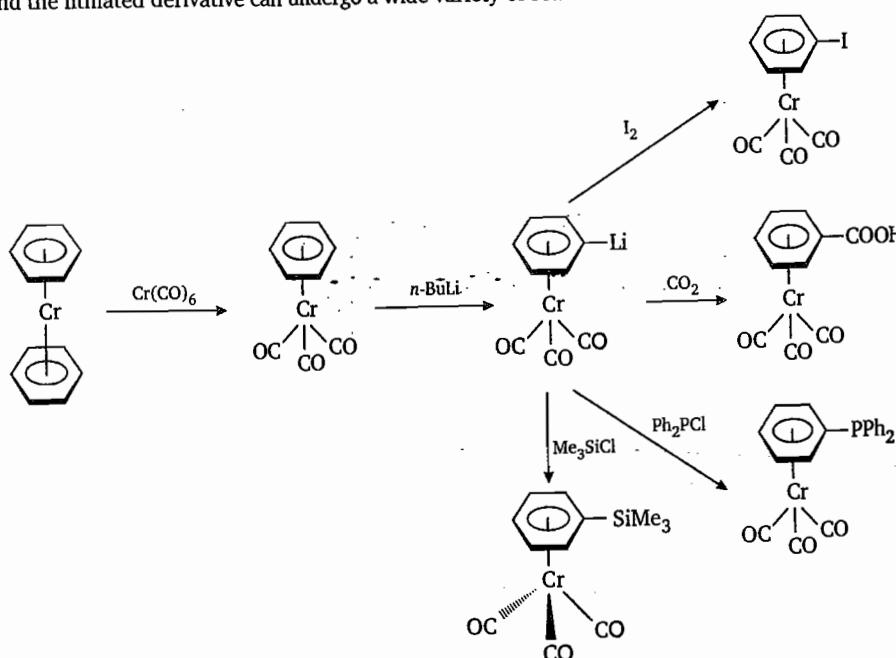


Cr, Mo and W form air sensitive 18 electron complexes,  $\text{M}(\eta^6-\text{C}_6\text{H}_6)_2$ . The Cr complex is readily oxidized to 17e air stable yellow  $[\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2]^+$ . The ease of oxidation precludes  $\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2$  from undergoing electrophilic substitution reactions. The electrophiles oxidize  $\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2$  to  $[\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2]^+$  preventing the further reaction.

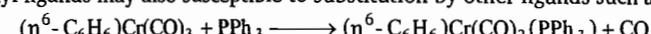
The arene ring in these compounds can be subjected lithiation with  $n\text{-BuLi}$  and is a precursor for other derivatives. The electron withdrawing nature of carbonyl groups from arene ring make it less susceptible to electrophilic attack than the free arene but more susceptible to attack by nucleophiles.



Similar to  $\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2$ , the arene ligand in  $(\eta^6-\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  can be subjected to lithiation and the lithiated derivative can undergo a wide variety of reactions as shown below:



The carbonyl ligands may also susceptible to substitution by other ligands such as:



#### $\eta^4$ -Cyclobutadiene Complexes

Cyclobutadiene does not have  $4n+2\pi$ -electrons, where  $n$  is an integer and, therefore, is anti-aromatic. This free diene is unstable due to its anti-aromatic character and ring strain. Cyclobutadiene can be stabilized by coordination to a low oxidation state metal atom, because the LUMO of free butadiene is populated by back donation. As cyclobutadiene gains two more  $\pi$ -electrons, the diene electronic structure resembles the aromatic six electron dianion  $\text{C}_4\text{H}_4^{2-}$ . Ligand to metal  $\sigma$ -donation prevents the ligand from accumulating excessive negative charge. This is one of the best example of free and bound forms of the ligand being substantially different from one another.

#### Cycloheptatriene Complexes :

Cycloheptatriene [Fig. 6.23 (a)] is a six  $\pi$ -electron donor and it can form complexes similar to those of benzene but differing in the localization of  $\pi$ -electrons in  $\text{C}_7\text{H}_8$ . The cycloheptatriene ligand coordinates to a metal as triene and the ring is folded with  $\text{CH}_2$  group bent away from the metal [Fig. 6.23(b)]

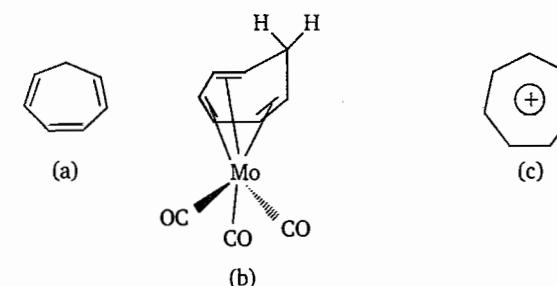
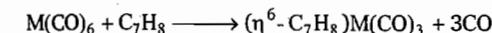
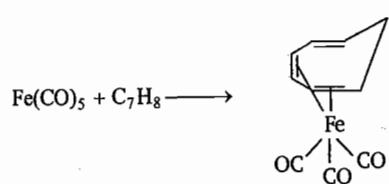


Fig. 6.23 Structure of (a) Cycloheptatriene (b)  $(\eta^6-\text{C}_7\text{H}_8)\text{Mo}(\text{CO})_3$  (c) Tropylium ion.

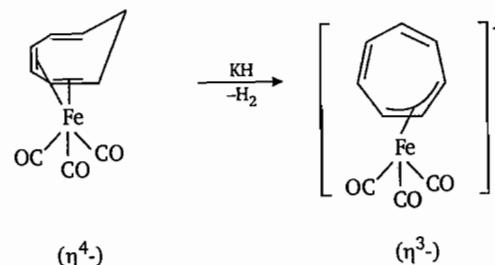
When cycloheptatriene  $\text{C}_7\text{H}_8$  reacts with  $\text{M}(\text{CO})_6$  (where  $\text{M}=\text{Cr}, \text{Mo}, \text{W}$ ), it will replace three CO ligands and add to the metal as a six electron donor via the three  $\pi$ -bonds.



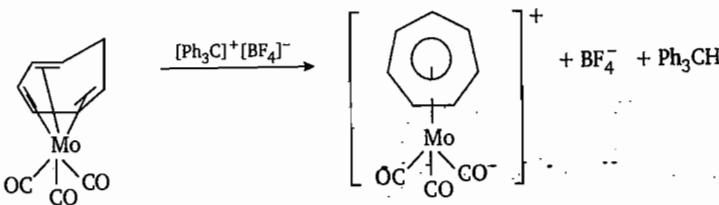
$\text{Fe}(\text{CO})_5$  reacts with cycloheptatriene to give  $(\eta^4-\text{C}_7\text{H}_8)\text{Fe}(\text{CO})_3$  complex, an 18 e and stable species in which cycloheptatriene acts an  $\eta^4$ , four electron donor diene.



Deprotonation of  $(\eta^4\text{-C}_7\text{H}_8)\text{Fe}(\text{CO})_3$  generates a coordinated  $\text{C}_7\text{H}_7^-$  ligand which bonds in an  $\eta^3$ -fashion allowing the metal to retain 18 electron.

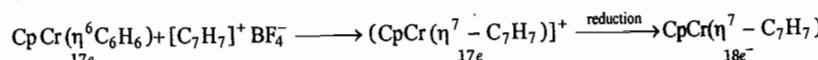


The abstraction of an  $\text{H}^+$  from cycloheptatriene gives the planar cycloheptatrienylum (tropylium) cation  $\text{C}_7\text{H}_7^+$  [Fig. 6.23 (c)] which is aromatic and  $6\pi$ -electron donor. It can coordinate to the metal through all the seven carbon atoms. The aromatic  $\text{C}_7\text{H}_7^+$  is more stable than  $\text{C}_7\text{H}_7^-$  and  $\text{C}_7\text{H}_7^-$  species.



The  $\text{C}_7\text{H}_7^+$  ring is planar with equal C—C bond lengths.

$\text{C}_7\text{H}_7^-$  is considered as  $\text{C}_7\text{H}_7^-$  for electron counting and oxidation state assignments.



Cycloheptatriene ligand may also act in  $\eta^1$ ,  $\eta^3$  and  $\eta^5$  bonding modes.

Some times an  $\text{H}^+$  may be removed from the cycloheptatriene,  $\text{C}_7\text{H}_8$  to give cycloheptatrienyl anion,  $\text{C}_7\text{H}_7^-$  which may then act as an 8 electron donor and coordinates to a metal through all carbon atoms.

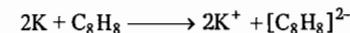


### Cyclooctatetraene Complexes

Cyclooctatetraene (Cot),  $\text{C}_8\text{H}_8$  is non-aromatic and has a tub-shaped conformation.

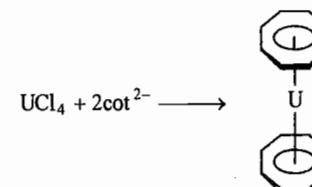


Cyclooctatetraene ligand reacts with an active metal such as K to form the salt  $\text{K}_2\text{cot}$  which contains cyclooctatetraenide anion,  $\text{C}_8\text{H}_8^{2-}$



The cot dianion is aromatic and planar and has  $10\pi$  electrons in eight  $\pi$ -orbitals. The cot dianion reacts with tetrapositive ions such as  $\text{U}^{4+}$ ,  $\text{Np}^{4+}$ ,  $\text{Th}^{4+}$  to form a neutral metallocene.

For example,

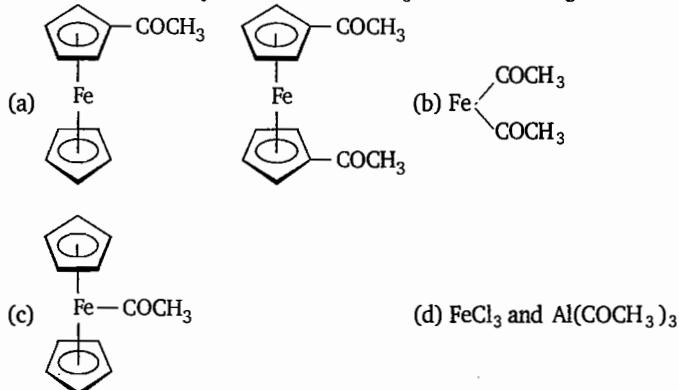


In these complexes the  $\text{cot}^{2-}$  rings are planar. The early transition metals such Ti, Zr, Hf can also form complexes with  $\text{cot}^{2-}$  but in these complexes the ring can be planar or puckered. Cot ligand can also act as an  $\eta^2$ ,  $\eta^4$  or  $\eta^6$ -species. In the case of  $\eta^2$ ,  $\eta^4$  and  $\eta^6$ -complexes the ring is puckered rather than planar.



## Objective Questions

1. The reaction of acetyl chloride and  $\text{AlCl}_3$  with ferrocene gives :



2. Oxidation occurs very easily in case of :

- |  |  |
|--|--|
| (a) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]$ | (b) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]$   |
| (c) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}]$ | (d) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}^+]$ |

3. The reaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CH}_3)(\text{CO})_2]$  with  $\text{PPh}_3$  results in :

- |  |  |
|--|--|
| (a) $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CH}_3)(\text{CO})(\text{PPh}_3)] + \text{CO}$ |  |
| (b) $[(\eta^1\text{-C}_5\text{H}_5)\text{Fe}(\text{CH}_3)(\text{CO})_2(\text{PPh}_3)]$           |  |
| (c) $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{COCH}_3)(\text{CO})(\text{PPh}_3)]$           |  |
| (d) $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{COCH}_3)(\text{PPh}_3)] + \text{CO}$          |  |

4. The stable cyclopentadienyl complex of beryllium is :

- |   |   |
|---|---|
| (a) $[\text{Be}(\eta^5\text{-C}_5\text{H}_5)_2]$                            | (b) $[\text{Be}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_5\text{H}_5)]$ |
| (c) $[\text{Be}(\eta^1\text{-C}_5\text{H}_5)(\eta^3\text{-C}_5\text{H}_5)]$ | (d) $[\text{Be}(\eta^1\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)]$ |

5. A compound A having the composition  $\text{FeC}_9\text{H}_8\text{O}_3$  shows one signal at 2.5 ppm and another one around 5.0 ppm in its  $^1\text{H}$  NMR spectrum. The IR spectrum of this compound shows, two bands around 1900 and  $1680\text{ cm}^{-1}$ . The compound follows the 18 electron rule. Of the following statements for A, the correct one is/are :

- |                                     |                                 |
|-------------------------------------|---------------------------------|
| (A) It has $\eta^5\text{-Cp}$ group | (B) It has a terminal CO ligand |
| (C) It has a $\text{CH}_3$ ligand   | (D) It has Fe—H bond            |
| (a) (A) and (B) only                | (b) (C) only                    |
| (c) (A) and (C) only                | (d) (B) and (D) only            |

6. The oxidation state of iron in  $[\text{Fe}(\eta^5\text{-Cp})_2][\text{BF}_4^-]$  is :

- |        |        |
|--------|--------|
| (a) +1 | (b) +2 |
| (c) +3 | (d) +4 |

7. The complexes  $\text{V}(\text{C}_6\text{O}_6)_2$  and  $\text{Cr}(\text{C}_6\text{O}_6)_2$  are both readily oxidized in air to their respective cations. The number of unpaired electrons, respectively, in each are :

- |         |         |
|---------|---------|
| (a) 0,0 | (b) 1,0 |
| (c) 0,1 | (d) 1,1 |

8. The reaction of allyl bromide and  $\text{NaCpFe}(\text{CO})_2$  gives a compound with the molecular formula  $(\text{C}_3\text{H}_5)\text{CpFe}(\text{CO})_2$ . The hapticity and number of electrons donated by the allyl group (according to the ionic method) respectively are :

- |                  |                   |
|------------------|-------------------|
| (a) one and two  | (b) three and two |
| (c) two and four | (d) four and four |

9. The substitution of  $\eta^5\text{-Cp}$  group with nitric oxide is easiest for :

- |                                     |                                       |
|-------------------------------------|---------------------------------------|
| (a) $(\eta^5\text{-Cp})_2\text{Fe}$ | (b) $(\eta^5\text{-Cp})_2\text{CoCl}$ |
| (c) $(\eta^5\text{-Cp})_2\text{Ni}$ | (d) $(\eta^5\text{-Cp})_2\text{Co}$   |

10. The ligand/ligands that is/are fluxional in the complex  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_5)(\text{CO})_2]$  is/are :

- |  |  |
|--|--|
| (a) $\eta^5\text{-C}_5\text{H}_5$        | (b) $\eta^1\text{-C}_5\text{H}_5$        |
| (c) $\eta^1\text{-C}_5\text{H}_5$ and CO | (d) $\eta^5\text{-C}_5\text{H}_5$ and CO |

11. The bonding of cyclopentadienyl in  $\text{Ti}(\text{Cp})_4$  is such that :

- |   |  |
|---|--|
| (a) all Cp rings are pentahapto                                       |  |
| (b) one Cp ring is pentahapto and the other three rings are monohapto |  |
| (c) two Cp rings are monohapto and the other two rings are pentahapto |  |
| (d) all Cp rings are monohapto  |  |

12. Though cyclobutadiene ( $\text{C}_4\text{H}_4$ ) is highly unstable and readily polymerizes in its free state, its transition metal complexes could be isolated because :

- |  |  |
|--|--|
| (a) it engages in long-range interaction with transition metals  |  |
| (b) it gains stability due to formation of $\text{C}_4\text{H}_4^{2-}$ on binding to transition metals |  |
| (c) its polymerization ability reduces in presence of transition metal                                 |  |
| (d) it becomes stable in presence of transition metals due to formation of $\text{C}_4\text{H}_4^{2+}$ |  |

13. The sandwich complex  $\eta\text{-CpCoC}_n\text{H}_n$  is an 18 electron species, when 'n' is :

- |       |       |
|-------|-------|
| (a) 6 | (b) 4 |
| (c) 3 | (d) 5 |

14. The correct order of energy level of d-orbitals in ferrocene is :

- |  |  |
|--|--|
| (a) $d_{x^2-y^2}, d_{xy} < d_{z^2} < d_{xy}, d_{yz}$ | (b) $d_{z^2} < d_{xz}, d_{yz} < d_{x^2-y^2}, d_{xy}$ |
| (c) $d_{x^2-y^2}, d_{xy} < d_{xz}, d_{yz} < d_{z^2}$ | (d) $d_{yz}, d_{xz} < d_{x^2-y^2}, d_{xy} < d_{z^2}$ |

15. The correct formulation for tetra(cyclopentadienyl) titanium(IV) complex is :  
 (a)  $[\text{Ti}(\eta^5-\text{C}_5\text{H}_5)_4]$       (b)  $[\text{Ti}(\eta^1-\text{C}_5\text{H}_5)_4]$   
 (c)  $[\text{Ti}(\eta^5-\text{C}_5\text{H}_5)(\eta^1-\text{C}_5\text{H}_5)_3]$       (d)  $[\text{Ti}(\eta^5-\text{C}_5\text{H}_5)_2(\eta^1-\text{C}_5\text{H}_5)_2]$
16. Which one of the following statements about the ferrocene is False ?  
 (a) It obeys the 18-electron rule      (b) It is diamagnetic  
 (c) It is an orange solid      (d) It resists electrophilic substitution
17. The product(s) of the reaction of  $[\text{Fe}(\eta^5-\text{C}_5\text{H}_5)(\text{CH}_3)(\text{CO})_2]$  and  $\text{PPh}_3$  is/are :  
 (a)  $[\text{Fe}(\eta^5-\text{C}_5\text{H}_5)(\text{CH}_3)(\text{CO})_2(\text{PPh}_3)]$   
 (b)  $[\text{Fe}(\eta^5-\text{C}_5\text{H}_5)(\text{COCH}_3)(\text{CO})(\text{PPh}_3)]$   
 (c)  $[\text{Fe}(\eta^5-\text{C}_5\text{H}_5)(\text{CH}_3)(\text{CO})(\text{PPh}_3)] + \text{CO}$   
 (d)  $[\text{Fe}(\eta^5-\text{C}_5\text{H}_4\text{CH}_3)(\text{H})(\text{CO})(\text{PPh}_3)] + \text{CO}$



## Subjective Questions

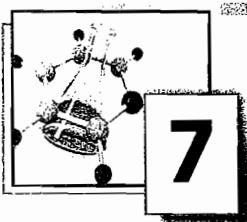
- Discuss the bonding and structure of ferrocene. How ferrocene reacts with :  
 (i) 2 moles of  $\text{CH}_3\text{COCl}$  in presence of  $\text{AlCl}_3$ .  
 (ii)  $\text{CH}_3\text{Br}$  in presence of  $\text{AlCl}_3$ .  
 (iii) Acetic anhydride in presence of  $\text{H}_3\text{PO}_4$ .
- Cyclopentadienyl ring in the ferrocene have aromatic character but cyclopentadiene itself has no such character. Explain.
- When  $\text{FeCp}_2$  is oxidized to  $\text{FeCp}^+$ , what will be the effect on the Fe—C bond length ?
- Which of the following compound would be more stable ?  
 (a)  $\text{Rh}(\eta^5-\text{C}_5\text{H}_5)_2$  or  $\text{Ru}(\eta^5-\text{C}_5\text{H}_5)$   
 (b)
- The compound  $\text{Ni}(\eta^5-\text{C}_5\text{H}_5)_2$  react with strong acid to give  $[\text{Ni}(\eta^5-\text{C}_5\text{H}_5)(\eta^4-\text{C}_5\text{H}_6)]^+$  whereas  $\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2$  reacts with strong acid to give  $[\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2\text{H}]^+$ . Give the explanation for the different sites of protonation of  $\text{Ni}(\eta^5-\text{C}_5\text{H}_5)_2$  and  $\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2$ . Also write the structures of the products.
- Write the products of the following reactions. More than one products may be possible.
  - $2\text{Na} + 2\text{C}_2\text{H}_5 \xrightarrow{\text{THF}}$
  - $2\text{Na}[\text{C}_5\text{H}_5] + \text{MnCl}_2 \xrightarrow{\text{THF}}$
  - $\text{Ni}[\eta^5-\text{C}_5\text{H}_5] + \text{NO} \longrightarrow$
  - $\text{Ni}[\eta^5-\text{C}_5\text{H}_5] + \text{Ni}(\text{CO})_4 \longrightarrow$
  - $\text{Ni}[\eta^5-\text{C}_5\text{H}_5] + \text{Na} / \text{Hg} \xrightarrow{\text{EtOH}}$
  - $\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2 + \text{CH}_3\text{COCl}(1 \text{ mol}) \xrightarrow{\text{AlCl}_3}$
  - $\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2 + \text{CH}_3\text{COCl}(2 \text{ moles}) \xrightarrow{\text{AlCl}_3}$
  - $\text{Cr}(\text{Co})_6 + \text{C}_6\text{H}_6 \longrightarrow$
- The compound  $\text{W}(\eta^5-\text{C}_5\text{H}_5)(\text{H})(\text{CO})_3$  reacts with  $\text{C}_3\text{H}_6$  to give three products A, B and C. Identify and draw the structure of compounds A, B and C. Each compound obey the 18-electron rule.

## ANSWERS

- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (a)  | 2. (b)  | 3. (a)  | 4. (d)  | 5. (a)  | 6. (c)  | 7. (b)  |
| 8. (a)  | 9. (c)  | 10. (b) | 11. (c) | 12. (b) | 13. (b) | 14. (a) |
| 15. (d) | 16. (d) | 17. (c) |         |         |         |         |

8. The compound  $\text{Ni}_3(\eta^5-\text{C}_5\text{H}_5)_3(\text{CO})_2$  shows a single CO stretching absorption band in IR spectrum at  $1761 \text{ cm}^{-1}$ . This compound has  $D_{3h}$  point group. Draw the structure of this compound. Does this compound obey 18-electron rule.
9. (a) Give two reactions of ferrocene which show it is more reactive than benzene.  
 (b) Explain why direct nitration of ferrocene is not possible? How can you get nitroderivative of ferrocene?

□□□



## Catalysis

### Catalysis

A thermodynamically favourable reactions may be slow at modest temperatures and, therefore, are not of much value for synthesis. The rate of reaction can be accelerated by increasing temperature but it requires high energy and, therefore, it is very expensive. Higher temperatures may also induce competing side reactions that will cause the reduction in yield of the required product. The rate of reaction of such thermodynamically favourable reactions can be accelerated using a catalyst. A catalyst is a substance that increases the rate of a thermodynamically allowed reaction by lowering the activation energy of barrier for the process without itself being consumed. A catalyst does not affect the Gibbs free energy of the overall reaction because  $G$  is a state function. The reaction which are not thermodynamically favourable can not be made favourable using catalyst. A catalyst is used in substoichiometric amount to bring about a reaction at a temperature below that required for uncatalyzed thermal reaction. If several reaction paths are possible, a catalyst may increase product specificity by lowering activation energy for desired path or by raising it for another.

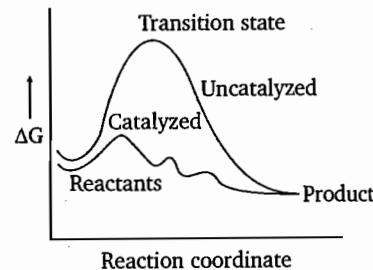
A catalyst combines with the reactants or substrates to form transition state which finally produces the reaction products and regenerates the catalyst.

The catalyst further enters the catalytic cycle and combines the reactants again and again. A typical catalyst may participate in a catalytic cycle  $10^1 - 10^6$  times or more.

Catalysts are classified into two categories—homogeneous and heterogeneous. The homogeneous catalysts are soluble in reaction mixture whereas the heterogeneous catalysts are insoluble. Homogeneous catalysts function at low temperatures and pressures and usually give good selectivity (for the product) but the great disadvantage of the homogeneous catalyst is that they are difficult to separate from the product because they mix with the products. If a stable product is formed with the catalyst, then it would be the final product and the catalytic cycle will stop and hence it is really become difficult to separate from the product. On the other hand, heterogeneous catalysts require

relatively higher temperatures and pressures and frequently lead to a mixture of products but its great advantage is that they are easily separated from the reaction products.

For most transition metal catalysts, the catalyzed pathway is completely changed from the pathway of the uncatalyzed reaction. (Figure 7.1)



**Fig. 7.1**

The free energy profile of an uncatalyzed reaction contains a high energy transition state whereas the catalyzed reaction contains multi-steps with no high peaks and no deep depressions.

If a catalyzed pathway is passed through an energy minimum lower than the energy of products, there will be an energy sink and a different products other than the desired will obtained.

Many transition metal organometallic compounds are important catalysts in organic synthesis, both in the industrial and the laboratory processes. Organometallic catalyst are usually homogeneous catalysts.

**Table 7.1 : Comparison of Homogeneous and Heterogeneous Catalysts**

S. No.	Homogeneous Catalysts	Heterogeneous Catalysts
1.	Soluble in the reaction mixture	Insoluble in the reaction mixture.
2.	Requires low temperature (< 250°C)	Requires high temperature
3.	More product selective	Less product selective.
4.	Reaction mechanism is well understood	Reaction mechanism is not well understood.
5.	Product separation is not easy	Product separation is easy.
6.	Expensive	Economic
7.	Catalyst separation is difficult	Catalyst separation is easy (by filtration)

### Catalytic Cycles

A catalysed reaction occurs in cycles called as catalytic cycles where the active form of the catalyst gets regenerated. A catalytic cycle consists of a series of stoichiometric reactions (often reversible) that form a closed loop. Turn over (TO) describes one loop through catalytic cycle. The slow step in a catalytic cycle is called the turnover limiting step. Usually one equivalent of a reactant is converted into one equivalent of product per equivalent of catalyst. The number of passes or **turn** through the catalytic cycle before the catalyst becomes deactivated is called the turnover number. Turnover number can also be defined as number of moles of a reactant converted by one mole of catalyst or number of moles of product formed per mole of catalyst. Turnover number (TON) can be calculated as:

$$\text{TON} = \frac{\text{Moles of reactant}}{\text{Moles of catalyst}} \times \% \text{ yield of product (in decimal)}$$

Higher the value of TON, longer will be the life of the catalyst.

The turnover number per unit time is called as turnover frequency (TOF) i.e., number of moles of product per mole of the catalyst per unit time is called the turn over frequency.

$$\text{TOF} = \frac{\text{Moles of reactant}}{\text{Time} \times \text{Moles of catalyst}} \times \% \text{ yield of product}$$

$$\text{or} \quad \text{TOF} = \frac{\text{TON}}{\text{Time}} \quad \text{Unit of TOF is time}^{-1}$$

### Application of Organometallic Compounds as Homogeneous Catalysts

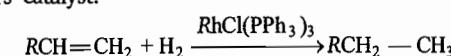
#### 1. Hydrogenation of Alkenes using Wilkinson's Catalyst

The reaction of hydrogen gas with alkenes is thermodynamically allowed but it does not take place at room temperature and pressure.

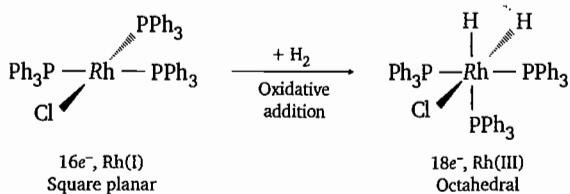


Several heterogeneous catalysts such as Ni, Cu, Pd, Pt are known to bring about hydrogenation of alkenes, alkynes and other unsaturated compounds fast and complete. The heterogeneous catalysts may be deposited on an inert solid support such as alumina.

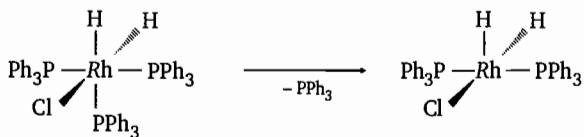
One of the most studied and first effective homogeneous catalyst, active at room temperature and atmospheric pressure is the Rh (I) (16-electron  $d^8$ )-square planar complex  $\text{RhCl}(\text{PPh}_3)_3$  which is known as Wilkinson's catalyst.



The dominant cycle (Figure 7.2) for hydrogenation of an alkene by Wilkinson's catalyst involves the oxidative addition of  $\text{H}_2$  to the 16-electron Rh (I) complex  $\text{RhCl}(\text{PPh}_3)_3$  to give an 18-electron Rh (III) dihydrido complex.

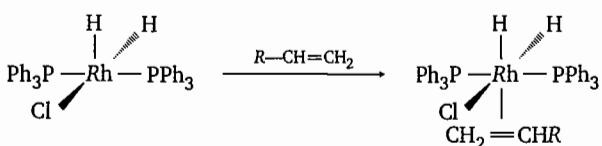


The NMR studies show that addition of alkene occurs by dissociative mechanism. The hydride ion ( $\text{H}^-$ ) has *high trans* effect and labilizes the  $\text{PPPh}_3$  ligand *trans* to  $\text{H}^-$  ligand. Therefore, a  $\text{PPPh}_3$  ligand *trans* to  $\text{H}^-$  ligand is dissociated to give a coordinatively unsaturated complex.

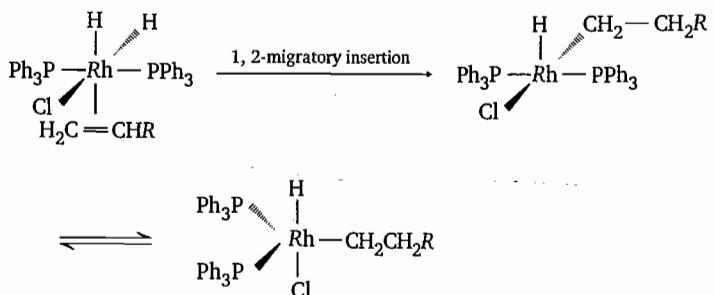


It is also possible to dissociate  $\text{Cl}^-$  which is also *trans* to  $\text{H}^-$  ligand and has much less *trans* effect but the larger size of  $\text{PPPh}_3$  (*i.e.*, more steric hindrance) ligand seems to be one factor that enhances its dissociation, and this provides more space for incoming large size alkene ligand.

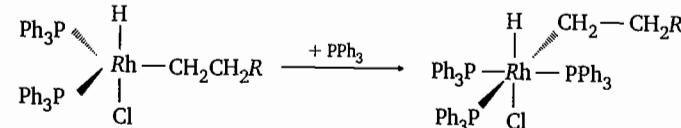
The coordinatively unsaturated complex interacts with alkene to form alkene complex.



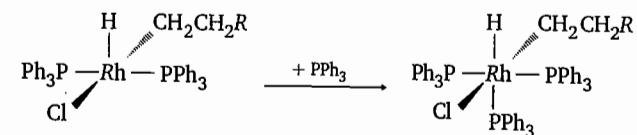
Hydrogen transfer from the rhodium atom into the coordinated alkene (1,2-migratory insertion) gives a transient 16-electron alkyl complex.



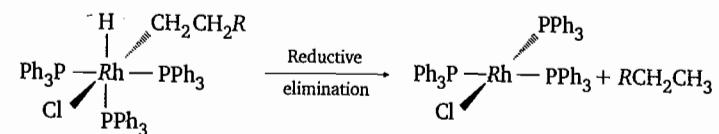
This alkyl complex takes on a phosphine ligand to produce an octahedral complex.



OR

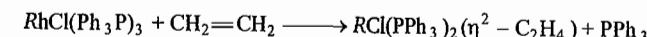


Now the hydrogen migrates to the carbon which results in the reductive elimination of alkane and formation of  $\text{RhCl}(\text{PPPh}_3)_3$ .



The catalyst reenters the catalytic cycle.

Among the alkenes, neither the smallest alkene,  $\text{CH}_2=\text{CH}_2$  nor very sterically crowded or hindered alkenes are hydrogenated. This is due to the reason that ethylene forms a very stable rhodium ethylene complex which does not undergo oxidative addition with  $\text{H}_2$  while the sterically hindered alkenes are blocked from coordination by the bulky ligands such as triphenylphosphine. If the alkene has several double bonds, only the least hindered of these is hydrogenated. Ethylene occupies the vacant coordination site created when  $\text{PPPh}_3$  dissociates from Wilkinson's catalyst and, therefore, serves as an inhibitor to hydrogenation.



A Catalytic reaction can be represented by a closed loop, called as Tolman catalytic loop (Figure 7.2.). The catalytic cycle involves the continuous cycle of various catalytic species and reactants and products entering and leaving the loop at appropriate places.

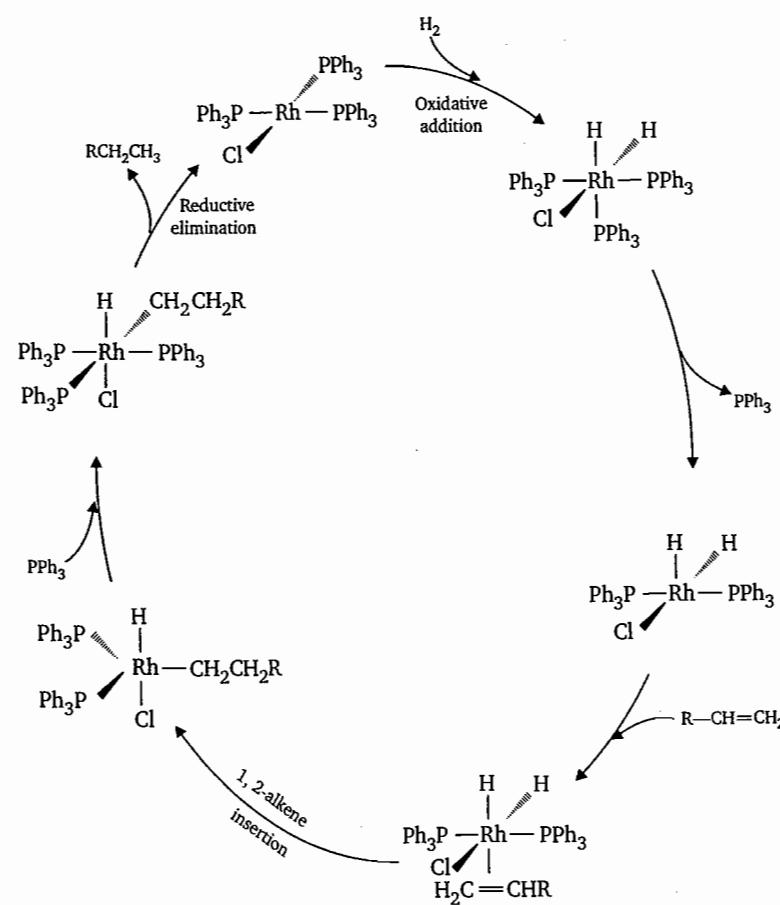
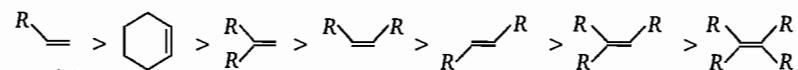


Fig. 7.2

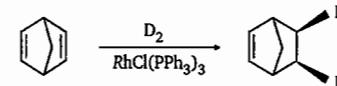
Salient features of Wilkinson's catalysts are given below:

1. Rate of hydrogenation of terminal alkynes is greater than that of terminal alkenes.
2. Rate of hydrogenation of conjugated dienes is slower than that of isolated alkenes.
3. Rate of hydrogenation of internal and branched alkenes and alkynes is slower than that of terminal ones.
4. Steric hindrance decreases the rate of hydrogenation i.e., more number of alkyl groups on alkene, slower will be the rate of hydrogenation.
5. Rate of hydrogenation of *cis*-alkenes is greater than that of *trans*-alkenes.
6. The alkenes having polar groups are hydrogenated more rapidly than those having no such groups because the polar functional groups helps the coordination of alkenes to the catalyst.

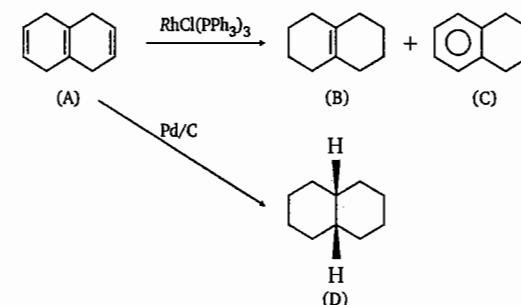
Rate of substituted alkenes follow the order:



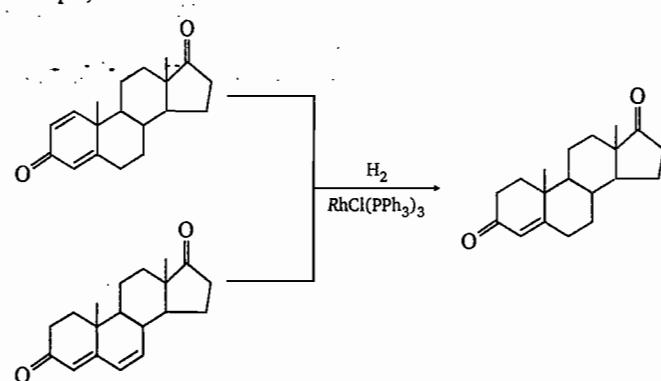
In certain cases the hydrogen gives *syn* addition to the alkene. For example,



Wilkinson Catalyst reduces the triene (A) mainly to the octalin (B) and isomerises to less extent to give tetralin (C). On the other hand, heterogeneous catalysts give none of these products but only the fully saturated decalin (D).



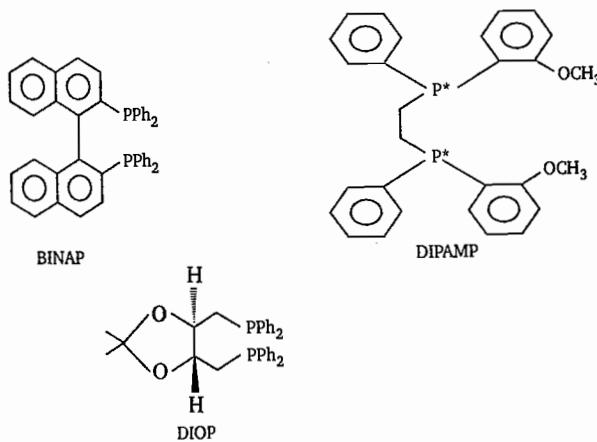
If a compound contains two or more double bonds, the least hindered double bonds are reduced. Therefore, Wilkinson catalyst is selective for hydrogenation of  $\text{C}=\text{C}$  bonds that are not sterically hindered. For example,



The functional groups such as  $-\text{CN}$ ,  $-\text{NO}_2$ ,  $-\text{COOR}$ ,  $-\text{CONH}_2$  and  $-\text{COOH}$  are not reduced by Wilkinson catalyst, though they can be reduced by heterogeneous catalysts. The  $\text{C}=\text{O}$  and  $\text{C}=\text{N}$  bonds of ketones and imines are easily reduced by Wilkinson Catalyst.

### Asymmetric Hydrogenation

When chiral chelating phosphine ligands are used in place of triphenylphosphine in the Wilkinson catalyst, the catalyst can be used to synthesize optically active compounds (asymmetric hydrogenation) such as pharmaceuticals. Some examples of chiral phosphines are (Fig. 7.3) :



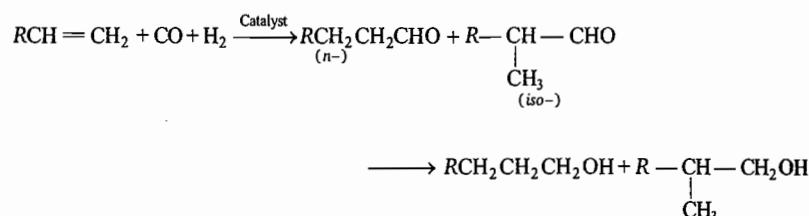
**Fig. 7.3 Chiral diphosphine ligands used in asymmetric hydrogenation**

If hydrogenation of an alkene leads to enantiomeric products, then the alkene is prochiral which means that it must have a structure that leads to R or S chirality when complexed to the metal. The prochiral chiral alkene becomes chiral upon coordination to the catalyst that already contains a chiral phosphine ligand and two diastereomeric complexes are produced. In favourable cases the desirable one of these is hydrogenated more rapidly to give the biologically active form of pharmaceuticals. This is due to the reason that the diastereomers, in general, have different stabilities and labilities. Therefore, one of the R or S enantiomers is formed. This makes the hydrogenation enantioselective.

If the catalyst is achiral,  $\text{RhCl}(\text{PPh}_3)_3$ , then the product of hydrogenation of the prochiral alkene is racemic mixture.

### Hydroformylation or Oxo Process

This reaction was discovered by Otto Roelen in 1938. The reaction of an alkene with CO and  $\text{H}_2$  catalyzed by cobalt or rhodium carbonyl complexes to form aldehyde containing one carbon atom more than the original alkene is called hydroformylation.



Aldehydes produced by hydroformylation are usually reduced to alcohols that are used as solvents plasticizers and in the synthesis of detergents. The term hydroformylation is used because of the addition of formaldehyde to the alkene.

The most widely accepted mechanism for the catalytic cycle for cobalt based catalyst  $\text{Co}_2(\text{CO})_8$  was proposed by Heck and Breslow in 1961 (Figure 7.4). In this catalytic cycle, the actual catalyst is 16-electron, four coordinate  $\text{Co}^1$  complex,  $\text{HCo}(\text{CO})_3$ . This species is not readily available, instead catalytic precursor  $\text{Co}_2(\text{CO})_8$  is introduced that form  $\text{HCo}(\text{CO})_3$  under reaction conditions.

For this catalytic cycle,  $\text{Co}_2(\text{CO})_8$  and  $\text{H}_2$  are introduced which react to give  $\text{HCo}(\text{CO})_4$  (an 18 electron species) which then losses a CO to give  $\text{HCo}(\text{CO})_3$  (a 16 electron species) and creates a vacant coordination site required for alkene. The alkene coordinates to this vacant site to form an 18-electron complex which undergoes migratory insertion of the olefin into the C-H bond and therefore, another 16-electron complex having vacant coordination site is formed. A CO ligand is then coordinated to the vacant site to form  $\text{RCH}_2\text{CH}_2\text{Co}(\text{CO})_4$  complex. Now insertion of a CO ligand of  $\text{RCH}_2\text{CH}_2\text{Co}(\text{CO})_4$  occurs into the alkyl-cobalt bond to give the acyl-cobalt complex

$\text{O}$   
 $\text{RCH}_2\text{CH}_2\text{C}=\text{Co}(\text{CO})_3$ .

The reactant  $\text{H}_2$  is added oxidatively to the coordinatively unsaturated cobalt-acyl complex to give a  $\text{Co}(\text{III})$  complex which finally undergoes reductive elimination of product,  $\text{RCH}_2\text{CH}_2\text{CHO}$  and regenerates the active catalyst  $\text{HCo}(\text{CO})_3$ .

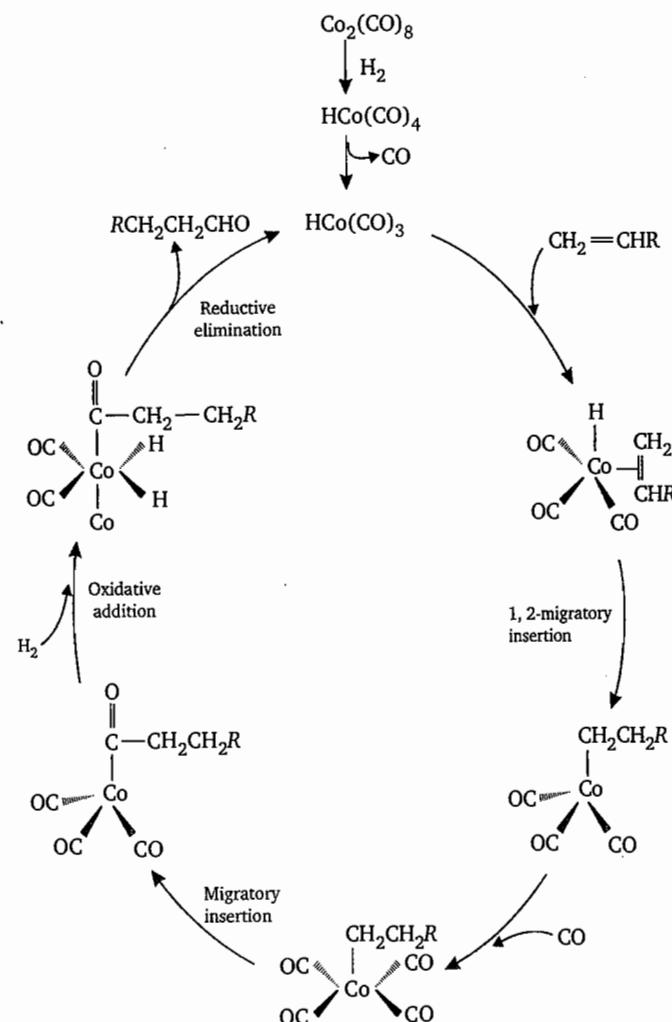


Fig. 7.4

The cobalt carbonyl complex catalyst has some disadvantages:

1. It operates at high temperature ( $140 - 175^\circ\text{C}$ ) and high pressure ( $200 - 250 \text{ atm.}$ ).
2. Straight chain ( $n -$ ) as well as branched chain ( $iso -$ ) aldehydes are formed. The  $n : iso$  ratio is found to be  $3 : 1$  which is not a good ratio. The  $n : iso$  ratio should be high because straight chain aldehydes are more biodegradable than the branch ones.

If the catalyst  $\text{HCo}(\text{CO})_4$  is modified by replacing one  $\text{CO}$  by  $\text{PBu}_3$  ( $\text{Bu} = n - \text{butyl}$ ) to give  $\text{HCo}(\text{CO})_3(\text{PBu}_3)$ , the selectivity of the catalyst increases to give high  $n : iso$  ratio ( $9 : 1$ ), but this catalyst reduces the rate of reaction. Therefore, this catalyst operates at higher temperature ( $175^\circ\text{C}$ ) and higher pressure ( $50 - 100 \text{ atm.}$ ). If more highly phosphine substituted rhodium complex  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  or  $\text{HRh}(\text{CO})(\text{PR}_3)_3$ , which is highly reactive and more selective, is used, the  $n : iso$  ratio ( $16 : 1$ ) is increased. This catalyst operates at lower temperature ( $90 - 120^\circ\text{C}$ ) and lower pressure ( $50 - 100 \text{ atm.}$ ). The proposed catalytic cycle of hydroformylation using  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  catalyst is shown in Figure 7.5.

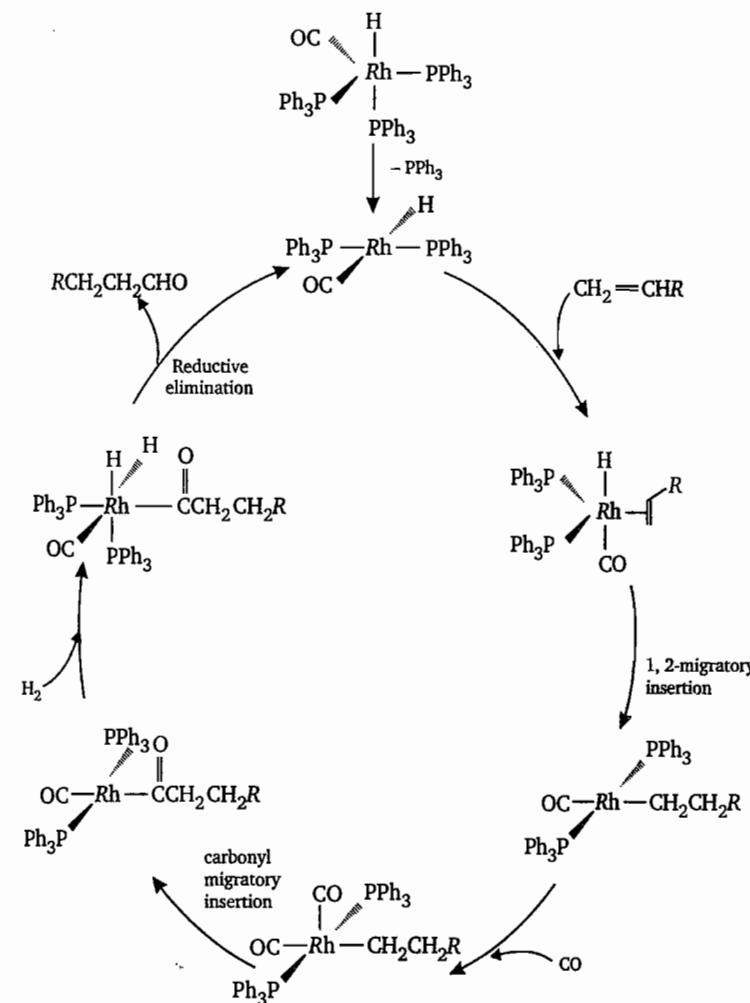
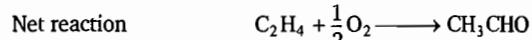
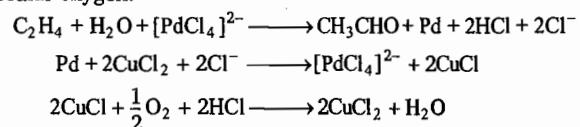


Fig. 7.5

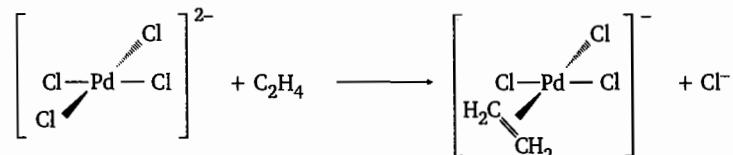
### Wacker Process

This process was developed by Wacker in 1950. The addition of molecular oxygen to alkene in the presence of catalyst  $[PdCl_4]^{2-}$  is called the Wacker process. This process is primarily used to produce acetaldehyde from ethene and molecular oxygen in aqueous solution using  $[PdCl_4]^{2-}$  as catalyst and  $CuCl_2$  as cocatalyst which reoxidizes Pd(0) back to Pd(II). The CuCl produced is reoxidized by molecular oxygen.

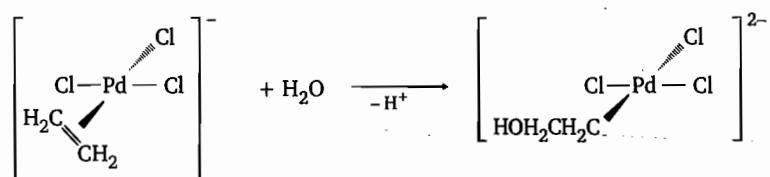


The reaction proceeds through the following mechanism:

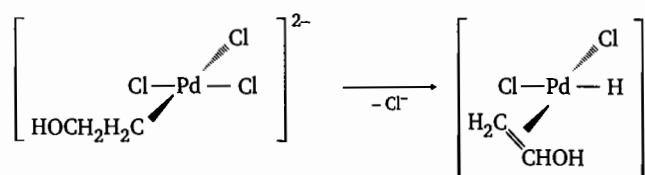
$C_2H_4$  forms metal ethene  $\pi$  complex with  $[PdCl_4]^{2-}$  replacing one  $Cl^-$  from  $[PdCl_4]^{2-}$



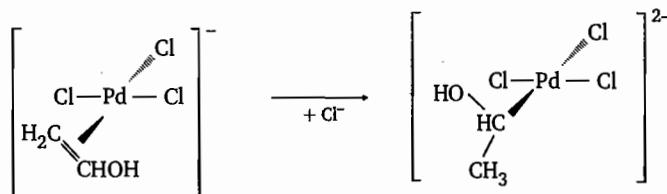
It may be possible to occur coordination of water molecule to the metal which loses a proton  $H^+$  resulting in an  $OH^-$  group bound to the metal followed by a migratory insertion of the  $OH^-$  group on the alkene. But this step involves the nucleophilic attack of  $H_2O$  with loss of  $H^+$  from the solution on the coordinated ethene to form a  $\sigma$ -bonded  $CH_2CH_2OH$  group rather than an insertion reaction involving an  $OH^-$  group.



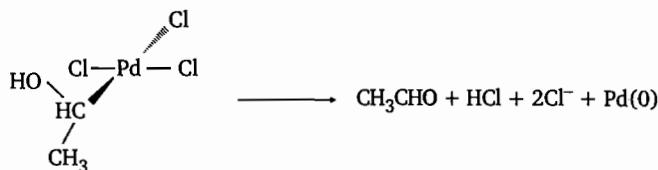
The next step involves the  $\beta$ -hydrogen elimination with the formation of Pd-H bond and loss of one  $Cl^-$  ligand. As a result  $\beta$ -hydroxyl ethyl  $\sigma$  complex converts into a vinyl alcohol  $\pi$ -complex.



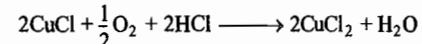
Then migratory insertion results in the formation of  $\sigma$  bonded  $CH(OH)CH_3$  group.



In the last step elimination of  $CH_3CHO$ ,  $H^+$  and  $Cl^-$  with the reduction of Pd(II) to Pd(0) occurs.



The catalyst  $[PdCl_4]^{2-}$  can be recovered by the reaction with  $CuCl_2$ . The cuprous chloride formed is reoxidized back to  $CuCl_2$  by oxygen.



The catalytic cycle for Wacker process is shown in Fig. 7.6.

The Wacker process is not widely used because other processes are more effective.

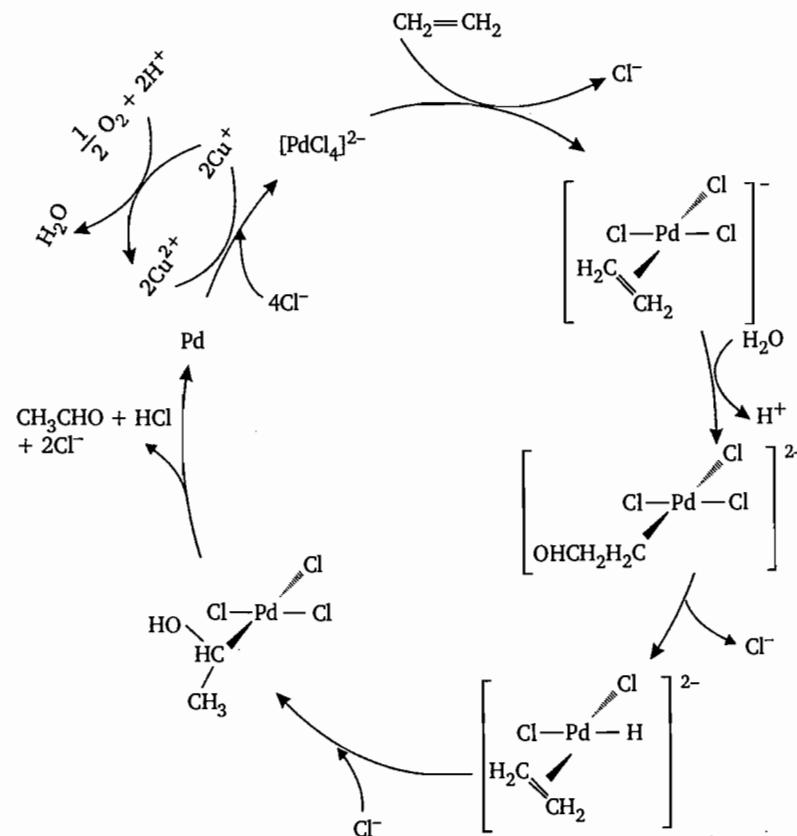
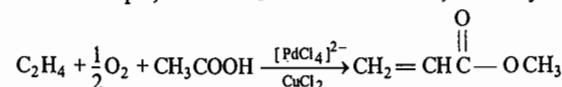


Fig. 7.6

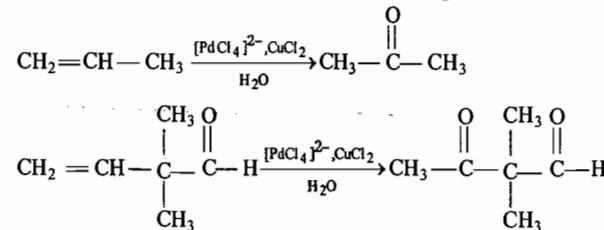
$[\text{PtCl}_4]^{2-}$  can also be used in Wacker process because alkene ligands coordinated to Pt(II) are also susceptible to nucleophilic attack. But only  $[\text{PdCl}_4]^{2-}$  is used in the catalytic system because 4d series Pd(II) complexes are more labile than 5d series Pt(II) complexes. Furthermore, the standard reduction potential of Pd(II) to Pd(0) is more favourable than for the corresponding Pt(II)/Pt(0) couple.

If the solvent other than water is used, the final step does not occur and the complex dissociates to give the vinyl product. For example, if acetic acid is used as solvent, then vinyl acetates is formed.



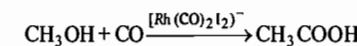
If an alcohol is used as solvent vinyl alkyl ethers are formed.

If substituted alkene is used, ketone is formed as the product.

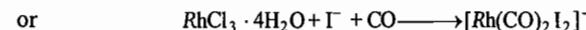
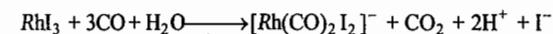


### Monsanto Acetic Acid Process

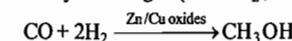
Acetic acid is a major organic compound that is manufactured in enormous quantities. One of the most important processes for the production of glacial acetic acid is the Monsanto process. This process involves the reaction of methanol with CO in the presence of  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  catalyst to form acetic acid.



The reaction of methanol with CO is also called as carbonylation. The catalyst  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  is obtained by the reaction of  $\text{RhI}_3$  with CO in aqueous solution.



Methanol is prepared from synthesis gas ( $\text{CO} + \text{H}_2$ ) in the presence of Zn/Cu oxides.



The catalytic cycle for Monsanto process is shown in Figure 7.7.

Methanol has almost 100% selectivity for  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  catalyst. This catalyst is 16-electron and the 4-coordinate complex and, therefore, it is coordinatively unsaturated. The formal oxidation state of Rh is +1. The first step is the rate determining step and is the oxidative addition of iodomethane to the four coordinate (coordinatively unsaturated), 16-electron complex  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  to give six coordinate, 18-electron complex  $[(\text{H}_3\text{C})\text{RhI}_3(\text{CO})_2]^-$ . This step is followed by CO migratory insertion resulting in a 16-electron acyl complex which gains CO ligand to form an 18-electron complex  $[\text{RhI}_3(\text{CO})_3(\text{COCH}_3)]^-$ . This complex undergoes reductive elimination of acetyl iodide  $\text{CH}_3\text{COI}$  with the regeneration of catalyst  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ . The acetyl iodide is then hydrolyzed by water to give acetic acid and HI.



Methyliodide is regenerated by the reaction of methanol with HI.



This reaction is feasible because of the soft-soft interaction of  $\text{CH}_3$  and I and hard-hard interaction of  $\text{H}^+$  and  $\text{OH}^-$  that leads to the formation of water.

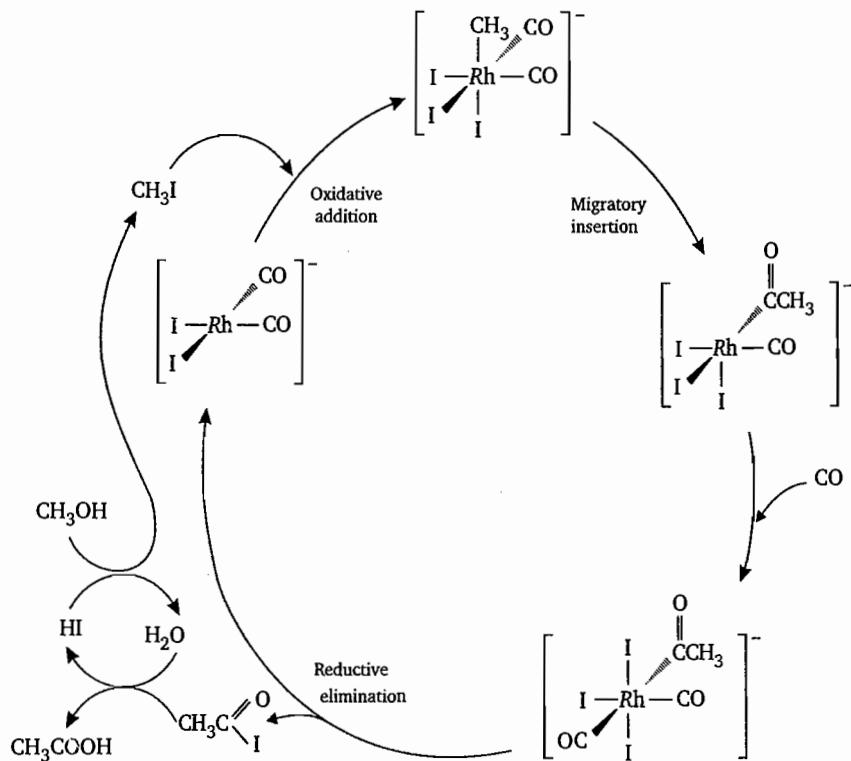


Fig. 7.7

Although cobalt and iridium complexes can also be used as catalyst and chloride and bromide ligands can also be incorporated but best results are obtained when  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  catalyst is used because the soft ligand  $\text{I}^-$  ion combines strongly with metal Rh(I). Therefore, oxidative addition of  $\text{CH}_3\text{I}$  (soft  $\text{CH}_3$  and soft  $\text{I}^-$ ) becomes easy.

### Cativa Process

In 1996, British Petroleum (BP) chemicals has produced a new method for manufacture of acetic acid which is called as cativa process. This process involves iridium catalyst  $[\text{IrI}_2(\text{CO})_2]^-$  instead of rhodium catalyst  $[\text{RhI}_2(\text{CO})_2]^-$ . The mechanism of the cativa process is similar to that of the Monsanto process (Figure. 7.8) but this process involves metal promoters such as  $\text{InI}_3$  and  $[\text{RuI}_2(\text{CO})_3]_2$ .

The first step involves the oxidative addition of  $\text{CH}_3\text{I}$  to  $[\text{IrI}_2(\text{CO})_2]^-$  catalyst to form 18-electron Ir(III) octahedral complex  $[\text{CH}_3\text{IrI}_3(\text{CO})_2]^-$ . In the next step an iodide ligand is transferred from  $[\text{CH}_3\text{IrI}_3(\text{CO})_2]^-$  to the promoter which creates a vacant site on catalyst so that the third CO ligand coordinates to the catalyst to form an octahedral complex. It has been observed that the migratory insertion of CO occurs much more rapidly in the neutral complex than in the anionic precursor. Now an iodide ligand is transferred back to the iridium followed by reductive elimination of acetyl iodide with the regeneration of catalyst  $[\text{IrI}_2(\text{CO})_2]^-$ . The catalytic cycle for cativa process is shown in Fig. 7.8.

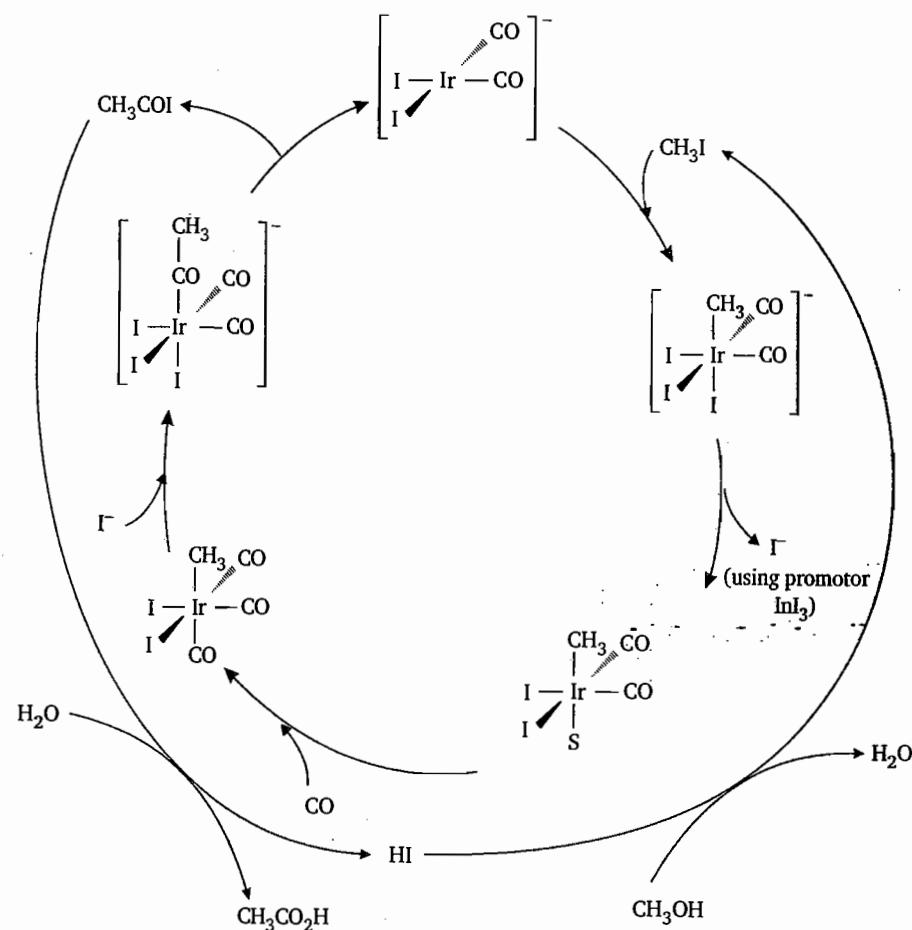


Fig. 7.8: Catalytic cycle for cativa process

The acetyl iodide is then hydrolyzed by water to give acetic acid and HI.



The starting material methanol is converted to methyl iodide (used in first step) by the reaction of HI.

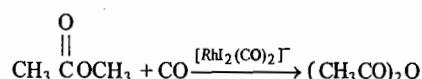


Salient features of cativa process are given below:

- The first step (oxidative addition) in the cativa process is much more faster (about 150 times) than that of monsanto process.
- In this process the rate determining step is the migratory insertion of CO rather than the oxidative addition as in Monsanto process.
- This process operates at lower water concentrations and produces less biproducts. Therefore, high purity acetic acid is formed more cheaply than in the Monsanto process.
- Iridium catalyst is more selective for methanol, and its cost is much less than that of rhodium.
- The promoter facilitates the removal of iodide ion from the catalyst in the second step and, therefore, reduces standing concentration of iodide ion. This is a slow step as compared to the oxidative addition. The promoter enhances the rate of slower step of the catalytic cycle.

### Tennessee Eastman Acetic Anhydride Process

The Tennessee Eastman acetic anhydride process converts methyl acetate to acetic anhydride using  $[\text{RhI}_2(\text{CO})_2]^-$  complex as catalyst.



The steps involved in this process are similar to those for the production of acetic acid by the Monsanto process. This process involves the replacement of : methanol by methylacetate, water by acetic acid, (as water can not be present in the synthesis of acetic anhydride) acetic acid by acetic anhydride and HI by LiI. LiI reacts with methyl acetate to give methyl iodide and lithium acetate.



Acetyl iodide is formed in the same manner as described in the Monsanto process of acetic acid. Acetyl iodide reacts with lithium acetate to give final product, acetic anhydride.



The catalytic cycle for Tennessee Eastman process is shown in Figure 7.9.

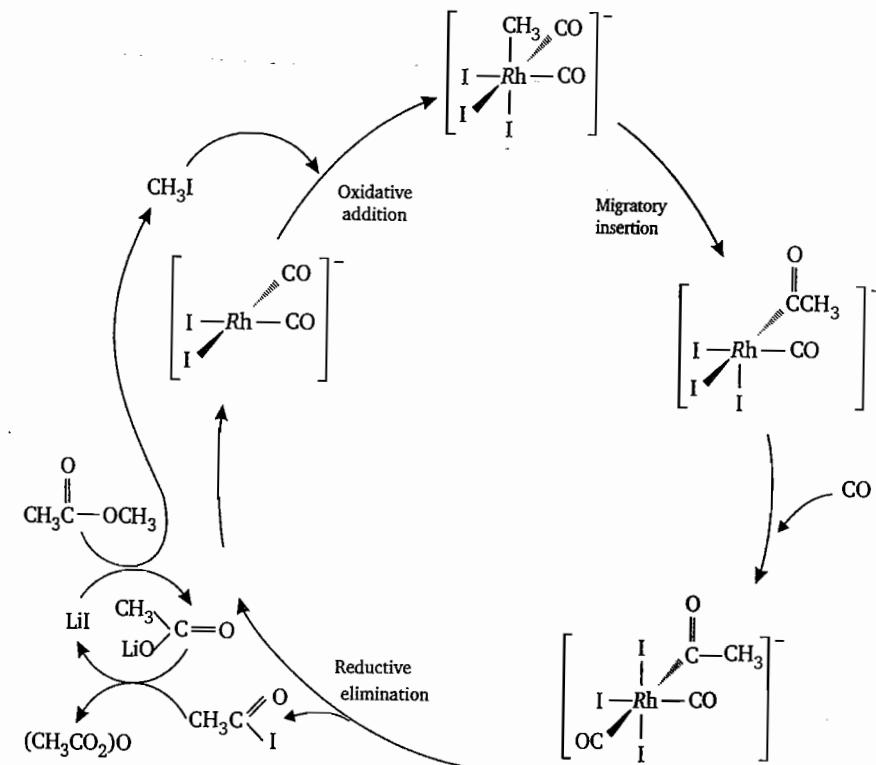
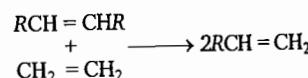
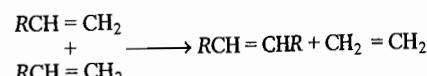
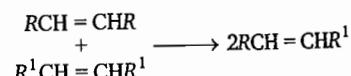


Fig. 7.9

Other alkali metal iodides do not function as well as LiI. For example, if LiI is replaced by NaI, the rate of reaction slows by a factor of  $\approx 2.5$ .

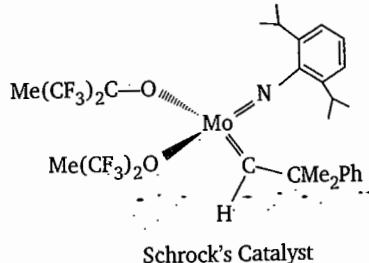
## Alkene (Olefin) Metathesis

Alkene metathesis is a reaction in which the strongest bond in the alkene (the C=C double bond) is broken during the reaction and then rearranged in a statistical fashion in the presence of certain transition metal compounds, mainly the carbenes, as catalysts.

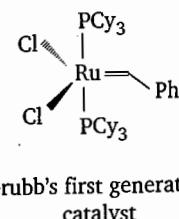


In these reactions one carbon of the double bond of one alkene along with all the groups or substituents on it exchanges with one carbon of the double bond of another alkene along with all the groups or substituents attached to it.

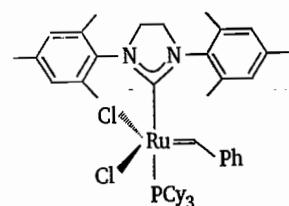
The catalysts which are used in alkene metathesis are mainly Schrock's catalyst (developed by Schrock) and Grubbs' catalyst (developed by Grubbs).



Schrock's Catalyst



Grubbs's first generation catalyst

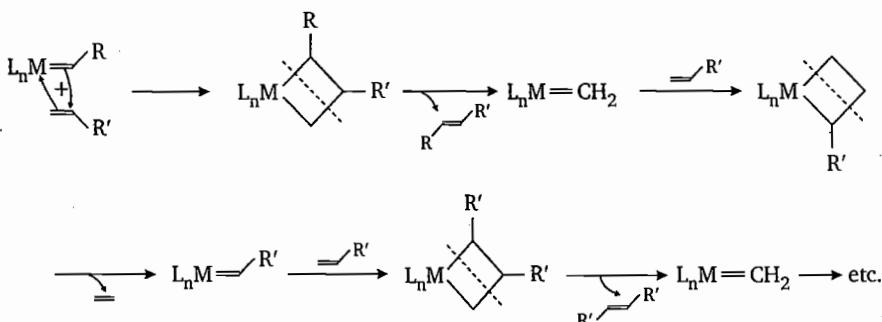


Grubbs's second generation catalyst

Schrock's and Grubbs's catalysts are homogeneous catalysts.

In Grubbs' catalyst, tricyclohexylphosphine (Pcy) is preferred over PR<sub>3</sub> ligand because its steric hindrance and strongly electron donating properties lead to enhanced catalytic activity. The Grubbs's second generation have higher catalytic activity in alkene metathesis reactions and are tolerant of a large range of functional groups, they, therefore, have widespread applications.

Herisson and Chauvin suggested the most appropriate mechanism for alkene metathesis reactions. The mechanism involves formation of metallacyclobutane from an initial carbene catalyst with an incoming alkene and C—C bond cleavage in a different way (along the dotted line as shown in Scheme 7.1) to generate the new alkene and a new carbene which acts as a chain carrier. If this process is repeated several number of times, an equilibrium mixture of alkenes is obtained. If the groups on the acyclic alkene are different, one metal carbene will be favoured over the other and only one alkene product will be obtained.



Scheme 7.1

With the initial alkylidene catalyst precursor, the consumption of the initial complex together with the appearance of chain carrying alkylidene species and metallacycles has been demonstrated by NMR spectroscopy.

Various types of alkene metathesis reactions depending on the nature of the substrates and products in catalytic reaction are given below :

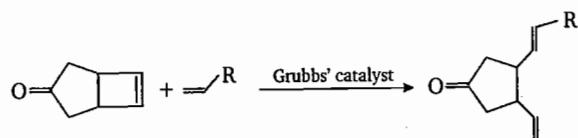
**1. Simple Metathesis :** The metathesis reaction which involves only one type of substrate is called the simple metathesis.



**2. Cross Metathesis :** The metathesis reaction which involves the two different substrates is called the cross metathesis.

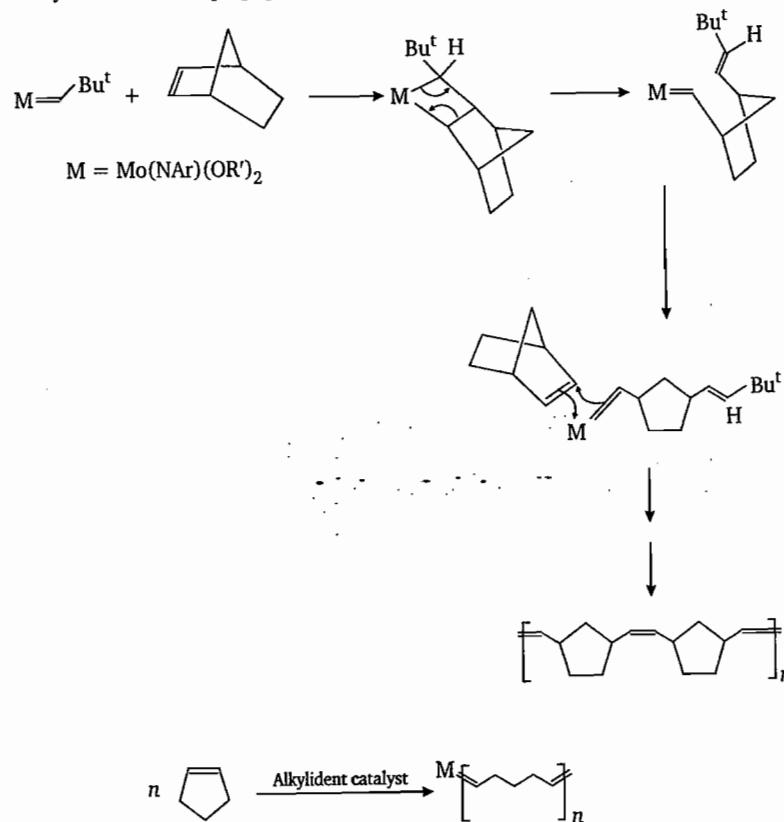


**3. Ring Opening Metathesis (ROM) :** The cyclic alkenes which have strained rings often undergo ring opening metathesis in the presence of another alkene and the catalyst. The strain in the ring causes the opening of ring. for example,

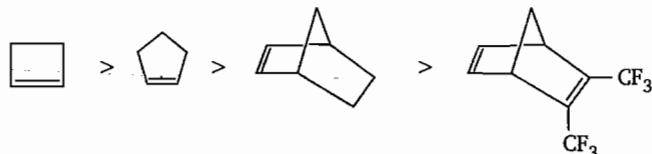


#### 4. Ring Opening Metathesis Polymerization (ROMP)

Cyclic alkenes having strained rings undergo ring opening metathesis polymerization in the presence of metal carbene catalyst but in the absence of another alkene which leads to the ring opening metathesis. The driving force of the reaction is itself ring strain. The metal carbene catalyst attacks the double bond in the ring structure forming a highly strained metallacyclobutane intermediate. The ring then opens forming the growing part of the polymer: a linear chain double bonded to metal with a terminal double bond as well. The new carbene reacts with the double bond on the next cyclic alkene and propagates the chain.



The order of ring strain in cyclic alkenes follow the order :

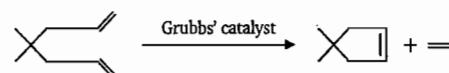


Only the unsubstituted bonds of cyclic alkene are ring opened. It is difficult to ROM or ROMP of tri- and tetra substituted cyclic alkenes or larger ring with Grubbs' first generation catalyst and they require more active Grubbs' second generation catalyst. ROMP of larger rings and those of which are sterically hindered is possible only with more active catalysts like the Grubbs' second generation catalyst.

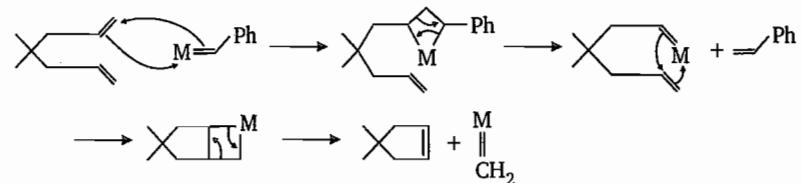
Alkenes such as the cyclohexenes have little or no ring strain and, therefore, can not be easily polymerized with the usual catalysts.

#### 5. Ring Closing Metathesis (RCM) :

RCM is simply an intramolecular alkene metathesis forming the cycloalkene with less or no ring strain and a volatile alkene. Removal of the volatile alkene drives the equilibrium to the ring closed product. The alkenes or alkynes having two terminal double or triple bonds undergo ring closing metathesis.

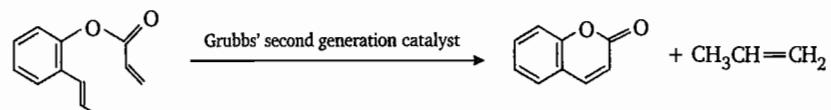


#### Mechanism :



where  $\text{M} = \text{RuCl}_2(\text{PCy}_3)_2$

RCM using Grubbs' second generation catalyst is shown below:



#### 6. Acyclic Diene Metathesis Polymerization (ADMET) :

The ADMET of alkenes is used to polymerize terminal dienes to polyenes. It is a type of step growth condensation polymerization whereas the other metathesis polymerization reactions such

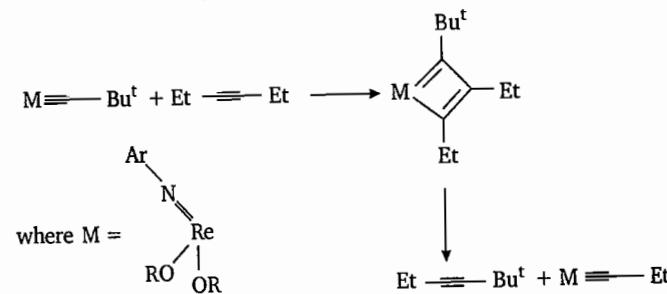
ROMP are chain growth addition polymerization. ADMET is derived by the removal of volatile ethylene gas (ROMP is derived by the release of ring strain).

### Enyne Metathesis (EM)

The reaction between an alkyne and an alkene in the presence of metal carbene as catalyst resulting in a 1,3-diene product is called enyne metathesis reaction. The reaction may be either inter molecular or intramolecular. If the reaction is intramolecular, then it would be a ring closing enyne metathesis, RCEYM.

### Alkyne Metathesis

Alkynes undergo metathesis reactions similar to alkenes but in alkyne metathesis reactions the catalysts used are transition metal carbynes instead of metal carbenes. The intermediates in these reactions formed are metallacyclobutadiene species, formed from the addition of an alkyne across a metal-carbon triple bond of the metal carbyne complex. Terminal alkynes undergo metathesis less readily than those of substituted alkynes.



### Alkene Polymerization : Ziegler-Natta Catalyst :

The polyalkenes such as polyethylene and polypropylene are most common and useful class of synthetic polymers. These are most often prepared by use of organometallic catalysts, either in solution or supported on solid surface. In 1950s, Karl Ziegler in Germany discovered that, in hydrocarbon solution  $TiCl_4$  reacts with  $AlEt_3$  to give polymeric  $TiCl_3$ , a solid with a layer structure and then a hydrocarbon insoluble titanium (III) alkyl which functions as the heterogeneous catalyst. Thus Ziegler-Natta catalyst is a binary mixture of  $TiCl_4$  and  $AlEt_3$ . Ziegler has used this catalyst to polymerize ethene stereospecifically to give polyethylene or polyethene polymer. This catalyst operates at 1 atm, pressure and moderate temperature. Soon thereafter G.Natta in Italy used this catalyst for stereospecific polymerization of propene to give polypropylene. This catalyst is, therefore, called as Ziegler-Natta catalyst. This catalyst is advantageous to industry because it can be easily recovered by filtration. Ziegler and Natta jointly received Nobel Prize in chemistry for their work in 1963. A highly plausible mechanism for Ziegler-Natta catalyst given by Casser and Arlman is given in Figure. 7.10.

Alkene polymerization occurs at defect sites in the crystal lattice where the metal is coordinatively unsaturated. A  $TiCl_5$  unit of polymeric  $TiCl_3$  is the starting point with a vacant coordination site.

The alkyl aluminium (a Lewis acid) alkylates the titanium atom on the surface of solid to give a coordinatively unsaturated titanium alkyl complex which acts as a Lewis acid.  $Et_2AlCl$  is used as cocatalyst. This titanium complex accepts  $\pi$ -electron density from alkene (ethene or propene) on its vacant coordination site. The coordinated alkene then undergoes a migratory insertion into metalalkyl bond (similar to Wilkinson catalyst except that an alkyl group migrates to alkene rather than a hydrogen). This migratory insertion provides an another coordinatively vacant site for further coordination of another alkene and, therefore, lengthen the polymer chain. The release of the polymer from the titanium atom occurs by  $\beta$ -hydrogen elimination, and the chain is terminated.

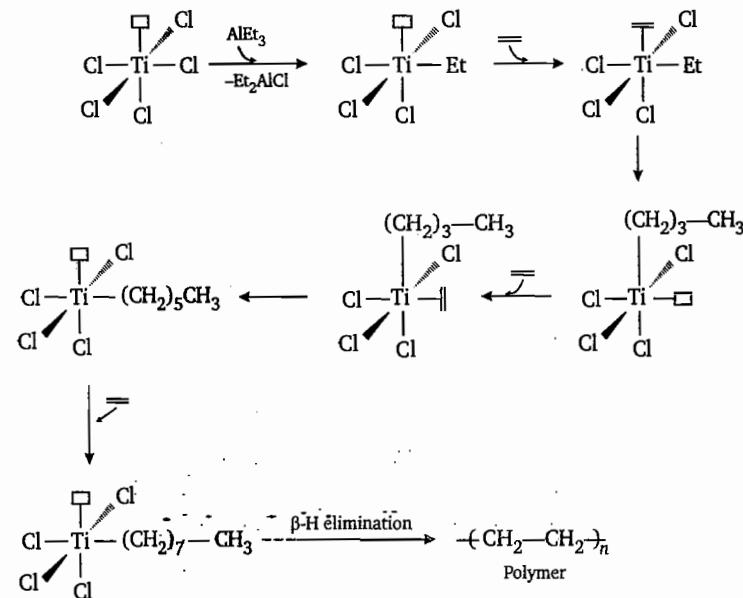
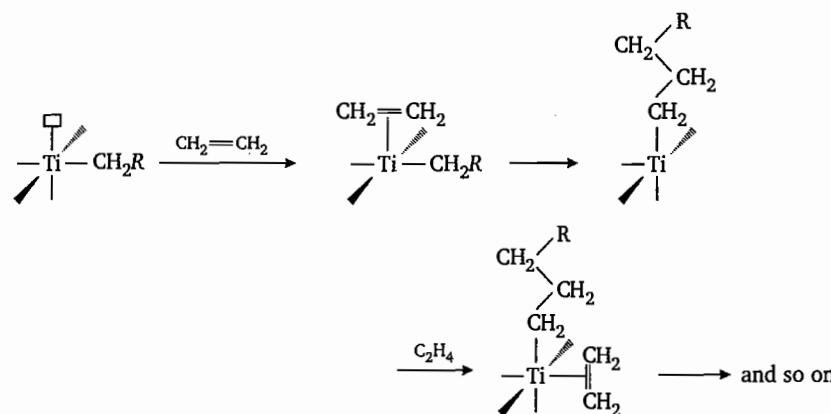


Fig. 7.10.

An alternate mechanism involving a four membered metallacyclobutane intermediate and an  $\alpha$ -hydride elimination has also been proposed by Green and Rooney. This mechanism involves the initial formation of alkylidene from the titanium-alkyl complex followed by the addition of alkene to form a metallacyclobutane. Then a product is formed in which ethylene is inserted into the original metal-alkyl bond.

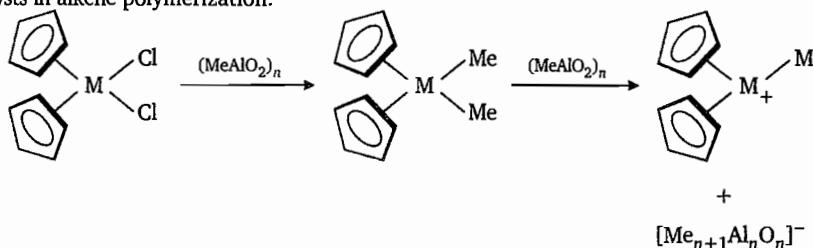
But it has been suggested experimentally by Grubbs that the Cossee-Arlman mechanism is favourable for most of the polymerization reactions.



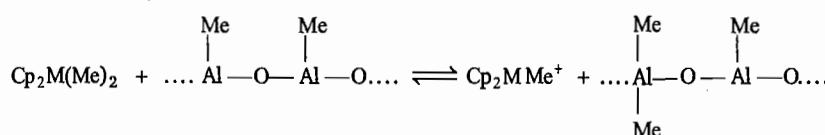
In 1960, modified Ziegler-Natta catalysts have been developed for the polymerization of propylene based on  $\text{TiCl}_4$  supported on  $\text{MgCl}_2$ .

The polymerization reactions at the active sites of Ziegler-Natta Catalysts are influenced by the electronic and steric environment of the crystal lattice because the active metal centre occupies a position on the surface of the crystal. It is the one of the drawbacks of these catalysts.

The homogeneous organometallic catalysts based on group 4 metallocene dichloride such as titanocene dichloride ( $\text{Cp}_2\text{TiCl}_2$ ), hafnocene dichloride ( $\text{Cp}_2\text{HfCl}_2$ ) and Zirconocene dichloride ( $\text{Cp}_2\text{ZrCl}_2$ ) also have high catalytic activity in the presence of lewis acid organoaluminium polymers, methylaluminoxane MAO,  $(\text{MeAlO})_n$ . When these catalysts react with  $(\text{MeAlO})_n$  having, on average, one methyl group per aluminium atom, cationic complexes  $[\text{Cp}_2\text{MMe}]^+$  (where M = Ti, Zr, Hf) are formed. The cationic complexes  $[\text{Cp}_2\text{MMe}]^+$  which are coordinatively unsaturated are the active catalysts in alkene polymerization.

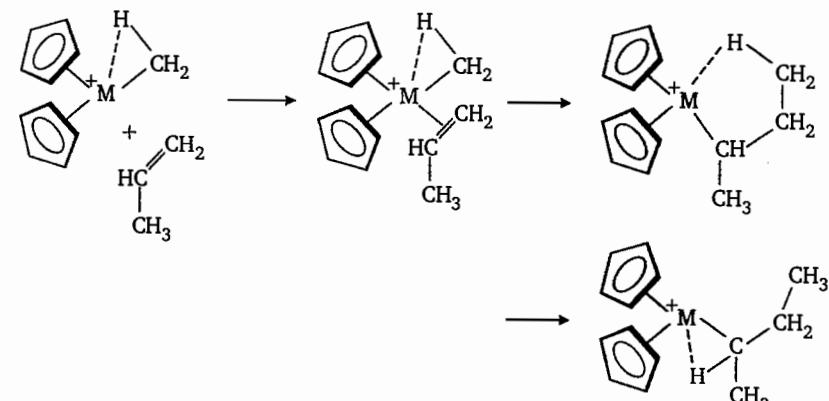


The MAO polymer abstracts a  $\text{Me}^-$  or  $\text{Cl}^-$  or an  $\text{OR}^-$  ion from the Metallocene.



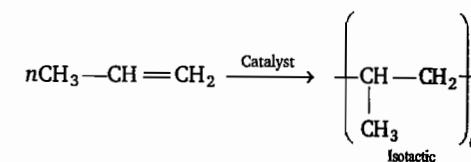
The complex ion  $[\text{Cp}_2\text{MMe}]^+$  with anionic counter ions such as  $\text{B}(\text{C}_6\text{H}_5)_4^-$ , are found to be highly reactive catalysts. The cationic complex ions  $[\text{Cp}_2\text{MMe}]^+$  are partly stabilized by C—H—M agostic interactions.

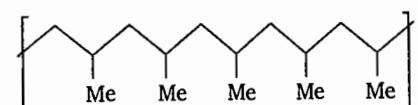
The mechanism of polymer chain propagation for these homogeneous catalysts is similar to that for heterogeneous catalysts.



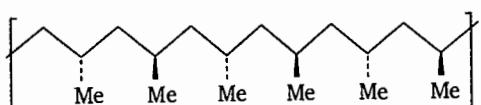
The coordinatively unsaturated complex cation  $(\text{Cp}_2\text{MMe})^+$  coordinates an alkane next to the M—Me bond into which it then inserts to give a M—Pr group. When the alkene is ethylene, the polymerization continues to give long chain polyethylene but with propylene (or propene), the polymer of too short length chain is obtained.

The polymerization of propylene with either homogeneous or heterogeneous catalyst has a major problem with the stereoregularity of process. The polymerization of propylene gives either two crystalline or amorphous solids. The heterogeneous catalyst gives only the isotactic form in which the  $\text{CH}_3$  groups are on the same side of the chain. The another crystalline form of polymer in which the alternate alkyl groups on the chain are on opposite sides is called the syndiotactic polymer. If the groups in the polymer of propylene have random orientation of  $\text{CH}_3$  groups along the polymeric chain, then they are called atactic polymers. The atactic polymers are weak plastics. The polypropylene polymers obtained by using Ziegler-Natta catalysts are highly crystalline because of regular structure.

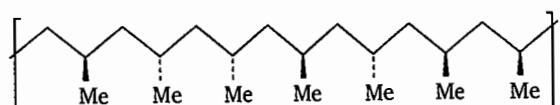




Isotactic polypropylene



Syndiotactic polypropylene



Atactic polypropylene Polymer

The activity of catalysts increases in the order :



If the metallocene catalyst (Fig. 7.11) is a chiral, then it is possible to produce optically active polypropylene.

For example, chiral Zirconium Catalyst produces optically active polypropylene polymer.

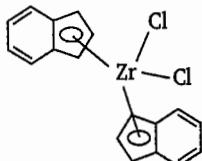
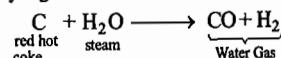


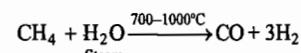
Fig. 7.11

### Water Gas Reaction : Fischer-Tropsch Process

The reaction of red hot coke and steam is called water gas reaction. In this reaction mixture of  $H_2$  and CO is formed and because of its origin it is called as water gas. The mixture of  $H_2$  and CO is also called as synthesis gas or syn gas.



Synthesis gas or syn gas can be obtained by mixing natural gas, mainly methane with steam at higher temperatures and pressure over a heterogeneous catalyst, Ni. This process is called steam reforming.



This reaction is an important source of hydrogen as the natural hydrocarbons are depleted.

The ratio of  $H_2$  to CO in synthesis gas can be varied with the water gas shift reaction in which water is reduced to hydrogen by reaction with CO.



The water gas shift is an equilibrium reaction and an important source of hydrogen. This reaction is favoured thermodynamically at  $400^\circ\text{C}$ ,  $\Delta G^\circ = -14.0 \text{ kJ mol}^{-1}$ .

Since the hydrogen is more versatile industrial chemical than water gas, it becomes necessary to increase the concentration of hydrogen. Also, in the synthesis of some organic compounds hydrogen is used 3-4 times the carbon atoms.

The water gas shift reaction is usually catalyzed heterogeneously over  $Fe_3O_4$ , Fe-Cr or Zn-Cu oxides. Use of heterogeneous catalysts requires a high temperatures and pressures.

On the other hand, the homogeneous catalysts such as  $[Fe(CO)_5]$ ,  $[HFe(CO)_4]^-$ ,  $[Pt(PPr_3^i)_3]$ ,  $[Ru(bpy)_2(CO)Cl]^+$  have been developed that can perform the same functions under much milder conditions.

In the mechanism Fig. 7.12 proposed for homogeneous iron carbonyl catalyst, the coordinated CO ligand undergoes nucleophilic attack by  $OH^-$  followed by decarboxylation of the resulting metallacarboxylic acid to give  $[HFe(CO)_4]^-$ . Protonation of this anionic hydride liberates  $H_2$  and regenerates the catalyst.

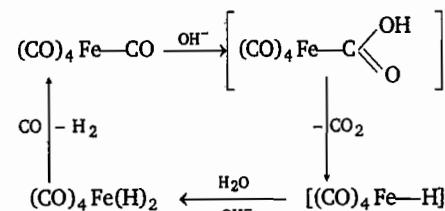


Fig. 7.12

The platinum catalyst is more interesting as it activates both  $H_2O$  and CO and, therefore, no added base is required. The mechanism of the platinum catalyst is shown in Fig. 7.13.

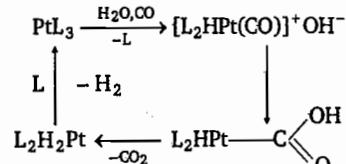


Fig. 7.13

A scheme for the reaction catalyzed by  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  is given in Fig. 7.14

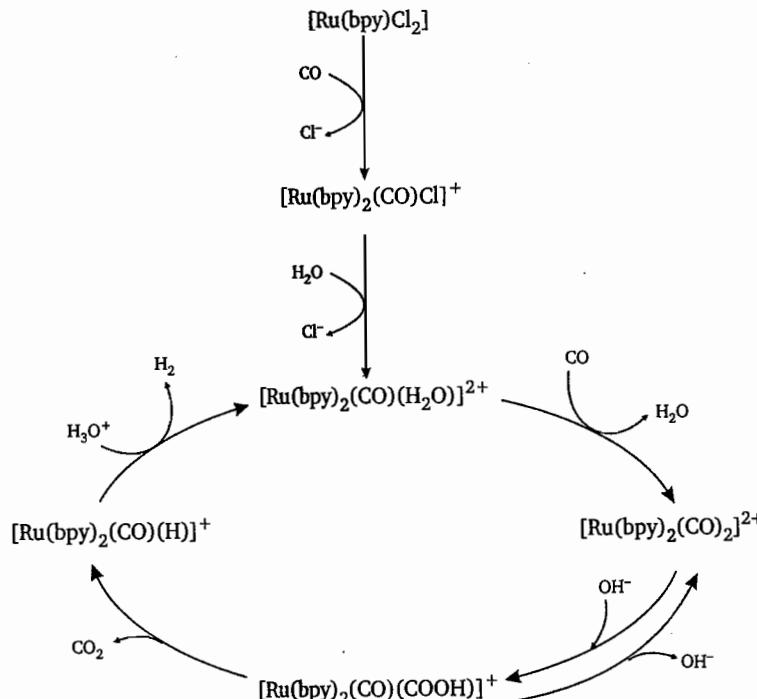


Fig. 7.14

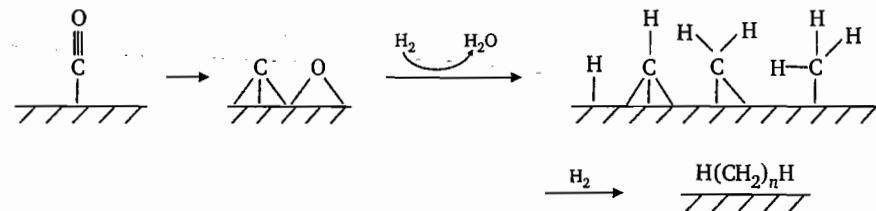
Substitution of  $\text{H}_2\text{O}$  for  $\text{Cl}^-$  in  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  results in  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H}_2\text{O})]^{2+}$ . In the next step  $\text{CO}$ -ligand displaces water to give  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  which undergoes nucleophilic attack by  $\text{OH}^-$  to give  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COOH})]^+$ . Now decarboxylation occurs with the formation of  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H})]^+$ . The final step involves the protonation of  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H})]^+$  followed by liberation of  $\text{H}_2$  gas and regeneration of the catalyst.

The synthesis gas is the starting material for many industrial chemicals.

The **Fischer-Tropsch** reaction converts synthesis gas into hydrocarbons (Linear + branched alkanes and alkenes) or oxygenates such as alcohol, aldehydes and ketones, depending upon the nature of heterogeneous catalysts.

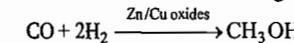
The metal carbonyl clusters are used as heterogeneous catalysts in the Fischer-Tropsch reaction for the conversion of  $\text{CO}$  into hydrocarbons. The original mechanism proposed by Fischer and Tropsch involves the adsorption of  $\text{CO}$  on the surface of catalyst. The conversion of  $\text{CO}$  into hydrocarbons involves the cleavage of  $\text{C}-\text{O}$  bond followed by the formation of  $\text{C}-\text{H}$  and  $\text{C}-\text{C}$

bonds on the surface of the catalyst and finally hydrogenolysis produces  $\text{CH}_2$  groups which then polymerized to give alkane.



The metal carbonyl clusters such as  $\text{Rh}_6(\text{CO})_{16}$ ,  $\text{Fe}_5\text{C}(\text{CO})_5$ ,  $\text{Fe}_6\text{C}(\text{CO})_{17}$ , and  $\text{Ru}_6\text{C}(\text{CO})_{17}$  are the known heterogeneous catalysts for Fischer-Tropsch reaction. If the alkane undergoes  $\beta-\text{H}$  elimination, an alkene is formed.

Synthesis gas can be converted into methanol using  $\text{CO}$  or  $\text{Zn}/\text{Cu}$  oxides catalysts.

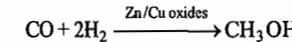


### Synthetic Gasoline

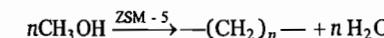
We have seen that coke or coal or natural gas (mainly methane) can be converted to the synthesis gas ( $\text{CO} + \text{H}_2$ ).



The synthesis gas can be converted into methanol using  $\text{Zn}/\text{Cu}$  oxides catalyst.



Mobil has developed a method for converting methanol to gasoline using ZSM-5 as catalyst.

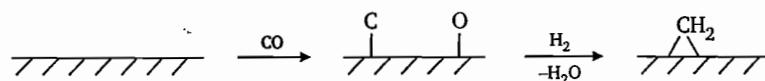


The zeolite acts as an acid catalyst and eliminates water molecules from methanol.

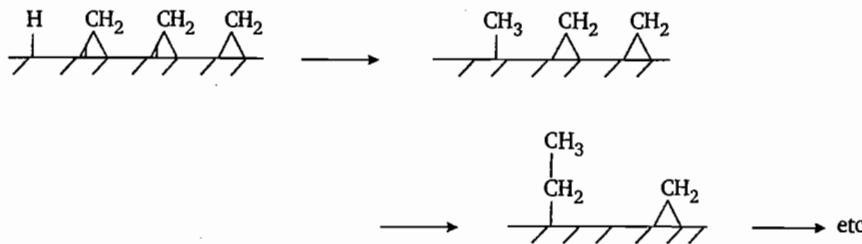
The synthetic Zeolite ZSM-5 has interlinked channels with elliptical cross-sections and the effective pore size intermediate between the smallest and the largest known zeolites leading to the shape selective properties of zeolite catalysts. The pore size is comparable to the size of the gasoline molecule. The insertion of methylene groups continues until the molecule is so large that it fills the channel which it has occupied.

The shape and size of channels play an important role in the selectivity of the gasoline.

The heterogeneous catalysts such as metallic iron and cobalt on alumina can also be used for synthesis of gasoline (a hydrocarbon fuel) from synthesis gas. Carbon monoxides dissociates on the surface of the catalyst to form surface carbides and these are hydrogenated to produce surface carbenes.



Carbene insertion into a metal-hydrogen bond produces a methyl group that can undergo carbene insertion in a propagating manner.



## Objective Questions

- The catalyst used for polymerization of olefins is generated from:
  - (a)  $\text{Ru}(\text{PPh}_3)_3\text{Cl}$
  - (b)  $\text{TiCl}_4$  and  $\text{AlEt}_3$
  - (c)  $\text{PdCl}_2$  and  $\text{CuCl}$
  - (d)  $\text{Co}_2(\text{CO})_9$  and  $\text{Na}$
- Which of the following is not suitable as catalyst for hydroformylation?
  - (a)  $\text{HCo}(\text{CO})_4$
  - (b)  $\text{HCo}(\text{CO})_4\text{PBu}_3$
  - (c)  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$
  - (d)  $\text{H}_2\text{Rh}(\text{PPh}_3)_2\text{Cl}$
- The catalyst used for the oxidation of ethylene to acetaldehyde is:
  - (a)  $\text{Ru}(\text{PPh}_3)_3\text{Cl}$
  - (b)  $\text{PdCl}_2$  and  $\text{CuCl}$
  - (c)  $\text{TiCl}_4$  and  $\text{AlEt}_3$
  - (d)  $\text{Co}_2(\text{CO})_8$  and  $\text{H}_2$
- Regarding the catalytic cycle of hydrogenation of alkanes involving  $\text{RhCl}(\text{PPh}_3)_3$  as the catalyst, the correct statement is:
  - (a) only 18-electron Rh complex is involved
  - (b) 14- and 16- and 18-electron Rh complexes are involved
  - (c) 14- and 16-electron Rh complexes are involved
  - (d) 16- and 18-electron Rh complexes are involved
- In hydroformylation reaction using  $[\text{Rh}(\text{PPh}_3)_3(\text{CO})(\text{H})]$  as the catalyst, addition of excess  $\text{PPh}_3$  would :
  - (a) increase the rate of reaction
  - (b) decrease the rate of reaction
  - (c) not influence the rate of reaction
  - (d) stop the reaction
- $[\text{Ru}(\text{C}_2\text{H}_5)\text{Cl}(\text{PPh}_3)_3]$  is stable only under a pressure of ethene because:
  - (a) it is a 16-electron complex
  - (b) it forms an 18-electron adduct with ethene
  - (c) one of the decomposition products is ethene
  - (d) it prevents  $\alpha$ -elimination of ethene
- The catalyst involved in carrying out the metathesis of 1-butene to give ethylene and 3-hexene is:
  - (a)  $\begin{array}{c} \text{PCY}_3 \\ | \\ \text{Cl} > \text{Ru} = \text{C}_6\text{H}_3 \\ | \\ \text{Cl} \\ \text{PCY}_3 \end{array}$
  - (b)  $\text{Na}_2\text{PdCl}_4$
  - (c)  $\text{Co}_2(\text{CO})_8\text{H}_2$
  - (d)  $\text{RhCl}(\text{PPh}_3)_3$
- Wilkinson catalyst is used for:
  - (a) Hydrogenation
  - (b) Epoxidation
  - (c) Polymerization
  - (d) Metathesis reaction

9. The catalyst used in the conversion of ethylene to acetaldehyde using Wacker process:  
 (a)  $\text{HCo}(\text{CO})_4$   
 (b)  $[\text{PdCl}_4]^{2-}$   
 (c)  $\text{V}_2\text{O}_5$   
 (d)  $\text{TiCl}_4$  in the presence of  $\text{Al}(\text{C}_2\text{H}_5)_3$
10. In a homogeneous catalytic reaction, 1.0 M of a substance and 1.0  $\mu\text{M}$  of a catalyst yields 1.0 mM of a product in 10 seconds. The turnover frequency (TOF) of the reaction ( $\text{s}^{-1}$ ) is:  
 (a)  $10^{-2}$   
 (b)  $10^2$   
 (c)  $10^{-3}$   
 (d)  $10^3$
11. The homogeneous catalyst that is used in the hydroformylation or hydrocarbonylation is based on:  
 (a) Co  
 (b) Cr  
 (c) Ti  
 (d) V
12. Metals used in automobile catalytic converters are:  
 (a) Pt and Pd  
 (b) Pt and Rh  
 (c) Pd and Rh  
 (d) Rh and Ni
13. Require matching of items of Column I with the appropriate items in Column II. Choose the correct one from the alternatives (a), (b), and (d).

	<b>Column-I</b>		<b>Column-II</b>
P	Wilkinson's catalyst	I	$\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2$
Q	Speier's catalyst	II	Hydrosilylation
R	Water gas shift catalyst	III	$\text{RhCl}(\text{PPh}_3)_3$
S	Zeolite ZSM-5 catalyst	IV	Synthetic gasoline
		V	Hydroformylation
		VI	Zinc-copper oxide

- (a) P = III, Q = II, R = VI, S = IV  
 (b) P = I, Q = V, R = III, S = IV  
 (c) P = V, Q = II, R = VI, S = IV  
 (d) P = III, Q = VI, R = IV, S = II

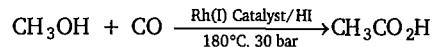
14. Match the List-I and List-II and choose the correct option.

	<b>Column-I</b>		<b>Column-II</b>
P	$(\text{PPh}_3)_3\text{RhCl}$	1.	Friedel Crafts catalyst
Q	$[\text{Rh}(\text{CO})_2\text{I}_2]^-$	2.	Hydroformylation of alkanes
R	$[\text{PdCl}_4]^{2-}$	3.	Hydrogenation catalyst
S	$[\text{HCo}(\text{CO})_4]$	4.	The Wacker process
		5.	Monsanto catalyst for acetic acid
		6.	Reppe catalyst

- (a) P = 3, Q = 5, R = 4, S = 2  
 (b) P = 4, Q = 1, R = 6, S = 2  
 (c) P = 5, Q = 4, R = 2, S = 1  
 (d) P = 3, Q = 2, R = 1, S = 5
15. The reaction of  $\text{H}_2$  with Wilkinson catalyst results in:  
 (a) "cis" addition of  $\text{H}_2$  and metal oxidation state change of -2  
 (b) "trans" addition of  $\text{H}_2$  and metal oxidation state change of +2  
 (c) "trans" addition of  $\text{H}_2$  and metal oxidation state change of -2  
 (d) "cis" addition of  $\text{H}_2$  and metal oxidation state change of +2
16. Active catalytic species for hydroformylation is:  
 (a)  $\text{RuCl}_2(\text{PPh}_3)_3$   
 (b)  $\text{HCo}(\text{CO})_3$   
 (c)  $\text{RuCl}(\text{PPh}_3)_3$   
 (d)  $\text{K}_2\text{PtCl}_6$
17. Wilkinson's catalyst is :  
 (a)  $[\text{Ru}(\text{CO})_2\text{I}_2]^-$   
 (b)  $(\text{Ph}_3\text{P})_3\text{RhCl}$   
 (c)  $\text{Co}_2(\text{CO})_8$   
 (d)  $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}$
18. Hydroformylation reactions are catalyzed by:  
 (a)  $\text{TiCl}_4$  and  $\text{AlEt}_3$   
 (b)  $\text{CaCl}_2$  and  $\text{NaOEt}$   
 (c)  $\text{Ni}(\text{CO})_4$   
 (d)  $\text{Co}_2(\text{CO})_8$
19. Wilkinson's catalyst :  
 (a) is coordinatively saturated  
 (b) does not obey the 18-electron rule  
 (c) is used for oxidation of alcohols  
 (d) is an Ir complex used in preparation of important pharmaceutical products
20. Match the catalyzed conversions listed in Column I with the appropriate catalysts listed in Column II.
- |   | <b>Column-I</b>   |    | <b>Column-II</b>                       |
|---|---|----|--|
| P | $\text{RCH}=\text{CH}_2 + \text{H}_2 + \text{CO} \rightarrow \text{RCH}_2\text{CH}_2\text{CHO}$ | 1. | $[\text{RhI}_2(\text{CO})_2]^-$        |
| Q | $\text{CH}_2=\text{CH}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_3\text{CHO}$             | 2. | $\text{Co}_2(\text{CO})_8$             |
| R | $\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}$                           | 3. | $\text{Rh}(\text{PPh}_3)_3\text{Cl}$   |
| S | $\text{RCH}=\text{CH}_2 + \text{H}_2 \rightarrow \text{RCH}_2\text{CH}_3$                       | 4. | $\text{PdCl}_2 + [\text{CuCl}_4]^{2-}$ |

- (a)  $\text{HCo}(\text{CO})_8$   
 (b)  $\text{H}_4\text{Co}(\text{CO})_3$   
 (c)  $\text{H}_2\text{Co}(\text{CO})_4$   
 (d)  $\text{HCo}(\text{CO})_4$

22. In monsanto acetic acid process shown below, the role of HI is :



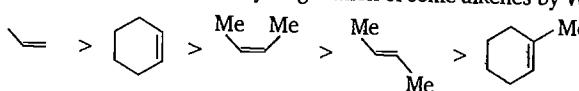
- (a) to convert  $\text{CH}_3\text{OH}$  to a stronger nucleophile  $\text{CH}_3\text{O}^-$   
 (b) to reduce the Rh(I) catalyst to Rh(0) species  
 (c) to reduce a Rh(III) active species to a Rh(I) species in the catalytic cycle  
 (d) to convert  $\text{CH}_3\text{OH}$  to  $\text{CH}_3\text{I}$



## Subjective Questions

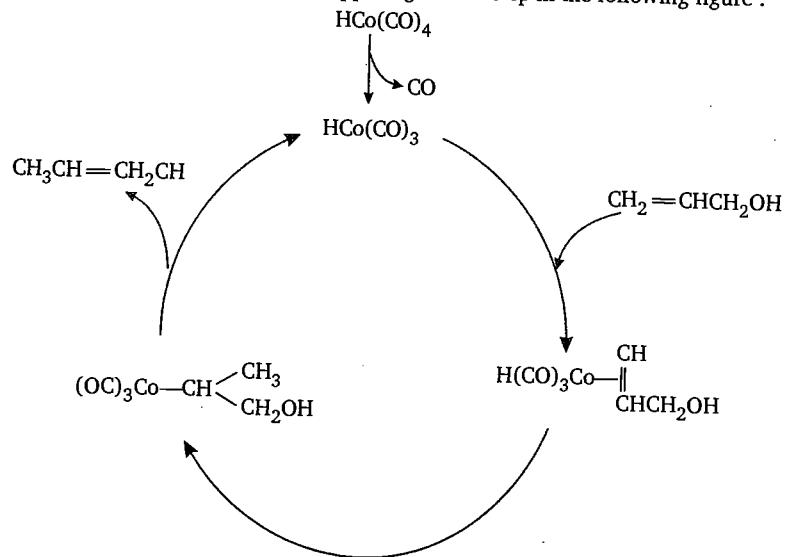
1. Write the plausible mechanism for the catalytic hydrogenation of alkenes using Wilkinson's catalyst,  $\text{ClRh}(\text{PPh}_3)_3$ . Identify the reaction type of each step.
2. Draw the catalytic cycle for the Zeigler-natta polymerization of propene. Comment about the polymer that formed.
3. Write the mechanism for hydroformylation reaction using  $\text{RhH}(\text{CO})(\text{PPh}_3)_2$  as the catalyst.
4. Define the following terms :
 

(a) Catalyst	(b) Catalytic cycle
(c) Catalyst support	(d) Selectivity
(e) Turnover number	(f) Turnover frequency
(g) Homogenous and heterogenous catalysts	(h) Tollman loop
5. The trend in the rate of hydrogenation of some alkenes by Wilkinson's catalyst is :



Explain this trend and identify the step in the catalytic cycle that is most affected.

6. Give the description of what is happening in each step in the following figure :

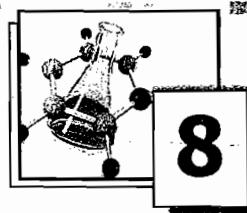


## ANSWERS

- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (b)  | 2. (d)  | 3. (d)  | 4. (d)  | 5. (b)  | 6. (b)  | 7. (a)  |
| 8. (a)  | 9. (b)  | 10. (b) | 11. (a) | 12. (a) | 13. (a) | 14. (a) |
| 15. (d) | 16. (b) | 17. (b) | 18. (d) | 19. (b) | 20. (c) | 21. (a) |
| 22. (d) | 23. (b) |         |         |         |         |         |

7. Write the catalytic cycle involved in the Monsanto process and Tennessee-Eastman process.
8. The complex  $\text{Rh}(\text{H})(\text{CO})_2(\text{PPh}_3)_2$  can be used in the catalytic synthesis of *n*-pentanal from an alkene having one less carbon. Give the mechanism for this process.

□□□



## Coupling Reactions

### Coupling Reactions

Organometallic chemistry has provided several reactions which involve in the formation of carbon-carbon or carbon-heteroatom bonds. These reactions are called coupling reactions. In these reactions two organic fragments are coupled with the aid of a metal catalyst. Usually two types of coupling reactions have been recognized :

1. Homocoupling reactions in which two identical organic fragments are coupled together, for example, conversion of alkyl halide ( $\text{RX}$ ) to alkane ( $\text{R}-\text{R}$ ), conversion of iodobenzene ( $\text{PhI}$ ) to biphenyl ( $\text{Ph}-\text{Ph}$ ).
2. Cross coupling reactions in which two different organic fragments are coupled together, for example, bromobenzene ( $\text{PhBr}$ ) reacts with vinyl chloride to give styrene ( $\text{PhCH=CH}_2$ ).

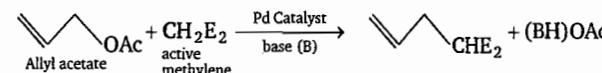
### Cross Coupling Reactions

These reactions are usually catalyzed by a number of palladium complexes or by a mixture of  $\text{Pd}(\text{OAc})_2$  and  $\text{PR}_3$ . Various steps in these reactions involved are: oxidative addition, reductive elimination, migratory insertion, transmetallation,  $\beta$ -elimination and/or  $\alpha$ -elimination. Some important cross coupling reactions are:

1. Tsuji-Trost reaction
2. Mizoroki-Heck reaction
3. Miyaura-Suzuki coupling
4. Stille coupling
5. Negishi coupling
6. Sonogashira coupling
7. Kumada coupling
8. Hiyama coupling
9. Buchwald-Hartwig amination or coupling

### 1. Tsuji - Trost Reaction

The Tsuji-Trost reaction is the palladium catalyzed allylation of nucleophiles such as active methylenes, enolates, amines and phenols with allylic compounds such as allyl acetates and allyl halides.



The catalytic cycle (Fig. 8.1) involves the following steps :

- (1) Formation of Pd-olefin complex.
- (2) Oxidative addition of allylic acetate to Pd(0) catalyst to form  $\eta^3$ -allyl complex.
- (3) Nucleophilic addition of carbanion derived from the deprotonation of active methylene compound.
- (4) Decomplexation or regeneration of catalyst.

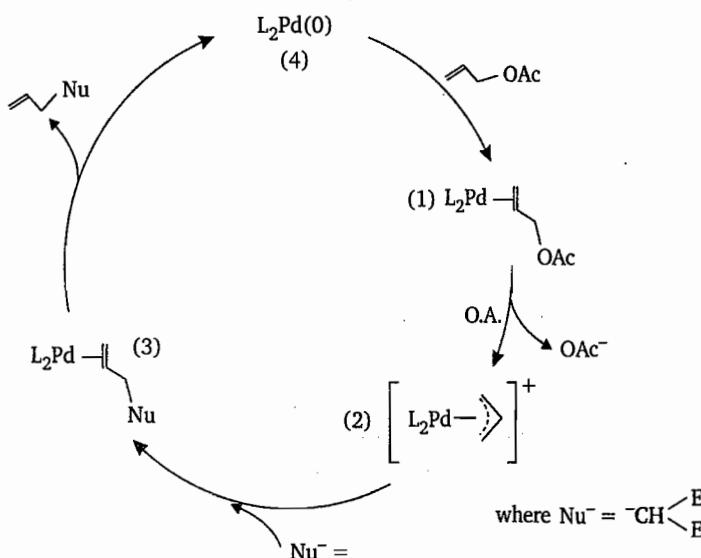
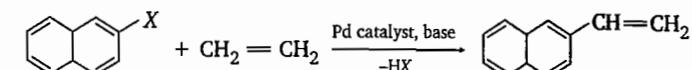
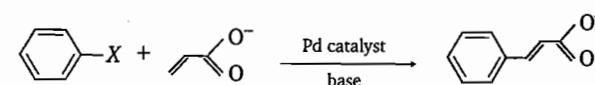
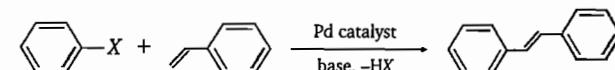
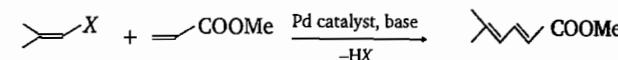


Fig. 8.1

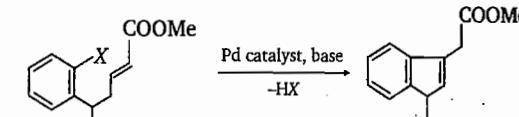
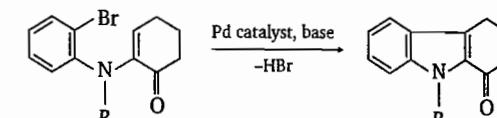
### 2. Mizoroki - Heck Reaction OR Heck Reaction

This reaction was independently discovered by T-Mizoroki and R. F. Heck. This reaction involves the substitution of the vinylic hydrogen of an alkene with a vinyl, aryl or benzyl group of their halides in the presence of palladium catalyst and a base. The coupling may be either inter-molecular or intramolecular. For example,

#### Intermolecular Heck reactions :



#### Interamolecular Heck Reactions :



A base such as triethylamine, potassium carbonate or sodium acetate is necessary to remove the liberated acid, HX. The catalyst may be Pd ( $\text{PPh}_3$ )<sub>4</sub> or in situ Pd ( $\text{OAc}$ )<sub>2</sub> /  $\text{PPh}_3$ . This reaction is stereoselective with a propensity for *trans* coupling as the palladium halide group and the bulky organic residue move away from each other in the reaction sequence in a bond rotation step.

The Heck reactions are mainly carried out in the polar aprotic solvents such as MeCN, DMSO or dimethylacetamide (DMAc).

The catalytic cycle for the Heck reaction is shown in Fig. 8.2.

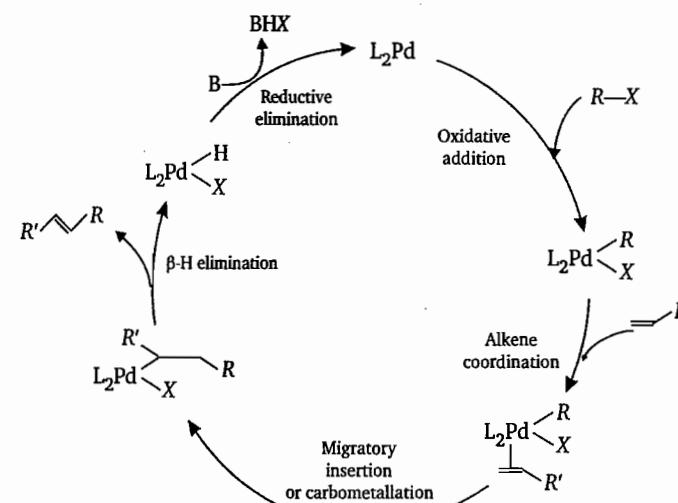
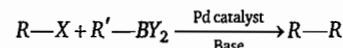


Fig. 8.2 Catalytic cycle for Heck reaction

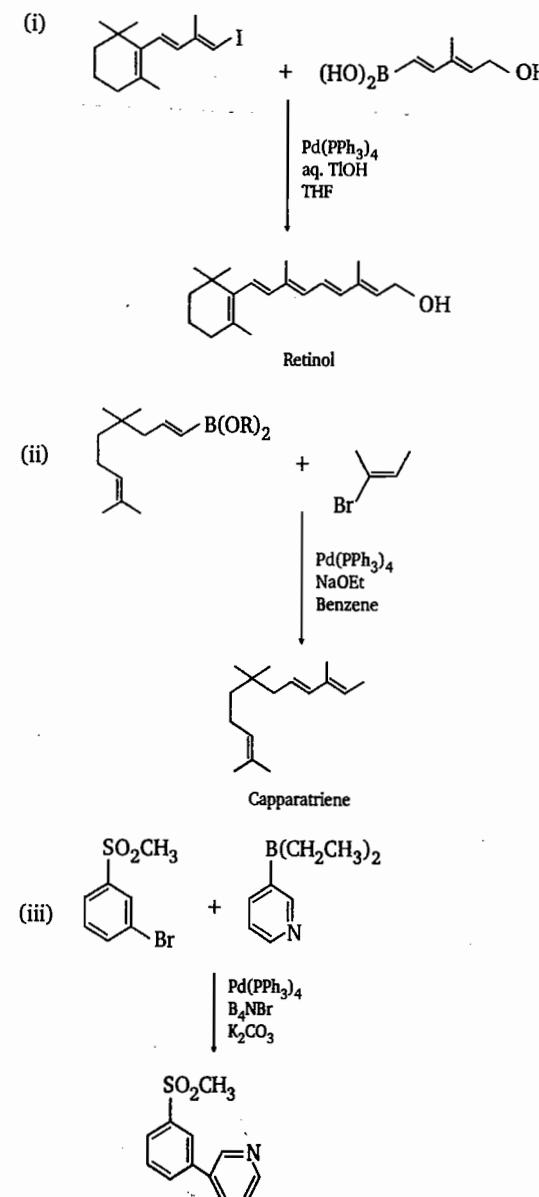
(R = vinyl, aryl, benzyl; X = halide; R' = electron withdrawing group).

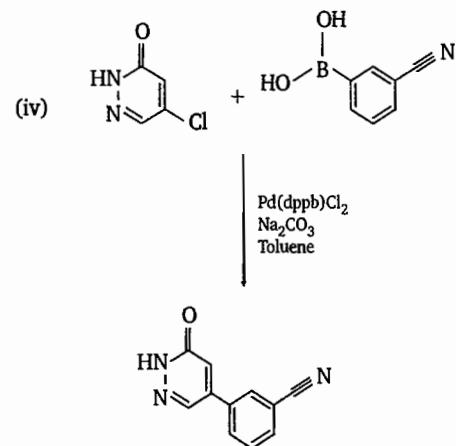
### 3. Miyaura - Suzuki Coupling

The Suzuki coupling reaction involves the cross coupling of organic halides with organoboron compounds (usually a boronic acid) in the presence of Pd(0) complex catalyst and a base.

 $X = I, Br$  $BY_2 = B(OH)_3, B(OR)_2$  $R =$  aryl, alkenyl and alkyl (under special conditions) $R' =$  allyl, alkenyl, alkynyl, aryl, benzylBase =  $Et_3N, NaOEt, Na_2CO_3, TlOH$  etc.Pd Catalyst =  $Pd(PPh_3)_4, PdCl_2(PR_3)_2, Pd(OAc)_2, Pd(dppb)Cl_2$ 

This is one of the most widely used reactions in synthetic organic chemistry for carbon - carbon bond formation as this reaction is highly tolerant of many different functional groups in the coupling partners. This reaction is widely used to synthesize poly-olefins, styrenes and substituted biphenyls. This reaction requires milder conditions than that for Heck reaction. The boron containing biproducts are non-toxic (unlike the Stille coupling which results in tin based biproducts), this reaction, therefore, is preferred in pharmaceutical industry. The important examples of this reaction are given below :



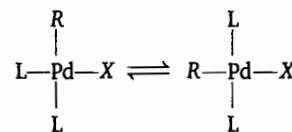


### Mechanism

The catalytic cycle for Suzuki coupling is shown in Fig. 8.3

The first step involves the oxidative addition of organic halide (1) to  $\text{Pd}(0)$  catalyst (2) to form the organopalladium complex (3) which reacts with base to give intermediate (4). This intermediate (4) via transmetallation with the boron- ate complex (5) forms organopalladium complex (6) with the removal of compound (7). The reductive elimination in compound (6) forms the desired product (8) and regenerates the  $\text{Pd}(0)$  catalyst.

The oxidative addition initially forms the *cis* palladium complex which rapidly isomerizes to the *trans* complex.



### Coupling Reactions

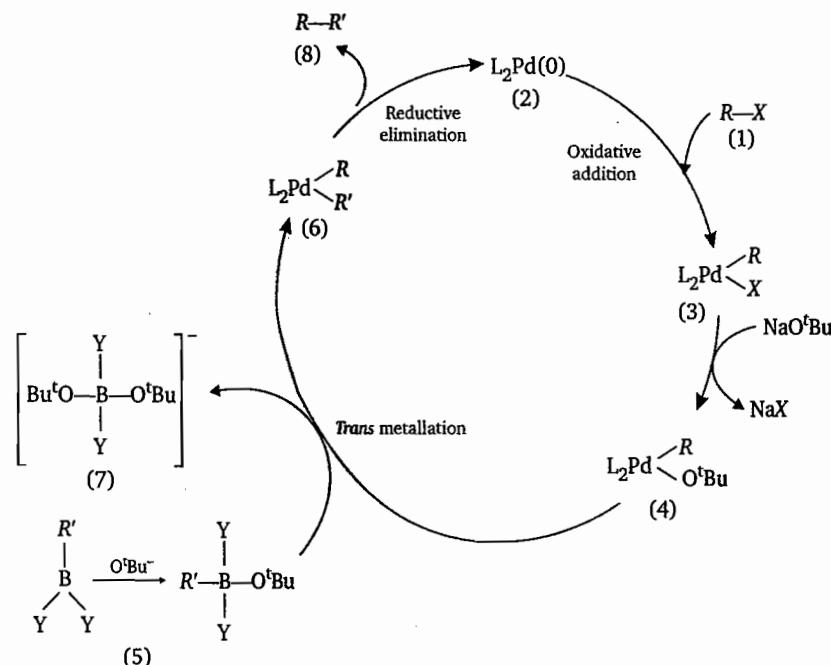
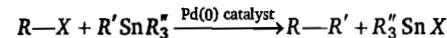


Fig. 8.3 Catalytic cycle for Suzuki coupling

The organoboron compounds undergo *trans* metathesis in the presence of a base because it activates the organoboron compounds. The activation of the boron atom enhances the polarization of the organic ligand and, therefore, facilitates *trans* metathesis as well as the formation of  $\text{R}-\text{Pd}-\text{O}^{\text{t}}\text{Bu}$  from  $\text{R}-\text{Pd}-\text{X}$ .

### 4. Stille Coupling

The stille coupling is a versatile alternative to the Suzuki coupling. In this reaction organoboron is replaced by organotin (*i.e.* organo stannanes). This reaction does not require a base. The stille coupling reaction involve the cross coupling of organohalides or pseudohalides with organotin compounds in the presence of  $\text{Pd}(0)$  catalysts. This reaction has very few limitations on  $\text{R}-\text{groups}$ .



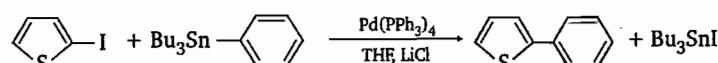
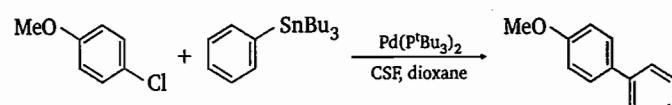
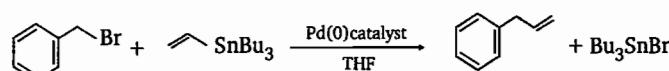
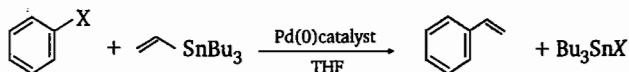
$\text{X} = \text{Br}, \text{I}, \text{OSO}_2\text{CF}_3, \text{Cl}$  (when L is large =  $\text{P}^{\text{t}}\text{Bu}_3$ )

$\text{R}$  = allyl, alkenyl, aryl, benzyl, acyl

$\text{R}'$  = allyl, alkenyl, alkynyl, aryl, benzyl, acetonyl

$\text{R}''$  = Me, *n*-Bu

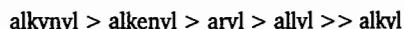
Some examples of Stille coupling reactions are given below:



The main drawback of the Stille coupling reaction is that the organotin compounds are toxic and have poor solubility in water due to their low polarity. All reactions that are developed by Suzuki coupling, are also developed by the Stille coupling reaction but Stille did not get the noble prize because the biproducts are organotin which are toxic.

Unlike Suzuki coupling, no activation of organotin compounds is required. The R group of the halide covers a wide range but should not have  $\beta$ -hydrogens as this will initiate  $\beta$ -H elimination rather than the reductive elimination.

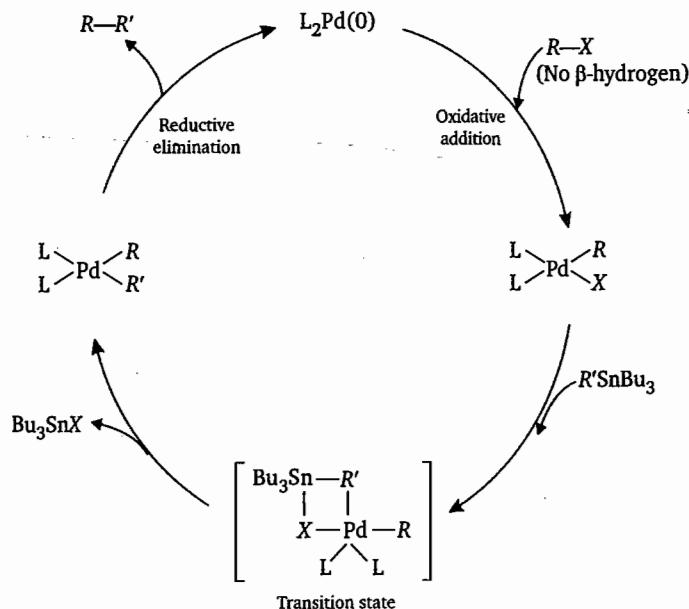
As the tin bears four organic groups, the rates of transmetalation follows the order:



The Stille coupling has some advantages :

1. Organotin compounds are readily prepared and purified.
2. It runs under neutral conditions making it even more tolerant of different functional groups than the Suzuki coupling.

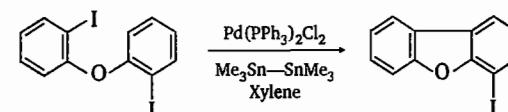
The catalytic cycle for the Stille coupling is shown in Fig. 8.4.



**Fig. 8.4. Catalytic cycle for the Stille coupling.**

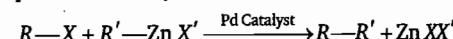
### The Stille-Kelly Coupling

Palladium catalyzed intramolecular cross coupling using hexabutyl distannane or hexaethyl distannane is called the Stille-Kelly coupling.



### 5. Negishi Coupling

Negishi coupling involves the cross coupling of an organohalide with organozinc compounds in the presence of nickel or palladium catalyst.



The leaving group X = Cl, Br, I, triflate. If X = Cl the Negishi coupling is slow.

R = alkenyl, allyl, aryl, benzyl, alkynyl

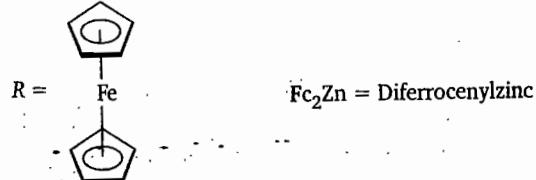
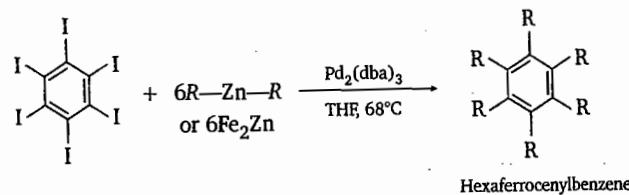
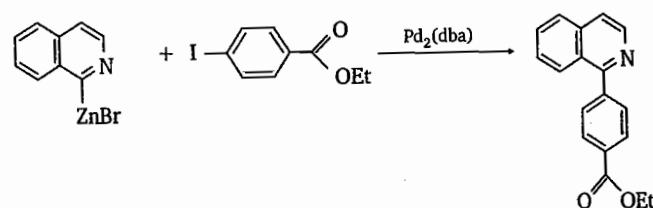
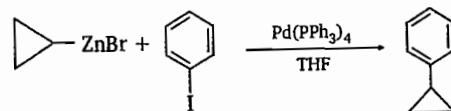
X' = Cl, Br, I

R' = alkyl, alkenyl, allyl, aryl

$L = PR_3, PPh_3, dppe, BiNAP$

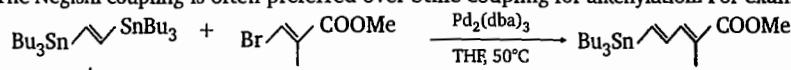
Palladium catalysts usually have high chemical yields and higher functional group tolerance.

Some examples of the Negishi coupling are given below:



$\text{Pd}_2(\text{dba})_3 = \text{tris (dibenzylideneacetone) dipalladium(0)}$

The Negishi coupling is often preferred over Stille coupling for alkenylation. For example,



The active catalyst in this reaction is Ni or Pd in zero oxidation state. The reaction proceeds through the oxidative addition of the organohalide to the catalyst followed by transmetalation and then reductive elimination. (Fig. 8.5)

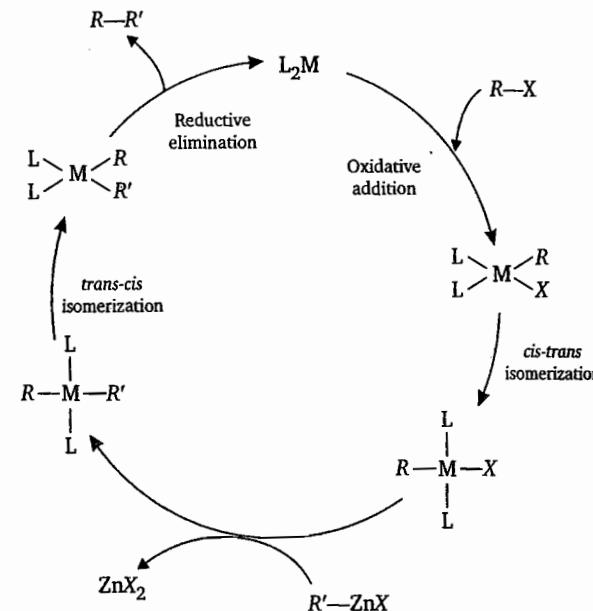
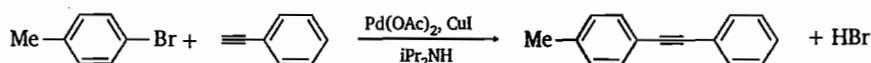
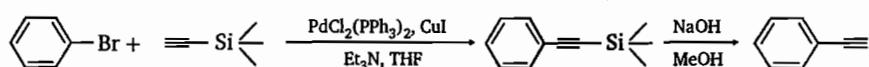
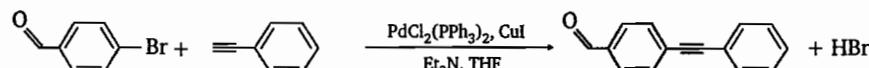
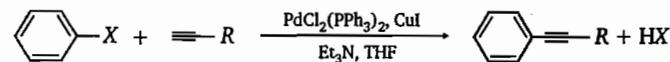


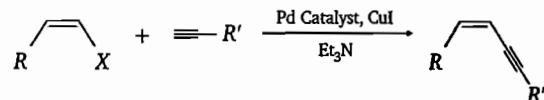
Fig. 8.5 Catalytic cycle for Negishi coupling

## 6. Sonogashira Coupling

The Sonogashira coupling involves the cross coupling of terminal alkyne with allyl or aryl halides in the presence of Pd catalyst, Cu (I) as a cocatalyst and an amine base.



In the Sonogashira coupling of alkene with alkyne, the geometry about double bond is usually retained.



The alkyne moiety is usually introduced in the form of its Cu(I) salt which is generated *in situ* from a Cu(I) salt such as CuI and a terminal alkyne in the presence of an amine base (Figure 8.6).

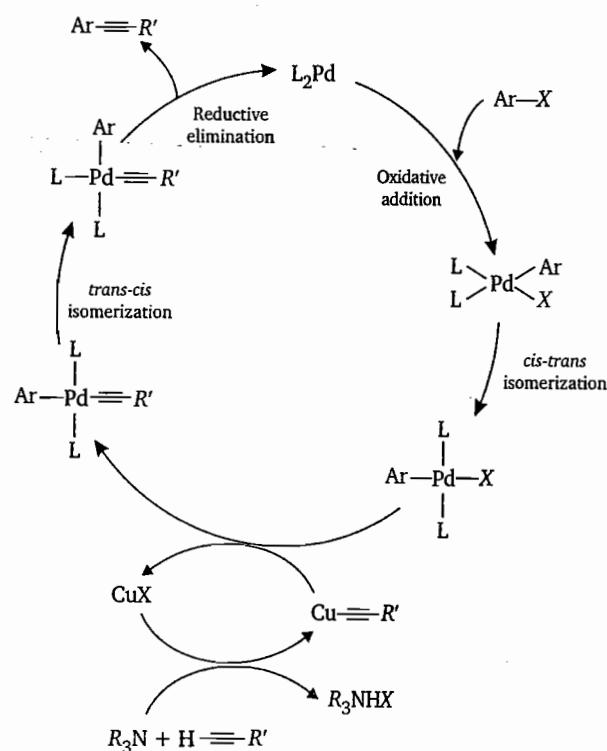
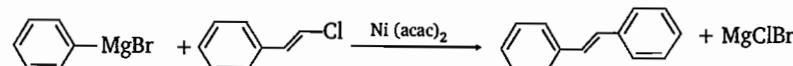
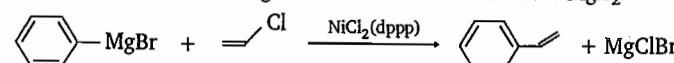
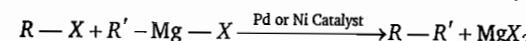


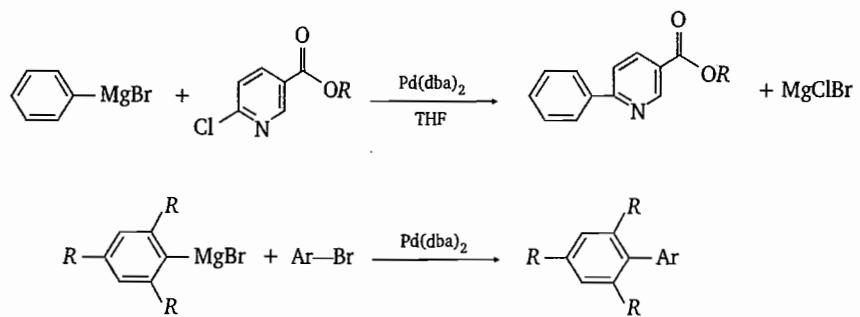
Fig. 8.6 Catalytic cycle for Sonogashira coupling.

## 7. Kumada Coupling

The Kumada coupling or Kumada-Corriu coupling was the first Pd or Ni catalyzed cross coupling, developed in 1972 independently by Kumada and Corriu.

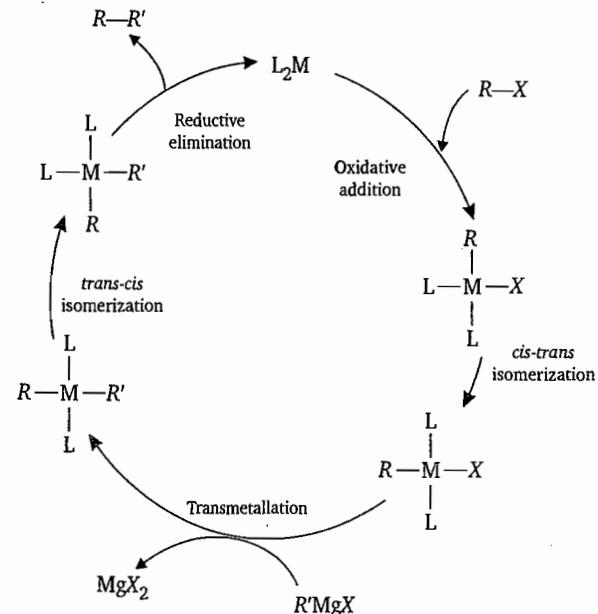
The Kumada coupling involves the cross coupling of an alkyl, vinyl or aryl halide or triflate with alkyl, alkenyl or aryl Grignard reagents in the presence of Ni or Pd catalysts.





When Pd Catalyst is used, order of reactivity of halides is : I > Br > Cl, when Ni catalyst is used, the order of reactivity is : Cl > I > Br.

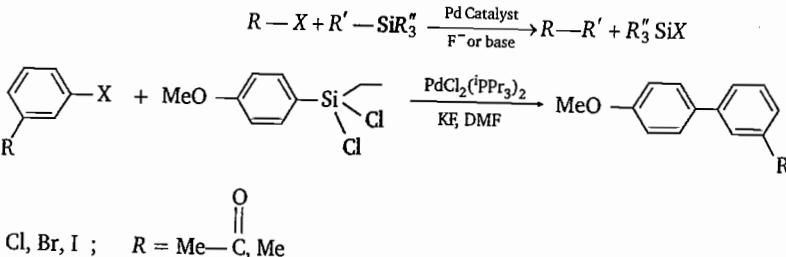
The Catalytic cycle for the Kumada coupling is shown in Figure 8.7.



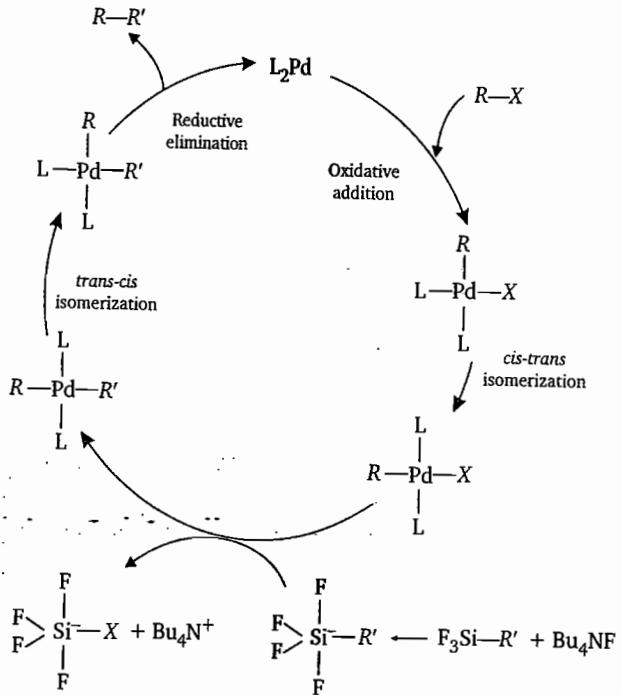
**Fig. 8.7.** Catalytic cycle for the Kumada coupling.

## 8. Hiyama Coupling

The Hiyama coupling involves the cross coupling between alkyl, alkenyl or aryl halides or pseudo-halides with organosilanes in the presence of Pd catalysts. This reaction is similar to the Suzuki coupling, but it requires an activating agent such as fluoride ions or a base. As with the Suzuki coupling, the transmetalation does not occur without activation by fluoride ions or a base.



The activation of the organosilane leads to the formation of pentavalent silicon compound (Figure 8.8).

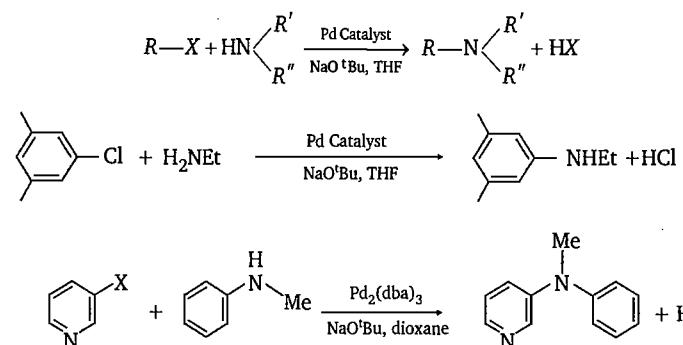


**Fig. 8.8.** Catalytic cycle for Hiyama coupling.

## 9. Buchwald- Hartwig Amination or Coupling

The Buchwald-Hartwig coupling involves the coupling of an aryl halide with an amine in the presence of catalyst and stoichiometric amount of a base such as  $\text{NaO}^\ddagger\text{Bu}$  to form aromatic amines (i.e., to form C—N bonds).

In 1995, Buchwald and Hartwig independently reported the palladium catalyzed coupling of aryl halides with amine nucleophiles in the presence of stoichiometric amount of base.



X = Cl, Br, I

The bulky as well as chelating ligand that increases the electron density at the metal facilitates oxidative addition and reductive elimination of the product. A base is required to deprotonate the amine substrate before or after coordination to palladium atom (Fig. 8.9).

The solvent also plays an important role in this reaction as compared to the other cross coupling reactions because of the heterogeneous nature of the reaction.

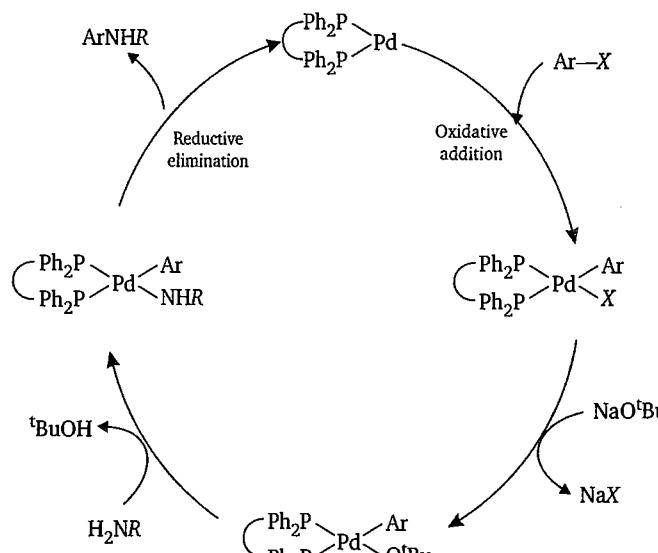
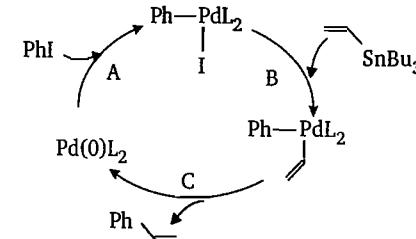


Fig. 8.9 Catalytic cycle for Buchwald-Hartwig coupling.

## Objective Questions

1. Consider the following reaction mechanism :



The steps A, B and C, respectively are :

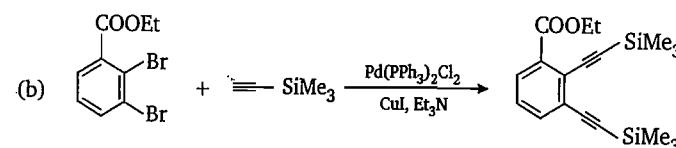
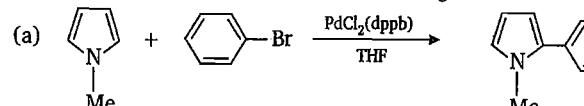
- oxidative addition; transmetallation; reductive elimination
- oxidative addition; carbopalladation;  $\beta$ -hydride elimination
- carbopalladation; transmetallation; reductive elimination
- metal halogen exchange; transmetallation; metal extrusion

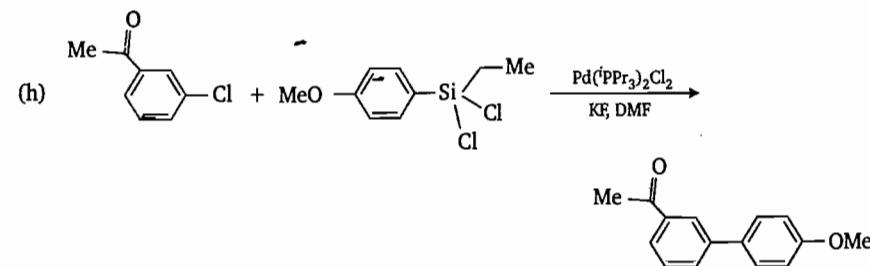
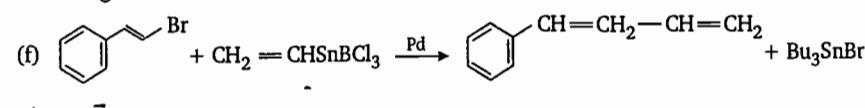
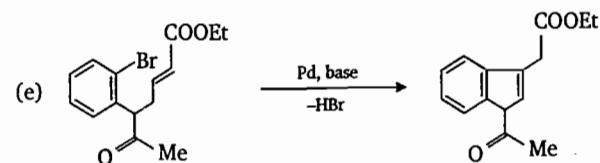
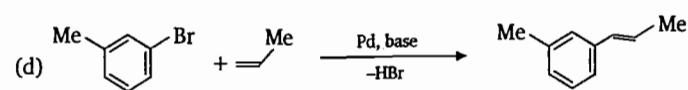
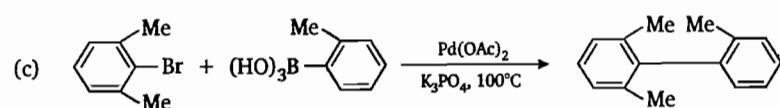
## ANSWERS

1. (a)

## Subjective Questions

1. Identify and name the reaction in the following transformations :



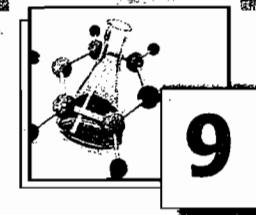


2. What are the basic difference between the Stille and Suzuki coupling reactions?

3. Write the short note on the following :

- |                              |                     |
|------------------------------|---------------------|
| (a) Suzuki coupling reaction | (b) Stille reaction |
| (c) Negishi coupling         | (d) Heck reaction   |
| (e) Kumada coupling          | (f) Hiyama coupling |
| (g) Sonogashira coupling     |                     |

□□□



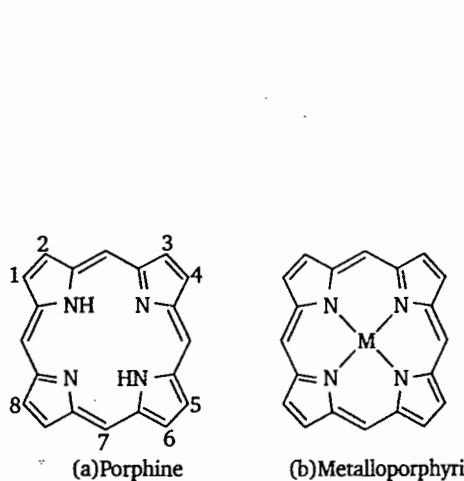
## Bioinorganic Chemistry

Bioinorganic chemistry is a relatively new and still growing interdisciplinary field of chemistry which largely focuses on the roles of metal ions in living systems.

### Metalloporphyrins

The metalloporphyrins are the complexes in which a metal ion is coordinated to four nitrogen atoms inside the cavity of the porphyrin ring in a square planar geometry. The axial sites are available for other ligands. Some examples of metalloporphyrins are hemoglobin, myoglobin, cytochromes and chlorophylls.

The porphyrin rings are the derivatives of a macrocyclic ligand called porphine. The porphine molecule consists of unsubstituted tetra-pyrole connected by methylidyne ( $\text{CH}$ ) bridges. These methylidyne carbon positions are labeled the  $\alpha, \beta, \gamma, \delta$  and 5, 10, 15, 20 positions in porphine and porphyrin rings respectively. The 5, 10, 15, 20-tetraphenyl derivatives (tpd) are readily available because of their ease of synthesis and purification. In porphyrin rings various groups are attached to the perimeter of porphine molecule. The porphyrin ring can accept two hydrogen ions to form the dication (i.e., + 2 diacid) or donate two protons to form dianion. In metalloporphyrin complexes the inner hydrogen atoms are replaced as protons by dipositive metal ions. Therefore the metal free porphyrin ligand has -2 charges. Since this macrocyclic ligand has a planar conjugated system of  $\pi$ -bonds around its perimeter, it is much more rigid macrocyclic ligand than the crown ethers. Therefore, the ligand is more selective for certain metal atoms than the crown ethers. It has a stronger preferences for the  $d^8\text{Ni}^{2+}$  ion. The other metal ions may add above or below the square plane. The structures of porphine molecule, metalloporphyrin and Fe-protoporphyrin IX or heme group are shown in Fig. 9.1.



**Fig. 9.1 Structure of (a) Porphine (b) Metalloporphyrin (c) Fe-protoporphyrin IX**

The porphyrin rings are rigid because of the delocalization of the  $\pi$ -electrons around the perimeter. The size of the cavity in the centre of porphyrin ring is ideal for accommodation of metal ions of the first transition series. If the metal ion is too small such as  $\text{Ni}^{2+}$ , the ring becomes ruffled to allow closer approach of nitrogen atoms to the metal ion. On the other hand, if the metal ion is too large, it can not fit into the cavity and occupies position above the ring which also becomes domed.

### Role of Iron in Living Systems

Iron is the most important transition metal involved in living systems, being vital for both plants and animals. In the living systems, iron has three well characterized systems :

- (1) Proteins that contain one or more porphyrin rings such as hemoglobin, myoglobin and cytochrome  $\text{P}_{450}$ .
- (2) Proteins that contain non-heme iron such as iron-sulphur compounds (ruberodoxin, ferredoxins, nitrogenase).
- (3) The non-heme diiron oxo-bridged compounds such as carboxylates (hemerythrin, ribonucleotide reductase and methane monooxygenase).

Some important naturally occurring iron proteins and their functions in living systems are listed in Table. 9.1.

**Table 9.1 : Iron Proteins and Their Functions**

Protein	Molar mass (approximate)	No. of Fe atoms per molecule	Oxidation state	Source	Nature of iron, heme (H) or non-heme (NH)	Functions
Hemoglobin $\text{H}_b$	64500	4	$\text{Fe}^{\text{II}}$	animals	H	Oxygen transport
Myoglobin $\text{M}_b$	17500	1	$\text{Fe}^{\text{II}}$	animals	H	Oxygen storage
Cytochromes	12500	4	$\text{Fe}^{\text{II}}$	plants, animals, bacteria	H	electron transfer
Ferredoxin	6000-12000	2-8	$\text{Fe}^{\text{II}}, \text{Fe}^{\text{III}}$	Bacteria, plants, animals	NH	Electron transfer
Ruberodoxin	6000	1	$\text{Fe}^{\text{III}}$	Bacteria	NH	Electron transfer
Ferritin	45000	20% Fe	$\text{Fe}^{\text{II}}$	animals	NH	Storage of iron
Transferrin	76000	2	$\text{Fe}^{\text{III}}$	animals	NH	Scavenging of iron
Hemerythrin $\text{H}_e$	108000	2	$\text{Fe}^{\text{II}}$	marine invertibrates	NH	Oxygen transport
FeMo Protein	220000	24-36	—	nitrogenase enzymes	NH	Nitrogen fixation in bacteria
Catalase	280000	—	$\text{Fe}^{\text{III}}$	Living organism	H	decomposition of $\text{H}_2\text{O}_2$
Peroxidase	44000	—	$\text{Fe}^{\text{III}}$	Living organism	H	decomposition of $\text{H}_2\text{O}_2$

### Hemoglobin and Myoglobin

Hemoglobin contains two parts : heme groups and globin proteins. A porphyrin ring containing an Fe atom is called a heme group. Cellular respiration is the process of using oxygen to break down glucose to produce  $\text{CO}_2$ , water and energy for use by the cell. It has molar mass of about 64500. Hemoglobin is found in red blood cells that are called erythrocytes and is responsible for their

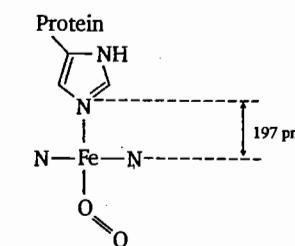
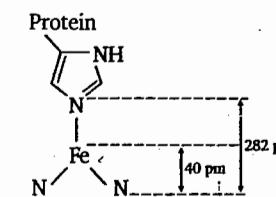
characteristic colour. Without hemoglobin the blood is either colourless or a different colour. Hemoglobin picks up the weak ligand dioxygen from the lungs or gills and carries dioxygen in arterial blood to the muscles, where the oxygen is transferred to another heme containing protein, myoglobin which stores it until oxygen is required to decompose glucose to produce energy,  $\text{CO}_2$  and water. Hemoglobin then uses certain amino acid groups to bind  $\text{CO}_2$  and carry it in venous blood back to the lungs.

Each hemoglobin molecule is made up of four subunits, each of which consists of a globin protein in the form of folded helix or spiral. The globin proteins are of two types : two are  $\alpha$  and two are  $\beta$ . An  $\alpha$  globin protein consists of 141 and an  $\beta$  globin protein consists of 146 amino acids. Each protein consists of one polar and one non-polar group. In hemoglobin which has no dioxygen attached (and is therefore called as deoxyhemoglobin or reduced hemoglobin), the protein is attached to Fe(II) protoporphyrin IX through imidazole nitrogen of histidine residue in such a way that the polar groups of each protein are on the outside of the structure leaving a hydrophobic interior. Therefore, the heme group is held in a water resistant protein pocket.

Perutz has suggested a mechanism for the cooperativity of the four heme groups in hemoglobin. In deoxyhemoglobin, iron is coordinated to four nitrogen atoms of the planar protoporphyrin IX and the fifth coordination site is occupied by nitrogen atom on imidazole of a proximal histidine of globin protein. The sixth vacant site trans to the imidazole nitrogen is vacant and reserved for dioxygen. In deoxyhemoglobin iron is present as high spin Fe(II) with one electron occupying the  $d_{x^2-y^2}$  orbital that points directly toward the nitrogen atoms of protoporphyrin IX. The presence of this electron increases the size of Fe(II) in these directions by repelling the lone pair of electrons on nitrogen atoms. As a consequence, Fe(II) becomes too large to fit easily within the hole provided by the planar protoporphyrin IX ring. The Fe(II) ion is, therefore, lies about 40 pm out of the plane in the direction of the histidine group, and the heme group is slightly bent into a domed shape (Fig.9.2) The iron atom in deoxyhemoglobin has square based pyramidal coordination.

The steric interactions between the histidine residue, the associated globin chain and heme group inhibit the free movement of the iron atom into the porphyrin ring.

Although  $\text{O}_2$  is not a strong ligand, the coordination of the dioxygen molecule trans to the histidine group as a sixth ligand alters the strength of the ligand field and causes the pairing of electrons on iron without affecting the oxidation state of iron. Therefore, Fe(II) becomes low spin and diamagnetic. In low spin Fe(II), the six d-electrons occupy the  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals. The  $d_{x^2-y^2}$  orbital is now empty and the previous effects of an electron present in this orbital in repelling the porphyrin nitrogen atoms is diminished. Therefore, the size of low spin Fe(II) becomes about 17 pm smaller than high spin Fe(II). Thus, the Fe(II) slips into the hole of an approximately planar porphyrin ring. As the iron slips into the hole, the imidazole side chain of histidine  $F_8$  also moves toward Fe atom, and the complex has an octahedral geometry. Recent X-ray studies show that dioxygen is bound in a bent fashion with an  $\text{Fe}—\text{O}—\text{O}$  angle of approximately  $130^\circ$ . There is strong evidence for hydrogen bonding between an imidazole N—H of a distal histidine and the bound dioxygen.



**Fig.9.2 The changes in heme of hemoglobin upon oxygenation**

There are four subunit for Hb

The four subunits of hemoglobin are linked with each other through salt bridges between the four polypeptide chains. These salt bridges are formed mainly due to electrostatic interaction between the  $-\text{NH}_3^+$  and  $-\text{COO}^-$  groups present on all the four polypeptide chains of hemoglobin. The protein structures in hemoglobin consists of a peptide backbone with various side chains. These side chains consist of a variety of non-polar (hydrocarbons), cationic (such as  $-\text{NH}_3^+$ ) and anionic (such as  $-\text{COO}^-$ ) groups. These salt bridges between the polypeptide chains in hemoglobin are now believed to introduce strain in the molecule. Therefore the deoxy form of hemoglobin is called tense state (or T state).

The movement of iron atom and imidazole side chain of histidine- $F_8$  toward the porphyrin plane results in breaking of some of the salt bridges. The breaking of these salt bridges reduces the strain in hemoglobin molecule. Therefore, the oxyform of hemoglobin is called relaxed state (i.e., R state). The T form of deoxyhemoglobin discourages the addition of first dioxygen molecule.

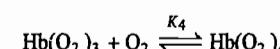
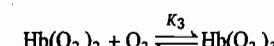
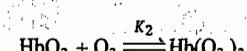
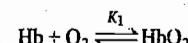
The bonding of one dioxygen molecule to a subunit of hemoglobin reduces the steric hindrance in the other subunits (due to breaking of salt bridges) and therefore encourages the bonding of dioxygen molecules to the iron atom of the second subunit which in turn encourages the third as well as fourth subunits. The binding of dioxygen molecule is most difficult in first subunit and easiest in the last subunit due to conformational change in the protein chain (or polypeptide chain). Initial addition of a dioxygen molecule to high spin Fe(II) triggers the oxygenation of deoxyhemoglobin. This is called cooperative effect.

3mp

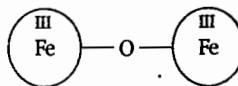
"The phenomenon where the addition of dioxygen to one heme subunit encourages addition of the dioxygen molecules to other heme subunits is known as cooperative effect."

The successive equilibrium constants for binding of dioxygen molecules to each of the four iron atoms follow the order:

$$K_1 < K_2 < K_3 < K_4$$



The fourth equilibrium constant ( $K_4$ ) is found to be much larger than the first ( $K_1$ ). This indicates that last  $O_2$  molecule is bound much more readily and tightly than the first. In the absence of conformational changes,  $K_4$  would be much smaller than  $K_1$ . As a result, as soon as one or two dioxygen molecules are bound to iron atoms, all the four iron atoms are readily oxygenated. Conversely, as one  $O_2$  molecule is removed from oxyhemoglobin the reverse conformational changes occur and successively decrease its affinity for oxygen. Therefore, initial removal of  $O_2$  molecule from deoxyhemoglobin triggers the removal of remaining  $O_2$  molecules. This phenomenon is also called as cooperative effect.

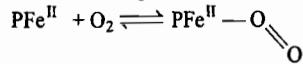


**Fig. 9.3.  $\mu$ -oxo dimer (hematin)**

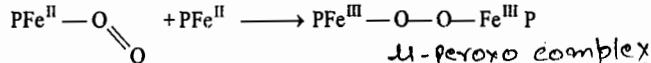
The naked heme, the iron-porphyrin complex without accompanying the polypeptide chains is oxidized to  $Fe(III)$  by dioxygen molecule in aqueous solution and is converted immediately into a stable  $\mu$ -oxo dimer (Fig. 9.3) known as hematin. In hematin iron is high spin  $Fe(III)$ . The hematin is unable to transport oxygen. The polypeptide chain can be removed by treatment with  $HCl$ /acetone. The polypeptide chain in hemoglobin and myoglobin prevents oxidation of  $Fe(II)$  because:

- (1) The hydrocarbon environment round the iron has a low dielectric constant and is hydrophobic and therefore act as a non-polar and provides non-aqueous environment.
- (2) It provides steric hindrance and does not allow the formation of hematin.

The mechanism of the formation of hematin is as follows: The first step involves the binding of the  $O_2$  molecule to  $Fe(II)$  of the heme group,  $PFe(II)$



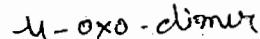
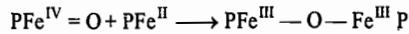
Second step involves the coordination of bound oxygen to second heme group forming  $\mu$ -peroxy complex.



Third step involves the cleavage of the peroxy complex into two ferryl complexes in which iron is present in + 4 formal oxidation state.



In the last step, the ferryl complex combines with another heme group resulting in the formation of hematin.



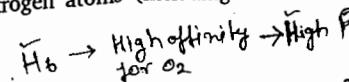
### Myoglobin (Mb)

Myoglobin (or deoxy-myoglobin) is a protein which has only one heme group per molecule and serves as an oxygen storage molecule in the muscles. It has molar mass of about 17000 and binds

dioxygen molecule more strongly than hemoglobin. The myoglobin molecule is similar to a single subunit of hemoglobin. Myoglobin is a five coordinate high spin  $Fe(II)$  complex with four of the coordination positions occupied by N-atoms of the porphyrin ring. The fifth position is occupied by an N atom of an imidazole group of a histidine residue (a globin protein). The protein consists of 153 amino acids. This protein restricts access to the  $Fe(II)$  by a second heme and reduces the formation of a hematin like  $Fe(III)$  dimer. The result is that the  $Fe(II)$  porphyrin complex survives long enough to bind and release dioxygen molecule. Such five coordinate heme complexes of  $Fe(II)$  are always high spin  $t_{2g}^4 e_g^2$  with one electron occupying the  $d_{x^2-y^2}$  orbital that points directly toward the four porphyrin nitrogen atoms. The presence of this electron increases the size of  $Fe(II)$  in these directions by repelling the lone pair of electrons of the nitrogen atoms.

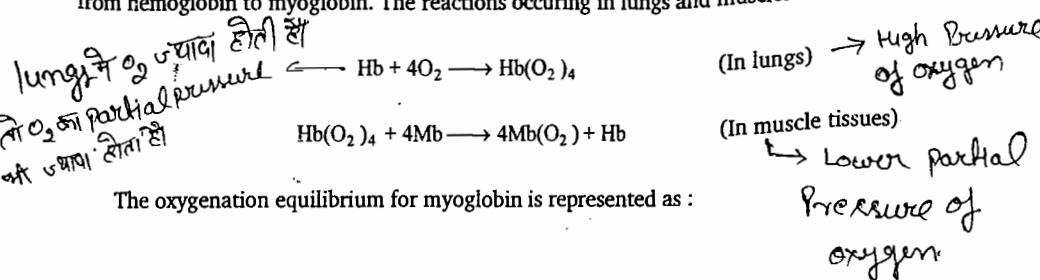
The size of  $Fe(II)$  is 92 pm in the square pyramidal arrangement which is considered to be pseudo-octahedral environment with the sixth ligand removed. The size of  $Fe(II)$  is so large that it can not fit into the hole of the planar porphyrin ring and therefore it lies about 40 pm away from the plane of the ring (Fig. 9.2). Therefore, high spin  $Fe(II)$  porphyrin complexes (in Hb and Mb) involves puckering and twisting of porphyrin ring.

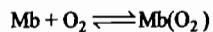
When a dioxygen molecule binds to  $Fe(II)$  at sixth coordination site *trans* to imidazole group of histidine residue, the complex converts to low spin  $Fe(II)$  octahedral complex and the electronic configuration changes to  $t_{2g}^6$  (i.e., the six d-electrons occupy the  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals leading to  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals empty). The previous effect of two electrons occupying the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals in repelling the N atoms on X, Y and Z axes diminishes. Therefore the low spin  $Fe(II)$  ion is smaller (75 pm) and slips into the hole in the planar porphyrin ring. As the  $Fe(II)$  ion moves, it pulls the imidazole group of histidine residue. Therefore, all the nitrogen atoms (including that of proximal histidine) approach more closer to the  $Fe(II)$  ion.



### The Physiology of Hemoglobin and Myoglobin

Hemoglobin has relatively high affinity for dioxygen at high partial pressure of dioxygen whereas myoglobin has relatively high affinity for dioxygen at lower partial pressure of dioxygen. In vertebrates dioxygen enters the blood in the lungs or gills where the partial pressure of dioxygen is relatively high and hemoglobin is virtually saturated with dioxygen in lungs. When hemoglobin carries dioxygen to muscle tissues, it experiences the lower partial pressure of dioxygen and its affinity for dioxygen has fallen off rapidly and in this situation affinity of myoglobin for dioxygen is relatively high. Therefore, in muscle tissues dioxygen is thermodynamically favourable transferred from hemoglobin to myoglobin. The reactions occurring in lungs and muscles tissues are as follows:





$$K_{\text{Mb}} = \frac{[\text{Mb(O}_2\text{)}]}{[\text{Mb}][\text{O}_2]}$$

If  $f$  is the fraction of myoglobin bearing oxygen and  $p_{\text{O}_2}$  is the equilibrium partial pressure of dioxygen, then

$$K = \frac{f}{(1-f)p_{\text{O}_2}} \Rightarrow K \cdot p_{\text{O}_2} = \frac{f}{(1-f)}$$

$$1 \times p_{\text{O}_2} - K \cdot p_{\text{O}_2} \cdot f = f$$

$$f = \frac{K \cdot p_{\text{O}_2}}{1 + K \cdot p_{\text{O}_2}}$$

$$1 \times p_{\text{O}_2} = f + K \cdot p_{\text{O}_2} \cdot f$$

$$1 \times p_{\text{O}_2} = (1 + K \cdot p_{\text{O}_2}) f$$

The equilibrium constant  $K$  is called the binding constant of myoglobin for  $\text{O}_2$ .

This is the equation for the hyperbolic curve for myoglobin (Fig. 9.4).

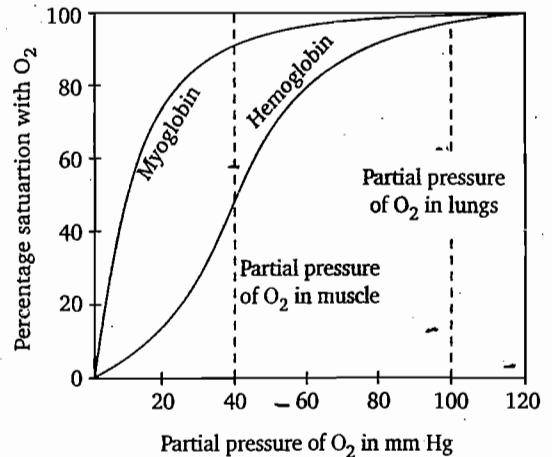


Fig. 9.4. Oxygen dissociation curves for hemoglobin and myoglobin, showing how hemoglobin is able to absorb  $\text{O}_2$  efficiently in the lungs yet transfer it to myoglobin in muscle tissue.

The hemoglobin curve does not follow such an equation. Hemoglobin has more complex behaviour as it has four heme subunits. It follows an empirically modified form with  $p_{\text{O}_2}$  replaced by  $p_{\text{O}_2}^n$ .

$$K = \frac{[\text{Mb(O}_2\text{)}_4]}{[\text{Hb}][\text{O}_2]^n}$$

$$K = \frac{f}{(1-f)p_{\text{O}_2}^n}$$

MUSCLE TISSUE  $\text{CO}_2$  जलावा करता है  $\text{CO}_2$  acidic होता है तो muscular tissue का pH को नियंत्रित करता है तो in muscular tissue  $\text{P}_{\text{O}_2}$  कम होता है  $\text{P}_{\text{CO}_2}$  ज्यादा होता है, pH कम होता है अब जो  $\text{CO}_2$  lungs में लायी जाती है उसका उपयोग  $\text{CO}_2, \text{HCO}_3^-$  की जड़ी भूमि में deoxy Hb

Bioinorganic Chemistry के साथ lungs में लायी जाती है पहले तो  $\text{CO}_2$  9-9

erythrocytes वाले red blood cell में enter करती है वहाँ पर carbonic anhydrase

or

$$f = \frac{K_{\text{p}_{\text{O}_2}^n}}{1 + K_{\text{p}_{\text{O}_2}^n}} \text{ enzyme CO}_2 को \text{H}_2\text{CO}_3 \text{ से convert करते हैं}$$

$$\text{H}_2\text{CO}_3 \text{ decomposes बनाता है } \text{HCO}_3^- \text{ जलावा वाला है Blood}$$

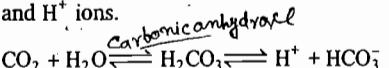
Where the exponent  $n$  is called the Hill constant. को pick करके lungs में ले जाती है For hemoglobin  $n = 2.8$  in the pH range of physiological importance in muscle tissues.

The exact value of  $n$  depends on pH of the biological system. When  $n$  exceeds the unity, the attachment of dioxygen to one heme group of hemoglobin increases the binding constant for next dioxygen which in turn increases the binding constant for the next one and so on. The exponent  $n = 2.8$  indicates that attachment of dioxygen to one heme subunit progressively increases its tendency to bind with the subsequent heme subunits of hemoglobin. Therefore, the exponent 2.8 reveals the cooperative effect of four heme subunits that produces the curves shown in Fig. 9.4.

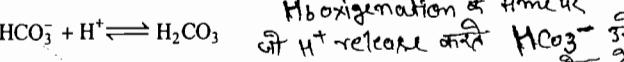
If the four heme subunits of hemoglobin act independently, they will give curve identical to that of myoglobin. The cooperative effect favours the attachment of more dioxygen molecules to the heme subunits of hemoglobin. Conversely, if only one dioxygen molecule is attached to a heme subunit of hemoglobin, it dissociates more readily than from a more oxygenated hemoglobin. This indicates that at low partial pressure of dioxygen hemoglobin is less oxygenated and tends to release dioxygen whereas at high partial pressure of dioxygen, hemoglobin is oxygenated almost to the same extent as if  $n = 1$ . This results in a sigmoidal curve for oxygenation of hemoglobin (Fig. 9.4). The curve shows that myoglobin binds dioxygen more strongly than the first dioxygen of hemoglobin. However, the fourth binding constant of hemoglobin is larger than that for myoglobin by a factor of about 50.

### Bohr's Effect

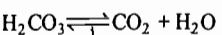
The cooperative effect is pH dependent. The affinity of hemoglobin for dioxygen decreases with decrease in pH. This is called Bohr effect. The  $\text{CO}_2$  released in muscle tissues is the end product of breakdown of glucose.  $\text{CO}_2$  being acidic, decreases the pH in muscle tissues and lowers the pH. The greater the muscular activity the more will be the release of  $\text{CO}_2$ . Therefore, in the muscles tissues, there is low  $p_{\text{O}_2}$ , low pH and high  $p_{\text{CO}_2}$ . In the muscle tissue  $\text{CO}_2$  is produced and is transported to the lungs. Most of the  $\text{CO}_2$  is transported in the form of soluble  $\text{HCO}_3^-$  ions.  $\text{CO}_2$  enters the erythrocytes (red blood cells) where the enzyme carbonic anhydrase converts it to  $\text{H}_2\text{CO}_3$  which dissociates into the  $\text{HCO}_3^-$  and  $\text{H}^+$  ions.



The formation of  $\text{HCO}_3^-$  ions is facilitated by the protein chains of deoxyhemoglobin which acts as a buffer by picking up the accompanying protons. The  $\text{HCO}_3^-$  ions travel in the solution in the serum of the venous blood back to the lungs. The release of proton from hemoglobin on oxygenation produces  $\text{H}_2\text{CO}_3$  from  $\text{HCO}_3^-$  ion.



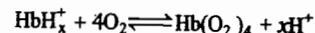
The carbonic anhydrase converts  $\text{H}_2\text{CO}_3$  into  $\text{CO}_2$  which is exhaled out. occupy कर रहा है तो पर्याप्त है



और  $\text{H}_2\text{CO}_3$  जला देता है पर्याप्त है

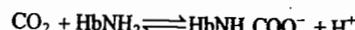
Carbonic anhydrase  $\text{H}_2\text{CO}_3$  को  $\text{CO}_2$  से convert करता है अब  $\text{CO}_2$  lungs आ गयी है और वहाँ से नासा पर्याप्त है

The oxygenated form of hemoglobin is more acidic than deoxygenated hemoglobin resulting in dissociation to produce protons from the molecule when dioxygen binds to it.



Where  $x$  is about 1. It means oxyhemoglobin releases one  $\text{H}^+$  for every dioxygen molecule binds. The protons are released from histidine residue of the protein chain.

About 10-15 % of  $\text{CO}_2$  is transported in erythrocytes as carbaminohemoglobin. In this form the  $\text{CO}_2$  is bound to the  $-\text{NH}_2$  group of the protein.



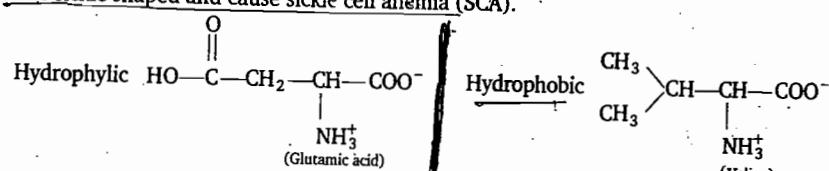
The reaction is rapid reversible and probably not catalyzed by an enzyme.

### ~~Ques~~ Poisoning Effect of CO and other ligands

Since  $\text{O}_2$  is neither a strong nor a soft ligand, it can not coordinate to the fairly soft  $\text{Fe}^{2+}$  ion if soft-base and strong ligand such as CO and  $\text{CN}^-$  are present. The dioxygen molecule serves as a strong  $\pi$ -acceptor ligand in its interaction with  $\text{Fe}^{2+}$  centre. The ligands such as  $\text{CO}$ ,  $\text{CN}^-$ ,  $\text{NO}$  and  $\text{PF}_3$  are stronger  $\pi$ -acceptors than  $\text{O}_2$  and can bind to  $\text{Fe}^{2+}$  centre more strongly than  $\text{O}_2$ . CO binds competitively at the same site on hemoglobin as does  $\text{O}_2$  and shows similar cooperative and Bohr effects. CO binding is more than 200 times stronger than  $\text{O}_2$  binding. The amount of  $\text{O}_2$  that can be carried by the remaining  $\text{Fe}^{2+}$  centres of the hemoglobin molecule is reduced if CO is bound to one of the heme subunits. Moreover, the  $\text{O}_2$  that is associated with hemoglobin molecules containing some CO is bound more strongly making the transfer of dioxygen from these hemoglobin molecules to the muscles tissues more difficult. Therefore, it prevents the transport of dioxygen and causes death eventually due to Asphyxia.

### Genetic Defects

**1. Sickle cell Anemia :** This is because of the mutant form of hemoglobin, where hydrophilic glutamic acid in one  $\beta$ -chain of globin proteins is replaced by hydrophobic valine which reduces the solubility of hemoglobin and prevents oxygen transport. During  $R \rightarrow T$  conversion hemoglobin polymerizes and becomes distorted. Because of deformed shape of hemoglobin, red blood cells become sickle shaped and cause sickle cell anemia (SCA).



**2. Absence of Methemoglobin Reductase :** Methemoglobin is a metalloprotein in which the iron in the heme group is in the  $\text{Fe}^{3+}$  state, not in the  $\text{Fe}^{2+}$  of normal hemoglobin. The size of  $\text{Fe}^{3+}$  ion is so small that it can fit into porphyrin ring of hemoglobin without binding oxygen and therefore, it prevents transfer of dioxygen. In human blood a trace amount (about 3 %) of methemoglobin is normally produced spontaneously.

However, the  $\text{Fe}^{3+}$  ion has an increased affinity for dioxygen binding. The binding of dioxygen to methemoglobin results in an increased affinity of dioxygen to other three heme subunits that still contain  $\text{Fe}^{2+}$  ions within the same hemoglobin molecule. This leads to an overall reduced ability of the red blood cells to release oxygen to muscle tissues.

The NADH-dependent enzyme methemoglobin reductase (diaphorase) converts the methemoglobin back to hemoglobin. A higher level of methemoglobin causes a disease called as methemoglobinemia which is a disorder.  $\text{NO}_2^- / \text{NO}_3^-$  makes oxidation of Fe faster than its reduction and causes intoxication.

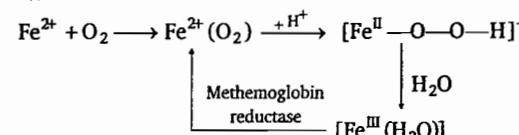


Fig. 9.5.

During the formation of oxyhemoglobin from hemoglobin and dioxygen, one electron is partially transferred from  $\text{Fe}^{2+}$  of heme to the bound oxygen forming a ferric superoxide complex anion Fig. 9.5.

### Electronic Spectra of Porphyrins and Metalloporphyrin

UV-visible spectroscopy is one of the most important technique for the characterization of macrocyclic ligands, porphyrins. The UV-visible absorption spectrum (Fig. 9.6) of the highly conjugated porphyrin ligand exhibit a strong absorption band at about 400 nm (the 'soret' band or B-band) and several weaker bands (Q-bands) at higher wavelengths (from 450 to 750 nm). Both the soret and Q bands in porphyrin systems arise from transition of electrons from porphyrin  $\pi$ -HOMO to the  $\pi^*$ -LUMO. It is the nature of metal centre and the substituents on the ring that affect the energies of these transitions and intensities of bands. Protonation of two of the inner nitrogen atoms or the insertion/change of metal atoms into the porphyrin usually strongly change the absorption spectrum. The metal ions ( $d^0, d^2, d^3$  or  $d^{10}$ ) in which the  $d\pi (d_{yz}, d_{zx})$  orbitals are relatively low in energy and do not form metal to ligand  $\pi$ -bonds have little effect on the porphyrin  $\pi$  to  $\pi^*$  energy gap in porphyrin absorption spectrum.

On the other hand the metal ions ( $d^n, n = 4 - 9$ ) having filled  $d\pi$  orbitals form metal to ligand  $\pi$ -bonds. This results in an increase in porphyrin  $\pi$  to  $\pi^*$  energy gap causing the electronic absorptions to undergo hypsochromic (blue) shifts.

→ The porphyrin ligand contains two  $\pi$ -HOMO of  $a_{1u}$  and  $a_{2u}$  symmetries and two  $\pi^*$  LUMO of  $e_g$  symmetry. An excited singlet state is formed with  $a_{2u}^1 e_g^1$  configuration by transfer of an electron from

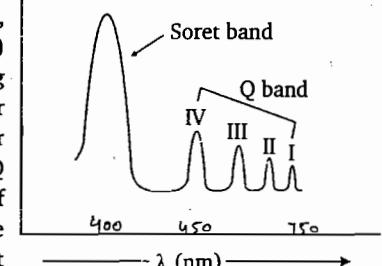


Fig. 9.6 Typical UV-Visible absorption spectrum of porphyrins

$a_{2g}$  orbital to an  $e_g$  orbital. These two excited states mix to form two new singlet states that are nearly 1 : 1 mixtures of the unmixed states.

An electronic transition to the higher energy mixed state, the  $S_2$  state is strongly allowed whereas an electronic transition to the lower energy mixed state, the  $S_1$  state is weakly allowed. The absorption band due to a transition to  $S_2$  state ( $S_0 \rightarrow S_2$ ) is the soret band and the band due to transition to the  $S_1$  state ( $S_0 \rightarrow S_1$ ) is the Q band.

Unlike most of the transition metal complexes, the colour of metallaporphyrins (either in oxidized or reduced form) is due to absorptions within the porphyrin ligand involving electronic transition from  $\pi$ -HOMO to  $\pi^*$  LUMO of porphyrin ring.

When metal inserted in porphyrin ring, Soret band become broad and Q-band disappears (Fig. 9.7). The soot and Q bands are characteristic of porphyrins.

Colour of hemoglobin (deoxy or oxy), myoglobin (deoxy or oxy), catalase (reduced or oxidized) and cytochromes is due to intraligand  $\pi$  to  $\pi^*$  transition.

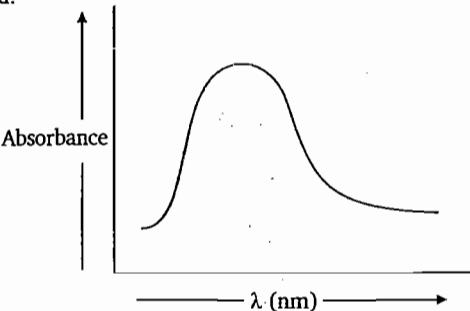


Fig. 9.7

### Hemerythrin

Hemerythrin is a non-heme iron containing protein found in marine invertebrates. Like hemoglobin and myoglobin, it contains  $\text{Fe}^{2+}$  ions and binds dioxygen reversibly. In the blood, hemerythrin (molecular mass = 108000) consists of eight subunits each with 113 amino acid residues and a two  $\text{Fe}(\text{II})$  ions active site. In the muscle tissues it contains fewer subunits. A major difference between hemoglobin and hemerythrin is in the binding of dioxygen. In hemoglobin one dioxygen binds per  $\text{Fe}(\text{II})$  ion whereas in hemerythrin one dioxygen binds to two  $\text{Fe}(\text{II})$  ions. Unlike hemoglobin, hemerythrin exhibits no cooperativity between the subunits during oxygen binding. Each subunit in hemerythrin consists of the two iron active site connected by three bridging groups, two of which are carboxyl anions from the glutamate and asparatate and the other is either  $\text{H}_2\text{O}$ ,  $\text{OH}^-$  or  $\text{O}_2^-$  but probably  $\text{OH}^-$ . The remaining ligands which complete an octahedron about one  $\text{Fe}(\text{II})$  and a five coordination about the other  $\text{Fe}(\text{II})$  ion are three imidazole nitrogen atoms of histidine residues on one  $\text{Fe}(\text{II})$  ion and two on the other [Fig. 9.8(a)]. The two  $\text{Fe}(\text{II})$  ions in deoxyhemerythrin are strongly antiferromagnetically coupled through the  $\text{Fe}-\text{O}-\text{Fe}$  bridge.

Dioxygen binds at the coordinatively unsaturated (vacant site) of the deoxyhemerythrin to give oxyhemerythrin. When dioxygen binds to the vacant site, two electrons are transferred from two  $\text{Fe}(\text{II})$  centre (one electron from each  $\text{Fe}(\text{II})$  of a subunit) to the dioxygen resulting in  $\text{Fe}(\text{III})$  and peroxide ( $\text{O}_2^-$ ). The proton from the hydroxo bridge shifts to the bound peroxide resulting in  $\text{HO}_2^-$  group [Fig. 9.8 (b)]. The  $\mu$ -oxobridging group is associated with bound  $\text{HO}_2^-$  group by hydrogen bonding.

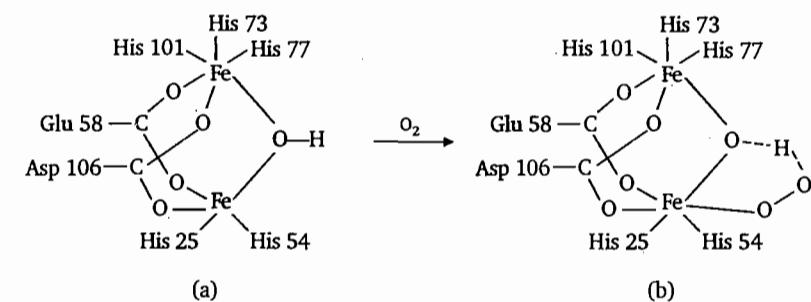


Fig. 9.8: Structure of (a) deoxyhemerythrin (b) oxyhemerythrin.

Mössbauer spectroscopy shows that the two  $\text{Fe}(\text{III})$  ions in oxyhemerythrin are in different environment. It is due to the reason that the peroxide ion is coordinated to one  $\text{Fe}(\text{III})$  ion not to the other. Raman spectroscopy has revealed the presence of a  $\mu$ ( $\text{O}-\text{O}$ ) stretching frequency at  $845 \text{ cm}^{-1}$ , a characteristic of a bound peroxide ion. Oxyhemerythrin contains antiferromagnetically coupled  $\text{Fe}(\text{III})$  ions. Due to antiferromagnetically oxyhemerythrin is diamagnetic and EPR inactive. In oxyhemerythrin both  $\text{Fe}(\text{III})$  ions are low spin ( $t_{2g}^5 e_g^0$ ).

When hemerythrin is oxidized to methemerythrin (the oxidized form of hemerythrin) which contains an oxo rather than hydroxo bridge, it does not bind dioxygen. The hemocyanin is the third system in nature after hemoglobin and hemerythrin for oxygen carrying from the point of intake to the muscle tissues where  $\text{O}_2$  is required.

### Hemocyanin

The name hemocyanin suggests the presence of heme group as well as the cyanide ion. But it has neither heme group nor the cyanide ion. The name simply means the blue blood. Hemocyanin is a copper containing protein which serves as an oxygen carrier in some invertebrates such as Mollusca (e.g., whelks, snails, squid) and Arthropoda (e.g., crabs, lobsters, shrimps). The deoxy form of hemocyanin contains  $\text{Cu}(\text{I})$  ion and is colourless. The dioxygen binding results in the blue  $\text{Cu}(\text{II})$  form. The blue colour of oxyhemocyanin is due to  $\text{O}_2^- \rightarrow \text{Cu}^{2+}$  LMCT. Like hemoglobin, hemocyanin molecule have several subunits and binds dioxygen cooperatively. The active sites contain two  $\text{Cu}(\text{I})$  ions (~360 pm apart) for binding of one dioxygen molecule. Each  $\text{Cu}(\text{I})$  ion is bound by three histidine residues (Fig. 9.9).

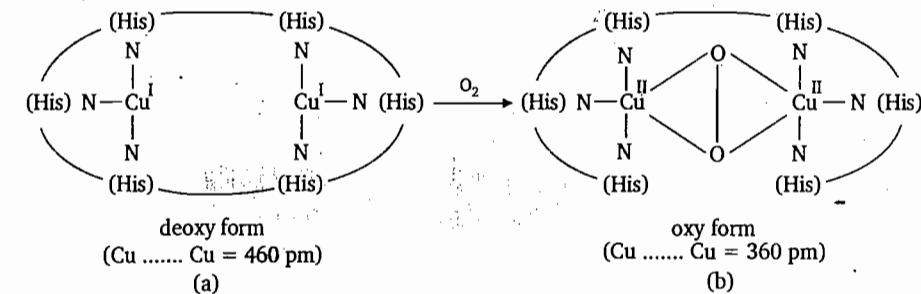


Fig. 9.9: Structure of (a) deoxyhemocyanin (b) oxyhemocyanin

Hemocyanin  
Colourless

Oxyhemocyanin  
(Blue colour due to  $\text{O}_2^- \rightarrow \text{Cu}^{2+}$  LMCT)

The dioxygen molecule oxidizes each Cu(I) ion to Cu(II) ion and itself is reduced to the peroxide ion ( $O_2^{2-}$ ). The two Cu(II) ions are bridged by the peroxide ion [Fig. 9.6(b)]. The resonance Raman spectroscopy reveals the formulation of  $\overset{\text{II}}{\text{Cu}}-\overset{\text{I}}{\text{O}}-\overset{\text{II}}{\text{O}}-\overset{\text{II}}{\text{Cu}}$  linkage :  $\nu(\text{O}-\text{O})$  is about  $750 \text{ cm}^{-1}$  compared with about  $800 \text{ cm}^{-1}$  for free  $\overset{\text{II}}{\text{O}_2^{2-}}$  ion. The Cu(II) ions are coupled antiferromagnetically with the  $\mu-\overset{\text{II}}{[\text{O}_2]^{2-}}$  ion being involved in a supexchange mechanism.

### Cytochromes

Cytochromes are found in both plants and animals and serve as electron carriers. They contain heme like prosthetic groups. A prosthetic group is a compound required by an enzyme to facilitate a particular reaction, such compounds are also called coenzymes. The peptide portion of an enzyme that requires a prosthetic group is called an apoenzyme while complete enzyme with prosthetic group is called the holoenzyme. There are three main types of cytochromes: Cytochrome a (Cyt-a), cytochrome b (Cyt-b) and cytochrome-c (Cyt-c). As in hemoglobin, the Fe(II) ion of heme group is attached to a N-atom of imidazole ring of histidine residue on one side of the porphyrin plane. The sixth coordination site of Fe(II) is occupied by a tightly bound S atom from a methionine residue of a protein. For this reason, the cytochromes are inert not only to oxygen but also to the poisons such as CO which affect the oxygen carriers.

The reduction potentials for cytochromes increase in the order : cyt-b (0.26 V) cyt-c (0.26 V) cyt-a (0.4 V) therefore the order of electron flow is :  $b \rightarrow c \rightarrow a \rightarrow O_2$ . The differences in reduction potentials for  $\text{Fe(II)} \rightarrow \text{Fe(III)}$  oxidation results from changes in the porphyrin substituents (Fig. 9.10), changes in the protein and in some cases changes in axial ligands.

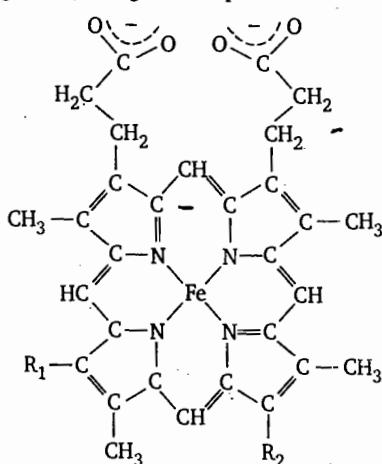
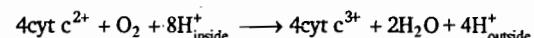


Fig. 9.10 Structure of heme groups

The electron transfer reactions allow energy from glucose oxidation to be released gradually and to be stored in the form of adenosine triphosphate (ATP) which is used when required by the cell. Cytochrome-c oxidase, the terminal member of the cytochrome chain which binds the inner membrane of the mitochondrion contains cytochrome-a, cytochrome-a<sub>3</sub> and two Cu(II) ions (Cu<sub>A</sub> and Cu<sub>B</sub>). Electron transfer involves the cytochrome-a and Cu<sub>A</sub>, electron being transferred from cytochrome c to Cu<sub>A</sub> and then to cytochrome-a. Cytochrome-a<sub>3</sub> and Cu<sub>B</sub> provide site for dioxygen binding and conversion of O<sub>2</sub> to H<sub>2</sub>O. Cytochrome a<sub>3</sub> and Cu<sub>B</sub> are five and three coordinated respectively and therefore bind dioxygen. The overall reaction catalyzed by cytochrome c oxidase enzyme is :

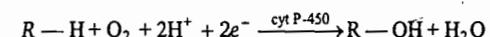


This indicates that cytochrome chain involves transport not only of electrons but also of protons across the mitochondrial membrane. The oxidized form of cytochrome a<sub>3</sub> is susceptible to bind CN<sup>-</sup> that renders cyanides toxic.

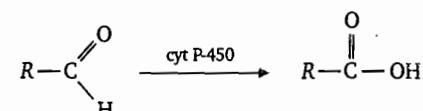
### Cytochrome P-450

Cytochrome P-450 are a group of cytochromes found in plants, animals and bacteria. It is named as pigment that absorbs at 450 nm with their CO complexes. This is due to  $\pi-\pi^*$  transition (blue to red) and this bond is called SORET bond. Cytochrome P-450 facilitates the cleavage of O<sub>2</sub> and functions as monooxygenase catalyzing the insertion of oxygen atoms into substrates. Oxygenases are enzymes that insert oxygen into the substrates. Monooxygenase inserts one oxygen atom and a dioxygenase inserts two oxygen atoms. Of the many possible substrates, the most important are molecules in which C—H bond is converted to C—OH groups. Some examples are:

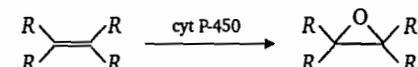
Conversion of an hydrocarbon RH to ROH.



Conversion of an aldehyde to the carboxylic acid.



Conversion of an alkene to epoxide.



Cytochrome P-450 enzymes are found in kidney where they oxidize insoluble hydrocarbons to water soluble R—OH compounds which then be excreted in the urine.

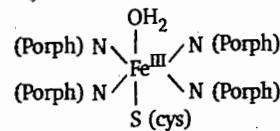
One oxygen atom is inserted into an organic substrate and one atom is reduced to H<sub>2</sub>O.

The active site in a cytochrome P-450 is heme similar to hemoglobin and myoglobin except that:

(i) Fe is present in Fe(III) state and it is low spin octahedral.

- (ii) One S-atom of cysteine is coordinated to Fe(III) instead of histidine in the proximal position.  
 (iii) Sixth coordination site is occupied by H<sub>2</sub>O.

The cytochrome P-450 enzymes have low spin octahedral Fe(III) active site.



Cytochrome P-450 enzymes have molar mass of about 50,000. The catalytic cycle for the action of cytochrome P-450 enzyme is shown in Fig. 9.11.

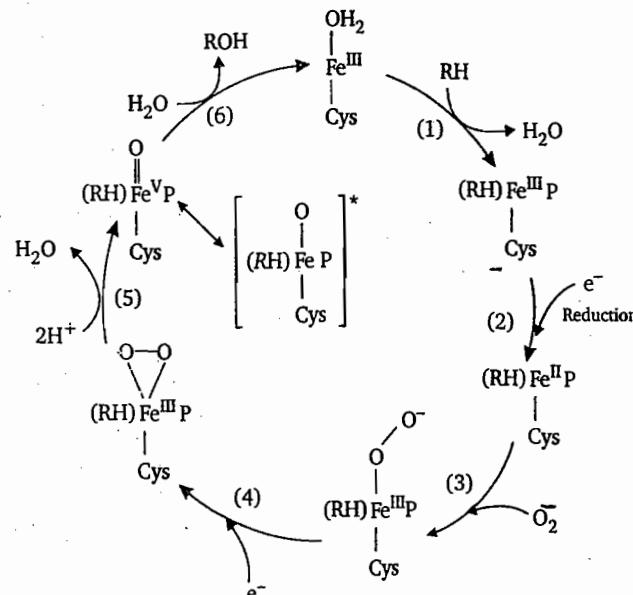


Fig. 9.11 Catalytic cycle for cytochrome P-450

In the first step, the organic substrate enters a hydrophobic pocket of the protein, near the Fe(III) centre expelling the water molecule from the iron axial coordination site to give a Fe(III) complex. In the second step, the Fe(III) complex is reduced by another enzymatic system to give high spin Fe(II) complex.

In the step 3, the dioxygen molecule binds to Fe(II) centre like hemoglobin and myoglobin followed by one electron transfer from Fe(II) to dioxygen to form an Fe(III)-superoxide complex. In the step 4, an another electron is added to give Fe(III)-peroxo complex. In step 5, the protonation of Fe(III)-peroxo complex leads to removing one oxide ion as water leaving an oxyferryl complex

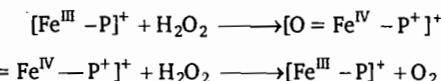
Fe(V)=O or oxygen double bonded to Fe(IV) with one electron having been oxidized from the π-HOMO of the porphyrin ring leaving it as a radical cation. In step 6, the organic substrate (R—H) is oxidized to R—OH with concomitant binding of an H<sub>2</sub>O ligand to the active site of the metalloenzyme which once again contains low spin Fe(III) centre.

### Catalases and Peroxidases

Peroxidase is a heme protein catalyzing oxidation of variety of substrates such as ascorbate, ferrocyanide, and cytochrome c by hydrogen peroxide. Catalase enzyme is found in nearly all living organisms. Catalases catalyze the disproportionation of hydrogen peroxide and organic peroxides. They also catalyze the oxidation of substrates by hydrogen peroxide. Catalase has one of the highest turnover numbers of all enzymes, one catalase molecule can convert millions of molecules of H<sub>2</sub>O<sub>2</sub> to water and oxygen each second.

Peroxidases and catalases have similarities in both structure and reaction mechanisms. Both have high spin Fe(III) heme active site, with imidazole nitrogen of histidine residue occupying the fifth coordination site. The sixth coordination site is occupied by a water ligand in the resting enzyme.

The reaction is believed to occur in two steps:



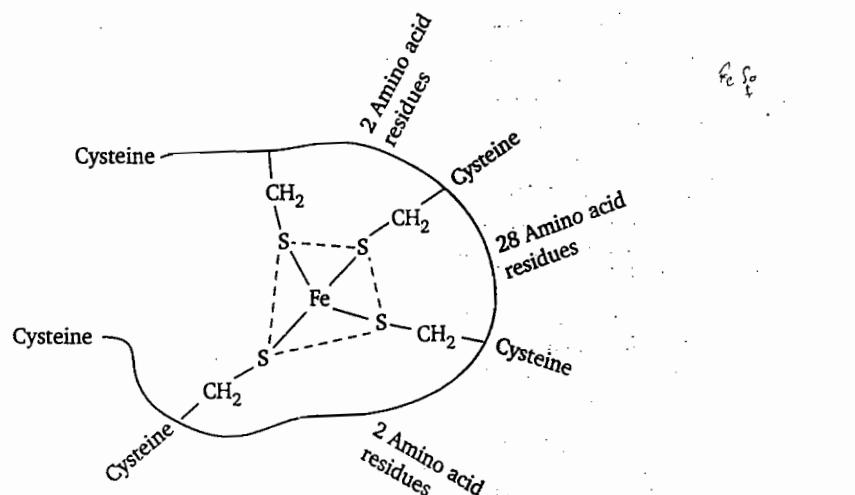
Where  $\text{Fe}^{\text{III}} - \text{P}$  is the heme group of the enzyme.  $\text{O} = \text{Fe}^{\text{IV}} - \text{P}$  is the mesomeric form of  $\text{O} = \text{Fe}^{\text{V}} - \text{P}$  which indicates that Fe(III) is not completely oxidized to Fe(V) but it receives one electron from the porphyrin ring. It means that Fe(III) is oxidized to Fe(IV) and porphyrin ring (P) is oxidized by one electron to porphyrin\* and the porphyrin ring containing one unpaired electron becomes a radical cation. The reactivity of the iron centre can be enhanced by the presence of Tyr-357 (tyrosinate at position 357) at the fifth (axial) position which assists the oxidation of the Fe(III) to Fe(IV). The optimum pH for human catalase is approximately 7. Hydrogen peroxide is harmful byproduct of several metabolic processes. To prevent damage to cells and tissues, it must be converted into H<sub>2</sub>O and O<sub>2</sub>. The colour of oxidized and reduced forms of catalase is due to π to π\* transition in the porphyrin ring.

### Iron-Sulfur Proteins

These are non-heme iron proteins and are responsible for electron transfer in plants and bacteria. These have relatively low molar mass (6000-12000) and contain one, two, four or eight Fe atoms. The iron atoms are coordinated to four sulfur atoms in an approximately tetrahedral manner. Since iron atoms are coordinated to S atoms tetrahedrally, the iron atoms have high spin configuration. They have low range of reduction potentials (-0.05 V to -0.5 V), therefore, they act as reducing agents in biochemical processes. Different types of these are involved in photosynthesis, nitrogen fixation and metabolic oxidation of sugars prior to involvement of the cytochromes.

### Ruberodoxin

Ruberodoxin is found in anaerobic bacteria where it participates in biological redox reactions. It is the simplest NHIP (non-heme iron protein) and contains only one Fe atom. The Fe atom is coordinated to four S atoms in distorted tetrahedral manner belonging to the amino acid cysteine in the protein chain. The iron is in the +3 oxidation state. The Fe—S distance is 224 to 233 pm and S—Fe—S bond angle is 104 to 114°. It has no labile sulfur (i.e., inorganic sulfur  $S^{2-}$  which can be liberated as  $H_2S$  by treatment with mineral acids, inorganic sulfur atoms are not part of the protein instead they form bridges between Fe atoms). The structure of ruberodoxin is shown in Fig. 9.12.



**Fig. 9.12** The environment of the iron in the ruberodoxin molecule.

When  $Fe(III)$  is reduced to  $Fe(II)$ , there is slight increase in the  $Fe-S$  distances but both  $Fe(III)$  and  $Fe(II)$  are high spin in tetrahedral geometry. Ruberodoxin is a one electron transfer agent.

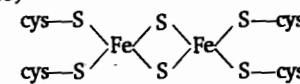
### Ferredoxins

NHIP with more than one iron atom are classified into three major categories: [2Fe—2S], [3Fe—4S] and [4Fe—4S].

#### [2Fe—2S] or $Fe_2S_2$ Ferredoxins

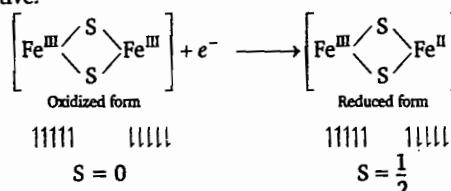
They are called as plant ferredoxins and act as one electron transfer agents. These are very acidic proteins. The active site consists of two di- $\mu$ -sulfido bridged high spin tetrahedral  $Fe(III)$  ions. The  $Fe(III)$  with  $S = \frac{5}{2}$  are antiferromagnetically coupled via bridging atoms and therefore are

diamagnetic and ESR inactive. Each iron atom is also coordinated with two non-labile sulfur atoms of terminal cysteine groups (Fig. 9.13)

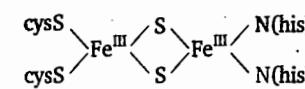


**Fig. 9.13** Structure of [2Fe—2S] ferredoxin

The ESR spectroscopy shows that the  $Fe^{+4}$  ions in reduced form are not equivalent but they exist as  $Fe(III)$  and  $Fe(II)$  rather than both having a fractional oxidation state of +2.5. In the reduced form the  $Fe(III)$  ( $d^5$ ) and  $Fe(II)$  ( $d^6$ ) electrons couple together resulting in one unpaired electron. Therefore it is EPR active.



If two cysteine units are replaced by two histidine residues, then the ferredoxin is called RIESKE protein (Fig. 9.14).



**Fig. 9.14**

#### [3Fe—4S] or $Fe_3S_4$ Ferredoxin

In recent years the existence of [3Fe—4S] ferredoxins has been established by Mössbauer spectroscopy. It contains cubane [4Fe—4S] structure with one corner removed (Fig. 9.15).

The  $Fe_3S_4$  cluster has 3Fe, four labile sulfurs and three non-labile sulfurs. In oxidized form it contains three high spin  $Fe(III)$  ions and in the reduced form it contains one  $Fe(II)$  and two  $Fe(III)$  ions. This suggests that it is a one electron transfer agent. In the reduced form  $Fe(II)$  and  $Fe(III)$  ions are also high spin. The two  $Fe(III)$  ions in oxidized form are coupled antiferromagnetically leaving the third  $Fe(III)$  ion paramagnetic ( $S = \frac{5}{2}$ ) and therefore it is ESR active. In the reduced form, the  $Fe(III)$  ions coupled antiferromagnetically leaving  $Fe(II)$  ion as paramagnetic ( $S = 2$ ) and therefore reduced form is also ESR active.

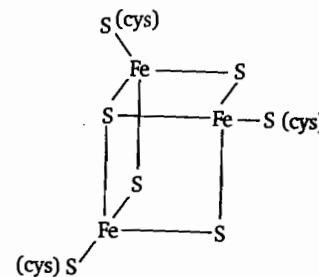
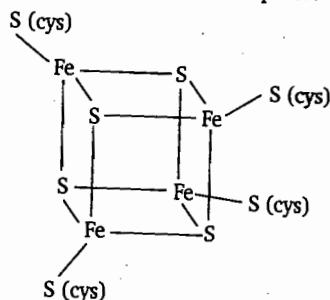


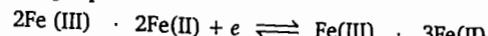
Fig. 9.15 Structure of [3Fe-4S] ferredoxin

### [4Fe—4S] or $\text{Fe}_4\text{S}_4$ Ferredoxins

These are the most common and most stable ferredoxins. These are found in bacteria and involve in anaerobic metabolism. The  $\text{Fe}_4\text{S}_4$  cluster consists of a cubane like cluster in which four Fe and four labile (or inorganic) S atoms are present on alternate corners of a cube. Therefore, it is called [4 Fe—4S] ferredoxin. In addition, each Fe atom is bounded to S atom of cysteine ligand (Fig. 9.16). Each Fe atom has approximately tetrahedral coordination sphere.

Fig. 9.16 Structure of  $\text{Fe}_4\text{S}_4$  Ferredoxins

[4Fe—4S] cluster acts as one electron transfer agent. It contains two Fe(III) and two Fe(II) ions in the oxidized form and one Fe(III) and three Fe(II) ions in the reduced form. In both forms Fe(II) and Fe(III) ions are high spin.



In oxidized form the two Fe(III) ions as well as the two Fe(II) ions are coupled antiferromagnetically resulting in  $S = 0$  and therefore, the oxidized form is diamagnetic and EPR inactive.

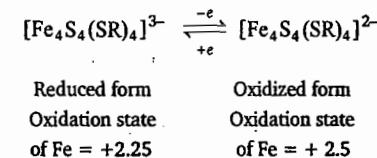
Fe(III)	Fe(III)	Fe(II)	Fe(II)
$d^5(\text{HS})$	$d^5(\text{HS})$	$d^6(\text{HS})$	$d^6(\text{HS})$
11111	11111	11111	11111
$S = 0$			

In the reduced form the Fe(III) and Fe(II) ions also couple antiferromagnetically resulting in  $S = \frac{1}{2}$ . Therefore, the reduced form is paramagnetic and EPR active.

Fe(III)	Fe(II)	Fe(II)	Fe(II)
$d^5(\text{HS})$	$d^6(\text{HS})$	$d^6(\text{HS})$	$d^6(\text{HS})$
11111	11111	11111	11111
$S = \frac{1}{2}$		$S = 0$	

The Mössbauer spectroscopy has shown that all the four iron atom are equivalent and regarded as electronically delocalized systems with oxidation states of + 2.5 (in oxidized form) and + 2.25 in the reduced form.

The synthetic analogues,  $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{x-}$  of ferredoxins  $[\text{Fe}_4\text{S}_4]^{n+}$  can be prepared by reacting  $\text{FeCl}_3$ ,  $\text{NaHS}$  and an appropriate thiol. The magnetic properties and EPR, electronic and Mössbauer spectra of the synthetic  $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}$  anion are similar to those of reduced ferredoxins.



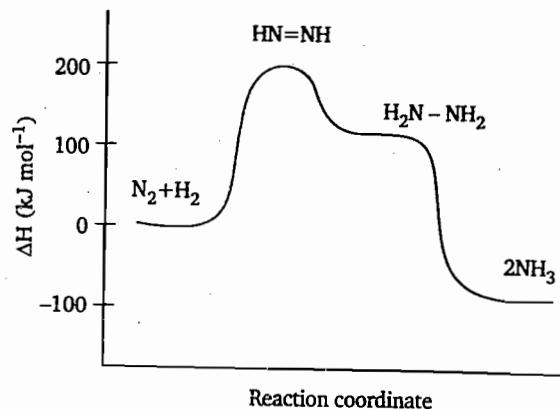
The oxidized form  $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$  can be further oxidized at high potentials of about + 0.35V. (therefore, these ferredoxins are called high potential iron sulfer proteins, HiPIP) to  $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{+}$  which is paramagnetic with  $S = \frac{1}{2}$  (due to antiferromagnetic coupling of Fe ions).

### Nitrogen Fixation

Nitrogen in chemically bound forms such as the amino acids, proteins and porphyrins, is one of the most important elements of life. On earth nitrogen is found as the elemental  $\text{N}_2$  and all forms of life are unable to utilize it as such. Nitrogen fixation is the process that converts atmospheric nitrogen into  $\text{NH}_3$ . There are two main processes for nitrogen fixation.

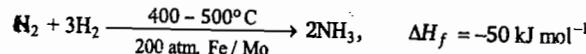
1. Biological process (By bacteria)
2. Industrial process (Haber-Bosch process)

In both the processes  $\text{N}_2$  is converted into  $\text{NH}_3$  breaking the  $\text{N}=\text{N}$  triple bond which has the highest bond dissociation energy ( $945 \text{ kJ mol}^{-1}$ ) of any homonuclear diatomic molecule. The barrier to form  $\text{NH}_3$  is not thermodynamic ( $\Delta H_f$  for  $\text{NH}_3 = -50 \text{ kJ mol}^{-1}$ ) but kinetic. The two intermediates before breaking of  $\text{N}=\text{N}$  triple bond completely,  $\text{HN}=\text{NH}$  (diazene) and  $\text{H}_2\text{N}-\text{NH}_2$  (hydrazine) are disfavoured thermodynamically because they have higher energies than either of the reactants or the products. (Fig. 9.17).



**Fig. 9.17 Energies of reactants, intermediate and the products along the reaction pathway**

The Haber-Bosch process involves the high temperature ( $400 - 500^\circ\text{C}$ ) and pressure (200 atm) and Fe/Mo catalyst. Therefore, this process is very expensive.



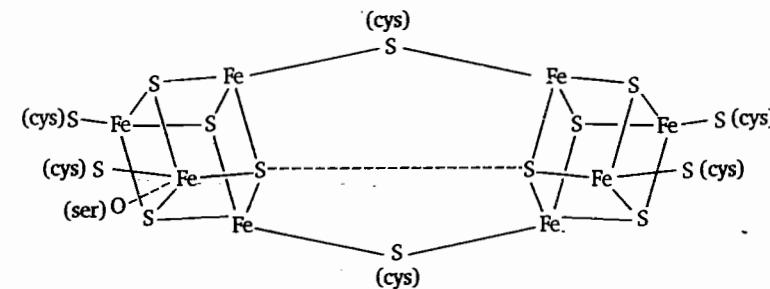
There is blue green algae, a wide variety of bacteria that can fix  $\text{N}_2$  in vivo (life natural process) at ambient temperature and pressure. These bacteria are either free living or form symbiotic association with plants or other organisms. The important bacteria which fix the nitrogen are : *Clostridium pasteurianum*, *Azotobacter vinelandii* and *Rhizobium*, the best known of which is *Rhizobium* which is found in the root nodules of leguminous plants such as clover, beans, peas and soya.

The ammonia so formed is used in amino acids and protein synthesis by plants. There are three types of nitrogenase enzymes:

1. Vanadium nitrogenase
2. Iron nitrogenase
3. Molybdenum nitrogenase

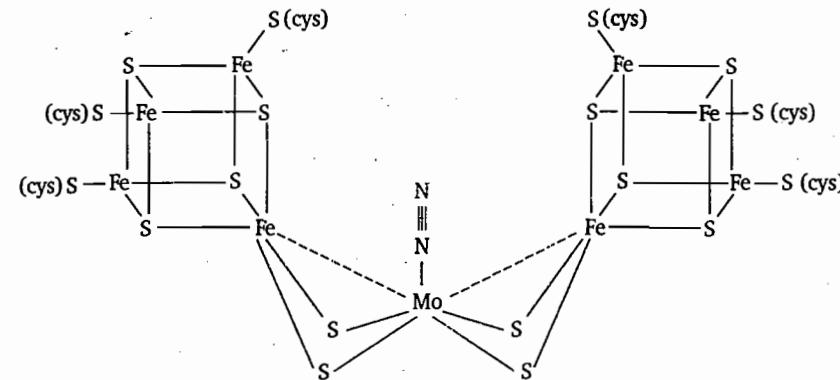
Nitrogenases are composed of two metalloproteins: an Fe protein and the MFe (M = Mo, V and Fe) protein as cofactor. The vanadium nitrogenase (containing Fe protein, a  $4\text{Fe} - 4\text{S}$  ferredoxin and FeV cofactor) has less activity than the molybdenum nitrogenase.

The presence of molybdenum is necessary component of most nitrogenases. These molybdenum nitrogenases consists of two different proteins: the Fe and MoFe proteins. The Fe protein has a molar mass of about 60,000. The Fe protein (called the P-cluster) has two  $\text{Fe}_4\text{S}_4$  units connected by two cysteine ligand bridges. These two units are also linked by a S...S bond (Fig. 9.18). In one  $\text{Fe}_4\text{S}_4$  unit there is a serine ligand attached to one of the iron atoms in addition to a cysteine ligand.



**Fig. 9.18 Structure of P-cluster in nitrogenase**

The molar mass of MoFe protein is 220,000 to 2,40,000. The most proposed structure of MoFe protein is shown in Fig. 9.19.



**Fig. 9.19 Structure of the active site of the Mo-Fe protein-nitrogenase**

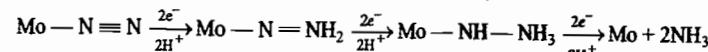
In MoFe protein, the Mo atom is linked to two  $\text{Fe}_4\text{S}_4$  units by two sulphide groups and Mo-Fe bonds. It is believed that the reduction of molecule nitrogen occurs at the Mo site of the enzyme. It is not clear whether the initial coordination of  $\text{N}_2$  occurs at an iron atom or a Mo atom, although most opinions favours the Mo atom.

The enzymes nitrogenases in various bacteria catalyzes the activation and reduction of dinitrogen to ammonia according to equation.



where  $P_i$  is inorganic phosphorus.

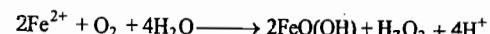
The electrons required in the reduction of  $\text{N}_2$  are transferred to nitrogen by the reduced form of ferredoxins and flavodoxins. The source of these electrons is the oxidation of pyruvate. The electrons are first transferred to the smaller protein (Fe protein or P-cluster). The reduced Fe protein transfers its reducing electron to the MoFe protein and then to the dinitrogen bound to Mo. A series of such electron transfer steps is:



The energy for this process is provided by the hydrolysis of ATP to ADP and  $P_i$ .

### Iron Storage and Transport : Ferritin and Transferrin

In humans and in many other higher animals iron is stored in ferritin and hemosiderin. Ferritin is composed of a protein coat (called as apoferritin) and an iron core. Twenty four proteins or peptide chains with about 175 amino acids are combined to form a protein coat (or apoferritin) which is a hollow sphere of about 100 Å in diameter. The iron core of ferritin contains about 45000 Fe(III) ions and some hydroxo as well as oxo and phosphate ligands. The iron core is similar to ferrihydrite,  $(\text{FeO} \cdot \text{OH})_8$  ( $\text{FeO} \cdot \text{H}_2\text{PO}_4$ ). The iron core is fit into the hollow shell of apoferritin to form ferritin. The phosphate groups in the iron core functions as terminators and linking group to the protein shell. Ferritin is found in liver, spleen and bone marrow. Ferritin is a water soluble crystalline substance. Ferritin contains eight hydrophilic and six hydrophobic channels. It is thought that Fe(III) ions enter via the hydrophilic channels and leave via hydrophobic channels. The mechanism by which Fe(III) ions enter and leave ferritin is not clear. The iron core can be formed only from aqueous Fe(II) ions so that oxidation of Fe(II) give Fe(III) ions as shown below:



The oxidation of Fe(II) ions is catalyzed by Fe ferroxidase enzyme. Oxidation of Fe(II) and hydrolysis produces one electron and an average of 2.5 protons.

Mössbauer spectroscopy and EXAFS show that Fe(III) in ferritin is high spin and surrounded by six oxygen atoms at a distance of 195 pm and six Fe(III) ions at a distance about 300 pm followed by  $\text{OH}^-$  ions octahedrally. The individual protein and apoprotein have molar masses 18500 and 445000 respectively. The formation of full iron core of 4500 Fe(III) ions produces a total of 4500 electrons and 11250 protons. Hemosiderin contains larger proportions of hydrous metal oxide and is water insoluble and is usually located within an intercellular membrane (lysosomes).

### Transferrin

Transferrin is a protein that binds Fe(III) very strongly [not Fe(II)] and transport it from the stomach into bloodstream. Transferrin proteins transport iron to the ferritin.

Humans and other animals absorb iron as Fe(II) from food in their digestive systems. As Fe(II) passes from the stomach (which is acidic) into the blood ( $\text{pH} = 7.4$ ), it is oxidized to Fe(III) in a process catalyzed by the copper metalloenzyme ceruloplasmin. The Fe(III) is then binds with transferrin protein and transported to bone marrow where it is released from transferrin protein after the reduction of Fe(III) to Fe(II) because Fe(II) binds less effectively to the transferrin and stored as ferritin. Fe(II) ion is then used to synthesise the other iron compounds such as hemoglobin, myoglobin, and the cytochromes. When a red blood cell become aged after an average of 16 weeks, the hemoglobin is decomposed and the iron is recovered by transferrin after oxidation to Fe(III).

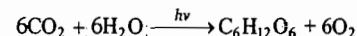
Transferrin have molar mass of about 80000 and contain two similar but not identical sites and bind only two Fe(III) ions. The Fe(III) ion is in a distorted octahedral environment of one N, three O and a chelating  $\text{CO}_3^{2-}$  or  $\text{HCO}_3^-$ . The binding constant is sufficiently high (about  $10^{26}$ ), therefore, transferrin act as extremely efficient scavenger of iron.

### Siderophores

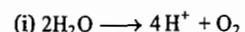
Siderophores are iron containing complexes which are found in most microorganisms and transport Fe(III). Siderophores are also known as siderochromes because some of them are intensely coloured. They have relatively low molar masses (500–1000). They are classified into several categories such as the ferrichromes, ferrioxamines and entrobactins. They are the chelating ligands and form chelates with Fe(III) ions. The complexes are high spin octahedral. These complexes are very stable but are labile which allow the iron to be transported and transferred within the bacteria.

### Photosynthesis

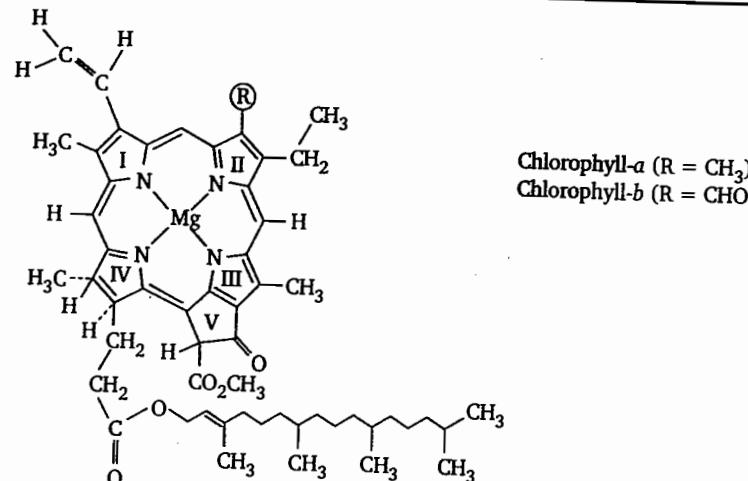
Photosynthesis is a redox process by which green plants convert water and atmospheric  $\text{CO}_2$  into carbohydrates such as glucose and release dioxygen by absorbing sun light. The overall reaction is:



This reaction involves the reduction of  $\text{CO}_2$  and oxidation of  $\text{H}_2\text{O}$  to  $\text{O}_2$ . It is a two step reaction:

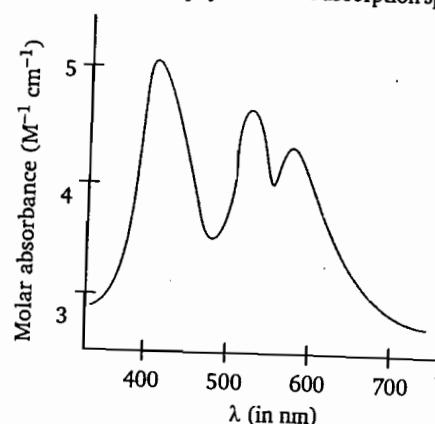


Photosynthesis occurs in the chloroplasts of the cells of the green plants. Photosynthesis is essentially a process by which sun light energy is converted into chemical energy in the form of adenosine triphosphate (ATP) and reduced nicotinamide adenine dinucleotide phosphate (NADPH). This energy permits the fixation of  $\text{CO}_2$  into carbohydrates with the liberation of dioxygen,  $\text{O}_2$ . Photosynthesis is initiated by the capture of light energy (usually referred to as light harvesting) in the photoreceptors of chlorophylls (chloros-green, phylon-leaf) found in chloroplasts in the green leaf. Many of the subsequent steps proceed in dark. The overall process is endothermic and involves more than one type of chlorophyll, ferredoxin, cytochromes, manganese complexes and a copper containing plastocyanin.

**Fig. 9.20 Structure of chlorophyll-a**

Chlorophylls are complexes of  $\text{Mg}^{2+}$  with porphyrin ring in which one of the pyrrole rings has been reduced. A porphine ring with one double bond reduced is called a chlorin. Therefore, chlorophylls are the complexes of  $\text{Mg}^{2+}$  with substituted chlorin. A fused cyclopentanone ring is also present (Fig. 9.20). In green plants there are two chlorophylls (a and b) differing in one of the side groups. Chlorophyll a (Chl-a) is shown in Fig. 9.17. Chlorophyll-b is the same except that for the  $-\text{CH}_3$  (in circle) which is  $-\text{CHO}$  in chlorophyll-b.

Chlorophylls in the chloroplast of plants leaf absorbs light in the red region of the visible spectrum (near 680–700 nm). The exact wave number depends upon the nature of the substituents. Chlorophylls are the green pigments. Chlorophyll-a has the absorption spectrum shown in Fig. 9.21.

**Fig. 9.21 The absorption spectrum of chlorophyll-a in the visible region**

The two bands are observed in the absorption spectrum of chlorophyll-a : the strong absorption band in the red (called 'Q band') and a comparatively weak band in blue to near UV (the Soret band). Both these bands arise from excitation of electrons from the porphyrin ring  $\pi\text{HOMO}$  to  $\pi^*\text{LUMO}$ . The non-absorbing radiations between these two bands accounts for the characteristic green colour of the plants leaf.

The initial absorption of light radiations is from the singlet ground state to a singlet excited state of the chlorophyll Q band ( ${}^1\text{Q}$ ). The chlorophylls in solution undergo rapid intersystem crossing into the lower energy spin triplet state ( ${}^3\text{Q}$ ). This state causes the photochemical electron transfer reactions of molecules in solution. The light absorbed by chlorophylls is transferred to the reaction centre.

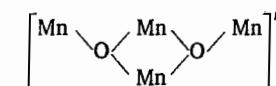
There are two photochemical reaction centres: Photosystem-I (PS-I) and Photosystem-II (PS-II). The initiating photosystem-II is called  $P_{680}$  as it absorbs at 680 nm and the subsequent photosystem-I is called  $P_{700}$  as it absorbs at 700 nm. The chlorophyll a site of PS-II absorbs quanta of higher energy than that of PS-I therefore, the two chlorophyll sites are distinguished as Chl- $a_2$  and  $a_1$  or alternatively  $P_{680}$  and  $P_{700}$ .

In addition to the chlorophylls at PS-I and PS-II reaction centres, there are several other pigments associated with the light harvesting complex.

The photosystem I involves chlorophyll-a along with other pigments and does not produce dioxygen. This photosystem is involved in the anaerobic bacteria. These bacteria oxidize  $\text{H}_2\text{S}$  to S or oxidize organic molecules instead of the usual reaction where  $\text{H}_2\text{O}$  is oxidized to  $\text{O}_2$ .

### Photosystem-II

In dark PS-II is in its ground, unexcited state in which it has no tendency to release an electron. When it absorbs sun light via antenna chlorophylls, it becomes excited such that it has a strong tendency to transfer its excited electron. It is, therefore, a strong reducing agent and it reduces the pheophytin (a chlorophyll like pigment lacking the  $\text{Mg}^{2+}$  ion) of the PS-II electron transfer chain. The loss of an electron causes PS-II to become positively charged and it then attracts electron from manganese protein (an  $\text{Mn}_4$  cluster).



The manganese protein contains three Mn(II) and one Mn(III). The oxidized manganese protein in turn attracts electron from water and catalyses the oxidation of  $\text{H}_2\text{O}$  to  $\text{O}_2$ .

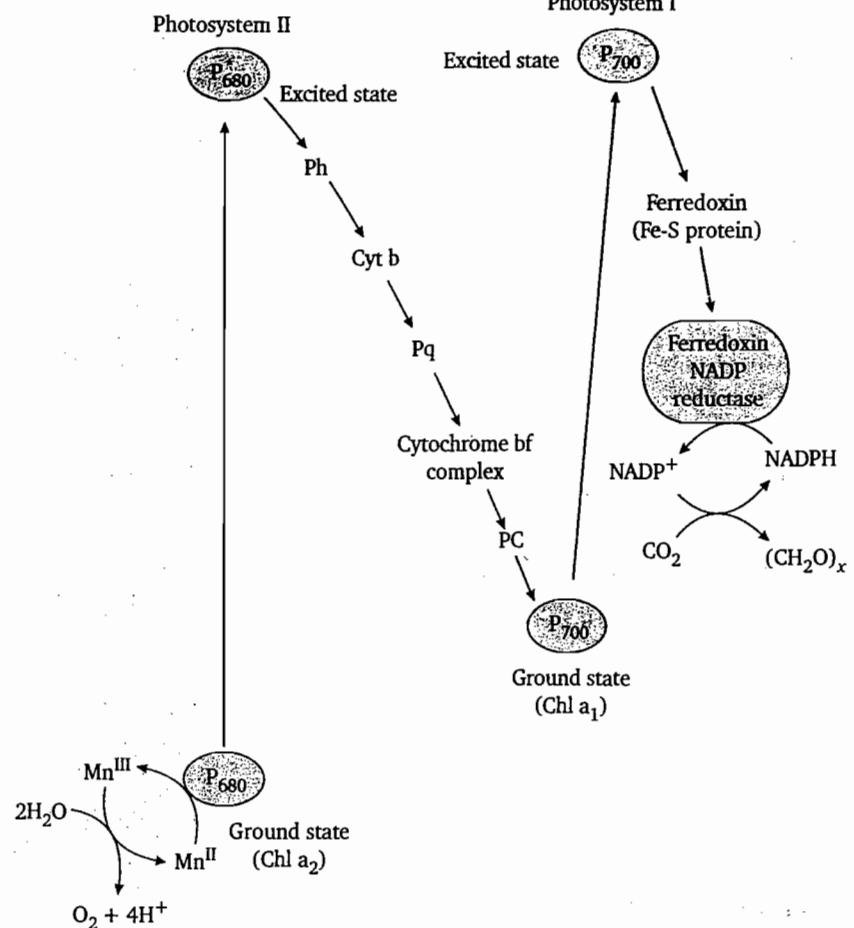


Fig. 9.22.

The electron from pheophytin is then transferred through various redox systems like plastoquinone, cytochromes, iron-sulphur protein and plastocyanin (plastocyanin is a copper protein in which the copper ion alternates between the Cu<sup>2+</sup> (oxidized) and Cu<sup>+</sup> (reduced) forms). At this point it leaves PS-II and moves on to PS-I. (Fig. 9.22)

### Photosystem-I

Photosystem-I involves chlorophyll-*a* and *b*. When PS-I absorbs light energy from chlorophylls, the antenna pigments (other pigments present in leaves to harvest some light and transfer its energy

to the reaction centre), the electron received from PS-II is, therefore, further excited and becomes a reducing agent. It passes on its electron to short chain of electron carriers, which reduces ferredoxin and the reduced form of ferredoxin reduces NADP<sup>+</sup> by the following reaction catalysed by the FAD enzyme called ferredoxin-NADP reductase (FAD or flavin adenine dinucleotide).

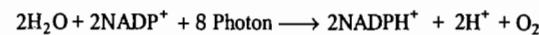


In brief, an electron of P<sub>700</sub> has been excited and transported to ferredoxin which in turn, reduces NADP<sup>+</sup>. This left P<sub>700</sub> an electron short. It is now P<sub>700</sub><sup>+</sup>, an oxidizing agent. It accepts an electron from plastocyanin (PC)

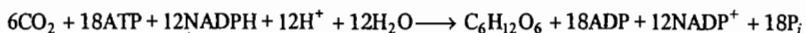


To go back further, we started with light absorption followed by exciting an electron on P<sub>680</sub>, the reaction centre on PS-II, this leaves P<sub>680</sub><sup>+</sup> which must have its electron restored so that it can revert to the ground state, ready for absorption of another light radiation to start a new cycle of reactions. The electron comes from water.

The net reaction of PS-II and PS-I is :



There are also cyclic dark reactions that produce ATP. NADPH and ATP involve in the conversion of CO<sub>2</sub> into glucose by the following net reaction.

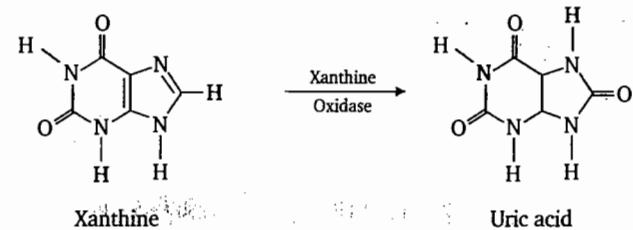


### Role of Mg<sup>2+</sup> Ion

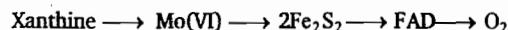
Mg<sup>2+</sup> is preferred in photosynthesis by chlorophyll because it binds strongly with chlorophyll and keep the macrocycle fairly rigid so that energy is not so readily dissipated by thermal vibrations.

### Xanthine Oxidase

The enzyme xanthine oxidase contains two identical subunits, each containing one molybdenum, two Fe<sub>2</sub>S<sub>2</sub> and FAD (flavin adenine dinucleotide) sites. It has molar mass of about 275000. Xanthine oxidase catalyzes the oxidation of xanthine to uric acid.



An excess of uric acid accumulation leads to gout, which can be treated with inhibitors of xanthine oxidase. In xanthine oxidase, the Mo(VI) site carries out the two electron oxidation of xanthine to uric acid and it self reduces to Mo(IV). The Mo(VI) site is regenerated by transferring electrons, one at a time, to the  $\text{Fe}_2\text{S}_2$  and FAD sites so that Mo(VI) becomes ready for oxidation of next equivalent of xanthine. The electron flow may be represented as :



$\text{Fe}_2\text{S}_2$  sites in xanthine oxidase play the same electron-transfer role as the  $\text{Fe}_2\text{S}_2$  ferredoxins play in photosynthesis.

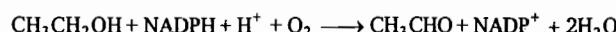
### Alcohol Dehydrogenase, Aldehyde Oxidase, Aldehyde Dehydrogenase

When ethanol is consumed, it is oxidized to extremely poisonous acetaldehyde. The oxidation of ethanol to acetaldehyde occurs in the liver by alcohol dehydrogenase.

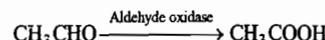


Alcohol dehydrogenases facilitate the oxidation of alcohols to aldehydes or ketones with the reduction of nicotinamide adenine dinucleotide ( $\text{NAD}^+$ ) to NADH. Alcohol dehydrogenase is a dimer of two subunits. It has two Zn atoms per subunit.

An another minor route of oxidation of ethanol to acetaldehyde involves cytochromes P-450 (which uses molecular oxygen) and NADPH.



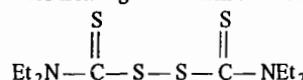
The oxidation of acetaldehyde to harmless acetic acid can be catalyzed by aldehyde oxidase enzyme.



The enzyme aldehyde oxidase is closely related to xanthine oxidase. It also contains two identical subunits, each containing one Mo, two  $\text{Fe}_2\text{S}_2$  and FAD sites. It has molar mass about 3,00,000. It oxidizes acetaldehyde to acetic acid via electron flow as shown below:



The drug antabuse is used for treating alcoholism which is a sulfur containing ligand, disulfiram.

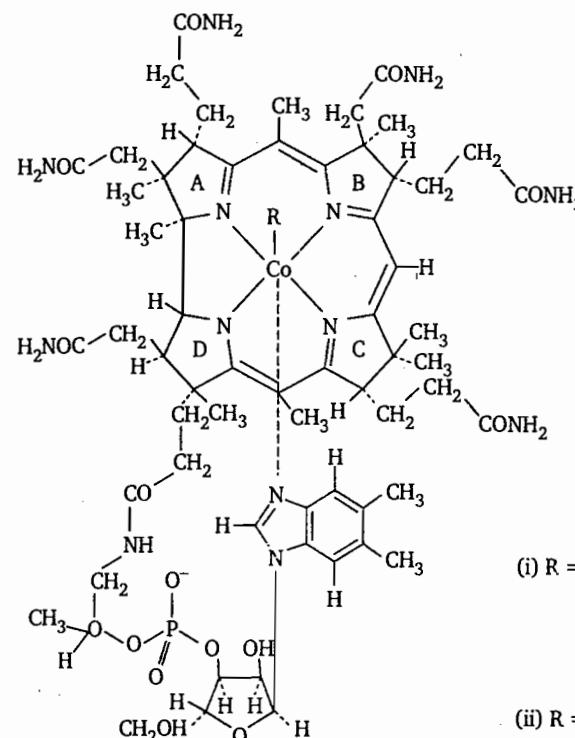


Another route of oxidation of acetaldehyde to acetic acid involves aldehydede hydrogenase and  $\text{NAD}^+$ .

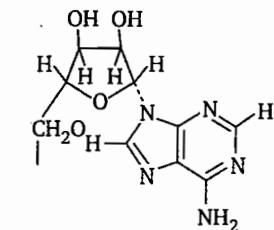


### Vitamin B<sub>12</sub> and Coenzyme B<sub>12</sub> or Cyanocobalamin

Vitamin B<sub>12</sub> and coenzyme B<sub>12</sub> are nature's only organometallic compounds. Vitamin B<sub>12</sub> was first isolated from liver extracts and it was observed that the deficiency of vitamin B<sub>12</sub> or B<sub>12</sub> coenzyme causes pernicious anemia in humans. In vitamin B<sub>12</sub> the Co(III) ion is coordinated to four N-atoms of a corrin ring. The corrin ring is modified porphyrin ring which has one less =CH- bridge between the two pyrrole rings than porphyrin ring. Therefore, corrin ring is less symmetric and less unsaturated than porphyrin ring. The fifth and sixth positions are occupied by an imidazole nitrogen and a cyanide ion. However in vivo, the cyanide ion is not present and the sixth position is occupied by loosely bound water molecule. (Fig. 9.23).



(i) R =

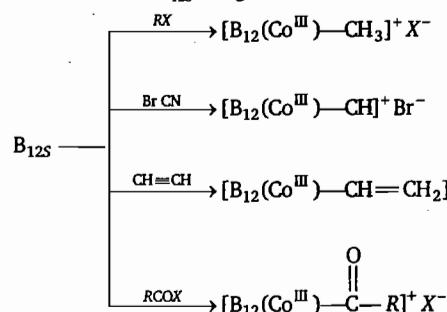


(ii) R = CN

Fig. 9.23 Structure of (i) Coenzyme B<sub>12</sub>, 5'-deoxyadenosylcobalamin, (ii) vitamin B<sub>12</sub>, cyanocobalamin

Incorporation of Co(III) into the corrin ring modifies the reduction potentials of cobalt and therefore, can be reduced by one electron to give vitamin B<sub>12r</sub> [Co(II) complex] or by two electrons to give vitamin B<sub>12s</sub> [Co(I) complex]. These reductions can be carried out in vivo by reduced ferredoxin.. The later is highly nucleophilic so readily undergoes alkylation.

Some reactions of vitamin B<sub>12s</sub> are given below:

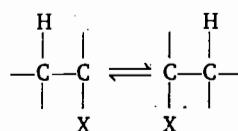


In Vitamin B<sub>12s</sub>, the R sight is empty and the 5-coordinate cobalt(I) atom is extremely reactive. In vitamin B<sub>12</sub> and its other derivative cobalt is present in + 3 oxidation state. Co(III) in these compounds is low spin octahedral field ( $d^6 \rightarrow t_{2g}^6 e_g^0$ ) and therefore they are diamagnetic and EPR inactive.

Vitamin B<sub>12</sub> and vitamin B<sub>12r</sub> are red and brown and these colours arise due to  $\pi - \pi^*$  transitions in corrin rings. The later is EPR active due to presence of an unpaired electron in  $d_{z^2}$  orbital. Co(II) is also low spin vitamin B<sub>12r</sub>. Co(I) in vitamin B<sub>12s</sub> is also EPR active due to presence of two unpaired electrons and its blue-green colour is due to  $\pi - \pi^*$  transitions.

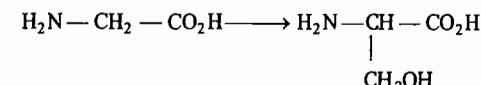
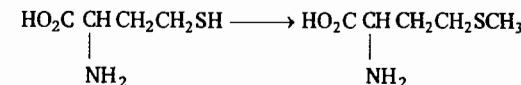
Unfortunately, certain bacteria can methylate not only sulfur in organic compounds but also some heavy metals such as Hg, Pb, Sn, Pd and Pt in aqueous solution to yield highly toxic species such as Hg(CH<sub>3</sub>) and Pb(CH<sub>3</sub>)<sub>4</sub>.

The reaction of adenosine triphosphate (ATP) with vitamin B<sub>12s</sub> yields direct cobalt-carbon bond between adenosyl and cobalt. The resulting molecule is known as B<sub>12</sub> coenzyme. It was the first organometallic compound discovered in living systems. In coenzyme B<sub>12</sub>, Co(III) is coordinated to carbon atom of an adenosyl ligand in place of CN<sup>-</sup> ligand. This coenzyme catalyses 1, 2 rearrangements of the general type:



Vitamin B<sub>12</sub> with CN<sup>-</sup> removed is called cobalamin, therefore, vitamin B<sub>12</sub> is called cyanocobalamin.

Coenzyme B<sub>12</sub> readily accepts a methyl group or hydroxy methyl group (bound to Co) that can be transferred to add a carbon to a substrate.



Coenzyme B<sub>12</sub> also reduces —CH(OH) group to —CH<sub>2</sub> group as the ribonucleic acid (RNA) is reduced to deoxyribonucleic acid (DNA).

The precise mechanism of these reactions involve the cleavage of Co—C bond. It may be noted that cobalt porphyrin analogues of vitamin B<sub>12</sub> can not be reduced to the Co(I) state under conditions where vitamin B<sub>12s</sub> is obtained. Therefore, this inability of the porphyrin ligand to stabilize the Co(I) is the reason why the corrin ring has been selected in place of porphyrin ring in the evolution of the B<sub>12</sub> cobalt complexes.

### Enzymes

Enzymes are larger protein molecules that catalyze large number of biochemical reactions. They increase the rate of biochemical reactions about 10<sup>6</sup> times compared to the uncatalyzed rate. They lower the activation energy for the formation of one product rather than the other and therefore are highly specific. The enzymes are composed of proteins.

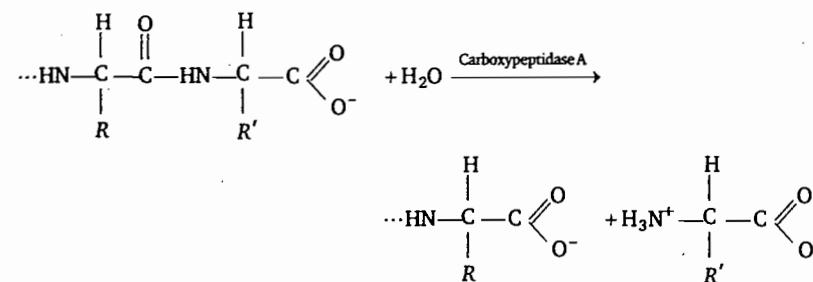
### Metalloenzymes

A metalloenzyme is an enzymatic protein in which a metal as metal ion is embedded in the cavity of the enzyme and forms strong bonds with the donor atoms of the protein. The donor atoms of proteins may be either soft bases such as S or hard bases such as O and N. In the similar way the metals may be either soft metals such as Cu<sup>+</sup>, Hg<sup>+</sup> and Cd<sup>2+</sup> or hard such as Fe<sup>3+</sup>, Zn<sup>2+</sup>. The protein part is called as an apoenzyme and a metal ion or complex metal ion is called a prosthetic group. For example, heme is prosthetic group in hemoglobin. A reversible bound group that combines with an enzyme for a particular reaction and then is released to combine with another is called as coenzyme. Both the prosthetic group and coenzyme are sometimes called cofactors.

### Zinc Metalloenzymes

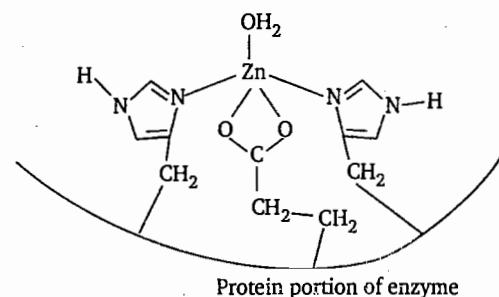
#### Carboxypeptidase-A

Carboxypeptidase A is a pancreatic metalloenzyme which catalyses the hydrolysis of peptide bonds in protein during the process of digestion.



The enzyme consists of a single protein chain of 307 amino acids and one  $Zn^{2+}$  ion. Molar mass of this enzyme is about 34,800.

The metal ion is coordinated to two N-atoms of two histidine residues (His-69 and His-196), to an oxygen atom of a glutamate residue (Glu-72) that acts as bidentate ligand and to a water molecule (Fig. 9.24).

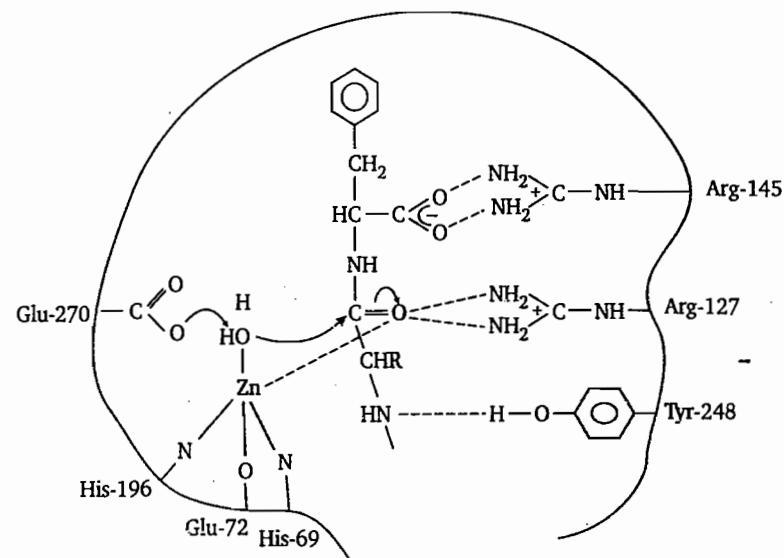


**Fig. 9.24** Structure of carboxypeptidase

The cavity has a hydrophobic pocket close to  $Zn^{2+}$  ion that can accommodate organic group of the peptide undergoing hydrolysis and therefore accounts for the higher efficiency with which hydrophobic C-terminal peptides are cleaved. The hydrophobic C-terminal peptides containing branched side chain or aromatic side chain such as  $C_6H_5 - CH_2 -$  or  $-CH_2C_6H_4OH$ . The carboxyl group of the substrate hydrogen bonds to an arginine (Arg-145) whereas the  $Zn^{2+}$  ion bonds to the oxygen of the peptide carbonyl group as shown in Fig. 9.25. The Arg-127 bonds to oxygen of carbonyl group of peptide of substrate and the phenolic group of Tyr-248 residue hydrogen bonds to  $-NH$  group of peptide of the substrate. The oxygen of the water molecule coordinated to  $Zn^{2+}$  ion bonds to the carbon of the carbonyl group of the peptide and free glutamate residue of the enzyme hydrogen bonds to hydrogen of the water ligand and  $H^+$  ion transfers from water to glutamate residue (Glu-270) leaving  $-OH$  group coordinated to  $Zn^{2+}$  ion.

In the next step  $C=O$  of carboxylic group of Glu-270 hydrogen bonds to H of  $-OH$  group coordinated to  $Zn^{2+}$  and  $H^+$  form  $-COOH$  group of Glu-270 is transferred to  $-NH$  group of the

substrate with breaking of C—N peptide bond of the substrate (Fig. 9.26). The glutamate residue abstracts a proton from  $-OH$  group coordinated to  $Zn^{2+}$  ion to form glutamic acid (Fig. 9.27). The hydrogen bonding to the carboxyl group by the Arg-145 and amide linkage by the Tyr-248 residues not only holds the substrate to the enzyme but also helps to break the C—N bond. In the final product of  $Zn^{2+}$ , the carbonyl of substrate binds in the bidentate fashion. Therefore, five coordination is maintained by switching the Glu-72 metal ligand from bidentate to monodentate because the metal moves toward Arg-127.



**Fig. 9.25**

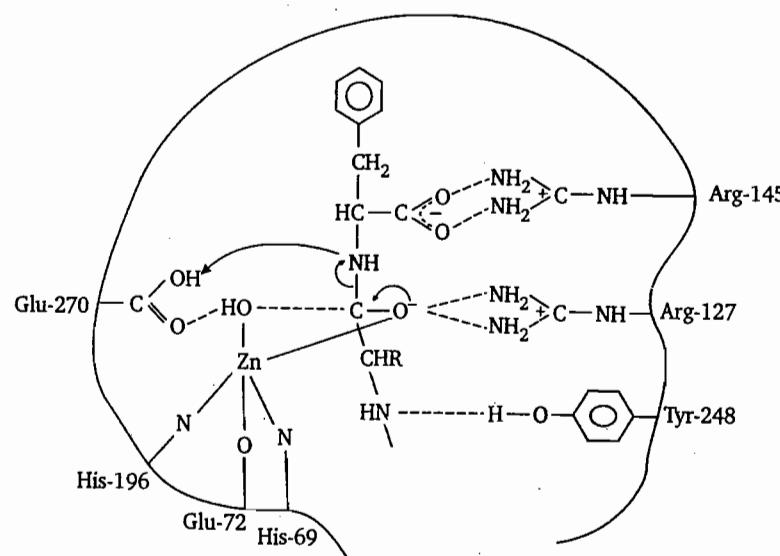


Fig. 9.26

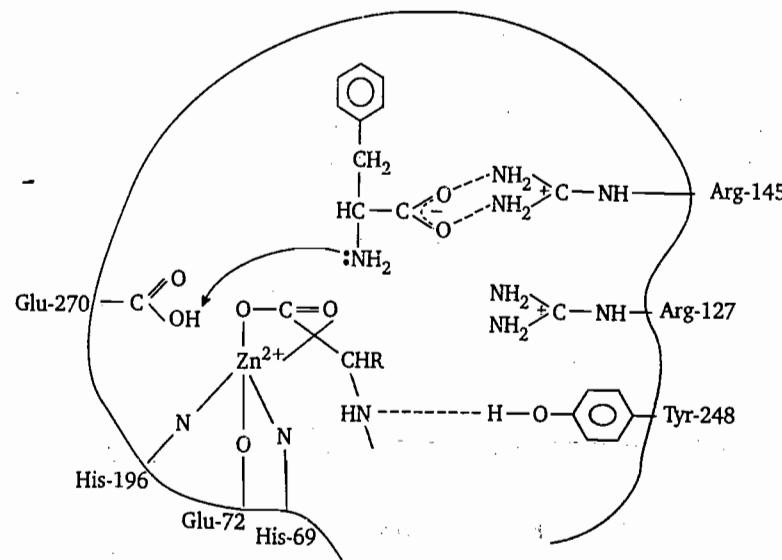


Fig. 9.27

### Carbonic Anhydrase

The uncatalysed following equilibrium is relatively very slow.



In the erythrocytes (red blood cells) the forward (hydration) reaction occurs during the uptake of  $CO_2$  by blood in tissue whereas the backward (dehydration) reaction occurs when  $CO_2$  is released in the lungs. The carbonic anhydrase enzyme increases the rate of this equilibrium by about one million times.

The molar mass of this enzyme is about 30,000 and it contains a single protein unit of 260 amino acids and the active site contains a  $Zn^{2+}$  ion coordinated tetrahedrally to three histidine imidazole nitrogen atoms (His-94, His-96 and His-119), and water molecule or hydroxide ion (Fig. 9.28). It contains other amino acids that may functions through hydrogen bonding, proton transfer etc.

The rates of forward and backward reactions in the  $CO_2$  hydration equilibrium increase as the pH is raised. The  $Zn^{2+}$  ion is more acidic in carbonic anhydrase than in carboxy peptidase. The presence of a neutral or less basic histidine residue instead of the glutamate residue contribute to the greater acidity of  $Zn^{2+}$  ion. Also, the three histidine residues are pulled back, therefore,  $Zn^{2+}$  ion becomes more electronegative and more acidic toward the fourth position. Thus the coordinated water becomes more polarized and losses  $H^+$  ion to give  $Zn - OH^-$ . The nucleophilic  $OH^-$  then attacks on the carbon atom of  $CO_2$  captured in the hydrophobic pocket near the  $Zn^{2+}$  ion, and a transient five coordinate  $Zn^{2+}$  ion is formed in which a carbonato oxygen from  $HCO_3^-$  coordinates to the  $Zn^{2+}$  ion. After rearrangement, the  $HCO_3^-$  ligand is replaced by  $H_2O$ . The protonation of  $H_2O$  ligand coordinated to  $Zn^{2+}$  ion then regenerate  $Zn - OH^-$  which then attacks another  $CO_2$  with the continuation of the catalytic cycle (Fig. 9.29).

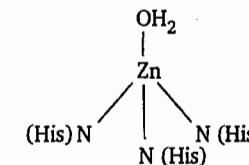


Fig. 9.28 Structure of carbonic anhydrase

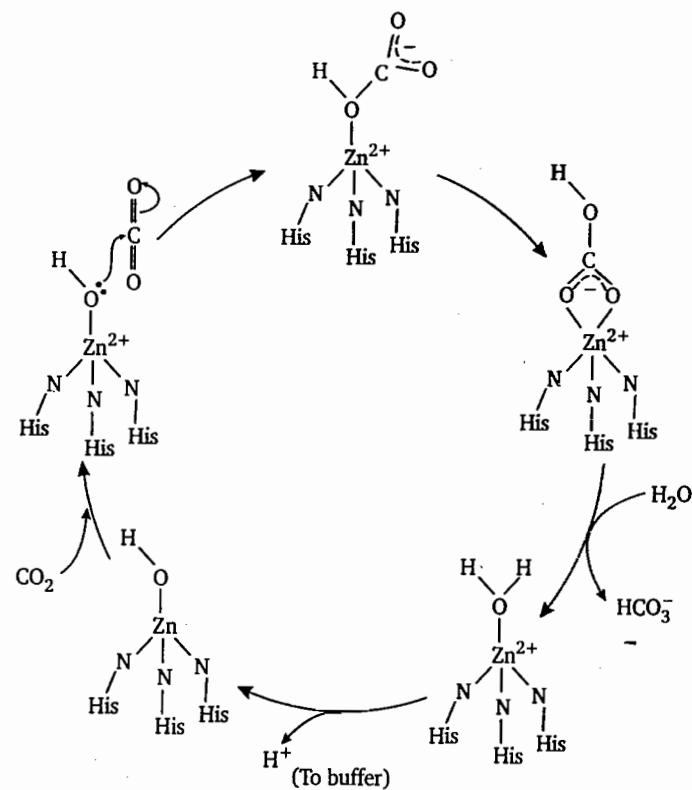


Fig. 9.29 Catalytic cycle of carbonic anhydrase

### Superoxide Dismutases (SOD)

In biochemistry, dismutation means the disproportionation reaction. It has been well established that the initial step in the electron transfer reduction of  $O_2$  produces the superoxide ion,  $O_2^-$ . The superoxide ion is toxic to cellular systems. The superoxide dismutase enzyme catalyses the dismutation (disproportionation) of superoxide ion into oxygen and hydrogen peroxide.



There are three types of superoxide dismutase:

- (1) Copper-zinc superoxide dismutase, CuZnSOD
- (2) Manganese superoxide dismutase, MnSOD
- (3) Iron superoxide dismutase, FeSOD

The former is called as bovine superoxide dismutase and found in mitochondria of eukaryotic cells and the later two are found in bacteria (prokaryotes). A crystal structure determination of CuZnSOD has shown that the  $Cu^{2+}$  and  $Zn^{2+}$  ions are coordinated to the imidazole of a histidine residue as shown in Fig. 9.30. The  $Cu^{2+}$  ion is a distorted square pyramidal site bound to four imidazole histidine nitrogen atoms and a water molecule, the  $Zn^{2+}$  ion is tetrahedrally coordinated to three nitrogens of imidazole of histidine residues and an oxygen of aspartate residue.

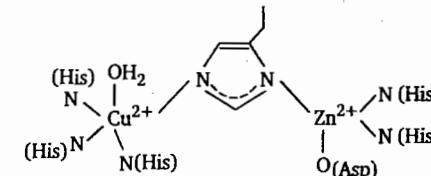


Fig. 9.30

The copper-zinc dismutase has molar mass of about 16000. It has been shown that the  $Cu^{2+}$  ion is the functional one whereas the  $Zn^{2+}$  ion is a supportive that holds the bridging imidazole histidine residue in place and provides structural stability.

The  $Cu^{2+}$  ion is more essential that can not be replaced by other metal while retaining activity. On the other hand, the  $Zn^{2+}$  ion can be replaced by other divalent metals such as Co or Cd with retention of most of the activity.

### Ceruloplasmin

Ceruloplasmin is an intensely blue copper protein. Its molar mass is about 1,35,000 with six or seven Cu atoms per molecule. This protein is found in plasma of most animals. It apparently plays an important role in the process of oxidizing Fe(II) to Fe(III) in the transfer of iron from ferritin to transferrin. It also participates in copper transport and storage. It is the deficiency of this protein which is responsible for Wilson's disease.

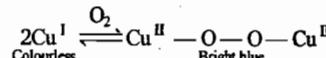
### Blue Copper Proteins :

These proteins contain active copper centre and the copper centres can be divided into three main types:

**Type 1 :** This type of centre is characterized by an intense blue colour because of strong absorption in the electronic spectrum at about  $\lambda_{max} = 600\text{nm}$  arising from cysteine (S)  $\rightarrow Cu^{II}$  charge transfer. This type of centre is EPR active because of the presence of one unpaired electron on  $Cu^{2+}$  and a narrow hyperfine splitting is observed.

**Type 2 :** Normal monomeric  $Cu(II)$  site is tetragonally coordinated. It exhibits normal EPR spectrum. It also exhibits electronic spectroscopic characteristics typical of  $Cu(II)$  ion.

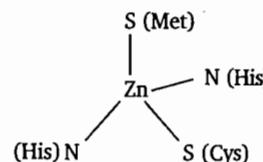
**Type 3 :** A pair of Cu(I) ions is about 360 pm apart and attached to protein through N-atoms of imidazole of histidine residues. The Cu<sub>2</sub>-unit can function as two electron transfer centre and involves in the reduction and transport of O<sub>2</sub> according to the following reversible reaction:



Cu(I) and Cu(II) ions are EPR inactive because Cu(I) with its  $d^{10}$  electronic configuration is diamagnetic and Cu(II) ions interact antiferromagnetically and become diamagnetic.

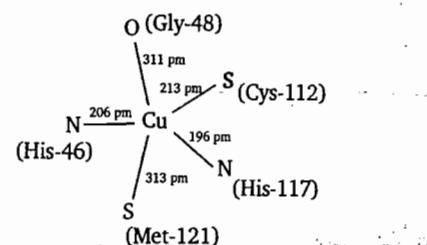
Blue copper proteins contain a minimum one Type 1 copper centre. Some important blue copper proteins are : Plastocyanin, stellacyanin, azurin, ceruloplasmin, laccase and ascorbic oxidase.

Type 1 Copper centres are found in **plastocyanin** and **azurin**. Plastocyanin is found in chloroplasts of green plants and blue-green algae. Plastocyanin has molar mass about 10500. It contains one copper atom per molecule. Plastocyanin is involved in electron transfer in photosynthesis (between PS I and PS II). The protein chain in a plastocyanin contains 97-104 amino acid residues. The copper centre in plastocyanin is coordinated to two N atoms of imidazoles of histidine residues, one S of methionine and one S of thiol of cysteine residues in distorted tetrahedral arrangement (or flattened tetrahedron) (Fig.9.31). The arrangement about copper centre involves three short bonds in a trigonal planar arrangement with fourth longer bond to S of methionine.



**Fig. 9.31 Structure of plastocyanin**

The blue copper protein **azurin** is found in bacteria and has molar mass about 16000. It also contains one Cu atom per molecule. The copper centre in azurin is trigonal bipyramidal. The two N atoms of imidazole of histidine residues and one S atom of cysteine residue in trigonal planar arrangement, one S of methionine and one O of glycine residues above and below the plane. There are three short bonds in the trigonal plane and two large bonds along the axis of the trigonal bipyramidal Cu—S (Met) and Cu—O (gly). (Fig. 9.32).

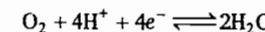


**Fig. 9.32 Structure of blue copper protein (azurin)**

The bond lengths shorten by 5-10 pm on going from Cu (I) to Cu(II). The coordination spheres can suite for both Cu(I) and Cu(II) and therefore, facilitate fast electron transfer. Since three donor atoms in trigonal plane are more closely bound to than the remaining donor atoms indicating the binding of Cu(I) is more favourable than that of Cu (II). This is supported by the high reduction potentials (+ .37 V for plastocyanin and + 0.31 V for azurin at about pH 7 for Cu<sup>2+</sup> → Cu<sup>+</sup>).

### Multicopper Blue Proteins

Multicopper blue copper proteins include ascorbic oxidase and laccase (oxidases are enzymes that use O<sub>2</sub> as an electron acceptor). These are the metalloenzymes which are found in variety of plants. They catalyze the four electron reduction of O<sub>2</sub> to H<sub>2</sub>O and at the same time, they catalyze the oxidation of organic substrates such as phenols, amines and ascorbate by O<sub>2</sub> (a one electron oxidation).



R<sup>•</sup> undergoes polymerization.

They contain all the three types of copper centres. Ascorbate oxidase contains a type 1 centre responsible for its blue colour along with triangular array of three other copper centres. Type 1 centre is indirectly connected to the Cu<sub>3</sub> unit by the protein chain. The coordination sphere of Type 1 centre is similar to that of oxidized form of plastocyanin with the metal bound by N atoms of imidazole of two histidine, S of one cysteine (Cu-S = 213 pm) and S of one methionine (Cu—S = 290 pm) residues. The trimer of Cu<sub>3</sub> unit lies within eight Histidine residues and can be subdivided into Type 2 and Type 3 Cu centres. Type 2 centre is coordinated to N atoms of imidazole of two histidine residues and an either H<sub>2</sub>O or OH<sup>−</sup> ligand. Type 3 centre contains two Cu atoms bridged by an O<sup>2−</sup> ligand. The two Cu atoms are coupled antiferromagnetically. Reduction of O<sub>2</sub> occurs at Cu<sub>3</sub> unit with the remote Type 1 centre acting as the main electron acceptor, removing from the organic substrates, detail of mechanism is not clear.

Laccase also has Type 1 copper centre along with a trimer of copper site containing Type 2 and Type 3 copper centres. The structure of Cu<sub>3</sub> unit is similar to that in ascorbate oxidase but Type 1 copper centre is three coordinated to S of one cysteine and two histidine residues in trigonal planar array and lacks the axial ligand present in the Type 1 copper centre in ascorbate oxidase.

### Non-Blue Copper Protein

**Galactase oxidase** is a non-blue copper protein and it is found in fungi where it catalyzes the oxidation of —CH<sub>2</sub>OH group in galactose to —CHO group by reducing O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>. It has molar mass about 68000. It contains one Cu atom coordinated to N atoms of imidazole of two histidine residues, O atoms of two tyrosine residues and O atom of an acetate ion in square pyramidal arrangement. The Cu (III) / Cu (I) couple involve in the 2-electron reduction of O<sub>2</sub>.

**Cytochrome-c oxidase** containing Cu and Fe is also a non-blue copper enzyme. Cytochrome-c oxidase is the terminal member of the respiratory chain in plants, animals, aerobic yeasts and some bacteria. It catalyses the reduction of  $O_2$  to  $H_2O$ .



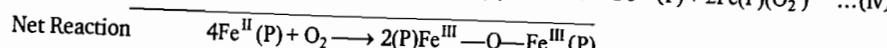
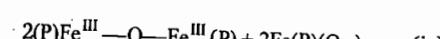
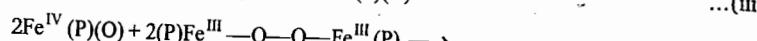
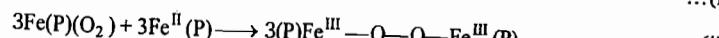
It is a large, complex, multisubunit enzyme containing two copper ions and two heme iron units. There are two kinds of copper sites,  $Cu_A$  and  $Cu_B$  and two kinds of heme iron units, heme-a and heme  $a_3$ . Electron transfer occurs from cytochrome-c to  $Cu_A$  and then to heme a.

Heme  $a_3$  (or cytochrome  $a_3$ ) and  $Cu_B$  provide the active site for  $O_2$  binding and its reduction to  $H_2O$ . Cytochrome-c oxidase is found associated with the inner mitochondrial membrane. Heme a and  $Cu_B$  sites are involved in pumping  $H^+$  ions (four  $H^+$  ions per  $O_2$  molecule) across the inner mitochondrial membrane. Cytochrome-c oxidase contains two  $Cu(I)$  ions and two  $Fe(II)$  heme centres. Oxidized form contains two  $Cu(II)$  ions and two  $Fe(III)$  heme centres.

Cytochrome-a in both oxidation states ( $Fe^{II}$  and  $Fe^{III}$ ) is low spin octahedral with two axial Histidine residues. In its oxidized form, it is EPR active. Addition of  $CN^-$  ion to the oxidized form or CO to reduced form does not perturb this centre. This indicates that  $CN^-$  ion does not bind to heme which is consistent with a six coordinate heme.  $Cu_A$  is dicopper site bridged by cystine residue. It also acts as an electron transfer site with a  $Cu_2S_2$  core. Histidine residue bound to  $Cu_A$  provide an electron transfer path between  $Cu_A$  and cytochrome a.

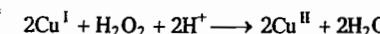
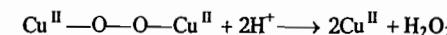
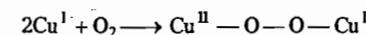
The cytochrome  $a_3$  can bind ligands such as  $CN^-$  to the oxidized form  $Fe(III)$  and CO to the reduced form ( $Fe^{II}$ ) which indicates that it is either five coordinate or it has readily displaceable ligand. It might be expected that two  $Cu(II)$  centres and two  $Fe(III)$  heme centres are EPR active. But it has been observed that low spin  $Fe(III)$  and  $Cu_A$  centres are EPR active and  $Fe(III)$  in cytochrome  $a_3$  and  $Cu_B$  centre are coupled antiferromagnetically and therefore are EPR inactive.

Dioxygen reacts with  $Fe(II)$  heme centre to form mononuclear dioxygen complex [Reaction-(i)]. These dioxygen complexes react rapidly with another  $Fe(II)$  heme centre to form binuclear peroxy bridged complex [Reaction (ii)]. These peroxy bridged complex are stable at low temperature but at higher temperature the peroxy linkage ( $O—O$ ) breaks and two equivalents of  $Fe(IV)$  oxo complex are formed. [Reaction (iii)]. The subsequent reactions of peroxy-bridged complexes with  $Fe(IV)$  oxo complexes give the  $\mu$ -oxo dimer [Reactions(iv)].

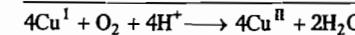


This reaction sequence indicates that, it is four electron reduction of one  $O_2$  molecule and the final products are the binuclear,  $O^{2-}$  bridged two  $Fe(III)$  heme complexes.

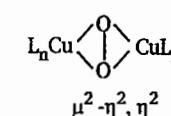
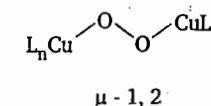
Copper(I) complexes also react with dioxygen to form peroxy bridged binuclear complexes. But these complexes do not undergo readily cleavage of peroxy linkage ( $O—O$  bond) because  $Cu(III)$  ion is not easily obtained as the  $Fe(IV)$  ion in an iron porphyrin complex. The stable bridged peroxy complex of  $Cu(II)$  is also difficult to obtain because the peroxy complexes either is protonated to give  $H_2O_2$  or is itself reduced by excess of  $Cu(I)$ .



Net Reaction



The bridged peroxy complex of  $Cu(II)$  may have either of the following structures.



### Essential and Trace Elements

There are many elements which are essential for biological reactions. Some of them are required in relatively large quantities and therefore, called macronutrients. These elements are Na, K, Mg, Ca, P, S, Cl along with four most abundant elements C, H, N, O in biological systems. There are also some elements which are required in small amounts, called as trace elements or micronutrients. These elements are : all the first row transition metals (except Sc and Ti) Mo and W (from second and third row transition metals respectively) and non-metals (B, Si, Se, F and I). Ni, Cd, Pd and As are ultratrace elements and are essential at very low concentrations (< 1 ppm). The elements are toxic at concentration above ultratrace level.

### The Biological Roles of some metal ions

About 30% of enzymes have a metal ion at their active sites. The metalloenzymes facilitates the variety of biological reactions shown in Table 9.2.

{ **Micro nutrients** } **3d** essential (except Sc, Ti)

**4d** only Mo

**5d** only W

Non-Metal → B, Si, Se, F and I

Ultratrace element  
 ↓  
 Ni, Cd, Pd, As

**Table 9.2**

Metal	Related Compounds	Action
Fe	Hemoglobin	Oxygen transport
	Myoglobin	Oxygen storage
	Hemerythrin	oxygen storage
	Oxygenases	Insertion of oxygen atoms into substrate
	Hydrogenases	Oxidation of H <sub>2</sub>
	Cytochrome P-450	Insertion of oxygen atom into substrate
	Catalase	Catalyze oxidation of substrates by H <sub>2</sub> O <sub>2</sub>
	peroxidase	Catalyze oxidation of substrates by H <sub>2</sub> O <sub>2</sub>
	Cytochromes	Electron transfer
	Ferredoxin	Electron transfer
	Ferritin	Iron storage
	Transferrin	Iron transport
	Siderophores	Iron transport
Co	Coenzyme B <sub>12</sub>	Methylation of organic compound
Cu	Amine oxidase	Oxidation of amine to aldehyde
	Ceruloplasmin	Transport of Fe from ferritin to transferrin, Cu storage and transport
	Hemocyanin	Oxygen carrier
Zn	Carboxypeptidase	Hydrolysis of peptide bonds
Mg	Chlorophyll Phosphotransferase	Photosynthesis Phosphate hydrolysis
Mn	Arginase	Electron transfer
Mg, Mn	Aminopeptidase	Catalyzes the cleavage of amino acid
Fe, Mo	Nitrogenase	Nitrogen fixation
Fe, Mo, Cu	Oxidase Reductase Hydroxylases	Redox reaction involving O <sub>2</sub> as electron acceptor Catalyzes reduction reactions Oxidative degradation of organic compounds
Cu, Zn, Mo	Superoxide dismutase	Dismutation of O <sub>2</sub> <sup>-</sup> into O <sub>2</sub> and H <sub>2</sub> O <sub>2</sub>
Mg, Cu, Zn	Phosphatases	Removed of phosphate group from substrate
Ni	Urease	Hydrolysis of urea into CO <sub>2</sub> and NH <sub>3</sub> .

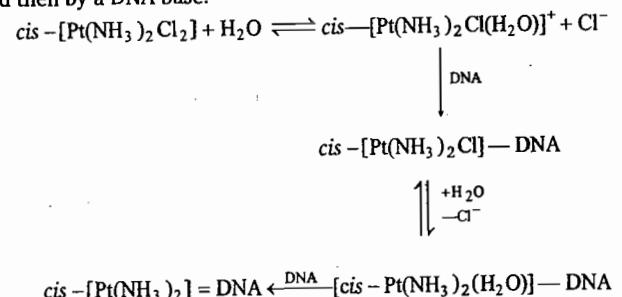
$\text{Na}^+$  and  $\text{K}^+$  ions are involved in Na-K pump, C, H, N and O along with P involve in amino acids, protein, DNA, NADP, ADP and ATP. Cr is essential for glucose metabolism in humans. Iodine is essential for thyroid gland, calcium serves as structural material in teeth, bones, shells and a number

of less well known calcium rich deposits. Calcium in teeth and bones have the composition  $\text{Ca}_{10}(\text{PO}_4)_6X_2$  where  $X = \text{F}, \text{Cl}$  or  $\text{OH}$  or a mixture of these. Fluorine is also essential for teeth and its deficiency causes dental caries.

## Metal complexes in Medicine

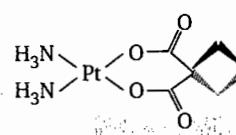
### Cisplatin: Anticancer Drug

In 1969, B. Rosenberg and Co-workers discovered the antitumor activity of simple square planar Pt(II) complex, *cis*-diamminedichloroplatinum(II) or cisplatin,  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ . This compound is used as chemotherapeutic agent to inhibit otherwise rapid division of tumor cells (*i.e.*, proliferation). The exact action of this complex is not known. Since the *trans*-isomer is inactive, therefore chelation or atleast coordination to donor atoms at *cis*-positions (*i.e.*, in close proximity) is an essential part of the activity. The proton nmr studies has suggested that platinum binds to N-7 atom of a pair of adjacent guanine bases of a fast growing tumor with the chloride ligands first being replaced by water molecules and then by a DNA base.



Cisplatin interacts with two adjacent guanine bases on DNA usually within the same strand (intrastand linking) or occasionally between strands (interstrand linking). Recent X-ray studies on a 12-base pair fragment of double stranded DNA has suggested that the binding of Pt distorts the local DNA structure and therefore, inhibits the cell division inherent in the proliferation of cancer cells. Cisplatin is most effective against testicular cancer. Cisplatin has negative side effects in kidney and neuro-toxicity.

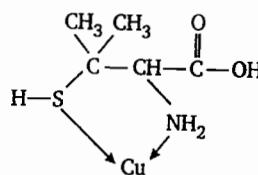
In order to avoid these serious side effects alternative platinum compounds have been developed. The most important of these is 'Carboplatin' (Fig. 9.33) in which the *cis*-chloride ligands are replaced by the O-chelate, cyclobutanedicarboxylate.



**Fig. 9.33** Structure of carboplatin

### Wilson's disease

Wilson's disease is caused by the overload of copper in the body. It is a genetic disease. Patients suffering from Wilson's disease have low levels of the copper storage protein ceruloplasmin and therefore, copper can not be tolerated even at normal levels. The Wilson's disease is responsible for liver disease, neurological damage and brown or green rings in the cornea of the eyes. Many chelating ligands can be used to remove the excess of copper but one of the best is **D-penicillamine**. This chelating ligand forms a complex with copper ions ( $Cu^I$  and  $Cu^{II}$ ) Fig. 9.34 that has intense purple colour and the molecular formula of the compound is  $[Cu_8^{I_4} Cu_6^{II}]_{12} Cl$ . The sulfhydryl group of D-penicillamine effects removal of copper as  $Cu(I)$  complex.

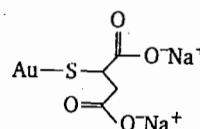


**Fig. 9.34 Structure of complex of Cu with D-penicillamine chelating ligand**

Chelation therapy using EDTA or 2, 3-dimercaptopropan-1-ol (BAL, British Anti-Lewisite) also causes the symptoms to disappear.

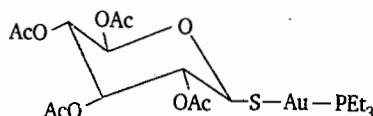
### Anti-Arthritis

Complexes of Au(I) have been used most successfully for the treatment of arthritic disorders in humans. These complexes used to treat arthritis were painfully administered as intramuscular injections. These complexes include  $Na_2[Au(S_2O_3)_2]$ , called Sanochrysin, sodium salt of thiomalate, called Myochrysin (Fig. 9.35).



**Fig. 9.35 Structure of Myochrysin**

More recently, the compound auranofin (Fig. 9.36) has been developed. It has the advantage that it can be administered orally and is effective.



**Fig. 9.36 Structure of Auranofin**

### Hypercalcemia

Hypercalcemia is a disease which causes the rapid loss of calcium from the bones of cancer patients. Gallium nitrate,  $Ga(NO_3)_3$  has been found to be most effective for treatment of hypercalcemia.

### Magnetic Resonance Imaging (MRI)

Nuclear magnetic resonance (NMR) spectroscopy can be used to image specific tissues of biological systems because of the differences in the relaxation times of water proton resonances usually brought about by metal ions which are paramagnetic. The useful metal ions for magnetic resonance imaging in humans are Gd(III), Fe(III) and Mn(II) ions. The paramagnetic character of these ions alters the relaxation of rate of nearby water protons and, therefore, the normal and diseased tissue can be distinguished. An advantage of paramagnetic MRI over radioisotopic imaging agents is that there is no possibility of radiation damage. Removal of excess of a metal from the body is called chelate therapy.

### Siderosis Disease

An excessive intake of iron causes various problems known as siderosis. Chelation therapy is also used to treat the excess of iron. The patients who suffer from deposits of iron in liver, kidney and heart, lead to failure of these organs. The excess of iron can be removed by using chelating ligand sachas desferrioxamine-B, a polypeptide having a very high affinity for Fe (III) but not for other. The concepts of soft and hard metals and ligands can be used for the process of designing therapeutic chelating agents.

## USE OF CHELATING AGENTS IN METAL POISONING : THE CHELATE THERAPY

### LEAD

Lead is a very poisonous metal. It is a cumulative poison, since it keeps on accumulating in the tissues of human body and plants.

### Harmful Effects of Lead

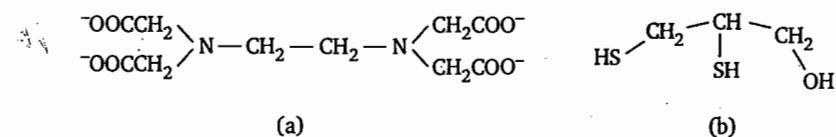
Lead has a strong affinity of complexing with oxo-groups of enzymes and inhibits all steps in the process of heme synthesis, porphyrin metabolism, protein synthesis by modifying transfer-RNA, acid phosphate, ATPase, carbonic anhydrase etc. Pb(II) also inhibits SH enzymes [less strongly than Cd(II) and Hg(II)] by interaction with cysteine residues in proteins.

### Symptoms of Lead Poisoning

Symptoms of lead poisoning are : anaemia, loss of appetite, headaches, nervous disorders, brain damage, liver damage, kidney damage, cholic and skin diseases.

### Treatment of Lead Poisoning

Lead poisoning can be treated by complexing and sequestering the lead by chelating ligands such as ethylenediamine tetraacetate  $\text{CaNa}_2(\text{EDTA})$  [Fig. 9.37(a)] or British anti-Lewisite, BAL [Fig. 9.37(b)] or penicillamine.



**Fig. 9.37 Structure of (a) EDTA (b) BAL**

### CADMIUM

Cadmium is extremely toxic. It accumulates in the kidneys and liver of human. It has a strong affinity for the  $-\text{SH}$  group of cysteine residues in protein and therefore inhibits SH enzymes. It also inhibits the action of zinc enzymes by displacing zinc.

### Symptoms of Cadmium Toxicity

Symptoms of cadmium toxicity are : disfunctions of kidneys, vomiting, irritation, hypertension, anaemia and a disease called Hai Itai in which the whole body feels serious pains and the bones begins to fracture very easily.

### MERCURY

Mercury having an appreciable vapour pressure is also extremely toxic. Monomethyl mercury,  $\text{CH}_3\text{Hg}$  and dimethyl mercury,  $(\text{CH}_3)_2\text{Hg}$  are more dangerous than metallic mercury itself and inorganic mercury compounds such as  $\text{HgCl}_2$ . These organomercury compounds are more readily absorbed in the gastrointestinal tract than  $\text{Hg}^{2+}$  salts because they have greater ability to penetrate biomembranes. They concentrate in blood and have immediate and permanent effect on brain and central nervous system because they bind to the  $-\text{SH}$  groups of cysteine residues in proteins.

### Symptoms of Mercury Toxicity

The symptoms of mercury toxicity are : central nervous disorders, headaches, irritability, fatigue, inability to make decisions, sleeplessness, diarrhoea, etc.

### Treatment of Mercury Toxicity

More rapid elimination of cadmium, mercury and lead requires the administration of chelating ligands such as 2, 3-dimercaptopropanol (i.e., British anti-Lewisite, BAL),  $\text{HSCH}_2\text{CH}(\text{SH})\text{CH}_2\text{OH}$  and N-acetyl penicillamine.

A very interesting natural detoxification has been discovered in bacteria resistant to mercury. Bacteria have developed resistance to heavy metals and detoxifying process is initiated and controlled by metalloregulatory proteins that are able selectively to identify metal ions. The most studied metalloregulatory proteins is mer R. It is a small DNA binding protein that controls transcription of the mer genes.

## DEFICIENCY SYMPTOMS OF SOME TRACE METALS

### ZINC

Zinc is very important for proper functioning of the immune system. The body of an adult human contains about 2g of zinc. There is some zinc in every one of the cells in the body but most of it is in the skin, hair, nails and eyes and in the prostate gland for males. The most easily absorbed form of zinc is zinc gluconate, zinc citrate and zinc monomethionate. Zinc sulphate is likely to upset the stomach. The infection fighting white blood cells contains a lot of zinc present in the body. The best food for zinc are organ meats such liver or kidneys, leafy grains, root vegetables such as carrots and potatoes. Zinc is important for:

- (i) Fighting off cold or flu : Zinc supplements assist to reduce the cold symptoms such as runny nose, coughing and sore throat.
- (ii) Zinc make skin, nails and hair healthy.
- (iii) Zinc helps in healing wounds.
- (iv) Zinc reduces the diabetic problems.
- (v) Zinc increases production of testosterone and other male hormones. Therefore, it reduces the male infertility.
- (vi) Zinc helps to preserve eye sight and improves memory.
- (vii) Zinc may help teenagers with pimples.

### Symptoms of Zinc Deficiency

- (i) Reduced growth of children.
- (ii) Reduced mental retardation.
- (iii) Slow wound healing.
- (iv) Frequent infections.
- (v) Skin irritation.
- (vi) Hair loss.
- (vii) Loss of sense of taste.

### Zinc Works Best with

- |               |                             |
|---------------|-----------------------------|
| (i) Vitamin A | (ii) Vitamin B <sub>6</sub> |
| (iii) Insulin | (iv) Vitamin D              |
| (v) Vitamin E | (vi) Glucose                |
| (vii) Mg      | (viii) Mn                   |

### Impacts of Excess of Zinc

Excess of zinc in the human body causes :

- |  |                            |
|--|----------------------------|
| (i) Dysfunction of the central nervous system          | (ii) Anaemia               |
| (iii) Diarrhoea  | (iv) Dizziness             |
| (v) Sore stomach                                       | (vi) Nausea                |
| (vii) Vomiting   | (viii) Alcohol intolerance |
| (ix) Electrolyte imbalance                             |                            |
| (x) Increase LDL cholesterol and lower HDL cholesterol |                            |

### COPPER

Copper is required in the formation of hemoglobin, red blood cells and bones. It helps in the formation of elastin and collagen making it necessary for wound healing. Copper works closely with iron for these functions. Copper is a vital component of a number of enzymes. Copper is essential for connective tissue formation, iron metabolism. It also acts as an antioxidant.

### Copper Sources

Main sources of copper are : Oysters (cooked), sunflower seeds, almonds, etc.

### Symptoms of Copper Deficiency

**Copper deficiency cause :** Deficiency of iron which can lead to anaemia, infections, osteoporoses, thinning of bones, thyroid gland dysfunction, heart disease, nervous system problems and increased blood fat level.

**Copper works best with** folic acid, vitamin B<sub>6</sub>, vitamin B<sub>12</sub>, amino acids, iron, zinc and Mn.

### Impact of Excess of Copper

**Excess of copper causes :** Fever, high blood pressure, diarrhoea, dizziness, depression, fatigue, irritability, joint and muscle pain, nausea, premature ageing, vomiting, wrinkling of skin, headache etc.

### COBALT

Cobalt is an essential trace mineral that is a constituent of vitamin B<sub>12</sub>. Cobalt is a necessary cofactor for making the thyroid hormone thyroxine. The most of the body's cobalt is stored in liver.

Main sources of cobalt are liver, clams, milk, nuts, fish, red meat, oysters. Cobalt works best with vitamin B<sub>12</sub>.

### Deficiency of Cobalt

A deficiency of cobalt may lead to a deficiency of vitamin B<sub>12</sub> and lead to pernicious anaemia. The symptoms of pernicious anaemia are :

- (i) bleeding gums.
- (ii) nausea, appetite loss and weight loss.
- (iii) weakness and tingling in the arms and legs.
- (iv) headache, confusion and poor memory.
- (v) sore tongue.

### Impact of Excess of Cobalt

The symptoms of excess of cobalt in the human body are :

- |                 |                  |
|-----------------|------------------|
| (i) nausea      | (ii) vomiting    |
| (iii) diarrhoea | (iv) skin rashes |

### IRON

Iron is the most important transition element involved in the living systems. The adult humans body contains about 4 g of iron. It plays a crucial roles in the transport and storage of dioxygen and electron transport. The important sources of iron are : green vegetable, squash, pumpkin seeds, liver, oysters beans, pulses, nuts (cashew, peanut, almond, pine, hazel nut), beef, lamb, Pork, wheat products, corn meal, strawberries, watermelon etc.

Deficiency of iron and oxygen causes anemia.

The symptoms of deficiency of iron an anemia are : difficulty maintaining body temperature, feeling tired and weak, decreased immune function which increases susceptibility to infection, fatigue, decreased memory,

Excess of iron causes stomach pain as the stomach lining becomes ulcerated, damage of internal organs particularly the brain and the liver.

Iron poisoning can be treated by chelate therapy using chelating agent such as deferoxamine.

Main Deficiency symptoms of some trace elements are given in Table. 9.3.

Table. 9.3 Deficiency Symptoms of Trace Elements

Element	Function	Main Deficiency Symptom
Chromium	Glucose metabolism	Impaired glucose metabolism
Cobalt	Vitamin B <sub>12</sub>	Anemia
Copper	Oxidative enzymes	Anemia, skeletal defects
Manganese	Mucopolysaccharide metabolism	Growth retardation
Molybdenum	Purine metabolism, aldehyde oxidation	Joint pain
Zinc	Nucleic acid metabolism	Poor wound healing

### Sodium Potassium Pump : Na<sup>+</sup>, K<sup>+</sup>-ATPase

Lipid soluble substance diffuse through the membrane lipid bilayer without the need for a carrier mechanism. This process is called passive diffusion. The movement of water soluble solutes and ions requires specific transmembrane proteins to facilitate transfer across the lipid bilayer. This process is called facilitated diffusion. Many of the facilitated diffusion processes move a solute against a concentration gradient. This requires an input of energy which is usually provided by hydrolysis of ATP. This facilitated diffusion that requires energy input is called active membrane transport.

An interesting example of active transport is the Na<sup>+</sup> / K<sup>+</sup> pump present in animal cells. This pumps Na<sup>+</sup> and K<sup>+</sup> out of and into the cell respectively using energy released by hydrolysis of ATP. The animal cells have intracellular fluid with low concentration of Na<sup>+</sup> (0.012 M) and high concentration of K<sup>+</sup> (0.14 M) as compared to extracellular fluid (blood and lymph) which contains high concentration of Na<sup>+</sup> (0.15 M) and low concentration of K<sup>+</sup> (0.004 M). (Fig. 9.38). The concentration of Na<sup>+</sup> and K<sup>+</sup> on the two sides of the cell membrane are interdependent suggesting that the same carrier protein transports Na<sup>+</sup> and K<sup>+</sup> ions. The carrier is an ATP-ase and the energy released by hydrolysis of one ATP to ADP + Pi is enough to pump three Na<sup>+</sup> ions out of the cell and two K<sup>+</sup> and one H<sup>+</sup> ions into the cell.

The concentration gradients (the difference in the intracellular and extracellular concentration) across the cell membrane produces an electrical potential difference across the cell membrane which is essential for functioning of nerve and muscle cells. To maintain this difference, Na<sup>+</sup> ions move into the cell via channels in the cell membrane but it is continuously pumped out again by means of the Na<sup>+</sup> / K<sup>+</sup> pump.

The Na<sup>+</sup> / K<sup>+</sup> pump is the key to functions such as cardiac and renal activity as well as all general transport processes into and out of the cell. The pump thus forms the basis for our ability to absorb a considerable number of nutrients, excrete waste products from the kidneys and regulate the water balance in the cells. If this little pump stopped pumping Na<sup>+</sup> ions out of the cell the later would rapidly swell up because of the infiltration of water and finally burst.

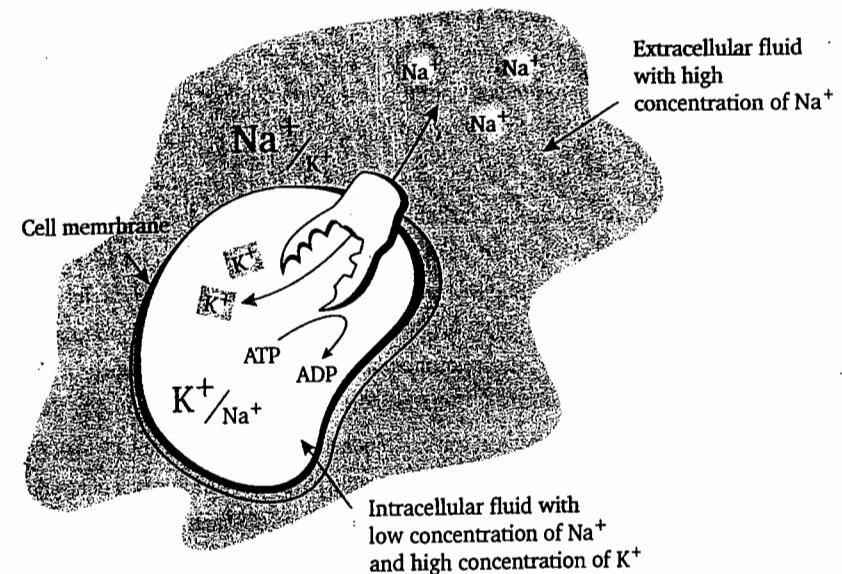


Fig. 9.38

The K<sup>+</sup> is required in the cell for glucose metabolism, protein synthesis and activation of many enzymes. Glucose and amino acids enter the cell in association with Na<sup>+</sup> which is favoured by the high concentration gradient. The Na<sup>+</sup> ions entering the cell in this way must then be pumped out again.

Skou did not use term Na<sup>+</sup> / K<sup>+</sup> pump regarding his discovery. He has stated that ATP-ase enzyme is responsible for the active transport of Na<sup>+</sup> and K<sup>+</sup> ions across the cell membrane and he described it as Na<sup>+</sup>, K<sup>+</sup>-ATPase. Therefore, Na<sup>+</sup> / K<sup>+</sup> pump is also called as Na<sup>+</sup>, K<sup>+</sup>-ATPase.

### Mechanism

The mechanism for ion transport involves the natural polyether which are called as ionophores (ion-bearers). Some natural ionophores for Na<sup>+</sup> and K<sup>+</sup> ions have oxygen donor atoms from carboxylates and cyclic peptides. Some of these are antibiotics such as nonactin and valinomycin. Nonactin is a member of a family of naturally occurring cyclic ionophores known as the macrotetrolide antibiotics.

Valinomycin is a natural, lipid soluble molecule that binds  $K^+$  and facilitates their transfer across cell membrane. Valinomycin and nonactin have selectivity for  $K^+$  over  $Na^+$  ion.

The  $Na^+ / K^+$  pump is also called the  $Na^+, K^+$ -ATPase because ATP is hydrolysed to give ADP + Pi and released energy which is used to  $Na^+$  and  $K^+$  ions pump out and into the cell respectively.  $Na^+, K^+$ -ATPase is composed of two dissimilar subunits  $\alpha$  and  $\beta$ . They are closely associated as dimeric pair ( $\alpha, \beta$ )<sub>2</sub> to form a tetramer ( $\alpha\beta$ )<sub>2</sub>.  $Na^+, K^+$ -ATPase contains two high affinity binding sites for ATP, one on each  $\alpha$ -subunit. These sites face the cytoplasmic surface of the cell membrane. The  $Na^+$  binding sites also face the cytoplasmic surface whereas the binding sites for  $K^+$  ions face the external surface of the cell membrane.  $Na^+, K^+$ -ATPase undergoes change in its shape (or conformation) due to the covalent attachment of phosphoryl group to the carboxyl group of a specific aspartic acid residue of  $\alpha$ -subunit. The phosphorylation occurs in the presence of  $Na^+$  and  $Mg^{2+}$ -ATP. The catalytic cycle for  $Na^+$  and  $K^+$  ion transport is illustrated in Fig. 9.39. The form (a) of the enzyme opens up toward the inner side of cell and binds three  $Na^+$  ions but not  $K^+$  ions. Once the  $Na^+$  ions are bound to the enzyme, an ATP molecule is bound to the enzyme and one of its phosphate groups (P) is transferred, i.e., there is hydrolysis of ATP to produce ADP and phosphorylated protein and to release energy. The enzyme changes its shape, opens up toward the outer side of the cell and releases  $Na^+$  ions. There are now binding sites for two  $K^+$  ions but not for  $Na^+$  ions on the outer side of the cell. When  $K^+$  ions bind, the phosphate group (P) is now hydrolyzed from the protein giving  $P_i$ . When  $K^+$  ions have been released inside the cell, the enzyme returns to the first stage-ready to bind new  $Na^+$  ions, so the cycle can begin all over again.

The net result is that hydrolysis of ATP pumps  $Na^+$  out and  $K^+$  in. The ratio is 3 $Na^+$  ions out and two  $K^+$  ions in. The overall equation is :

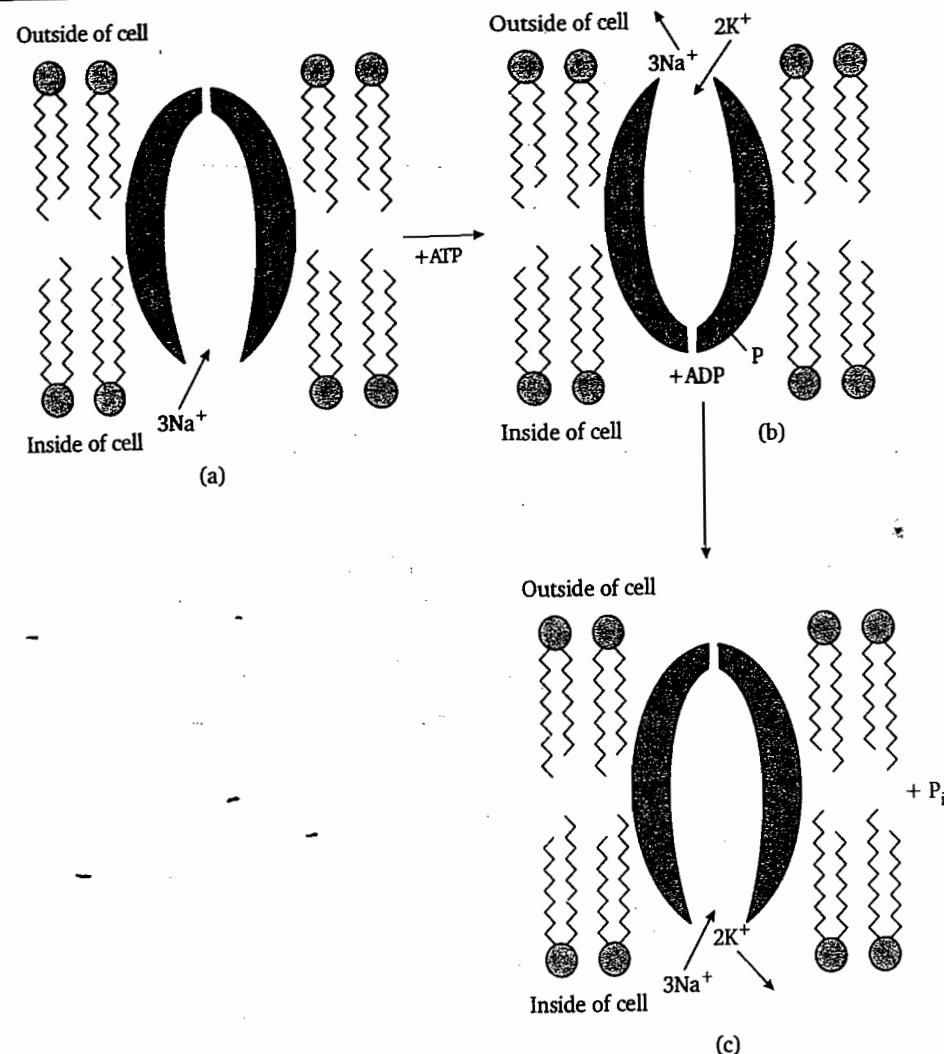
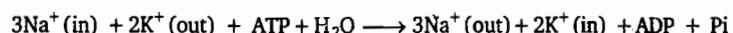


Fig. 9.39



## Objective Questions

1. Which of the following is a heme iron protein ?
  - (a) Ruberodoxin
  - (b) Transferrin
  - (c) Hemerythrin
  - (d) Cytochrome-c
  
2. In biological systems, the metal ions involved in electron transport are :
  - (a)  $\text{Na}^+$  and  $\text{K}^+$
  - (b)  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$
  - (c)  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$
  - (d)  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$
  
3. In the transformation of oxyhemoglobin to deoxyhemoglobin :
  - (a)  $\text{Fe}^{2+}$  in low spin state changes to  $\text{Fe}^{2+}$  in high spin state
  - (b)  $\text{Fe}^{2+}$  in low spin state changes to  $\text{Fe}^{3+}$  in low spin state
  - (c)  $\text{Fe}^{2+}$  in high spin state changes to  $\text{Fe}^{2+}$  in low spin state
  - (d)  $\text{Fe}^{2+}$  in high spin state changes to  $\text{Fe}^{2+}$  in high spin state
  
4. The oxygen free form of myoglobin is a :
  - (a) 5-coordinate high spin  $\text{Fe(II)}$  complex
  - (b) 6-coordinate low spin  $\text{Fe(II)}$  complex
  - (c) 5-coordinate high spin  $\text{Fe(III)}$  complex
  - (d) 5-coordinate low spin  $\text{Fe(III)}$
  
5. Iron-sulphur clusters in biological systems are involved in :
  - (a) proton transfer
  - (b) atom transfer
  - (c) group transfer
  - (d) electron transfer
  
6. In biological systems, the metal ion involved in the dioxygen transport besides Fe is :
  - (a) Co
  - (b) Zn
  - (c) Mg
  - (d) Cu
  
7. Myoglobin is a :
  - (a) catalyst for epoxidation reaction
  - (b) component in photosynthetic system
  - (c) nitrogen fixation enzyme
  - (d) di-oxygen binding metalloprotein
  
8. The oxidation state of iron in met-hemoglobin is :
  - (a) three
  - (b) two
  - (c) four
  - (d) zero
  
9. The metal ions present in the active site of nitrogenase enzyme cofactor are :
  - (a) Fe, Mo
  - (b) Fe, W
  - (c) Fe, Cu
  - (d) Fe, Ni
  
10. Which of the following metalloproteins converts oxygen to water :
  - (a) catalase
  - (b) cytochrome-c oxidase
  - (c) haloperoxidase
  - (d) hemoglobin

11. In oxyhemoglobin, the iron centre best described by which of the following ?
  - (a) high spin  $\text{Fe(II)}$
  - (b) high spin  $\text{Fe(III)}$
  - (c) low spin  $\text{Fe(III)}$
  - (d) low spin  $\text{Fe(II)}$
  
12. The metal atom present in the active site of carboxypeptidase enzyme is :
  - (a) cobalt
  - (b) zinc
  - (c) iron
  - (d) magnesium
  
13. The coordination geometry of  $\text{Cu(II)}$  in the type-1 copper protein plastocyanin is :
  - (a) square planar
  - (b) tetrahedral
  - (c) octahedral
  - (d) distorted tetrahedral
  
14. The ligand system present in vitamin  $\text{B}_{12}$  is :
  - (a) porphyrin
  - (b) corrin
  - (c) phthalocyanin
  - (d) crown ether
  
15. Carboxypeptidase contains :
  - (a)  $\text{Zn(II)}$  and hydrolysis  $\text{CO}_2$
  - (b)  $\text{Mg(II)}$  and hydrolysis  $\text{CO}_2$
  - (c)  $\text{Zn(II)}$  and hydrolysis peptide bonds
  - (d)  $\text{Mg(II)}$  and hydrolysis peptide bonds
  
16. In bacterial ruberodoxin, the number of iron atoms, sulfur bridges and cysteine ligands are :
 

Fe atom	Sulfur bridges	Cysteine
(a) 4	4	4
(b) 2	2	4
(c) 2	2	2
(d) 1	0	4
  
17. A well known naturally occurring organometallic compound is :
  - (a) vitamin  $\text{B}_{12}$  coenzyme
  - (b) chlorophyll
  - (c) cytochrome P-450
  - (d) myoglobin
  
18. Among the following pair of metal ions present in nature, the first one functions as an electron transfer agent and the second one catalyzes the hydrolysis reactions. The correct is :
  - (a) Fe and Zn
  - (b) Mg and Fe
  - (c) Co and Mo
  - (d) Ca and Cu
  
19. Match the Column-I and Column-II :
 

	Column-I		Column-II
P	Cytochrome-c	I	Molybdenum
Q	Calmodulin	II	Potassium
R	Chlorophyll	III	Magnesium
S	Alcohol dehydrogenase	IV	Zinc
		V	Iron
		VI	Calcium

- (a)  $P = I$ ,  $Q = II$ ,  $R = III$ ,  $S = IV$   
 (b)  $P = II$ ,  $Q = III$ ,  $R = IV$ ,  $S = V$   
 (c)  $P = V$ ,  $Q = IV$ ,  $R = VI$ ,  $S = IV$   
 (d)  $P = V$ ,  $Q = VI$ ,  $R = III$ ,  $S = IV$

**20.** Match the following metal in Column-I with the appropriate biomolecule in Column-II

	<b>Column-I</b>		<b>Column-II</b>
P	Zn	I	Phosphotransferase
Q	Cu	II	Peroxydase
R	Fe	III	Carboxypeptidase
		IV	Hemocyanine
		V	Nitrogenase



**21.** Storage of iron in the body is carried out by :



**22.** The changes (from A-D given below) which occur when O<sub>2</sub> binds to hemerythrin are :



**23.** patients suffering from Wilson's disease have :

- (a) low level of Cu-Zn superoxide dismutase
  - (b) high level of Cu-Zn superoxide dismutase
  - (c) low level of copper storage protein, ceruloplasmin
  - (d) high level of copper storage protein, ceruloplasmin

**24.** High dose of dietary supplement  $ZnSO_4$  for the cure of Zn deficiency :

- (a) reduces myoglobin
  - (b) increase iron level in blood
  - (c) increases copper level in brain
  - (d) reduces copper, iron and calcium level in body

**25.**  $Mg^{2+}$  is preferred in photosynthesis by chlorophyll because :

- (a) it has strong spin-orbit coupling
  - (b) it has weak spin-orbit coupling
  - (c) it is heavy metal
  - (d) it binds strongly with chlorophyll

- 26.** The transition metal present in vitamin B-12 is :



- 27.** The metal present in carbonic anhydrase is :



- 28.** Nature has chosen Zn(II) ion at the active site of many hydrolytic enzymes because :

- (a) Zn(II) is a poor Lewis acid
  - (b) Zn(II) does not have chemically accessible redox states
  - (c) Zn(II) forms both four and higher coordination complexes
  - (d) Zn(II) forms weak complexes with oxygen donor ligands

**29.** Match the Column-I with Column-II :

	<b>Column-I</b>		<b>Column-II</b>
P	Liver alcohol dehydrogenase	I	Cu at the active site
Q	Cytochrome-c oxidase	II	Fe and Cu at the active sites
R	Hemocyanin	III	Zn at the active site
S	Myoglobin	IV	Fe at the active site
		V	Mo at the active site
		VI	Cu and Zn at the active sites

- (a) P = VI, Q = II, R = I, S = IV  
 (b) P = III, Q = II, R = I, S = IV  
 (c) P = III, Q = II, R = IV, S = V  
 (d) P = V, Q = VI, R = I, S = II

**30.** Match the Column-I with Column-II :

	<b>Column-I</b>		<b>Column-II</b>
P	Ferritin	I	Electron transport
Q	Vitamin B <sub>12</sub>	II	Ionophore
R	Cytochromes	III	Oxygen transport
S	Valinomycin	IV	Nitrogen fixation
		V	Organometallic enzymes
		VI	Iron storage

- (a)  $P = VI$ ,  $Q = IV$ ,  $R = II$ ,  $S = I$   
 (b)  $P = I$ ,  $Q = III$ ,  $R = VI$ ,  $S = IV$   
 (c)  $P = III$ ,  $Q = V$ ,  $R = IV$ ,  $S = VI$   
 (d)  $P = VI$ ,  $Q = V$ ,  $R = I$ ,  $S = II$

ANSWERS

- 1.** (d)      **2.** (d)      **3.** (a)      **4.** (a)      **5.** (d)      **6.** (d)      **7.** (d)  
**8.** (a)      **9.** (a)      **10.** (b)      **11.** (d)      **12.** (b)      **13.** (d)      **14.** (b)  
**15.** (c)      **16.** (d)      **17.** (a)      **18.** (a)      **19.** (d)      **20.** (c)      **21.** (b)  
**22.** (b)      **23.** (c)      **24.** (d)      **25.** (d)      **26.** (c)      **27.** (c)      **28.** (b)  
**29.** (b)      **30.** (d)      **31.** (c)      **32.** (a)      **33.** (a)      **34.** (b)      **35.** (b)



## **Subjective Questions**

1. What is meant by active transport in Na/K pump ? Give a diagrammatic representation of the process and explain the mechanism involved in it.
  2. What are the functions of hemoglobin and myoglobin ? What changes occurs in the heme groups of hemoglobin on going from deoxy to oxy form ?
  3. In what parts of the human body are ferritin and transferrin found ? How is transferrin involved in the recycling of iron from the breakdown and synthesis of hemoglobin ?
  4. Where and in what form is iron stored in the human body ? How is it taken from the storage sites to the sites for incorporation into hemoglobin ?
  5. What are the differences between hemoglobin and myoglobin ? Hemoglobin acts as an oxygen carrier from lungs to muscles but as carbon dioxide carrier from the tissues to the lungs. Explain this cycle.
  6. Explain why heme group can not function as biological oxygen carrier in the absence of the globin chain ? What serves as trigger in the Perutz mechanism for oxygenation and deoxygenation of hemoglobin ?
  7. What special features of  $Zn^{2+}$  ion make it an excellent biocatalyst ? Substitution of  $Co^{2+}$  for  $Zn^{2+}$  ion gives a spectral probe. What special features of  $Co^{2+}$  ion are exploited and why does  $Zn^{2+}$  lacks them ?
  8. (a) Classify the elements according to their action in biological system.  
(b) What do you understand by essential and non-essential metal ions in the biosystem.
  9. What is the active metal in carboxypeptidase A. What is the coordination number and how is it satisfied ?
  10. (a) Explain the role of *cis*-platin in cancer therapy.  
(b) Why is *cis*-platin used by oncologists in preference to the *trans*-isomer.  
(c) What are ionophores.
  1. (a) Write the toxic effects of Pb(II). Give the reasons for its toxicity. How it can be treated.  
(b) Write the toxic effects of Hg(II) poisoning. Give the reasons for its toxicity. How it can be treated.  
(c) What are the impacts of excess and deficiency of  $Cu^{2+}$  and  $Co^{2+}$  ions in human body ?
  2. Explain with the help of a diagram the mechanism of sodium-potassium pump in human body and what is the source of energy for the function of this pump ?

13. Name the disease associated with the deficiency of zinc in the human body. Also list the symptoms associated with the disease.

□□□

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