

**AS-2156**  
**Organometallic Chemistry of transition metals**

**Model Answer**

**M. Sc. (Third Semester) Examination 2013**

**CHEMISTRY**

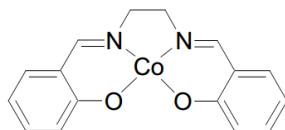
**Organometallic Chemistry of Transition Metals**

*Paper: CMT-303 (I)*

**Section- 'A'**

**(Short Answer Type Questions)**

1. (i)

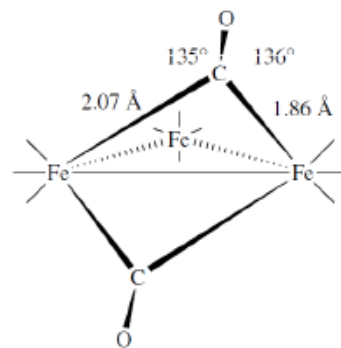


Co(salen)

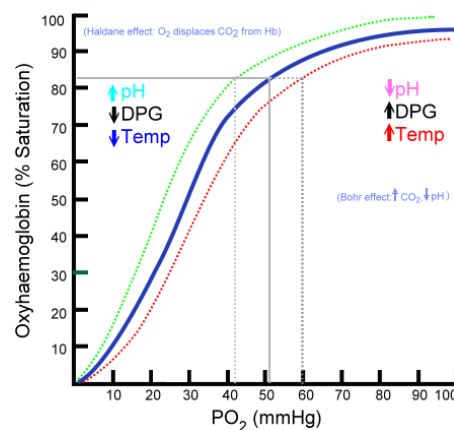
(ii) When oxygen binds to the iron complex of the porphyrin ring, the imidazole side-chain of the histidine residue interacting at the other pole of the iron is pulled toward the porphyrin ring. This interaction forces the plane of the ring sideways toward the outside of the tetramer, and also induces a strain in the protein helix containing the histidine as it moves nearer to the iron atom. In the tetrameric form of normal adult hemoglobin, the binding of oxygen is called cooperative effect. The binding affinity of hemoglobin for oxygen is increased by the oxygen saturation of the molecule, with the first oxygens bound influencing the shape of the binding sites for the next oxygens, in a way favorable for binding. This positive cooperative binding is achieved through steric conformational changes of the hemoglobin protein complex as

discussed above; i.e., when one subunit protein in hemoglobin becomes oxygenated, a conformational or structural change in the whole complex is initiated, causing the other subunits to gain an increased affinity for oxygen. As a consequence, the oxygen binding curve of hemoglobin is sigmoidal, or S-shaped, as opposed to the normal hyperbolic curve associated with non-cooperative binding.

(iii) The semi-bridging carbonyl compounds are those carbonyl compounds in which the CO is neither fully terminal nor fully bridging but intermediate between the two. The structure of one semi bridged carbonyl compound is given below.



(iv) The Bohr effect is a physiological phenomenon first described in 1904 by the Danish physiologist Christian Bohr, stating that hemoglobin's oxygen binding affinity is inversely related both to acidity and to the concentration of carbon dioxide. That is to say, a decrease in blood pH or an increase in blood CO<sub>2</sub> concentration will result in hemoglobin proteins releasing their loads of oxygen and a decrease in carbon dioxide or increase in pH will result in hemoglobin picking up more oxygen. Since carbon dioxide reacts with water to form carbonic acid, an increase in CO<sub>2</sub> results in a decrease in blood pH.



(v) General formula of Zeolites



Any two examples of the followings:

Faujasite, matrolite, Stilbite, Linde A, ZSM-5, Boggsite, Sodalite, Mordenite etc.

(vii) Write the evidence for the existence of  $(Ph_3P)_2RhCl$  complex in solution.

The evidence for dissociation of  $Ph_3P$  ligand from  $(Ph_3P)_3RhCl$  is indirect but persuasive:

- (a) For complexes with less sterically hindered phosphines e.g.  $(C_2H_5)_3P$ , the catalytic effect disappears-apparently steric repulsion forcing dissociation is necessary; and
- (b) With the corresponding iridium complex in which metal-phosphorous bond is stronger, no dissociation takes place and no catalysis is observed.

(viii) pre-catalyst is a compound or complex which during catalytic cycle generates or converts into the true catalyst which actually works as catalyst

For example in Wilkinson's catalyst  $(Ph_3P)_3RhCl$  is actually pre-catalyst but actual catalyst is  $(Ph_3P)_2RhCl$

### 3.6.2. Classification of Carbyne Complexes

Like carbene complexes, the carbyne complexes are also of two types :

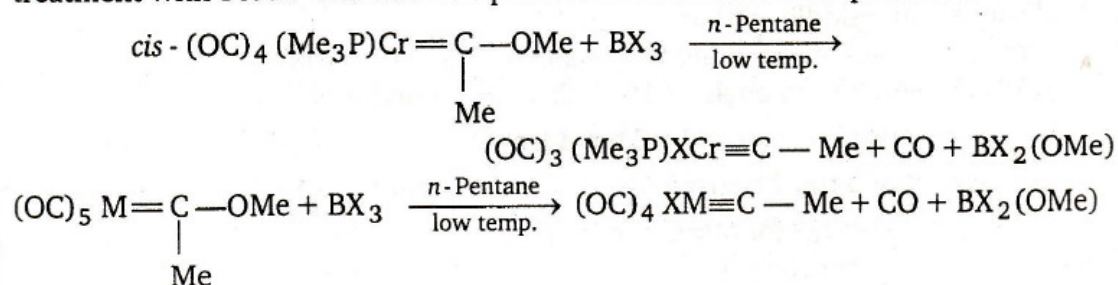
**(a) Fischer carbyne complexes :** The transition metal complexes formed by the doublet carbyne ligand are called Fischer carbyne complexes. The metal atom is present in low-valent state in such complexes. The carbyne carbon atom of Fischer carbyne complexes are electrophilic in nature. These are simply called carbyne complexes.

**(b) Schrock carbyne complexes :** The transition metal complexes formed by quartet carbyne ligand are called Schrock carbyne complexes. The metal atom is present in high-valent state in such complex. The carbyne carbon atom of Schrock carbyne complexes is nucleophilic in nature. The Schrock carbyne complexes are also called alkylidyne complexes.

However, the distinction between Fischer and Schrock carbyne complexes is less marked than for carbene complexes.

### 3.6.3. General Methods of Preparation

**[A]** The first carbyne complexes were synthesised by Fischer in 1973 by electrophilic abstraction of methoxide ion from a methoxy methyl carbene on treatment with boron trihalide in *n*-pentane solvent at low temperature.

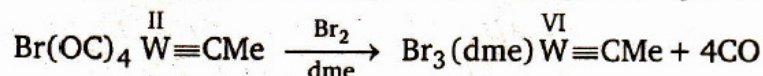




where M = Cr, Mo, W

X = Cl, Br, I

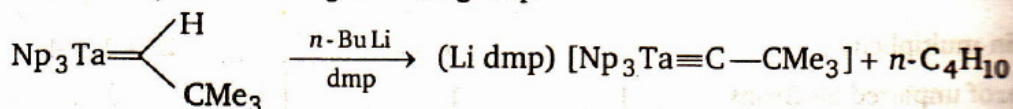
**[B]** The carbonyl ligands of Fischer carbyne complexes can be removed by careful and controlled oxidation forming Schrock carbyne complexes.



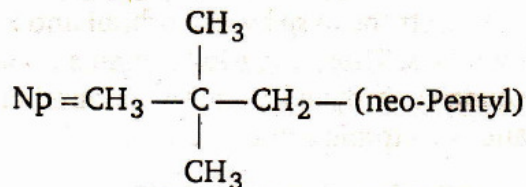
where, dme = MeOCH<sub>2</sub>CH<sub>2</sub>OMe

(1, 2-Dimethoxyethane)

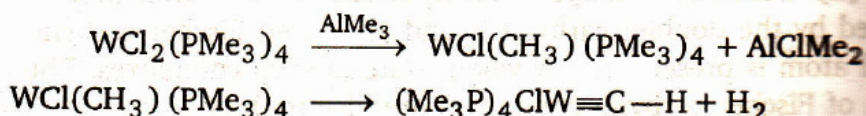
**[C]** The Schrock carbyne complexes can be made by deprotonation of alkylidene complexes having α-CH group.



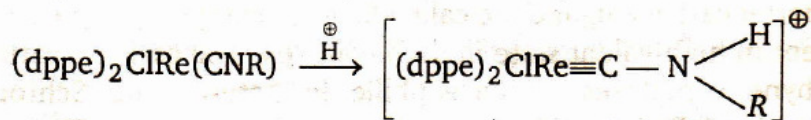
where, dmp = N, N'-Dimethylpiperazine



**[D]** The Schrock carbyne complexes can be prepared by direct α-elimination via methyl compound,



**[E]** The Schrock carbyne complexes can be prepared by the protonation of isocyanide complexes.



where, dppe = Ph<sub>2</sub>P—CH<sub>2</sub>—CH<sub>2</sub>—PPh<sub>2</sub>

1, 2-bis(diphenylphosphino)ethane

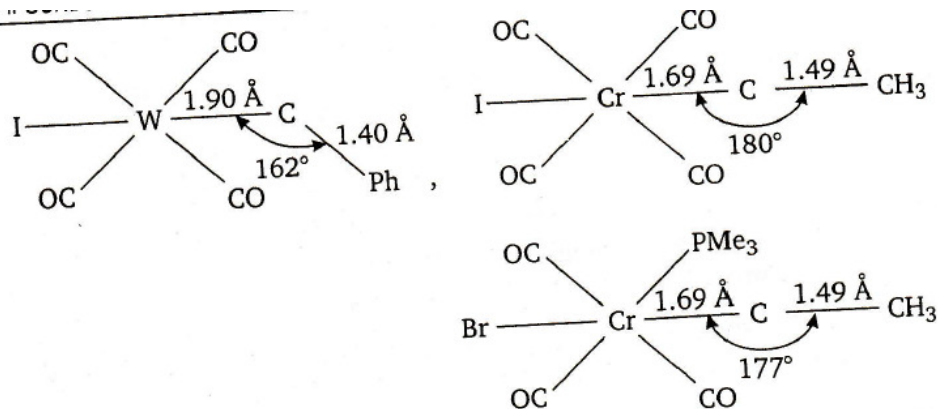
### 3.6.4. Structure and Bonding

The structures of transition metal carbyne complexes have been determined by various means viz., X-diffraction studies, IR and NMR spectral studies, etc. These studies suggest that the M≡C—C linkage of carbyne complexes is linear due to sp hybridisation on middle carbon atom. The M—C—C bond angle is ~ 180°. However, the M—C—C bond angle deviates from 180° in some cases, e.g., trans I(OC)<sub>4</sub>W≡C—Ph has an angle of 162°. The M≡C bond is very short.

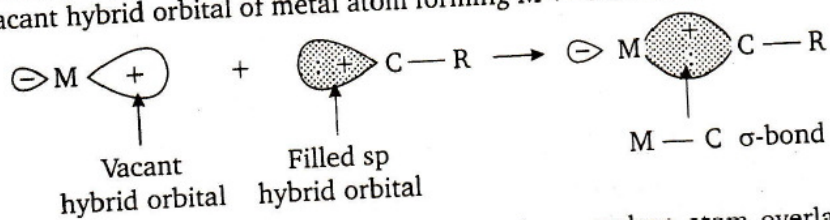
For first transition series, M≡C bond length = 1.65 – 1.75 Å

For second and third transition series, M≡C bond length = 1.75 – 1.90 Å

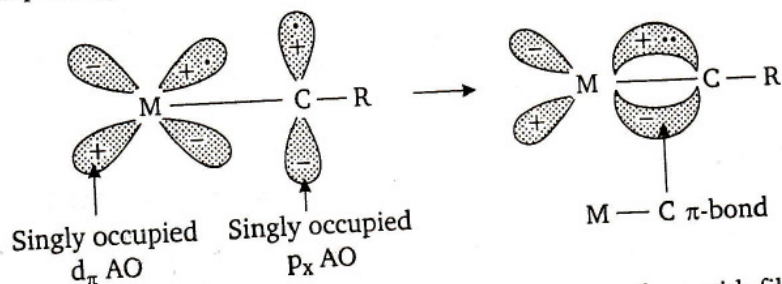
The force constants for M≡C bonds are comparable to those for M≡N bonds. Structures of some transition metal-carbyne complexes are given below.



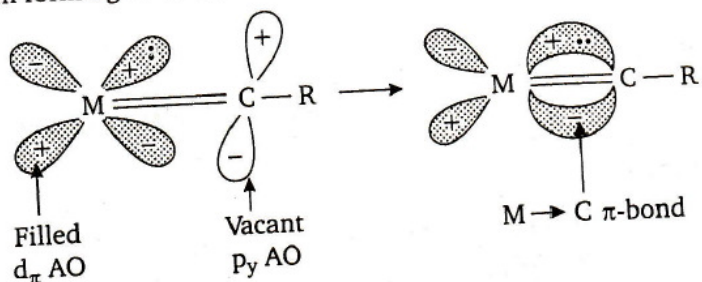
The doublet carbene ligand of Fischer carbene complexes acts as 3e donor ligand, i. e., LX type ligand. The filled  $sp$  hybrid orbital of doublet carbene overlaps with vacant hybrid orbital of metal atom forming  $M \leftarrow C$   $\sigma$  bond.



The singly occupied  $p_x$  AO of doublet carbene carbon atom overlaps with singly occupied  $d_\pi$  AO of metal forming  $M-C$   $\pi$  bond. It is called  $d_\pi - p_\pi$  bond.



The vacant  $p_y$  AO of doublet carbene carbon atom overlaps with filled  $d_\pi$  AO of metal atom forming  $M \rightarrow C$   $\pi$  bond. It is called  $d_\pi - p_\pi$  bond or back bond.

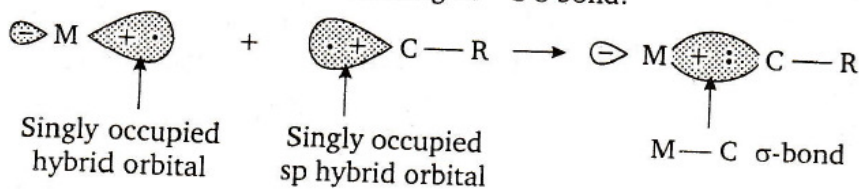


Thus, three covalent bonds are formed between metal atom and carbene carbon atom in Fischer carbene complexes.

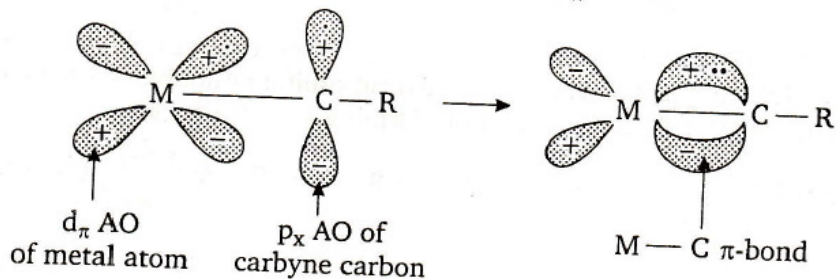
In the Schrock carbene complexes, quartet carbynes are involved which have three unpaired electrons. The quartet carbene also acts as a 3e donor ligand. But it is



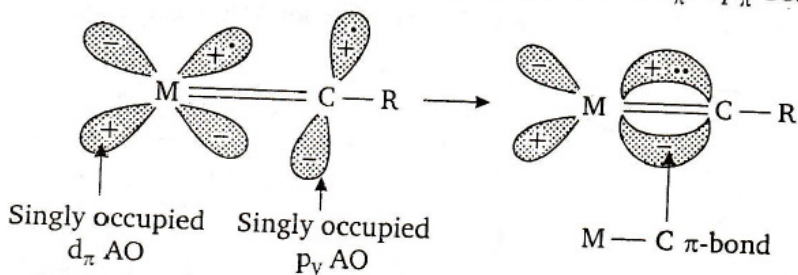
a  $X_3$  type ligand. The singly occupied  $sp$  hybrid orbital of quartet carbyne overlaps with hybrid orbital of metal atom forming  $M-C$   $\sigma$  bond.



The singly occupied  $p_x$  AO of quartet carbyne overlaps with the singly occupied  $d_\pi$  AO of metal atom forming  $M-C$   $d_\pi - p_\pi$  bond.



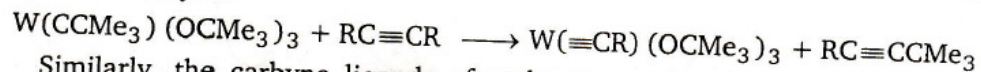
Similarly, the singly occupied  $p_y$  AO of quartet carbyne overlaps with the singly occupied  $d_\pi$  AO of metal atom forming another  $M-C$   $d_\pi - p_\pi$  bond.



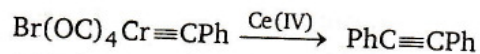
Thus, three covalent bonds are formed between metal atom and carbyne carbon atom in Schrock carbyne complexes.

### 3.6.5. Chemical Reactions

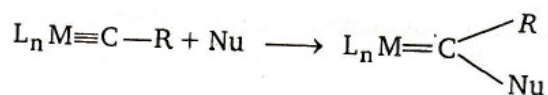
(a) A carbyne complex can couple with an alkyne to give another carbyne complex and alkyne.



Similarly, the carbyne ligands of carbyne complexes can couple together forming an alkyne.



(b) The carbyne carbon atom of Fischer carbyne complexes is electrophilic in nature and it can be attacked by nucleophiles such as  $PMe_3$ , pyridine, alkyllithium or isonitrile (Nu) to give a carbene complexes.



## Answer to question No. 2

(ii) Cobalt(III) dioxygen complexes : Co(III) complexes with Schiff-bases derived from salicylaldehyde and ethylenediamine, porphyrin derivatives, diethylenetriamine and ethylenediamine, *Co-Salens*. These complexes take up O<sub>2</sub> reversibly to form 1:1 and 2:1 Co:O<sub>2</sub> complexes (Fig. 9.13).

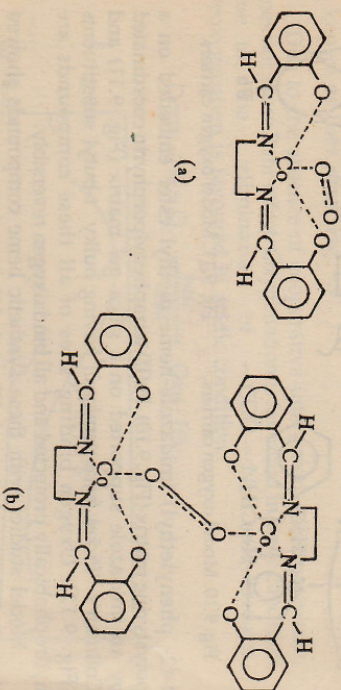


Fig. 9.13. Cobalt (II) dioxygen complexes (*Co-salens*)

In 1:1 Co: O<sub>2</sub> complexes, Co(II) transfers one electron to O<sub>2</sub>, which is reduced to a superoxide ion. 2:1 Co: O<sub>2</sub> complexes are generally peroxocomplexes due to transfer of two electrons to molecular oxygen, one by each of the two Co(II) ions.

(iii) Iridium (II) dioxygen complexes (*Vaska's Complexes*) : Bis-triphenylphosphorylchlorocarbonyl iridium(I), *trans*-Ir(Ph<sub>3</sub>P)<sub>2</sub>(Cl)(CO) binds one molecule of O<sub>2</sub> reversibly in benzene solution to give a photosensitive, diamagnetic dioxygen complex, Ir(Ph<sub>3</sub>P)<sub>2</sub>(Cl)(CO)(O<sub>2</sub>), having a dipole moment( $\mu$ ) of 5.9 D in solution.



X-ray study revealed a trigonal bipyramidal structure (Fig. 9.14) for the oxygenated complex, in which Ir, CO, Cl and O<sub>2</sub> lie in the equatorial plane and the two Ph<sub>3</sub>P molecules coordinate Ir axially from above and below the equatorial plane. The two oxygen atoms are equidistant from the central iridium.

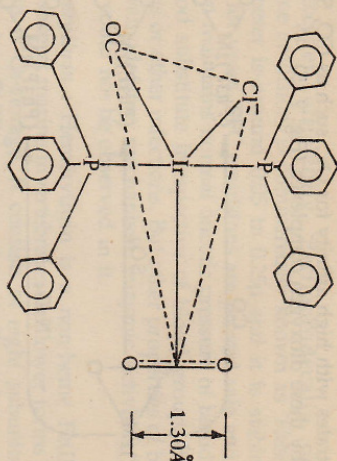
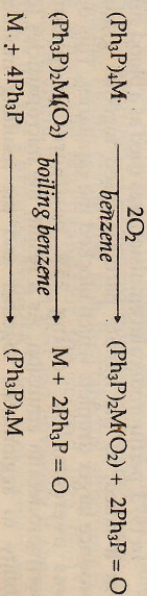


Fig. 9.14. Iridium (II) dioxygen complex (*Vaska's complex*).

O—O distance of 1.30Å in this compound corresponds to that of a superoxo complex. Reduction of O<sub>2</sub> to O<sub>2</sub><sup>-</sup> is effected by oxidation of Ir(I) (*d<sup>8</sup>*) to Ir(II) (*d<sup>7</sup>*) having one unpaired electron. Coupling of the unpaired electron spin of the coordinated superoxide ion with that of Ir(II) is responsible for diamagnetism of this complex. Polarity ( $\mu = 5.9\text{D}$ ) of the molecule is the result of charge transfer from Ir(I) to O<sub>2</sub> to give Ir(II) and O<sub>2</sub><sup>-</sup>. Replacement of Cl<sup>-</sup> by I<sup>-</sup> results in irreversible oxygenation with concomitant increase of O—O distance upto 1.51Å which is even greater than that in a peroxo complex. I<sup>-</sup> being more basic than Cl<sup>-</sup>, can transfer more electron density to Ir(I), which in turn can transfer more electron density to O<sub>2</sub>.

(iv) Platinum group metal dioxygen complexes : Tetrahedral complexes of the type M(Ph<sub>3</sub>P)<sub>4</sub>, where, M = Pt(0), Pd(0) and Ni(0) bind O<sub>2</sub> irreversibly in benzene solution to produce square planar dioxygen complexes, (Ph<sub>3</sub>P)<sub>2</sub>M(O<sub>2</sub>) having the metal ions in the bivalent state. O—O distances of 1.45Å in these compounds correspond to those in peroxo (O<sub>2</sub><sup>2-</sup>) complexes. These complexes decompose in boiling benzene to give oxidised ligand (Ph<sub>3</sub>P=O) and zero valent metals (M). The latter can again take up Ph<sub>3</sub>P ligands to start a fresh catalytic cycle.





### Answer to question No. 3 (i)

#### 9.2. Oxygen Carrying Proteins

Nature has designed four  $O_2$ -carrying proteins for transport and storage of oxygen in biological systems. These are: *hemoglobin*, *myoglobin*, *hemerythrin* and *hemocyanin*. Hemoglobin and myoglobin are Fe(II)-heme proteins, while hemerythrin is a non-heme Fe protein. On the other hand, hemocyanin contains copper at its oxygen binding site. There are reports of functioning of vanadium protein e.g., *vanadocytes*, as oxygen carriers, but details are yet to be explored.

(a) **Hemoglobin and Myoglobin**: *Hemoglobin (Hb)* and *myoglobin (Mb)* are responsible for the transport and storage of oxygen in higher animals. *viz.*, mammals. *Hb* transports oxygen from its source (lungs, skin and gills) to the site of its use inside the muscle cell where oxygen is transferred to *Mb* for use in mitochondrial oxidation (i.e., respiration).

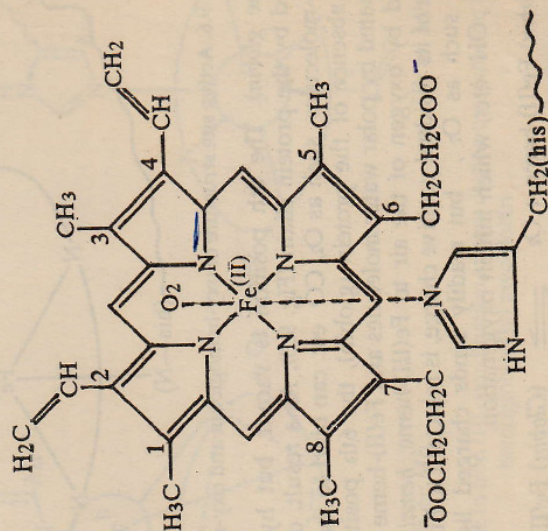


Fig. 9.5. The heme group in hemoglobin and myoglobin.



*Mb* is a monomeric protein ( $MW = 17,100$  daltons) having a single polypeptide chain that is not conducive of self association. On the other hand, *Hb* is a tetrameric protein ( $MW = 64500$  daltons), consisting of two  $\alpha$  and two  $\beta$  peptide chains interlinked through hydrogen bonded ( $\text{COO} \cdots \text{N H}_2$ ) interactions. Due to these salt bridge interactions (numbering as many as eight), the peptide chain in deoxy-*Hb* is constrained. X-ray diffraction study showed the disappearance of these salt bridges on oxygenation.

The active sites of both *Hb* and *Mb* contain the heme group, in which  $\text{Fe(II)}$  is equatorially coordinated by the four pyrrole nitrogen atoms of *protoporphyrin IX* (Fig. 9.5). The 5th position is coordinated by the imidazole nitrogen atom of a histidine of the protein chain

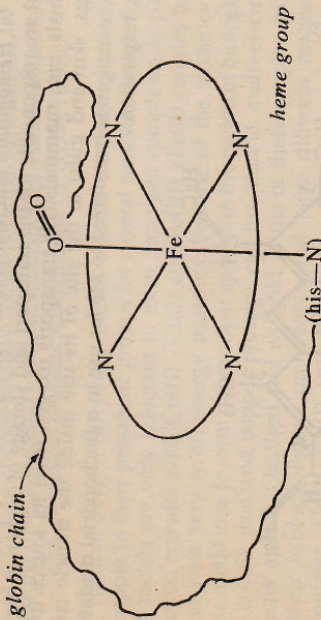
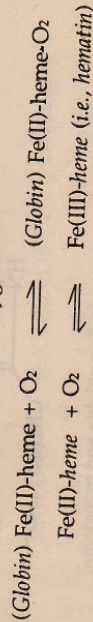


Fig. 9.6. Active site structure of oxy-hemoglobin and oxy-myoglobin.

(i.e., the *globin*). The 6th position is vacant, but hydrophobically shielded by the protein chain (Fig. 9.6). As a result, only non-polar neutral molecules such as  $\text{O}_2$ ,  $\text{CO}$  etc. can bind to the 6th position. In the absence of the protein (*globin*), the 6th position is readily coordinated by polar water molecules and  $\text{Fe(II)}$ -heme is irreversibly oxidised by oxygen of the air to  $\text{Fe(III)}$ -heme, *hematin*. The latter, because of its residual positive charge, is reluctant to bind uncharged ligands such as  $\text{O}_2$ , but readily binds charged ligand such as  $\text{CN}^-$ ,  $\text{S}^{2-}$ ,  $\text{OH}^-$  etc., which inhibit oxygenation.



Being 5-coordinated,  $\text{Fe(II)}$  in *Hb* and *Mb*, is present in high spin configuration.  $\text{Fe(II)-N}$  bond lengths in high spin  $\text{Fe(II)-N}$  compounds are  $\approx 2.18 \text{ \AA}$ , which is much greater than the mean radius ( $\approx 2.05 \text{ \AA}$ ) of the porphyrin cavity. Pentacoordinated iron(II) in deoxy-*Hb* and deoxy-*Mb* has a square pyramidal geometry and it is situated about  $0.8 \text{ \AA}$  out of the porphyrin plane (Fig. 9.7), being shifted towards the apically coordinated histidine. Oxygen binds to the  $\text{Fe(II)}$  heme at the vacant 6th position and the resulting octahedral field is sufficiently strong to transform high spin  $\text{Fe(II)}$  (radius  $0.92 \text{ \AA}$ ) to low spin  $\text{Fe(II)}$  (radius  $0.75 \text{ \AA}$ ). As a result of that,  $\text{Fe(II)}$  radius is contracted by about  $0.17 \text{ \AA}$  and  $\text{Fe(II)}$  in the active sites of oxy-*Hb* and oxy-*Mb* moves towards the porphyrin plane and ultimately sits in the porphyrin cavity. This movement of  $\text{Fe(II)}$  causes the coordinated histidine to move towards the porphyrin plane. This brings about a conformational change throughout the peptide chain amounting to rupture of some or all the  $-\text{COO} \cdots \text{N H}_2$  salt bridge interactions. The constrained hemoglobin tetramer then relaxes by exposing the 6th positions of

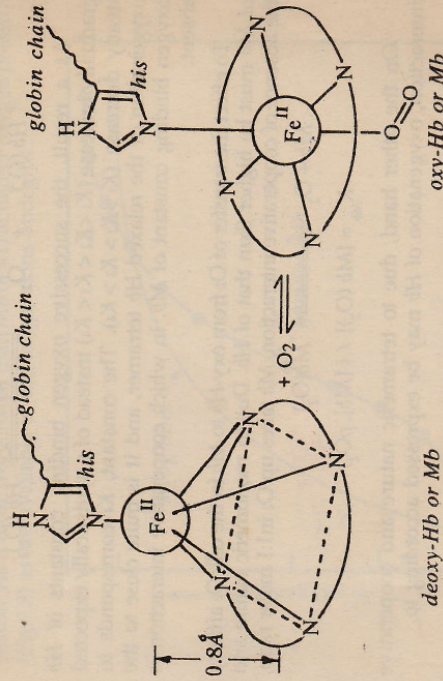


Fig. 9.7. Change in iron (II) coordination sphere during oxygenation of hemoglobin and myoglobin.

the remaining heme groups to oxygenation. This phenomenon is known as *cooperative interaction*. Oxygenation of *Hb* is autocatalytic due to this cooperative interaction. But such effects are absent in *Mb*



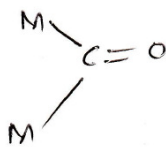
Carbonyl compounds : Semi-bridging Carbonyls :

↓  
Terminal & Symmetrical bridging & Unsymmetrical bridging

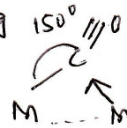


In Semi-bridging carbonyl the CO is neither fully terminal nor fully bridging but intermediate between the two. Semi-bridging carbonyl is 2e donor.

doubly bridging



triply bridging

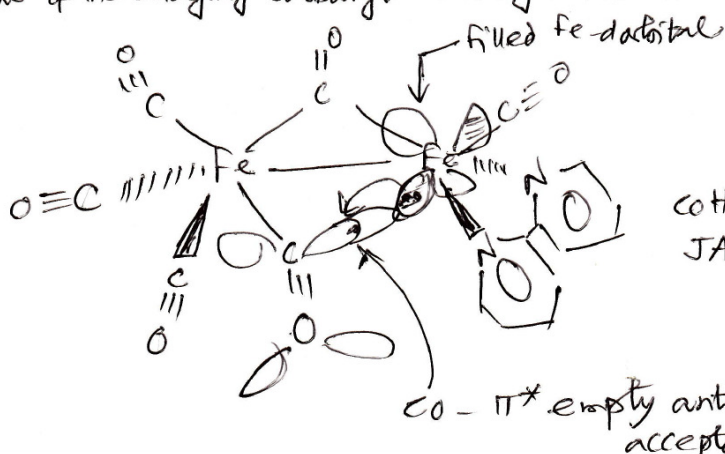


Terminal bridging  $M-C-O$  angle  $180^\circ$ , symmetrical is  $120^\circ$  and unsymmetrical the angle is  $\sim 150^\circ$ .

In semi-bridging carbonyl the  $\pi^*$  system accepts electron density from the second metal centre.

The C-O stretching frequency of semi-bridging carbonyl are lower than linear terminal carbonyls but higher than bridging carbonyls.

Example:- Substituting 2-carbonyl in  $Fe_2(\mu-CO)_3(CO)_6$  with a bipyridine ligand leads to a considerable change in the structure, particularly in the bridging CO region. The better  $\sigma$ -donating bipyridine ligand increases the electron density on that Fe-atom. This generates an asymmetrically charged complex. The higher partial negative charge on the bipy-substituted Fe-centre can be reduced by donating some of it specially into the  $\pi^*$  orbital of one of the bridging carbonyls turning it into a semi-bridging CO.



Cotton & Tsou  
JACS 1974, 96, 1233

Answer to Question No. 4(i)

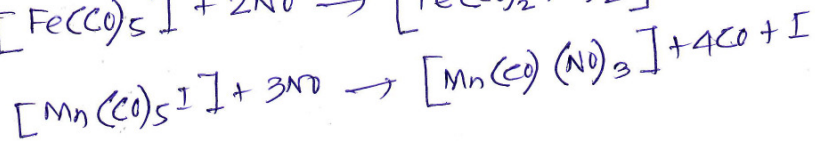
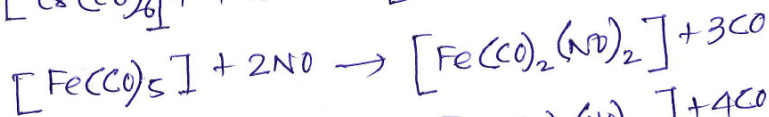
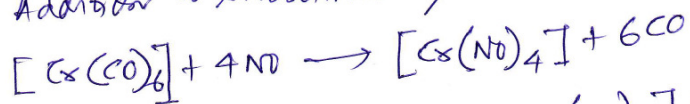
## Metal Nitrosyl Carbonyls :

NO - 11 electrons - one more than CO - which is occupying the antibonding  $\pi$  molecular orbital. NO readily forms  $\text{NO}^+$  - having the same no. of valence electrons like CO

NO - three electron donor CO - two electron donor  
Pure nitrosyl complex is rare  $\rightarrow \text{Cr}(\text{NO})_4$ .

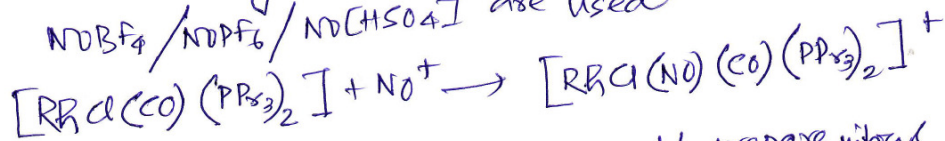
Unlike the carbonyls, NO complexes cannot be prepared directly by excess NO at high temp. and pressures the oxide tends to disproportionate at high temperatures and ~~changes~~ chances of oxidation of metal by it cannot be ruled out.

(i) Addition or substitution by NO

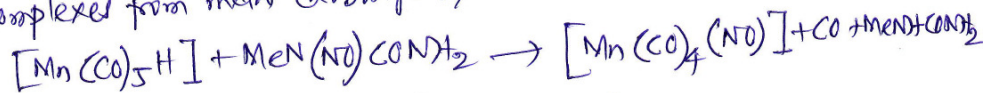


(ii) Methods involving  $\text{NO}^+$

$\text{NOBF}_4$  /  $\text{NOPF}_6$  /  $\text{NO}[\text{HSO}_4]$  are used



(iii) N-methyl-N-nitrosourea may also be used to prepare nitrosyl complexes from metal carbonyl hydrides



There exist three principal modes of bonding

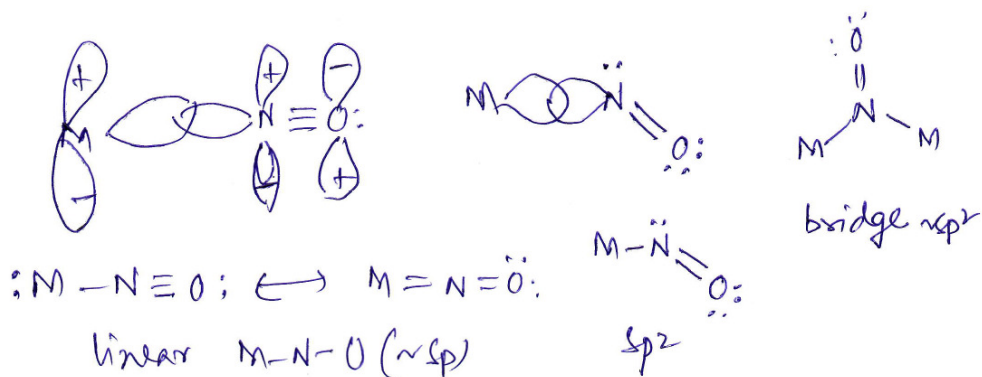
(i) terminal, linear  $\text{M}-\text{N}-\text{O}$  group. (angle -  $180^\circ$ )  
3e (str. fr.  $1650 - 1900 \text{ cm}^{-1}$ )

(ii) bent  $\text{MNO}$  group - (angle -  $120^\circ - 140^\circ$ )  
1e (str. fr.  $1525 - 1690 \text{ cm}^{-1}$ )

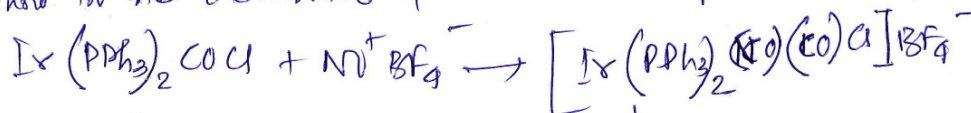


(iv) Bridging NO bond: doubly, triply and quadruply bridged nitric oxide ( $M_2$  - ir - 1480 - 1510  $cm^{-1}$ )  
 $M_3$  - is 1320  $cm^{-1}$ )

Symmetric and asymmetric bridges are known.

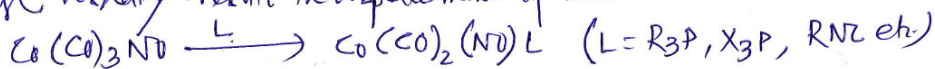


The first well characterized example of a bent nitroxyl ligand found in the derivative of the Vaska's compound.



Square pyramidal with a bent nitroxyl  $\angle Ir-N-O = 124^\circ$  at the apical position  $[Ir \text{ st. freq. } 1680 \text{ } cm^{-1}]$

Under comparable conditions M-CO and linear M-NO bonds are equally strong because of the fact that the M-C and M-N bond lengths differ  $\sim 7 \text{ pm}$ , which may be associated with the difference in size of the elements. However, substitution reactions on mixed nitroxyl carbonyl usually result in displacement of bonded CO rather than  $M^+$



This suggests that the M-N bond is stronger than the M-C bond

#### Answer to question no. 4 (a)

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- a) **Metal-Organic Frameworks** are compounds consisting of metal ions or clusters coordinated to often rigid organic molecules to form one-, two-, or three-dimensional structures that can be porous.
- b) More formally a metal–organic framework, abbreviated to MOF, is a coordination network with organic ligands containing potential voids. A coordination network is a coordination compound extending, through repeating coordination entities, in 1 dimension, but with cross-links between two or more individual chains, loops, or spiro-links, or a coordination compound extending through repeating coordination entities in 2 or 3 dimensions and finally a coordination polymer is a coordination compound with repeating coordination entities extending in 1, 2, or 3 dimensions.
- c) In some cases, the pores are stable during elimination of the guest molecules (often solvents) and can be used for the storage of gases such as hydrogen and carbon dioxide. Other possible applications of MOFs are in gas purification, in gas separation, in catalysis and as sensors.
- d) A metal-organic framework (MOF) is composed of two major components: a metal ion or cluster of metal ions and an organic molecule called a linker. The organic units are typically mono-, di-, tri-, or tetravalent ligands. The choice of metal and linker has significant effects on the structure and properties of the MOF. For example, the metal's coordination preference influences the size and shape of pores by dictating how many ligands can bind to the metal and in which orientation.

#### MOFs for hydrogen storage

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- e) Considerable interest has been shown in the development of non-petroleum energy carriers for use in transportation. Hydrogen is an attractive option because it has a high energy content (120 MJ/kg compared to 44 MJ/kg for gasoline), produces clean exhaust product (water vapor without CO<sub>2</sub> or NO<sub>x</sub>), and can be derived from a variety of primary energy sources. However, the specific energy of uncompressed hydrogen gas is very low, and considerable attention must be given to denser storage methods if hydrogen is to emerge as a serious option for energy storage.
- f) Proposed forms of reversible hydrogen storage include: compressed gas, cryogenic liquid, adsorption to high surface-area materials, chemical storage as metal hydrides, and various reactions of liquid fuels high in hydrogen content (whose products must be collected and recycled after use). Of these, compressed and liquid hydrogen are the most mature technologies and are the most suitable for immediate deployment. The United States Department of Energy (USDOE) projects that with further technological development, adsorptive or chemical storage may prove most effective for storage.
- g) Metal Organic Frameworks (MOFs) attract attention as materials for adsorptive hydrogen storage because of their exceptionally high specific surface areas and chemically tunable structures. MOFs can be thought of as a three-dimensional grid in which the vertices are metal ions or clusters of metal ions that are connected to each other by organic molecules called linkers. Hydrogen molecules are stored in a MOF

by adsorbing to its surface. Compared to an empty gas cylinder, a MOF-filled gas cylinder can store more gas because of adsorption that takes place on the surface of MOFs. (Note that molecular hydrogen adsorbs to the surface, not atomic hydrogen.) Furthermore, MOFs are free of dead-volume, so there is almost no loss of storage capacity as a result of space-blocking by non-accessible volume. Also, MOFs have a fully reversible uptake-and-release behavior: since the storage mechanism is based primarily on physisorption, there are no large activation barriers to be overcome when liberating the adsorbed hydrogen. The storage capacity of a MOF is limited by the liquid-phase density of hydrogen because the benefits provided by MOFs can be realized only if the hydrogen is in its gaseous state.

- h) In order to realize the benefits provided, such as adsorption, by MOFs hydrogen cannot be stored in them at densities greater than its liquid-phase density. The extent to which a gas can adsorb to a MOF's surface depends on the temperature and pressure of the gas. In general, adsorption increases with decreasing temperature and increasing pressure (until a maximum is reached, typically 20-30 bar, after which the adsorption capacity decreases)., However, MOFs to be used for hydrogen storage in automotive fuel cells need to operate efficiently at ambient temperature and pressures between 1 and 100 bar, as these are the values that are deemed safe for automotive applications.
- i) In 2012, the lab led by William A. Goddard III predicted that MOF-210 will have Hydrogen storage capacity of 2.90 delivery wt% (1-100 bar) at 298 K and 100 bar. Also that MOF-200 will have a Hydrogen storage capacity of 3.24 delivery wt% (1-100 bar) at 298 K and 100 bar. They also proposed new strategies to obtain higher interaction with H<sub>2</sub>. Such strategy consist on metalating the COF with alkaline metals such as Li. These complexes composed of Li, Na and K bound to benzene ligands (such as 1,3,5-benzenetribenzoate, the ligand used in MOF-177) have been synthesized by Kriech et al. and Goddard showed that the THF is important of their stability. If the metalation with alkaline is performed in the COFs, Goddard et al. calculated that two MOFs will reach the 2015 DOE target of 5.5 wt % at 298 K: MOF200-Li (6.34 delivery wt%) and MOF200-Na (5.94 6.34 delivery wt%) at 100 bar. Other strategies to increase the interaction of MOFs with molecular hydrogen have been reviewed recently.

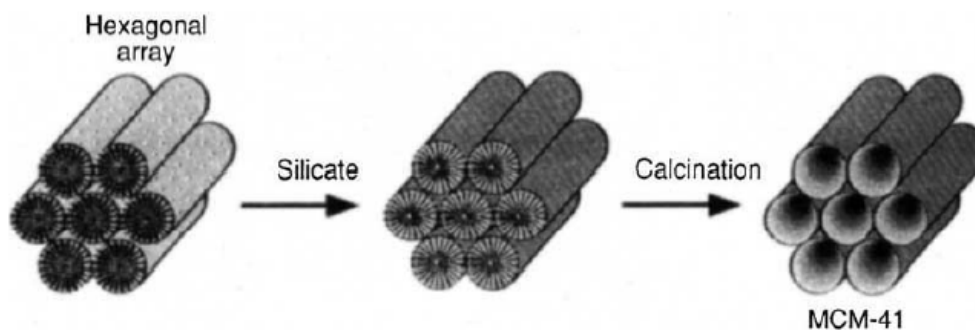
## B ) *Mesoporous materials:*

### Brief description of synthesis, characterization and application

Mesoporous inorganic solids (pore diameters of 20-50 nm) have found great utility as catalysts and sorption media because of their large internal surface area. Examples of mesoporous solids include silicas and modified layered materials. The well known members of this family of materials are described as M41S family of mesoporous silicas, which is firstly reported by C T Kresge , Mobil Company, scientist. The M41S silicas consisted of three mesophases, namely MCM-41 (Hexagonal,  $p6mm$ ), MCM-48 (cubic,  $Ia3d$ ) and MCM-50 (lamellar). They were synthesized via supramolecular templating mechanism using long chain alkyltrimethylammonium surfactants under basic conditions.

In a typical example the MCM-41 molecular sieve characterized here as follows: 200g of a solution containing 26 wt% hexadecyltrimethylammonium ion, as  $C_{16}H_{33}(CH_3)_3N^+OH/Cl$  (~30% hydroxide) was combined with 2 g of Catapal alumina, 100g of tetramethylammonium silicate solution (10%  $SiO_2$ , ratio of tetramethylammonium to  $SiO_2 = 1$ ) and 25 g of precipitated silica (HiSil), with stirring (molar ratio of  $C_{16}H_{33}(CH_3)_3N^+$  to  $Si < 1$ ). This mixture was placed in static autoclave at  $150^\circ C$  for 4 hours. After cooling it to room temperature, the solid product was recovered by filtration on Buchner funnel, washed it with water and dried it in air at ambient temperature. The as-synthesized product was then calcined at  $540^\circ C$  for one hour in flowing nitrogen, followed by six hours in flowing air. The as-synthesized product contains over 40 wt% of the original surfactant as reflected by its composition as molar: 1N, 19.6 C, 4.7 Si, 0.27 Al.

The three step cooperative organization mechanism proposed by Stucky and co-workers has proven to be consistent with the behaviour of mesoporous materials synthesis mixtures. In case of using cationic surfactant in basic condition the first step is triggered by electrostatic interactions. It corresponds to the displacement of the surfactant counterions by polydentate and polycharged inorganic anions leading to organic-inorganic ion-pairs, which self organize into liquid crystal-like mesophase. This is followed by cross-linking of the inorganic species, and formation of a rigid replica of the underlying liquid crystalline phase.

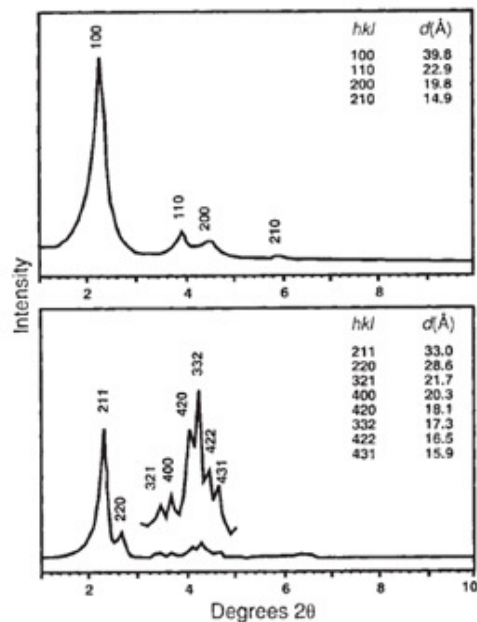


Cooperative templating mechanism

## Characterization:

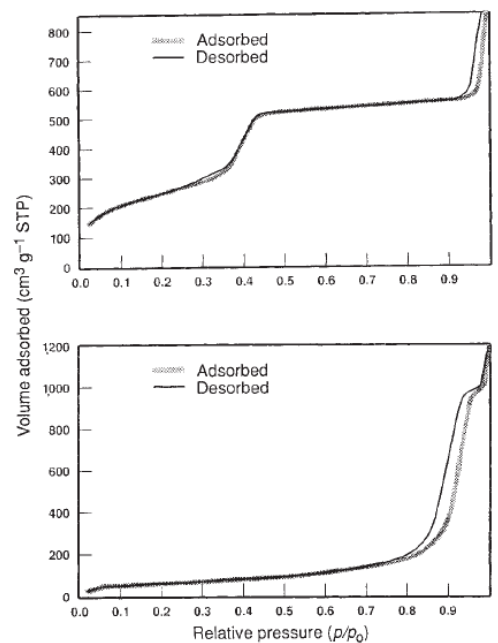
Brief description of the characterization through XRD, N<sub>2</sub>-adsorption and TEM

Fig. 1



a. Representative X-ray diffraction pattern of MCM-41. The pattern was obtained from a Scintag PAD automated diffraction system using  $\Theta$ - $\Theta$  geometry, Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and an energy-dispersive detector. b. Representative X-ray diffraction pattern of cubic (*Ia3d*) phase. Inset is expansion of region  $2\Theta = 3\text{-}5^\circ$ .

Fig.2



N<sub>2</sub> adsorption isotherm for MCM-41. b. N<sub>2</sub> adsorption isotherm for amorphous silica (BET surface area  $306 \text{ m}^2 \text{ g}^{-1}$ ). These isotherms were obtained on a Micromeritics Digisorb 2600 adsorption instrument using standard procedures. The isotherm for this MCM-41 shows the inflection characteristic of capillary condensation within the pores, where the  $p/p_0$  (relative N<sub>2</sub> pressure) position of the inflection point is related to the diameter of the pore being filled<sup>26,27</sup>  $\sim 40 \text{ \AA}$ . The significant adsorption at lower  $p/p_0$  ( $\sim 200 \text{ cm}^3 \text{ g}^{-1}$ ) is most probably due to monolayer coverage of the walls and not to the presence of microporous phases.

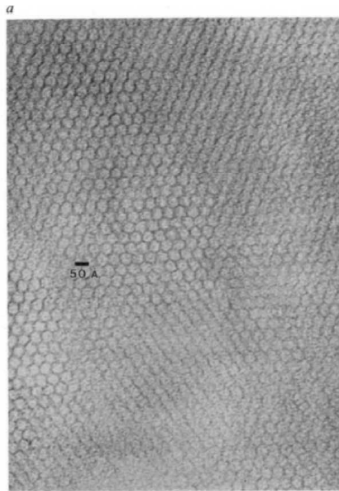


Fig.:  
3

Representative transmission electron micrograph of MCM-41. This image was obtained with a JEOL 200CX transmission electron microscope operated at 200 kV from a thin section prepared by ultramicrotomy. The instrument has an interpretable resolution of 4.5 Å and an effective 2-Å objective aperture was used to enhance image contrast.

### Applications

- \* Silicate mesoporous material modified on surface and framework were tested in a wide range of catalytic processes.
- \* It has also been used as molds or nanoreactors for the synthesis of other advanced materials such as metallic or semiconducting nanowires and nanoparticles, as well as nanoporous carbons, metals and polymers.
- \* Many mesostructured non-silica oxides and transition metal chalcogenides showed promising applications based on their unique electronic, magnetic or optical properties.

### 5

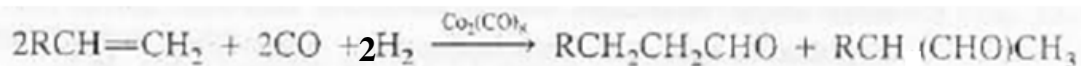
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**What is *hydroformylation* reaction and its main product? Name the catalyst for this reaction and discuss its widely accepted mechanism for the catalytic cycle. Is there any difference between *hydroformylation* and *oxo process*?**

#### Answer:

- \* The reaction of an alkene with carbon monoxide and hydrogen, catalyzed by cobalt or rhodium salts, to form an aldehyde is called hydroformylation.
- \* The name hydroformylation arises from the fact that in a formal sense a hydrogen atom and a formyl group are added across a double bond.
- \* The net result of process is extension of the carbon chain by one and introduction of oxygen into the molecule.
  
- \* It is also sometimes known as oxo process so there is no difference between hydroformylation and oxo process.

\* The main product of hydroformylation is aldehyde.



\* It was discovered by Roelen in 1938 and is the oldest and largest volume catalytic reaction of alkenes, with the conversion of propylene to butyraldehyde being the most important.

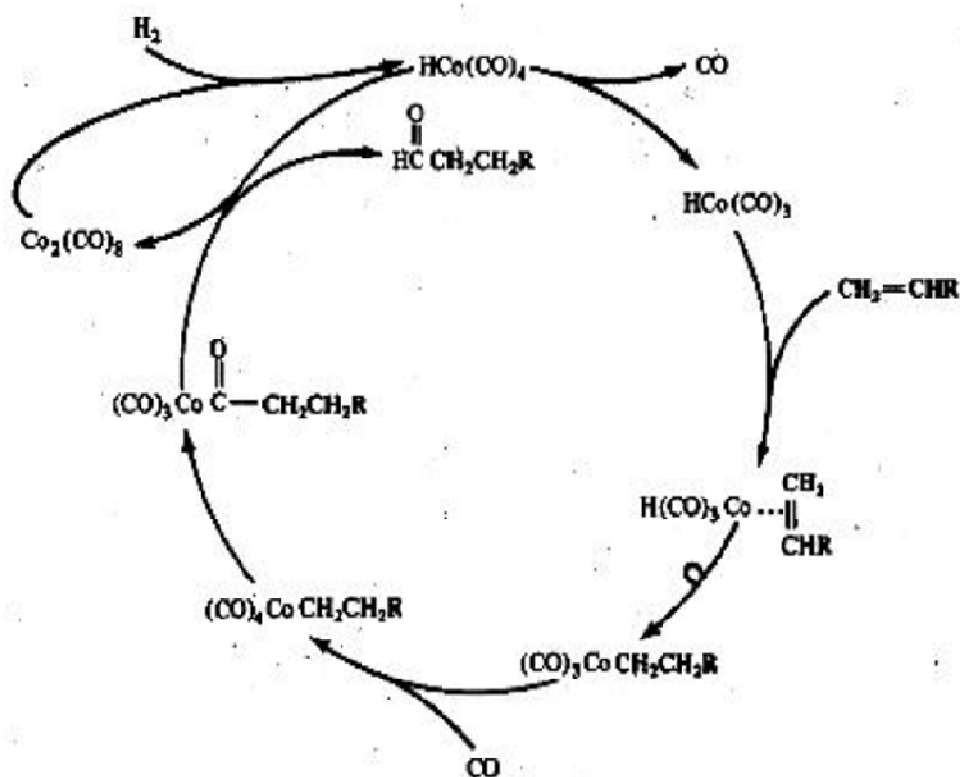
\* About 5 million tons of aldehydes and aldehyde derivatives (mostly alcohols) are produced annually making the process the most important industrial synthesis using a metal carbonyl complex as a catalyst.<sup>1</sup>

1. Orchin, M. *Acc. Chem. Res.* **1981**, *14*, 259-266.

The most widely accepted mechanism for the catalytic cycle is the following one proposed by Heck and Breslow.<sup>2</sup>

2. Heck, R. F. ; Breslow, D. S. *J. Am. Chem. Soc.* **1961**, *83*, 4023-4027.

Description of the following catalytic loop.



\* There are some disadvantages associated with the cobalt carbonyl catalyst when it is used to convert propylene to butyraldehyde. (Description of few points).

\* A modified cobalt catalyst,  $\text{HCo}(\text{CO})_3\text{PBu}_3$  developed by shell improves the linear to branched ratio but gives the slower reaction and therefore is run at higher temperatures ( $175^\circ\text{C}$  and 50-100 atm).

\* Union carbide has improved the ratio even more with various rhodium catalysts. The  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  catalyzes the reaction at  $90\text{-}110^\circ\text{C}$  and 12 atmospheres. They have also announced a new low-pressure hydroformylation rhodium catalyst modified with phosphites,  $\text{P}(\text{OR})_3$ , which works with less active alkenes such as 2-butene and 2-methylpropene.<sup>3</sup> the relatively high expense of rhodium requires that this catalyst be long lived and lost from the reaction system.

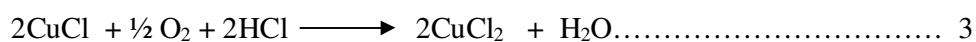
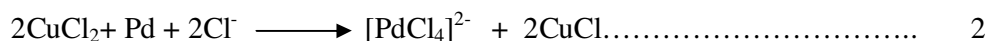
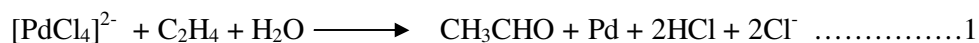
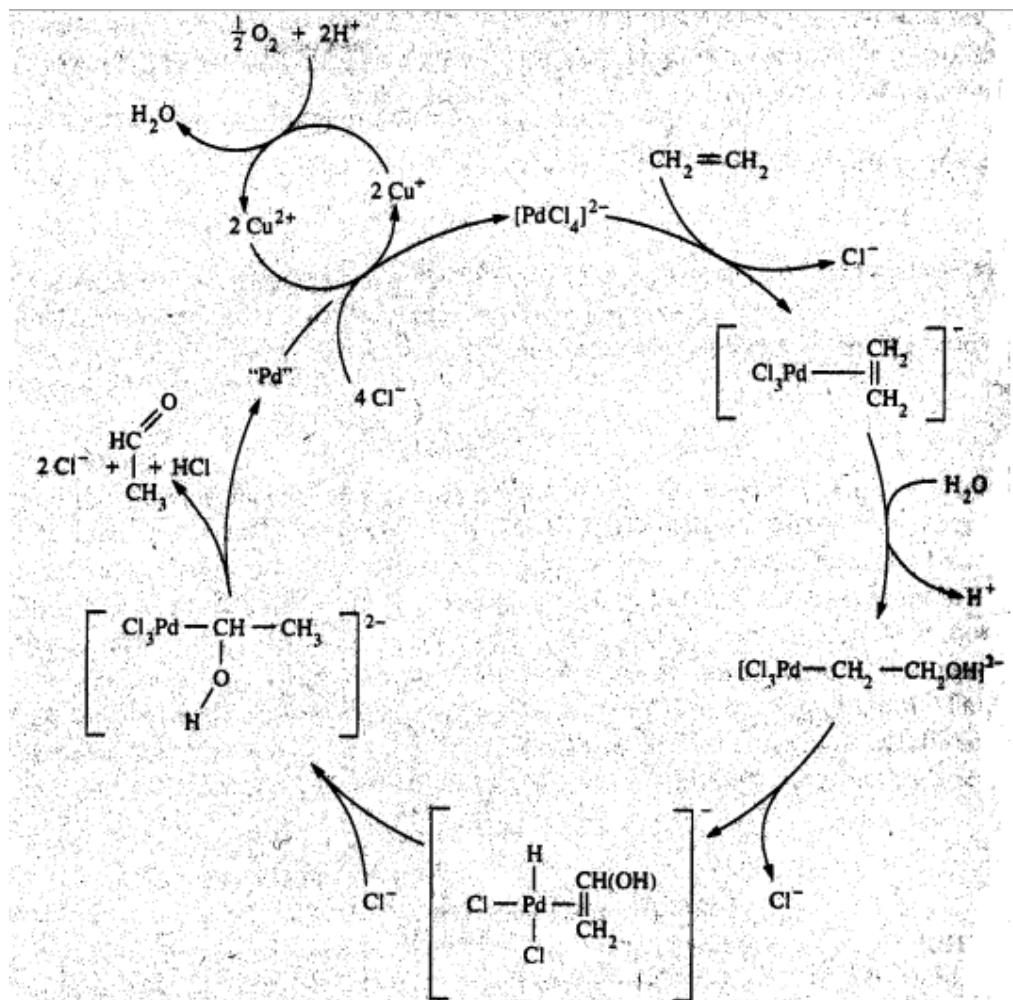
3. *Chem. Eng. News* **1988**, 66(41), 27.

6. The addition of molecular oxygen to ethylene provides acetaldehyde on an industrial scale and this reaction is catalyzed  $[\text{PdCl}_4]^{2-}$ . Name this process and its catalytic mechanism.

This process is known as Wacker Process and developed in Germany. About 4 million pounds of aldehydes are produced yearly by this method. Acetaldehyde is easily oxidized to acetic acid and the overall conversion of the ethylene to the acid represents a principal route to its synthesis. It has been said that “ the invention of the Wacker process was triumph of common sense.”<sup>1</sup>

1. Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York 1980; p102.





\* The first reaction is stoichiometric and would be of little value since palladium is expensive except that, in the presence of  $\text{Cu}^{2+}$ , palladium metal is oxidized back to  $\text{Pd}^{2+}$  before it precipitates (eqn.2).

The  $\text{Cu}^+$  produced is reoxidized by molecular oxygen. The mechanism for conversion of ethylene to acetaldehyde has been extensively studied and the intermediates shown in the above cycle are now accepted most chemists and researchers.<sup>2</sup>

2. (a) Backvall J. E. *et al.* J. Am. Chem. Soc. 1979, 101, 2411-2416; (b) Akermark, B. *et al.* 1987, 6, 2608-2610.

1.

(vi) What do you mean by Ruddlesden-Popper (R-P) oxides?

Ans: Ruddlesden-Popper (RP) oxides tend to exhibit high flexibility in terms of cation composition and oxygen content. As such they are good candidates for studying the effect of cation composition and oxygen content on various functional properties. In this

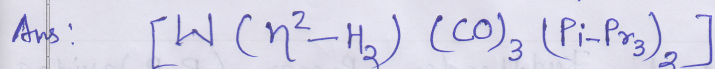
The ideal RP structure of  $A_2 \text{O}_{n-1} \text{B}_n \text{O}_{3n+1-\delta}$  is closely related to the basic perovskite structure as it is based on a perovskite-structured block,  $\text{O}_{n-1} \text{B}_n \text{O}_{3n-1}$  ( $n \geq 1$ ), consisting of  $n-1$   $\text{O}$  layers and  $n$   $\text{BO}_2$  layers. This block is sandwiched between two rock-salt-structured AO layers according to the layer sequence of  $\text{AO}-\text{BO}_2-(\text{O}-\text{BO}_2)_{n-1}-\text{AO}$ . The  $\delta$  in the formula,  $A_2 \text{O}_{n-1} \text{B}_n \text{O}_{3n+1-\delta}$ , denotes the degree of oxygen nonstoichiometry. ~~is~~ derived from

The RP phases are derived from the parent-perovskite phase by the addition of one extra AO layers, leading to a transition in the ab phase (plane) between two consecutive unit cells.

The oxygen-vacancy concentration of RP oxides is seldom presented on layer-by-layer basis; an overall oxygen nonstoichiometry parameter of  $\delta$  is usually given instead. The variation range of  $\delta$  is strongly influenced by the identical identity of the transition metal.

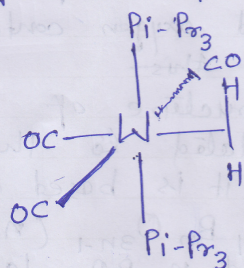


(ix) Name of the first synthesized metal hydride.



(1984)

This complex was prepared by G. Kubas by the reduction of corresponding halide in the presence of  $H_2$  gas.



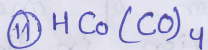
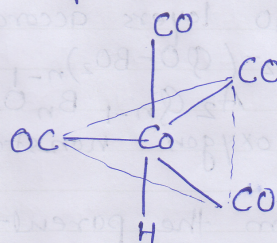
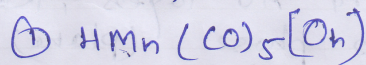
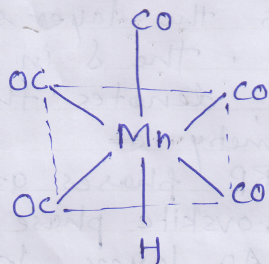
H-H distance :  $0.84 \text{ \AA}$

Chemical shift( $\delta$ ) :  $-4 \text{ ppm}$

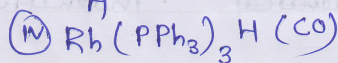
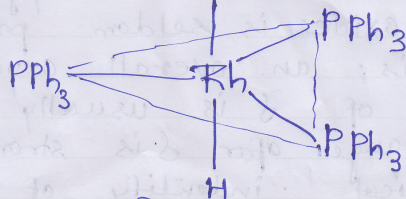
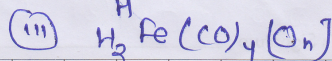
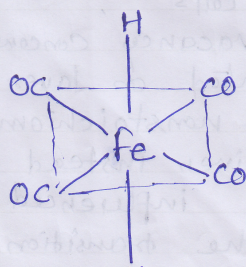
IR :  $2690 \text{ cm}^{-1}$

(x) Give two examples of metal carbonyl hydrides

Ans:



(Trigonal bipyramidal)

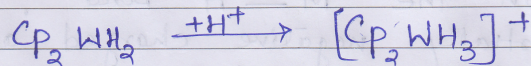
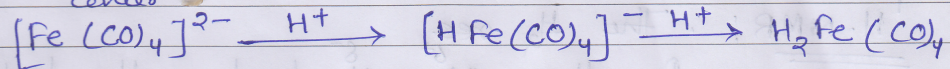




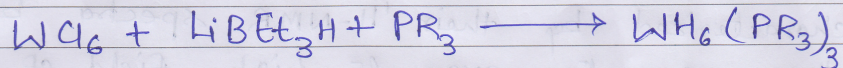
8. Write the synthetic method of metal hydrides and also discuss their  $^1\text{H-NMR}$  spectra.

Ans: The metal hydrides are synthesized by following methods:

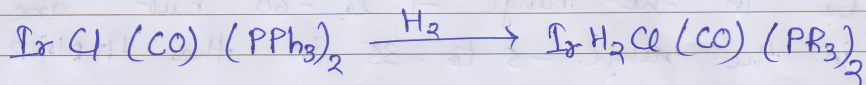
(i) Protonation: requires an electron rich basic metal center



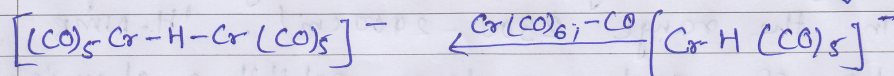
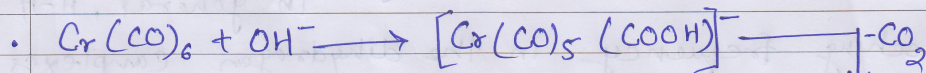
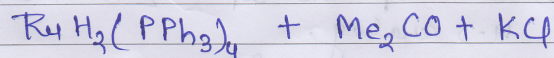
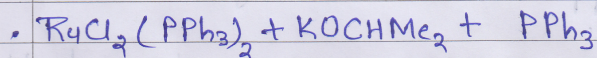
(ii) from Hydride donors:



(iii) from  $\text{H}_2$ :



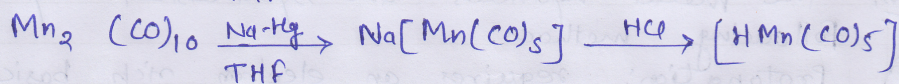
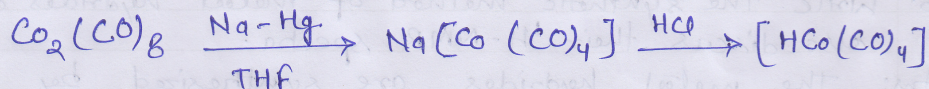
(iv) from a ligand ( $\beta$ -elimination)





4

(V) By acidification of Metal carbonylate anions:



<sup>1</sup>H-NMR: The  $\text{H}_2$  res. In the  $\text{M}^{\delta+} - \text{H}^{\delta-}$  bond, the hydrogen atom is partially negative charged and, therefore its proton is highly shielded by electron. The metal hydride complexes are therefore detected and characterized by their <sup>1</sup>H-NMR spectra because they resonate even to high field of TMS. (Tetramethylsilane). The chemical shift ( $\delta$ ) may be in the range -1 to -60 but are usually in the range -5 to -35 in the <sup>1</sup>H-NMR spectra of metal hydride complex.

- The <sup>1</sup>H-NMR appears in the range 0 to -10 $\delta$  in the metal hydrides.
- The presence of an H-H(D) bond is shown by the H,D coupling constant of 20-30 Hz in the <sup>1</sup>H-NMR spectrum of the H-D analog.

In general, H-H stretching frequency in the dihydrogen complexes lies in the range 2300 - 2900  $\text{cm}^{-1}$ . <sup>1</sup>H-NMR spectra of such complexes exhibit a chemical shift ( $\delta$ ) from 0 to -10. The H-H distance in di-

hydrogen complexes generally lies in the range of  $0.74 \text{ \AA}$  to  $1 \text{ \AA}$ . free  $\text{H}_2$  molecule is a very weak acid ( $\text{p}K_a = 35$ ) but  $\text{H}_2$  molecule coordinated to transition metal is a much stronger acid ( $\text{p}K_a = 0$  to  $20$ )