

**Module-2:**

**Metal Complexes and  
Organometallics**

## **Contents.....(6 hours)**

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**Inorganic complexes - structure, bonding and application;**

**Organometallics – introduction, stability, structure and applications of metal carbonyls, ferrocene and Grignard reagent;**

**Metals in biology: haemoglobin and chlorophyll- structure and property).**

# Inorganic Complexes: Structure, Bonding and Applications

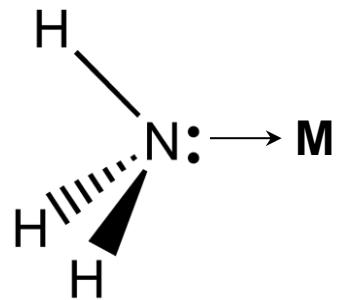
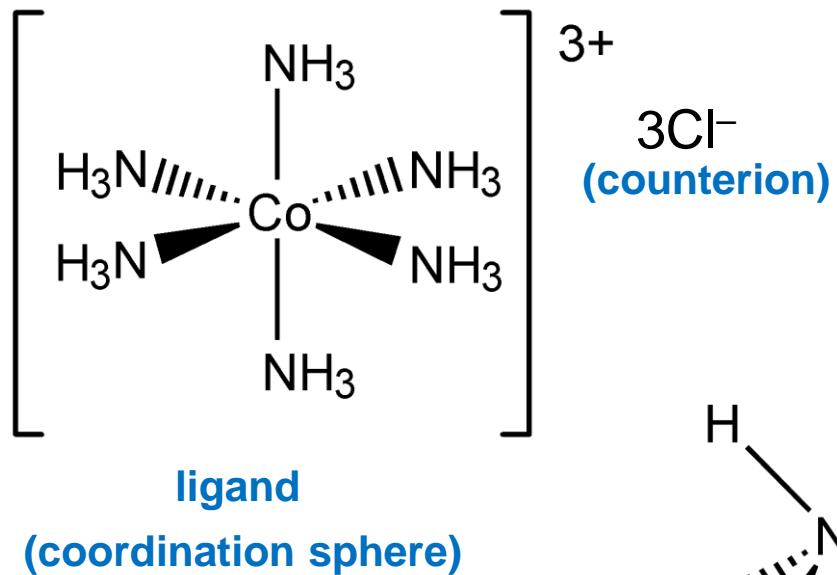
## ❖ Double Salt:

## Double Salts and Coordination Compounds

Ferric alum

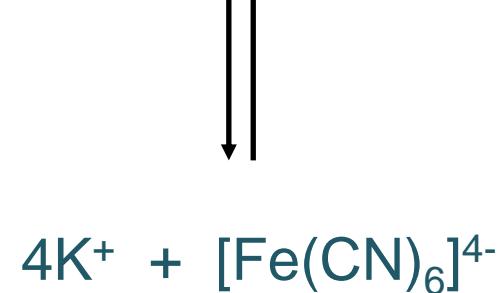
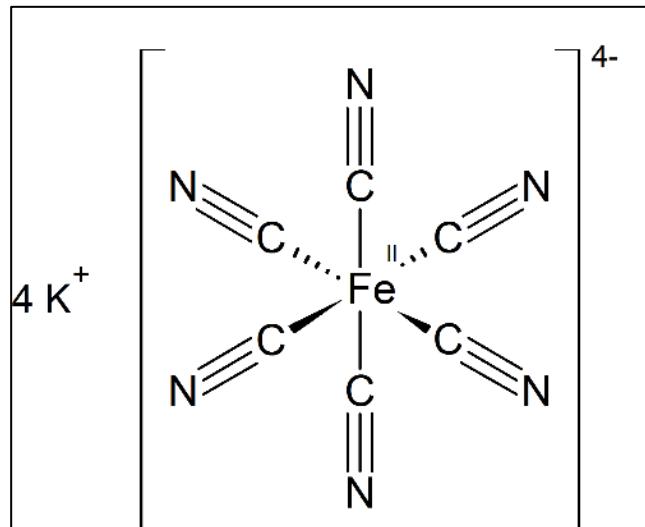
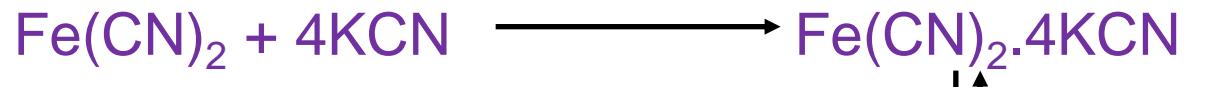


In water:  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Fe}^{3+}$



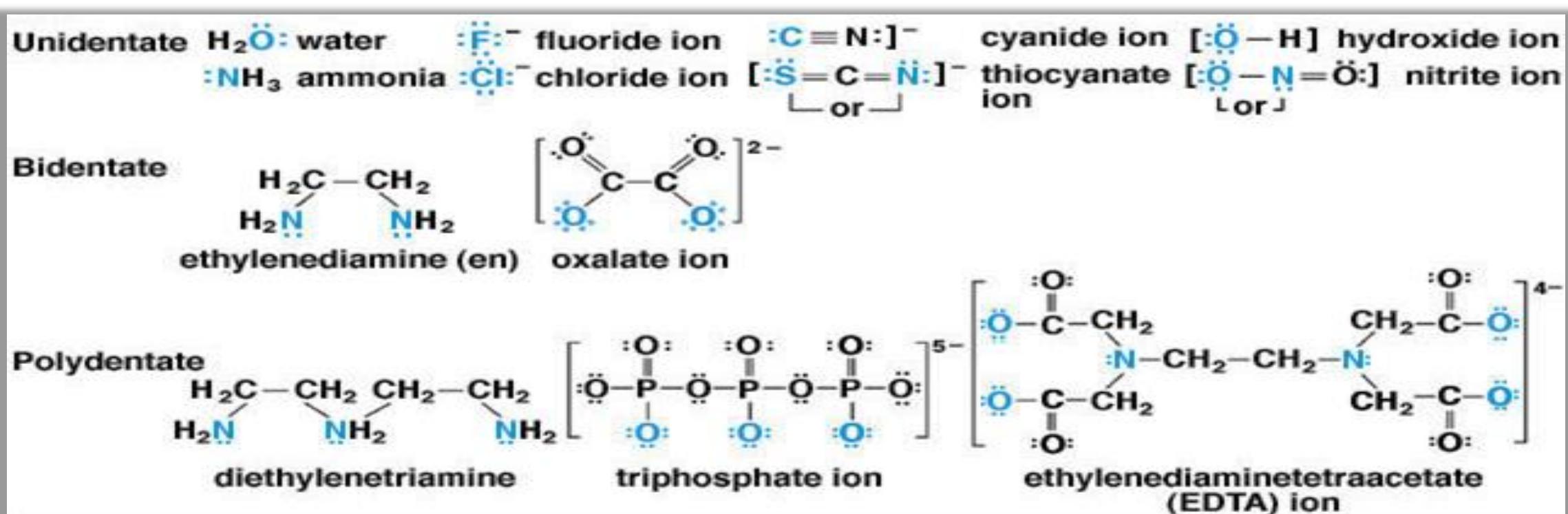
N forms a coordinate covalent bond to the metal

## ❖ Co-ordination Compounds



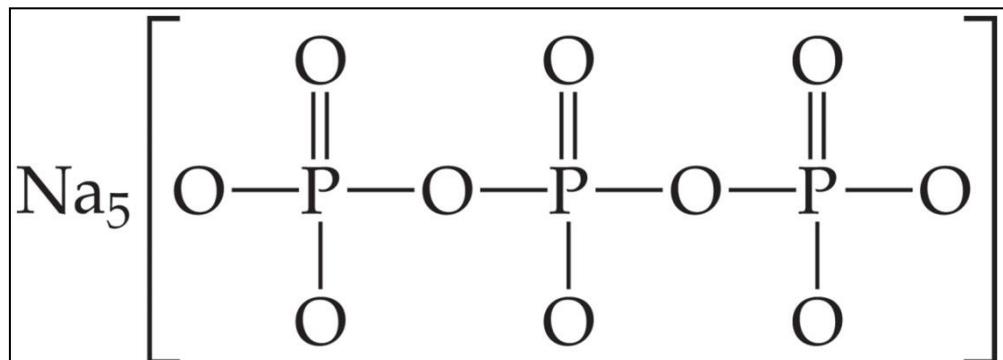
# Ligands

- Molecule or ion having a lone electron pair that can be used to form a bond to a metal ion (Lewis base).
- coordinate covalent bond:** metal-ligand bond
- monodentate** : one bond to metal ion
- bidentate** : two bond to metal ion
- polydentate** : more than two bonds to a metal ion possible

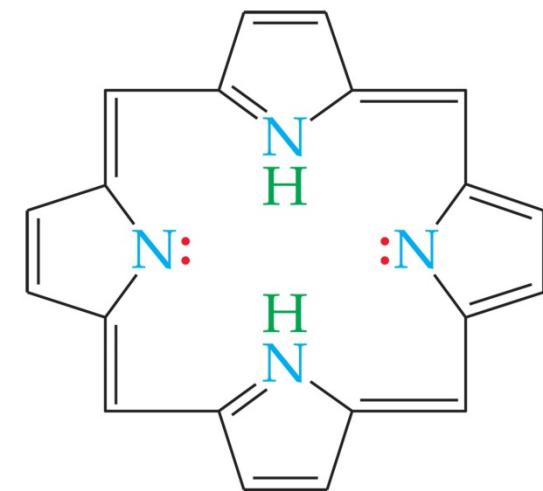


# Chelating Agents

- Bind to metal ions removing them from solution.
  - Phosphates are used to tie up  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in hard water to prevent them from interfering with detergents.



- Important biomolecules like heme and chlorophyll are porphyrins

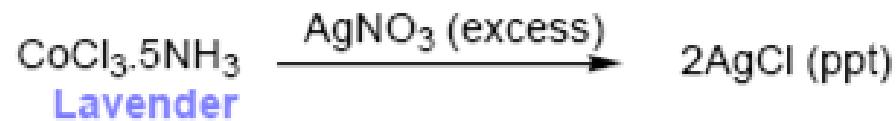
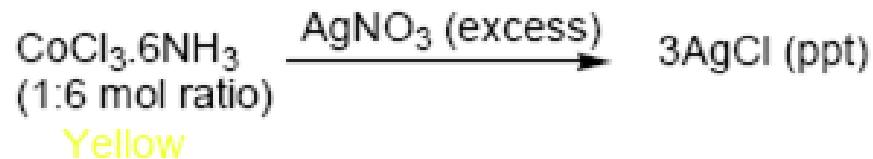


# Werner Coordination Theory

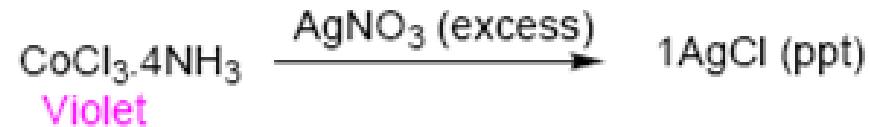
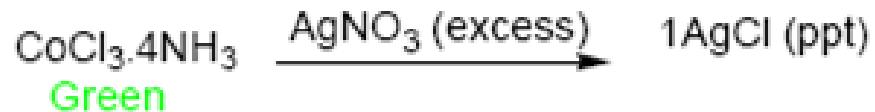
**Werner's Theory:** Alfred Werner, Swiss chemist put forward **a theory to explain the formation of complex compounds.**

Werner studied the following metal complexes:

- $\text{CoCl}_3$  forms four different compounds with  $\text{NH}_3$ .



One Cl does not react



## Limitations:

1. Bonding within coordination sphere.
2. Square planar (or) Tetrahedral

# Lewis Acid Base Theory - Gilbert N. Lewis, 1920s

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- ❖ Lewis Acid/Base reactions: Base: electron pair donor; Acid: electron pair acceptor
- ❖ Ligands: Lewis bases ; Metals: Lewis acids ; Coordinate covalent bonds
- ❖ Metal Complexes - Formation of a complex was described as an acid - base reaction according to Lewis

## Sidgwick's Rule

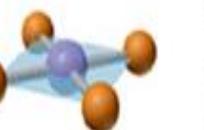
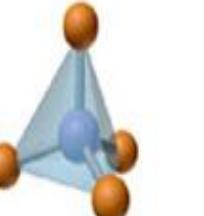
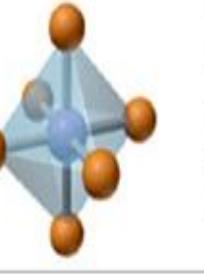
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- ❖ Sidgwick's Effective atomic number (EAN) rule is based on the octet theory of Lewis and this is the first attempt to account for the bonding in complexes.

# Valence Bond Theory (Linus Pauling, 1931)

**Valence bond theory** predicts that the bonding in a metal complex arises from overlap of filled ligand orbitals and vacant metal orbitals.

Coordination number	Hybridisation	Geometry	Examples
2	sp	Linear	$[\text{CuCl}_2]^-$ , $[\text{Ag}(\text{CN})_2]^-$
3	$\text{sp}^2$	Trigonal planar	$[\text{HgI}_3]^-$
4	$\text{sp}^3$	Tetrahedral	$[\text{Ni}(\text{CO})_4]$ , $[\text{NiCl}_4]^{2-}$
4	$\text{dsp}^2$	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{Pt}(\text{NH}_3)_4]^{2+}$
5	$\text{dsp}^3$ <i>(<math>d_{x^2-y^2}</math> orbital is involved)</i>	Trigonal bipyramidal	$\text{Fe}(\text{CO})_5$
6	$\text{d}^2\text{sp}^3$ <i>(<math>d_{z^2}</math> and <math>d_{x^2-y^2}</math> orbitals of inner shell are involved)</i>	Octahedral	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , $[\text{Fe}(\text{CN})_6]^{4-}$ , $[\text{Fe}(\text{CN})_6]^{3-}$ , $[\text{Co}(\text{NH}_3)_6]^{3+}$ <i>(Inner orbital complexes)</i>
6	$\text{sp}^3\text{d}^2$ <i>(<math>d_{z^2}</math> and <math>d_{x^2-y^2}</math> orbitals of the outer shell are involved)</i>	Octahedral	$[\text{FeF}_6]^{4-}$ , $[\text{CoF}_6]^{4-}$ , $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ <i>(Outer orbital complexes)</i>

Coordination Number	Shape	Examples
2	Linear	 $[\text{CuCl}_2]^-$ , $[\text{Ag}(\text{NH}_3)_2]^+$ , $[\text{AuCl}_2]^-$
4	Square planar	 $[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{PdCl}_4]^{2-}$ , $[\text{Pt}(\text{NH}_3)_4]^{2+}$ , $[\text{Cu}(\text{NH}_3)_4]^{2+}$
4	Tetrahedral	 $[\text{Cu}(\text{CN})_4]^{3-}$ , $[\text{Zn}(\text{NH}_3)_4]^{2+}$ , $[\text{CdCl}_4]^{2-}$ , $[\text{MnCl}_4]^{2-}$
6	Octahedral	 $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , $[\text{V}(\text{CN})_6]^{4-}$ , $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ , $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ , $[\text{FeCl}_6]^{3-}$ , $[\text{Co}(\text{en})_3]^{3+}$

# Tetrahedral Geometry

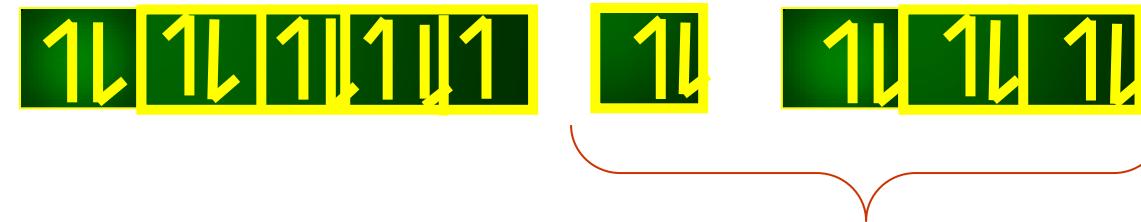
- Tetrahedral copper complex



Cu ground state  $3d^94s^2$



$\text{Cu}^{2+}$

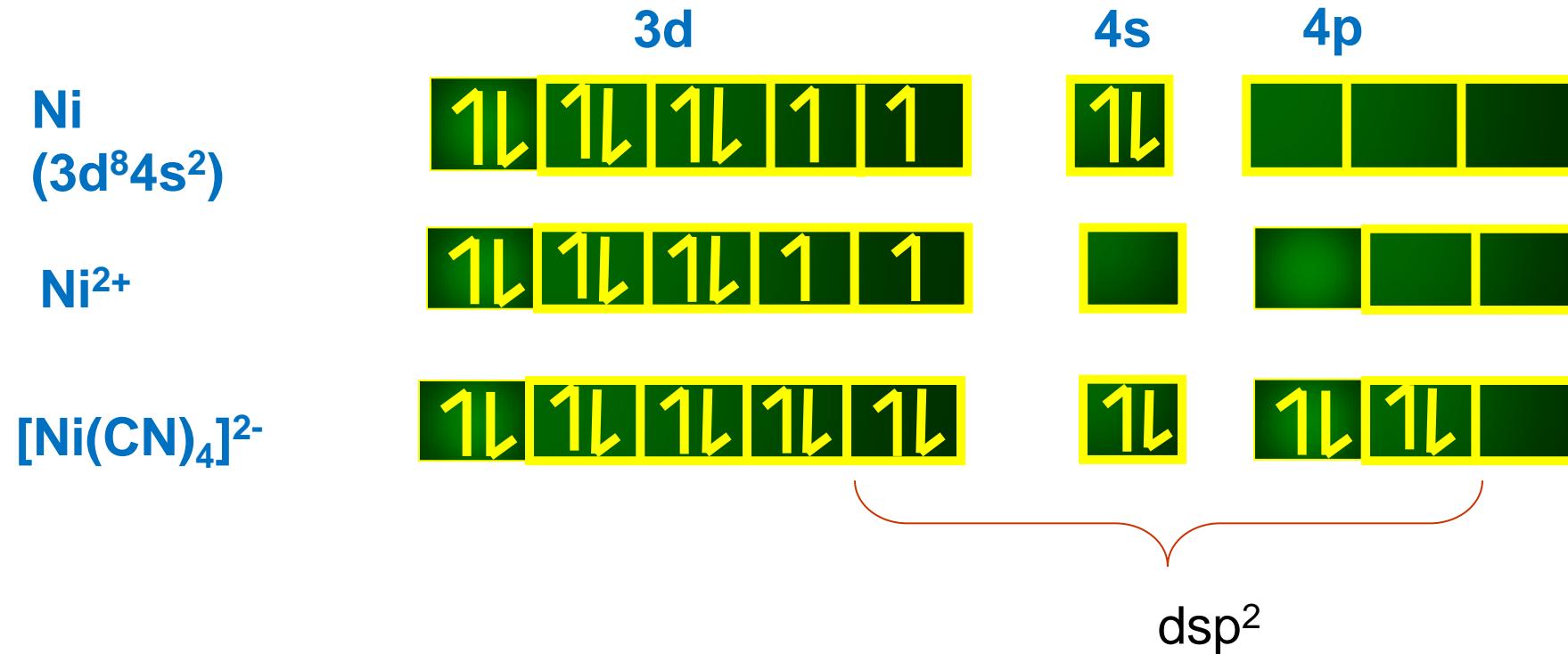


4 e<sup>-</sup> pairs by Cl<sup>-</sup> ions

- One unpaired electron - paramagnetic and attracted by magnets

# Square Planar Geometry

- Square planar nickel complex

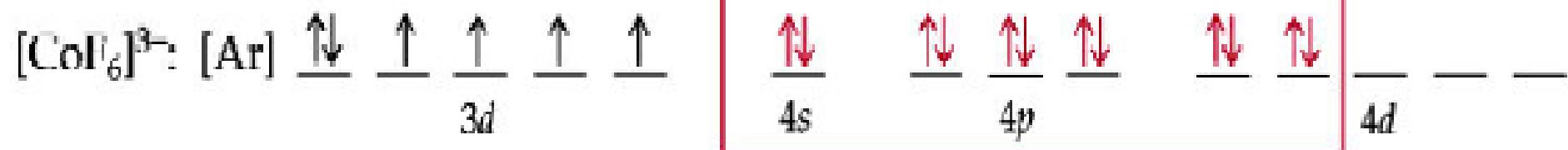


- All paired electrons – diamagnetic - weakly repelled by magnets

# Octahedral $sp^3d^2$ Geometry

Gives  $[CoF_6]^{3-}$  four unpaired electrons, which makes it paramagnetic and is called a *high-spin complex*.

Ground state Co=  $(3d^74s^2)$

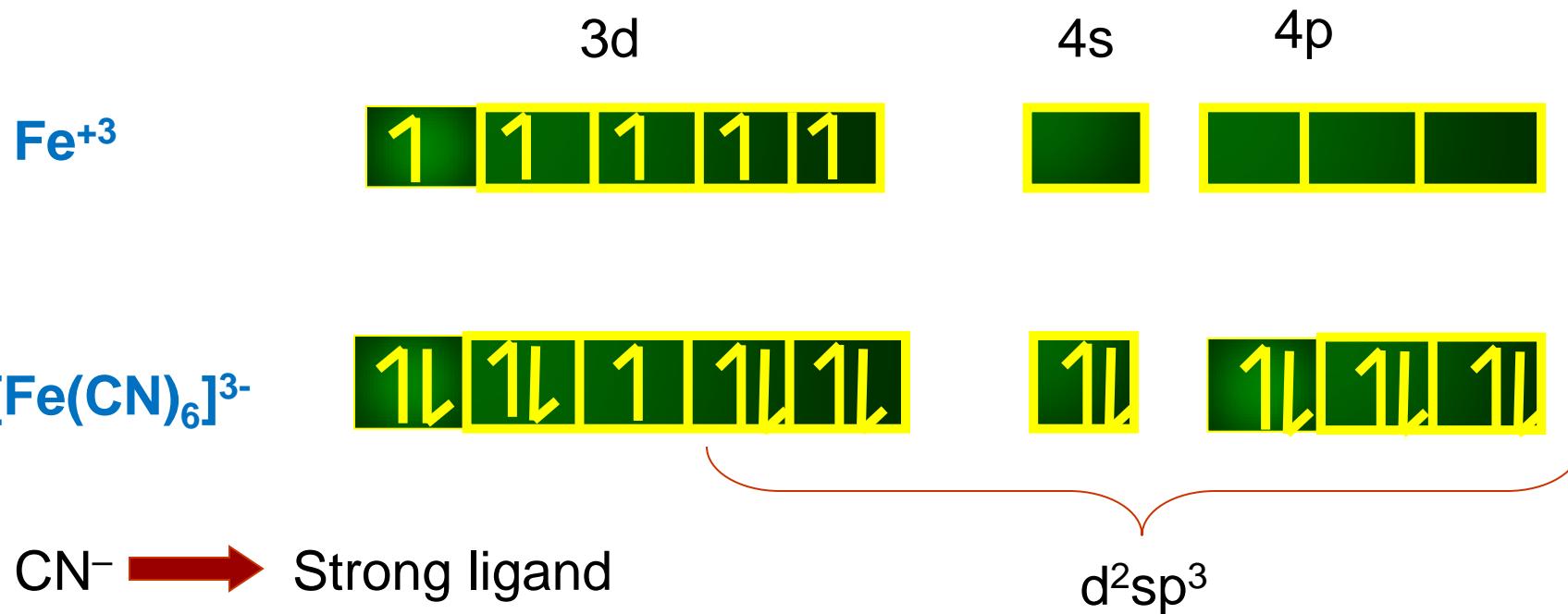


Six  $sp^3d^2$  bonds to the ligands

# Octahedral $d^2sp^3$ Geometry

$[\text{Fe}(\text{CN})_6]^{3-}$

Fe:  $(3\text{d}^6 4\text{s}^2)$



# Bonding in Coordination Compounds

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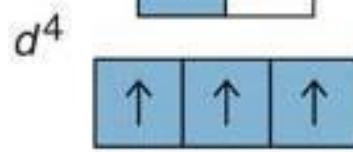
- ❖ Many of the properties of metal complexes are dictated by their electronic structures.

## Crystal field theory (CFT)

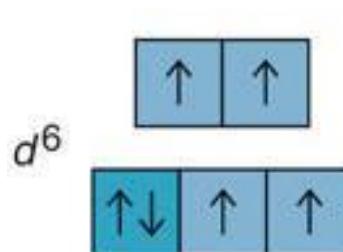
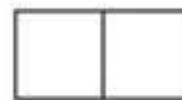
- ❖ Electronic structure can be explained by an ionic model that attributes formal charges on to the metals and ligands. This forms basis of crystal field theory (CFT), which is considered as the core concept in inorganic chemistry.
- ❖ Consider bonding in a complex to be an electrostatic attraction between a positively charged nucleus and the electrons of the ligands.
  - **Electrons on metal atom repel electrons on ligands.**
  - **Focus particularly on the  $d$ -electrons on the metal ion.**
- ❖ Ligand field theory (LFT) and the molecular orbital theory (MO) are considered sophisticated models as compared to CFT. LFT explains complexes, wherein, the interactions are covalent.

# Orbital occupancy for high- and low-spin complexes of d<sup>4</sup> through d<sup>7</sup> metal ions

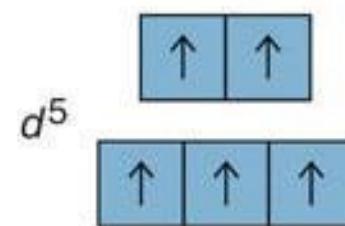
*high  
spin:  
weak-  
field  
ligand*



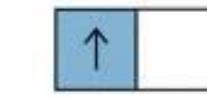
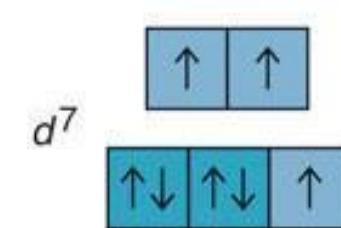
*low spin:  
strong-  
field ligand*



*high  
spin:  
weak-  
field  
ligand*



*low spin:  
strong-  
field ligand*

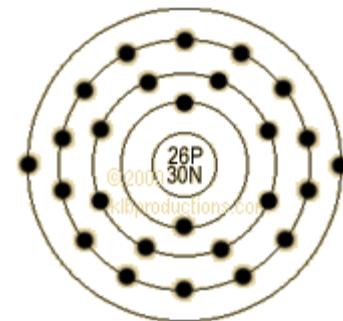
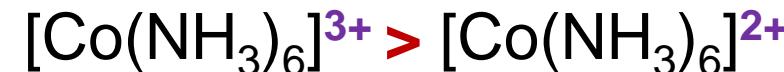


CFSE and electronic arrangements in octahedral complexes

Number of <i>d</i> electrons	Arrangement in weak ligand field			Arrangement in strong ligand field				
	<i>t</i> <sub>2g</sub>	<i>e</i> <sub>g</sub>	CFSE $\Delta_o$	Spin only magnetic moment $\mu_s(D)$	<i>t</i> <sub>2g</sub>	<i>e</i> <sub>g</sub>	CFSE $\Delta_o$	Spin only magnetic moment $\mu_s(D)$
<i>d</i> <sup>1</sup>	↑ [ ] [ ]	[ ] [ ]	-0.4	1.73	↑ [ ] [ ]	[ ] [ ]	-0.4	1.73
<i>d</i> <sup>2</sup>	↑ [ ↑ ] [ ]	[ ] [ ]	-0.8	2.83	↑ [ ↑ ] [ ]	[ ] [ ]	-0.8	2.83
<i>d</i> <sup>3</sup>	↑ [ ↑ ] [ ↑ ] [ ]	[ ] [ ]	-1.2	3.87	↑ [ ↑ ] [ ↑ ] [ ]	[ ] [ ]	-1.2	3.87
<i>d</i> <sup>4</sup>	↑ [ ↑ ] [ ↑ ] [ ↑ ] [ ]	[ ] [ ]	-1.2 +0.6 = -0.6	4.90	↑ ↓ [ ↑ ] [ ↑ ] [ ]	[ ] [ ]	-1.6	2.83
<i>d</i> <sup>5</sup>	↑ [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ]	[ ] [ ]	-1.2 +1.2 = -0.0	5.92	↑ ↓ [ ↑ ] [ ↑ ] [ ↑ ] [ ]	[ ] [ ]	-2.0	1.73
<i>d</i> <sup>6</sup>	↑ ↓ [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ]	[ ] [ ]	-1.6 +1.2 = -0.4	4.90	↑ ↓ [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ]	[ ] [ ]	-2.4	0.00
<i>d</i> <sup>7</sup>	↑ ↓ [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ]	[ ] [ ]	-2.0 +1.2 = -0.8	3.87	↑ ↓ [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ]	[ ] [ ]	-2.4 +0.6 = -1.8	1.73
<i>d</i> <sup>8</sup>	↑ ↓ [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ]	[ ] [ ]	-2.4 +1.2 = -1.2	2.83	↑ ↓ [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ]	[ ] [ ]	-2.4 +1.2 = -1.2	2.83
<i>d</i> <sup>9</sup>	↑ ↓ [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ]	[ ] [ ]	-2.4 +1.8 = -0.6	1.73	↑ ↓ [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ]	[ ] [ ]	-2.4 +1.8 = -0.6	1.73
<i>d</i> <sup>10</sup>	↑ ↓ [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ]	[ ] [ ]	-2.4 +2.4 = 0.0	0.00	↑ ↓ [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ↑ ] [ ]	[ ] [ ]	-2.4 +2.4 = 0.0	0.00

$\Delta_o$  is dependent on:

- Nature of the ligands
- The charge on the metal ion
- Whether the metal is a 3d, 4d, or 5d element



27  
Co

45  
Rh

77  
Ir



# Spectrochemical Series

- For a given ligand, the color depends on the oxidation state of the metal ion.



WEAKER FIELD

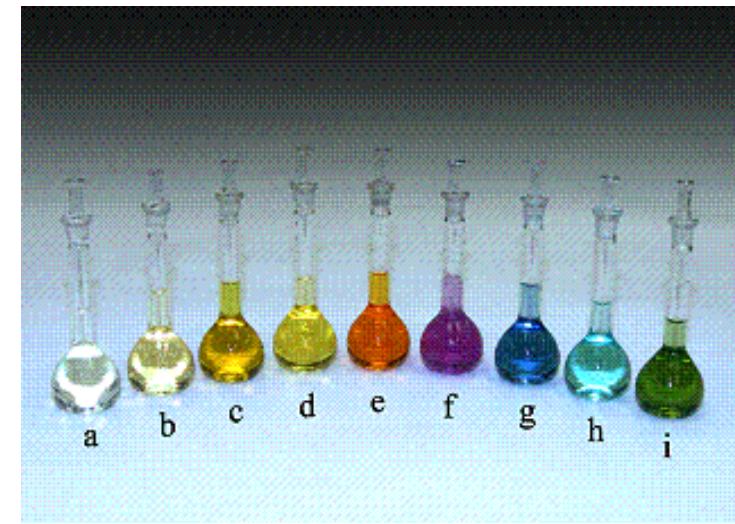
STRONGER FIELD

SMALLER  $\Delta$

LARGER  $\Delta$

LONGER  $\lambda$

SHORTER  $\lambda$



- Complexes of cobalt (III) show the shift in color due to the ligand.
- (a)  $\text{CN}^-$ , (b)  $\text{NO}_2^-$ , (c) phen, (d) en, (e)  $\text{NH}_3$ , (f) gly, (g)  $\text{H}_2\text{O}$ , (h)  $\text{ox}^{2-}$ , (i)  $\text{CO}_3^{2-}$

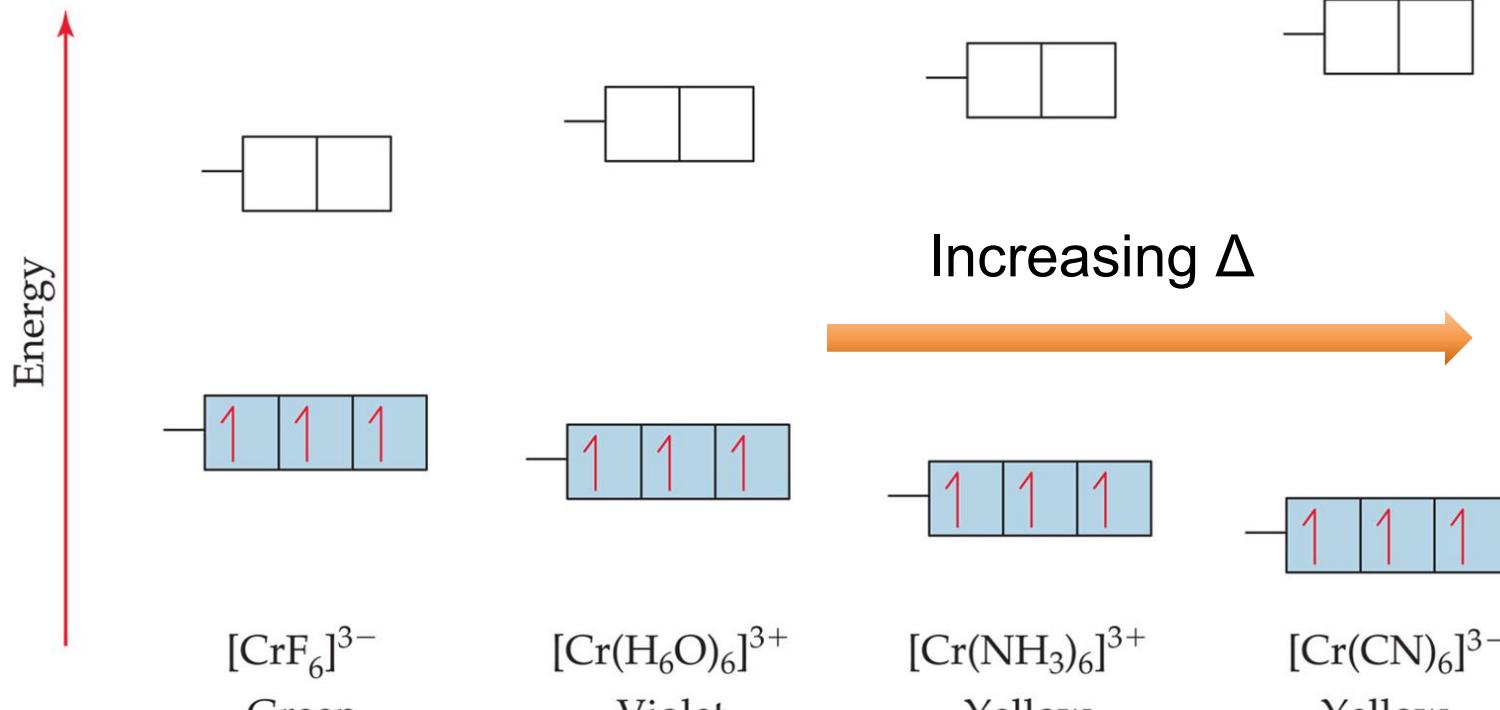
- For a given metal ion, the color depends on the ligand.

# Spectrochemical series (strength of ligand interaction)

## Effect of ligand on splitting energy



Increasing  $\Delta$



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Low spin – color variations shown with increasing CFSE

$(\text{Cr}^{3+} = 24 - 3 - 18 = d^3)$

# **Applications of Coordination Compounds**

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- ❖ Coordination compounds are of great importance.
- ❖ Play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine.
  - **Catalysis**
  - **Extraction of metal ions**
  - **Analytical chemistry (development of numerous analytical methods)**
  - **Hardness estimation -**
  - **Biological importance**
  - **Medicinal application**
  - **Industrial application**

# Extraction / Purification of metal



## □ Extraction

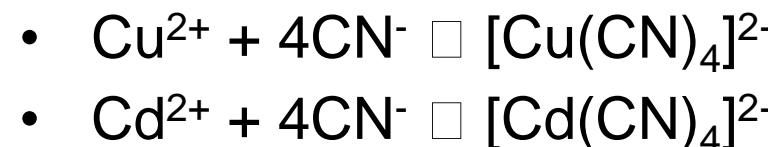
- ❖ processes of metals, like those of **silver and gold**, make use of complex formation.
- ❖ These noble metals are extracted from their ore by the formation of cyanide complexes - dicyanoargentite(I) -  $[\text{Ag}(\text{CN})_2]^-$  and dicyanoaurate (I) -  $[\text{Au}(\text{CN})_2]^-$  in the presence of oxygen and water, from which the metallic forms can be separated by the addition of zinc.
  - $\text{Ag}_2\text{S} + 4\text{NaCN} \rightarrow 2 \text{Na}[\text{Ag}(\text{CN})_2] + \text{Na}_2\text{S}$
  - $2 \text{Na}[\text{Ag}(\text{CN})_2] + \text{Zn} \rightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Ag}\downarrow$
- ❖ **Purification of metals** can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to  $[\text{Ni}(\text{CO})_4]$ , which is decomposed to yield pure nickel.

# Analytical chemistry

- ❖ In the qualitative methods of analysis, complex formation is of immense importance in the identification and separation of most inorganic ions.
- ❖ Familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis.

Examples of such reagents include EDTA, DMG (dimethylglyoxime),  $\alpha$ -nitroso,  $\beta$ -naphthol, cupron, etc.

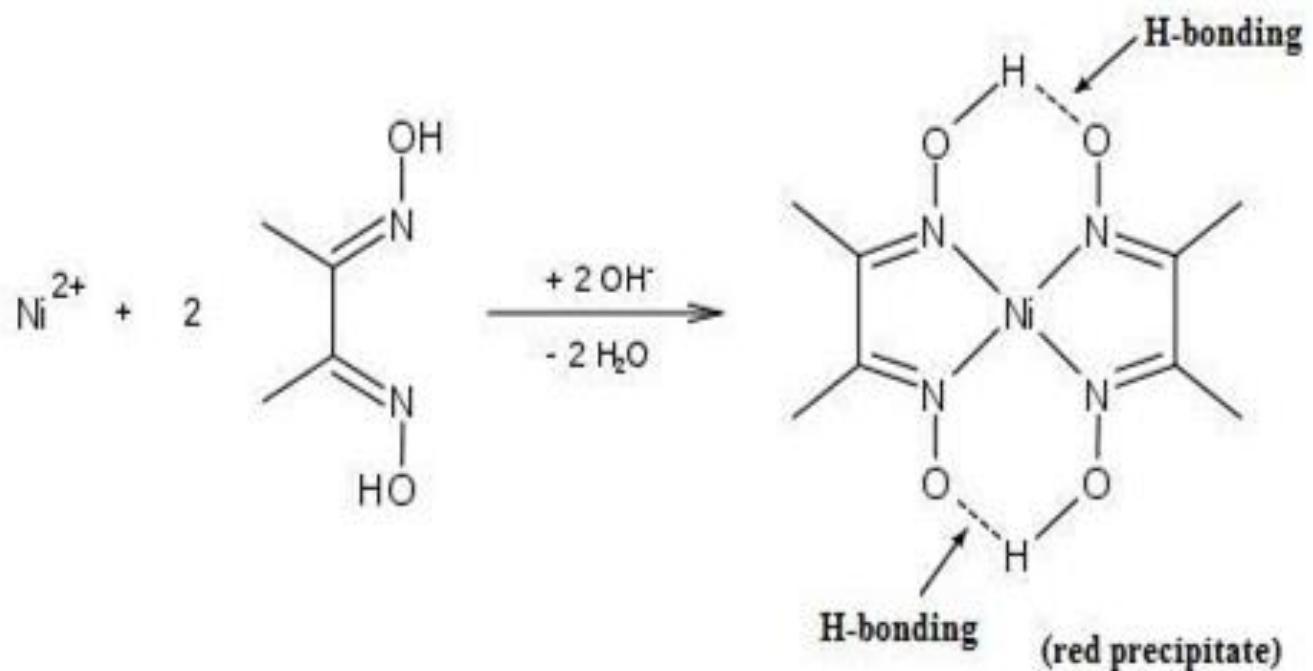
- ❖ Since Cu is more stable than Cd. Therefore, on passing  $H_2S$  only CdS is precipitated. Thus  $Cd^{2+}$  ion easily detected in the presence of  $Cu^{2+}$  ions.



- ❖ Presence of Co and Fe can be detected by the formation of blue and blood red color thiocyanate complexes respectively

# Detection of Complex formation

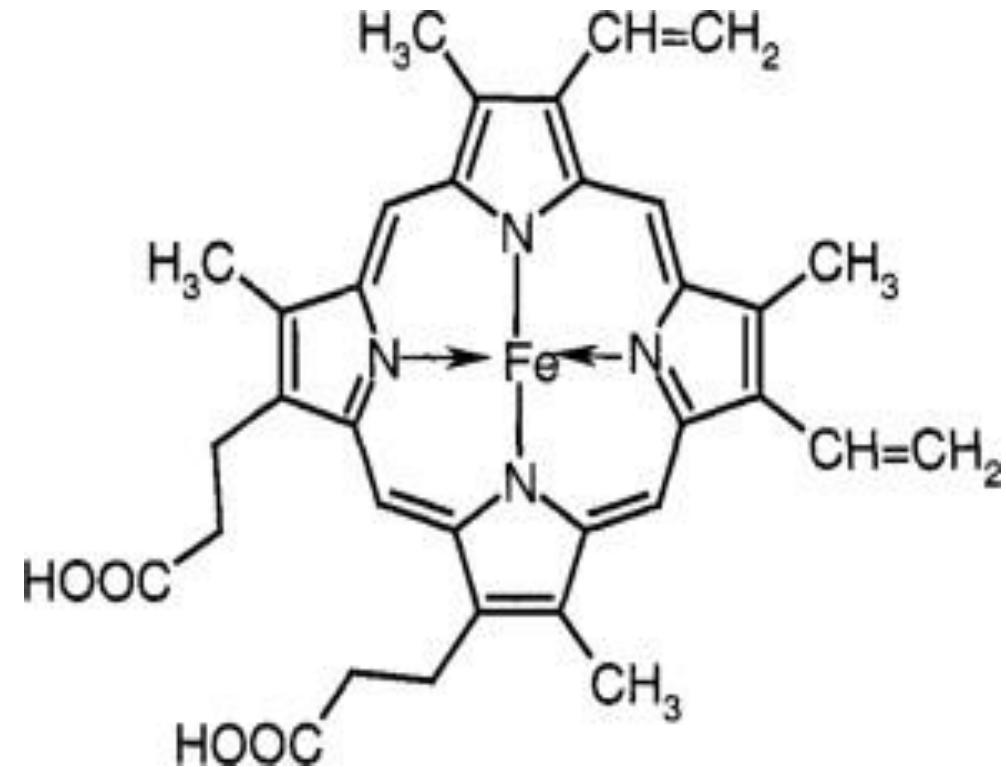
- ❖ Formation of Precipitate



- ❖  $\text{Ni}^{2+}$  and  $\text{Pd}^{2+}$  form insoluble colored precipitates with dimethyglyoxime

# Biological Importance

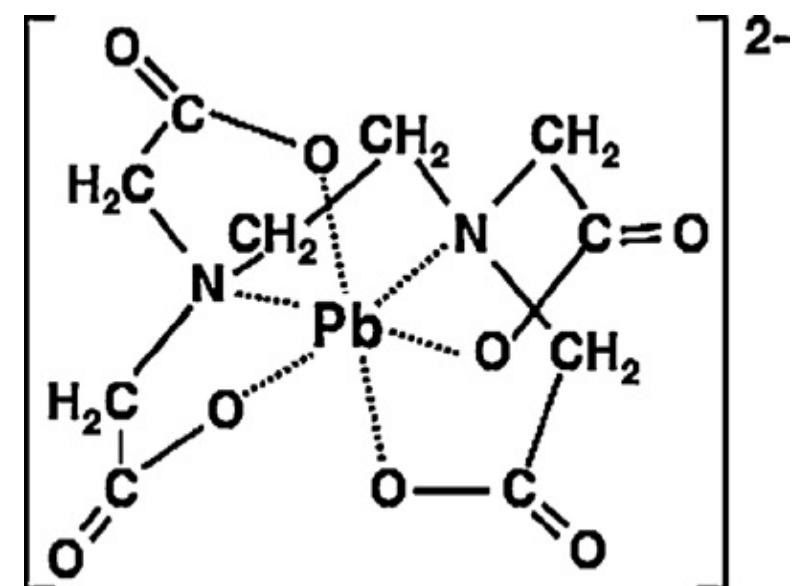
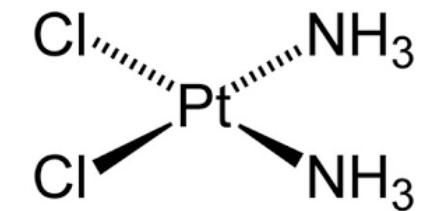
- ❖ Pigment responsible for photosynthesis, **chlorophyll**, is a coordination compound of magnesium.
  - ❖ **Haemoglobin**, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron.
  - ❖ **Vitamin B12**, cyanocobalamin, the anti-pernicious anaemia factor, is a coordination compound of cobalt.
  - ❖ Other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems)
  - ❖ Metalloprotein with the metal ion cofactor have many diverse functions including transport, storage, and signal transduction.



**Heme B:** Heme B is a porphyrin (four linked pyrrole rings) that readily binds iron, as shown. This is an example of a biomolecule that contains non-protein ligands for a transition metal.

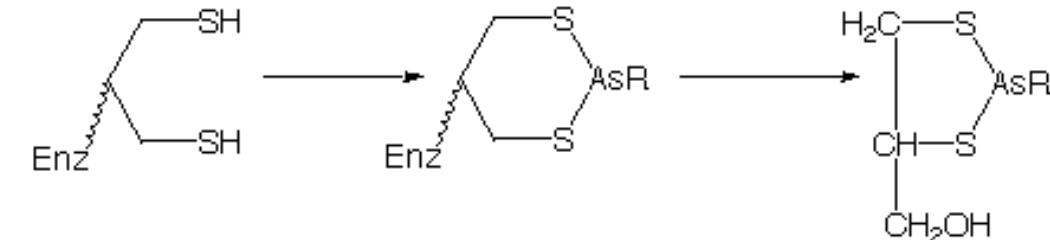
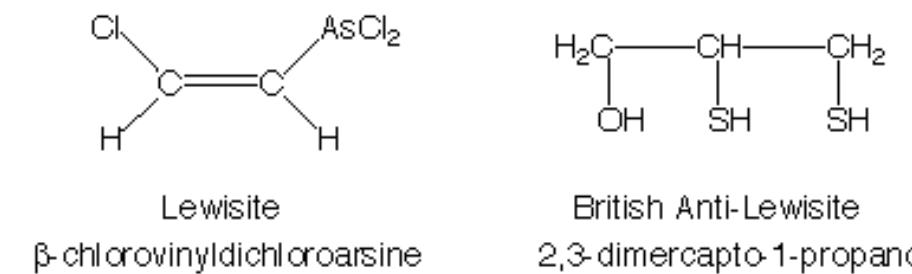
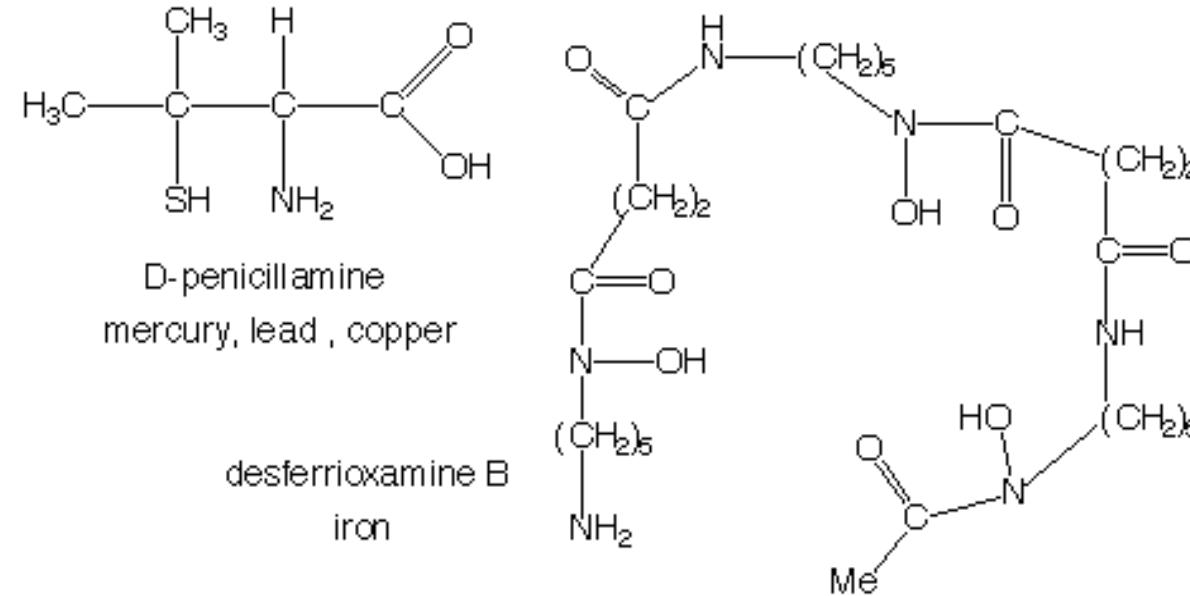
# Medicinal Application

- ❖ To treat problems caused by the presence of metals in toxic proportions in plant/animal systems, chelate therapy is used.
- Excess of copper and iron are removed by the chelating ligands D-penicillamine and desferrioxime B via the formation of coordination compounds.
- ❖ EDTA is used in the treatment of lead poisoning.
- ❖ Coordination compound of platinum effectively inhibit the growth of tumours. cisplatin - cis  $[\text{PtCl}_2(\text{NH}_3)_2]$ , and related compounds.



# Chelation therapy

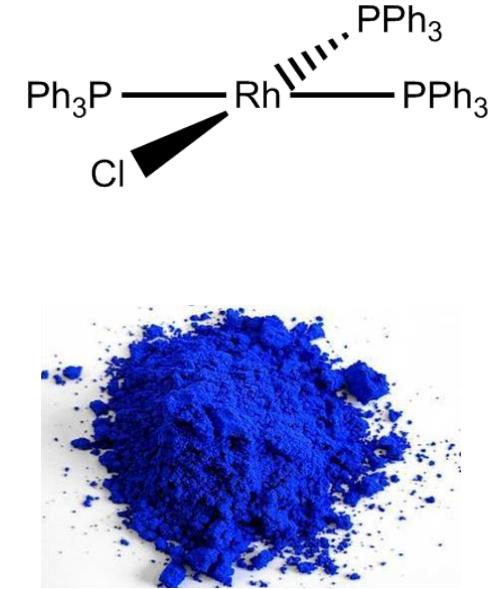
- ❖ D-penicillamine - Used in the treatment for poisoning by heavy metals, including Wilson's disease (build-up of copper in the body).
- ❖ Naturally occurring compounds such as desferrioxamine B, belong to a group of compounds called siderophores and are used by bacteria to assist in the uptake of iron, can also be used to remove unwanted iron by chelation therapy.



# Industrial applications

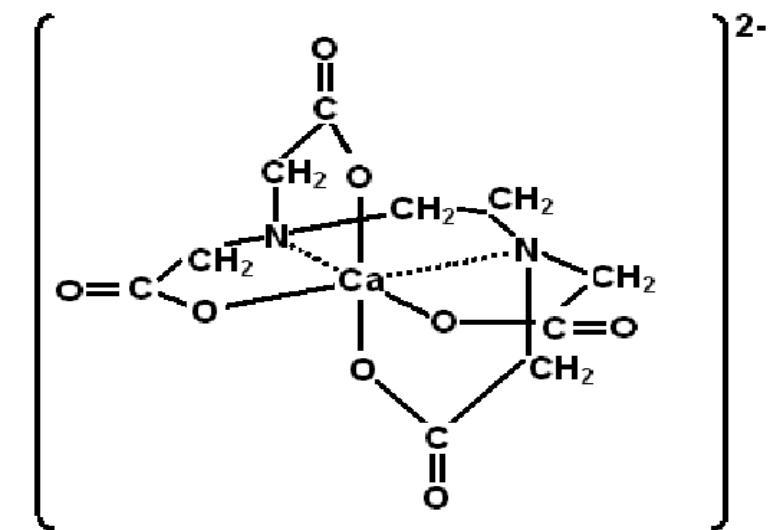
- Coordination compounds are used as catalysts for many industrial processes. Examples rhodium complex,  $[(\text{Ph}_3\text{P})_3\text{RhCl}]$ , a Wilkinson catalyst - hydrogenation of alkenes.
- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes,  $[\text{Ag}(\text{CN})_2]^-$  and  $[\text{Au}(\text{CN})_2]^-$  than from a solution of simple metal ions.
- In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the non decomposed  $\text{AgBr}$  to form a complex ion,  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ .
- Prussian blue – Mixture of hexacyanoFe(II) and Fe(III) -  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  inks, blueprinting, cosmetics, paints (commercial coloring agents)
- **History of Prussian blue:**

The first modern, artificially manufactured colour was Prussian blue. It was made by the colormaker Diesbach of Berlin in about 1704. Diesbach accidentally formed the blue pigment when experimenting with the oxidation of iron. The pigment was available to artists by 1724 and was extremely popular throughout the three centuries since its discovery.



# Hardness of water

- ❖ Hardness of water is estimated by titration with the sodium salt of EDTA.
- ❖ During titration, the calcium and magnesium ions in hard water form the stable complexes, Calcium EDTA and Magnesium EDTA.
- ❖ Hardness of water is estimated by simple titration with  $\text{Na}_2\text{EDTA}$ .
- ❖ The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.



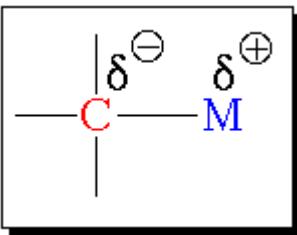
# Representative Metal Complexes in Catalysis

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- **Zeise's Salt** :  $K[Pt(C_2H_4)Cl_3]$
- **Magnus Green Salt** :  $[Pt(NH_3)_4][PtCl_4]$
- **Edman's Salt** :  $K[Co(NH_3)_2(NO_2)_4]$
- **Reinecke's Salt** :  $NH_4[Cr(NH_3)_2(NCS)_4]$
- **Vaska's Complex** :  $[Ir(CO)(PPh_3)_2Cl]$
- **Wilkinson's Catalyst** :  $[Rh(PPh_3)_3Cl]$

# Organometallics – Introduction, stability, structure and applications of metal carbonyls, ferrocene and Grignard reagent

# What are Organometallics?



- ❖ An area which bridges organic and inorganic chemistry.
- ❖ A branch of coordination chemistry where the complex has one or more metal-carbon bonds.

**C** always is more electronegative compared to **M**.

- ❖ The leading journals of the field define an "organometallic" compound as one in which there is a bonding interaction (ionic or covalent, localized or delocalized) between one or more carbon atoms of an organic group or molecule and a main group, transition, lanthanide, or actinide metal atom (or atoms)
- ❖ Following longstanding tradition, organic derivatives of metalloids such as **boron (B)**, **silicon (Si)**, **germanium (Ge)**, **arsenic (As)**, **tellurium (Te)** are also included in this definition.

**Zeise's Salt- The first transition metal organometallic compound:**

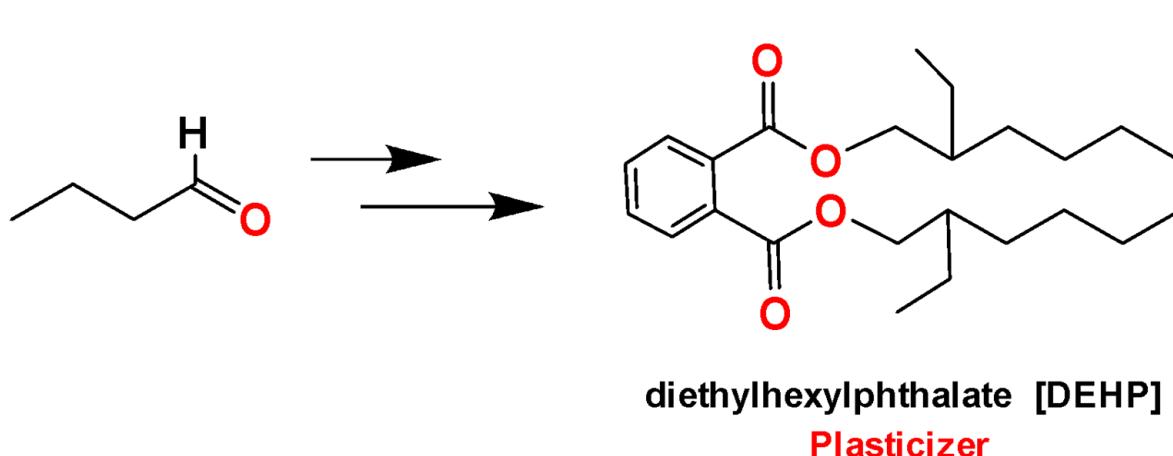
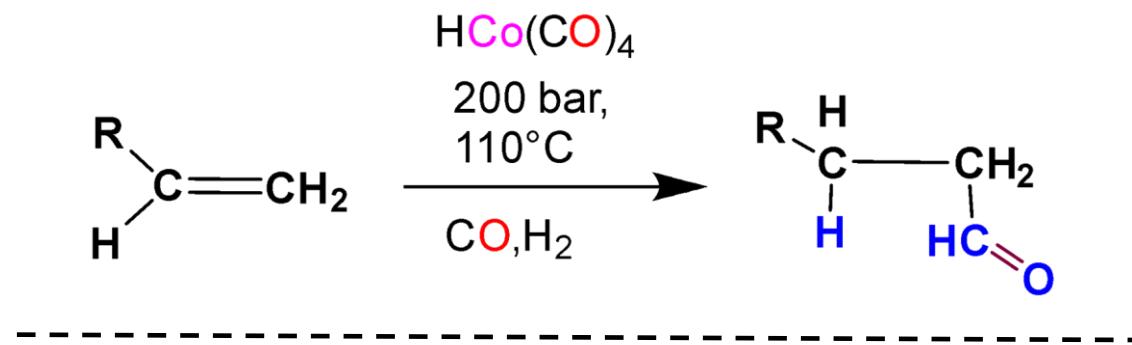
- ❖ Discovery 1827
- ❖ Structure ~ 150 years later



**First  $\sigma$ -bonded Organometallic Compound- Diethyl Zinc:**



# First organometallics in homogeneous catalysis- The Hydroformylation (1938)



First Industrial plant-  
hydroformylation



detergents

# Why are organometallics important?

❖ Are we dealing with 'a' special element?



- What is special about carbon?
  - Forms bonds with other carbon atoms (C-C) readily and they are strong (catenation)
  - Forms strong multiple bonds (C=C)
  - Forms very strong bonds with another special element H!!
  - Cyclic “C=C-C” fragments would be extra stable - **AROMATIC**

□ C and its electronic configuration!

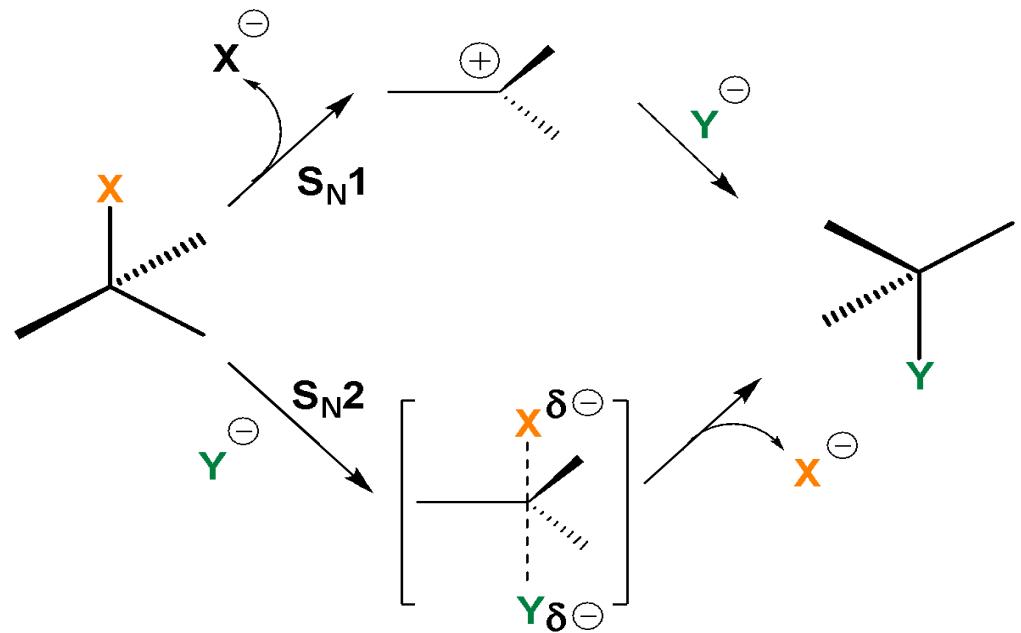


□ Why is this special ?

- To form a full shell, it would require 4 covalent bonds
- Gap between the 2s and 2p is just right!
- $1s^2 \quad 2s^1 \quad 2p_x^1 \quad 2p_y^1 \quad 2p_z^1$
- When 4 equivalent covalent bonds are formed, **no extra electrons / no vacant orbitals**

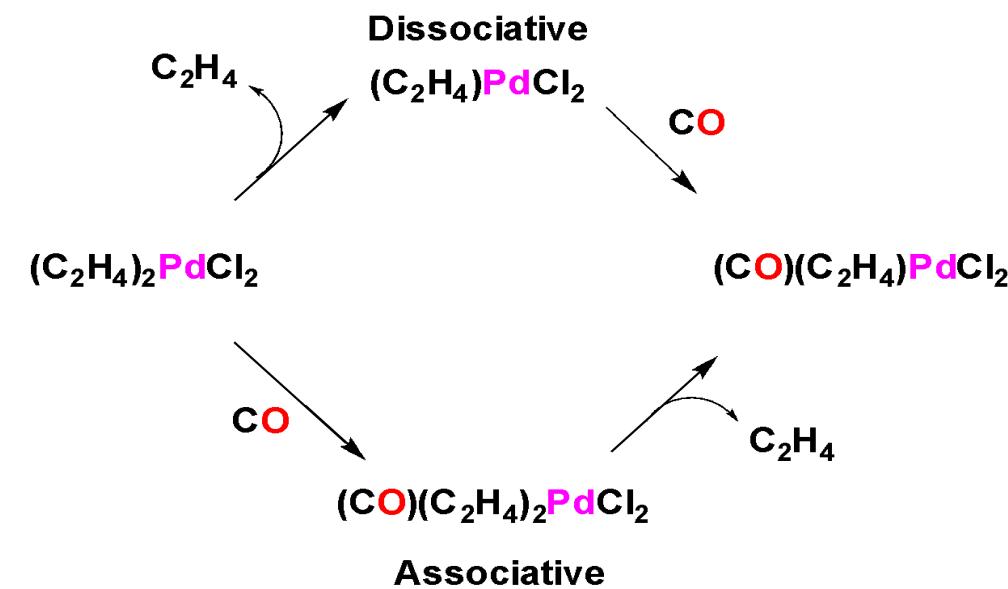
# Organic vs Organometallic reactivity

## Organic chemistry



- C-C/C-H bonds are covalent
- $C^{\delta+}-X^{\delta-}$  : polar (partly ionic)
- Reactivity dominated by nucleophilic attack at carbon atom
- $S_N2$  and  $S_N1$  like reactivity

## Organometallic chemistry



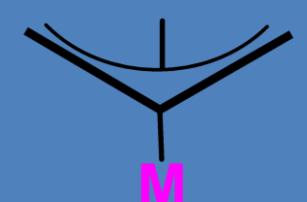
- C is the *negative end of the M-C bond* ("umpolung")
- Reactivity dominated by nucleophilic attack on metal atom and electrophilic attack on carbon Atom
- Associative and dissociative

# Some Important Ligand Nomenclature

$\eta^X$

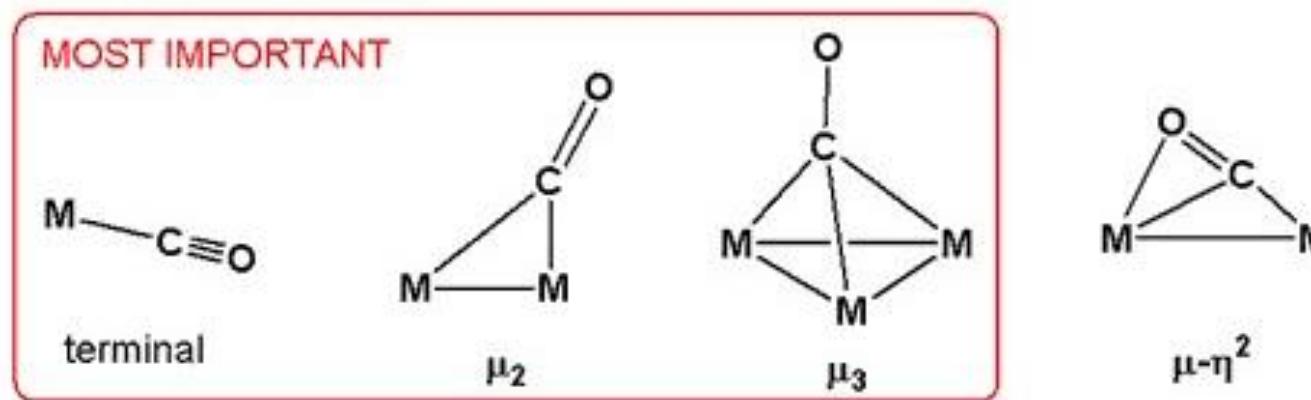
“eta-x” was originally developed to indicate how many carbons of a  $\pi$ -system were coordinated to a metal center. **Hapticity** is another word used to describe the bonding mode of a ligand to a metal center. An  $\eta^5$ -cyclopentadienyl ligand, for example, has all five carbons of the ring bonding to the transition metal center.

- $\eta^x$  values for carbon ligands where the  $x$  value is odd usually indicate *anionic* carbon ligands (e.g.,  $\eta^5$ -Cp,  $\eta^1$ -CH<sub>3</sub>,  $\eta^1$ -allyl or  $\eta^3$ -allyl,  $\eta^1$ -CH=CH<sub>2</sub>)
- The # of electrons donated (ionic method of electron counting) by the ligand is usually equal to  $x + 1$
- Even  $\eta^x$  values usually indicate *neutral* carbon  $\pi$ -system ligands (e.g.,  $\eta^6$ -C<sub>6</sub>H<sub>6</sub>,  $\eta^2$ -CH<sub>2</sub>=CH<sub>2</sub>,  $\eta^4$ -butadiene,  $\eta^4$ -cyclooctadiene)
- Number of electrons donated by the ligand in the even (*neutral*) case is usually just equal to  $x$ .

$\eta^5$ -Cp	$\eta^3$ -Cp		$\eta^1$ -allyl
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$\mu_x$

“mu-x” is the nomenclature used to indicate the presence of a **bridging ligand** between two or more metal centers. The x refers to the number of metal centers being bridged by the ligand. Usually, most authors omit  $x = 2$  and just use  $\mu$  to indicate that the ligand is bridging the simplest case of two metals.



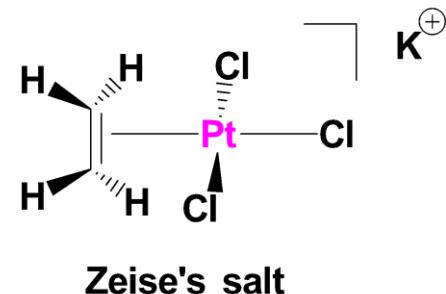
- ❖ bridging ligands are usually placed next to the metals in question, then followed by the other ligands (note that rules 1 & 2 take precedence):  $\text{Co}_2(\mu\text{-CO})_2(\text{CO})_6$ ,  $\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4$ ,  $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_2(\text{CO})_2$

❖ Organometallic compounds are classified into three classes.

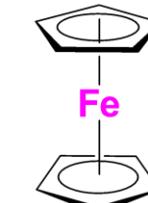
- (i) **Sigma ( $\sigma$ ) bonded organometallic compounds:** In these complexes, the metal atom and carbon atom of the ligand are joined together with a sigma bond,  
For Example:
  - (a) **Grignard reagents, R–Mg–X** where R is an alkyl or aryl group, and X is a halogen.
  - (b) **Zinc compounds of the formula  $R_2Zn$**  such as  $(C_2H_5)_2Zn$
  - Other similar compounds are  $(CH_3)_4Sn$ ,  $(C_2H_5)_4Pb$ ,  $Al_2(CH_3)_6$ ,  $Al_2(C_2H_5)_6$ ,  $Pb(CH_3)_4$  etc.  
 $Al_2(CH_3)_6$  is a dimeric compound and has a structure similar to diborane,  $(B_2H_6)$ . It is an electron deficient compound, and two methyl groups act as bridges between two aluminium atoms.

### (ii) Pi ( $\pi$ ) bonded organometallic compounds:

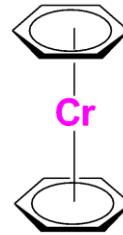
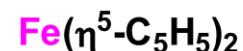
These are the compounds of metals with alkenes, alkynes, benzene and other ring compounds. In these complexes, the metal and ligand form a bond that involves the  $\pi$ -electrons of the ligand. Three common examples are Zeise's salt, ferrocene and dibenzene chromium. These are shown below.



Zeise's salt



Ferrocene

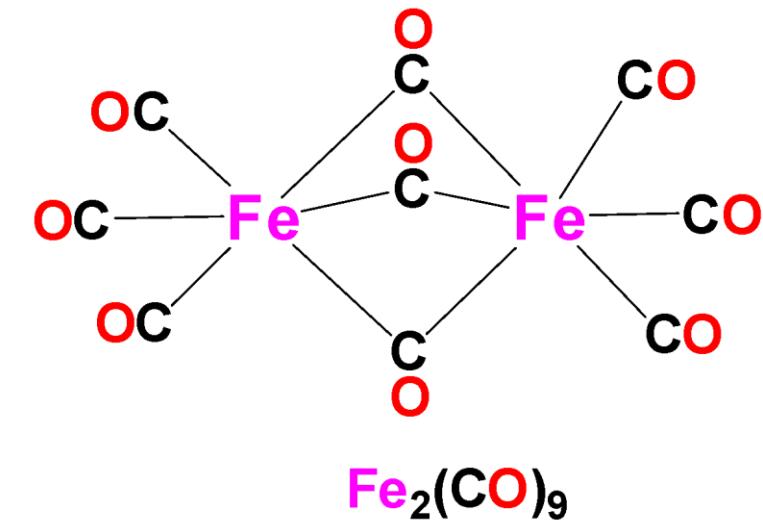
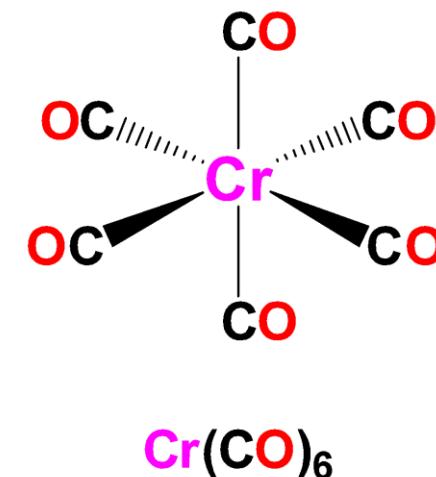
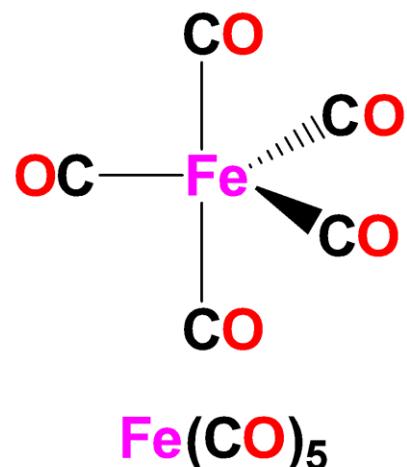
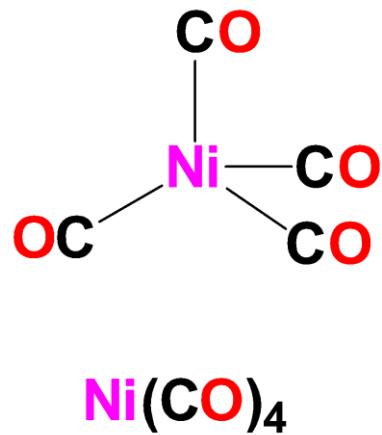


Dibenzene chromium



### (iii) Sigma and $\pi$ -bonded organometallic compounds

- Metal carbonyl compounds formed between metal and carbon monoxide, belong to this class. These compounds possess both  $\sigma$ -and  $\pi$ -bonding. Generally, oxidation state of metal atoms in these compounds is zero. Carbonyls may be mononuclear, bridged or polynuclear.



## Stability of Organometallic Compounds

- ❖ In general terms, the stability of an organometallic compound may refer to either its thermal stability, or resistance to chemical attack (by air and moisture). Obviously, these different types of stabilities would depend both on **thermodynamic** as well as **kinetic** factors.

The organometallic compounds are generally **hydrolysed** via nucleophilic attack by water, which is facilitated by:

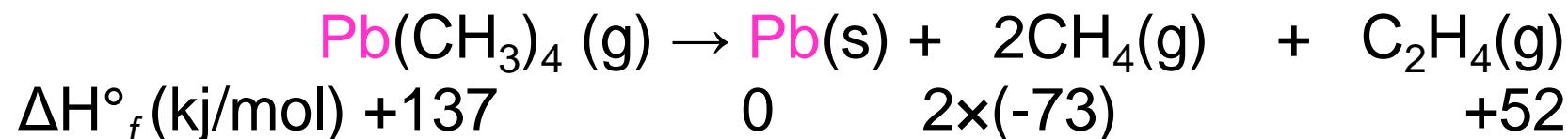
- (1) the presence of empty low-lying orbitals on the metal
- (2) the polarity of metal-carbon bonds. Rate of hydrolysis is dependent on M-C bond polarity – greater the polarity, faster will be the rate

## Thermal Stability

The thermodynamic stability of a compound relative to its constituent elements would obviously depend upon the standard free energies of formation,  $\Delta G^\circ_f$ , values for organometallic compounds, one has to rely on the known standard enthalpies of formation,  $\Delta H^\circ_f$ , making due allowance for plausible estimates for the contributions of the entropy terms  $T\Delta S$ , in the well-known relationship:

$$\Delta G = \Delta H - T\Delta S$$

For example, let us for the purpose of simplicity consider that tetramethyllead decomposes into lead, decomposes into lead, methane and ethane only, i.e.,

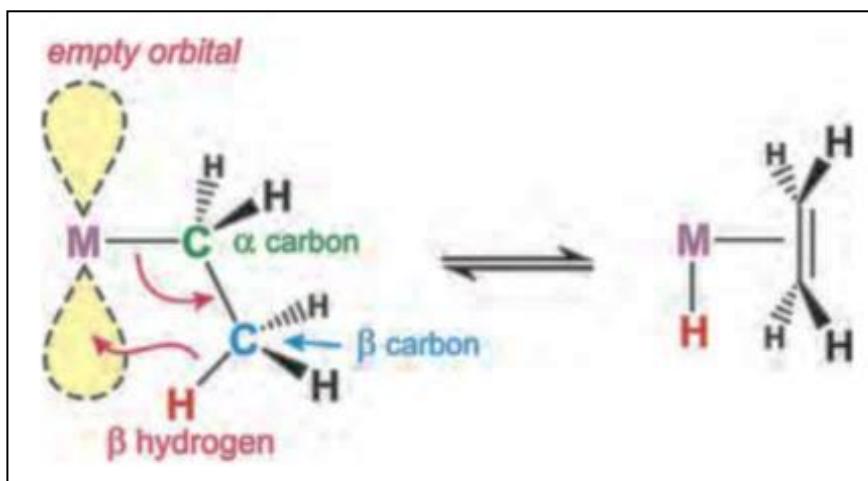


The standard enthalpy change  $\Delta H_m$  for this reaction would be given by the difference between the standard enthalpies of formation,  $\Delta H_f$ , for the products and reactants, i.e.,

$$\Delta H_m = -146 + 52 - 137 = -231 \text{ kJ mol}^{-1}$$

# Factors influencing the stability/ reactivity of Organometallics

- ❖ The thermodynamic stability of metal-alkene complexes is strongly affected by the nature of the alkene (and metal):
  - 1) **Electron-withdrawing groups** on the alkene generally **increase the strength of the metal-alkene bonding**, while **electron-donating groups** generally **decrease the stability**.
  - 2) In cases where *cis-trans* isomerism is possible, the more stable complex is almost always formed by the *cis*-alkene (steric factors).
  - 3) Presence of  $\beta$ -hydrogen in the alkyl chains attached to the metal

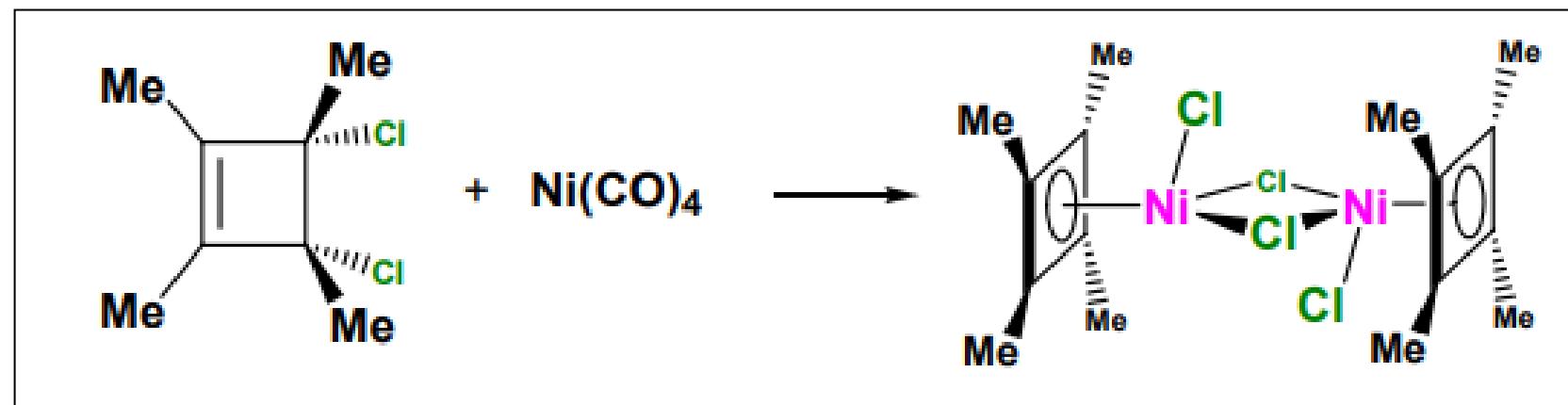


- The main driving force for  $\beta$ -hydride elimination is the formation of a stronger M-H bond (almost always stronger than M-alkyl) and the generation of an alkene ligand that reduces the unsaturation of the metal complex. The reverse reaction, however, also can occur and is called a migratory insertion.
- In order to prepare stable M-alkyl complexes one, therefore, often needs to stay away from alkyls with  $\beta$ -hydrogens (or avoid metals with empty coordination sites).

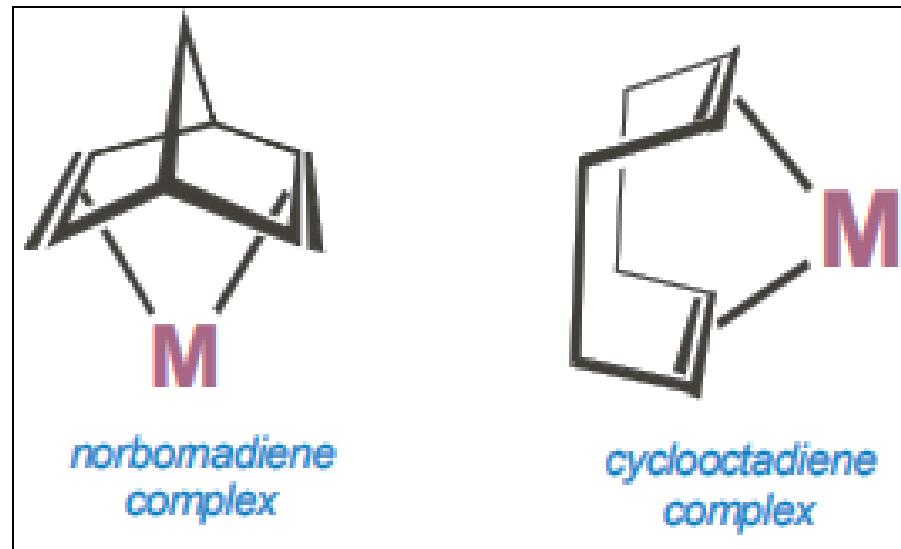
4. Metal complexes of ring-strained cycloalkenes (e.g., cyclopropene) display higher than expected stability. The ring strain raised the energy of the cycloalkene ring system making it a better donor to the metal center (better orbital energy matching). See the next section on cyclobutadiene for a particularly remarkable example.

Cyclic conjugated  $\pi$ -systems are aromatic if the number of  $\pi$ -electrons equals  $4n + 2$  (where n = an integer). Cyclobutadiene is an anti-aromatic since it has 4  $\pi$ -electrons. The anti-aromaticity combined with the ring strain makes this simple molecule too unstable to exist as a free organic compound.

The high stability of a cyclobutadiene coordinated to a metal arises from the mixing of the 4  $\pi$  electrons on the cyclobutadiene with one of the metal d orbitals that has 2 e- and the right symmetry to mix in and form a 6  $\pi$  electron aromatic system!



5. Chelating dienes show the expected stabilization from the chelate effect. The most common examples are norbornadiene and cyclooctadiene shown below. Note that these can still be easily substituted off the metal by stronger coordinating ligands such as phosphines.



## The 18-electron Rule or Effective atomic number (EAN)

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- ❖ The 18e rule is a way to help us decide whether a given d-block transition metal organometallic complex is likely to be stable. Not all the organic formulas we can write down correspond to stable species. **Recall:** Second row elements (B, C, N, O, F) have 4 valence orbitals ( $1s + 3p$ ) so they can accommodate up to 8 valence electrons--*the octet rule*.
- For example,  $\text{CH}_5$  requires a 5-valent carbon and is therefore not stable. Stable compounds, such as  $\text{CH}_4$ , have the noble gas octet, and so carbon can be thought of as following an 8e rule.
- **The 18e rule**, which applies to many low-valent transition metal complexes, follows a similar line of reasoning. **The metal now has one s, and three p orbitals, as before, but now also five d orbitals.** We need 18e to fill all nine orbitals; some come from the metal, the rest from the ligands. Therefore, we can expect that the low-lying MOs can accommodate up to 18 valence electrons--*The 18-Electron Rule*.
- ❖ The rule states that “***thermodynamically stable transition metal organometallic compounds are formed when the sum of the metal d electrons and the electrons conventionally considered as being supplied by the surrounding ligands equals 18***”

## Counting electrons for metal complex

To count the electrons of a metal complex, one must:

- a) **note any overall charge on the metal complex**
- b) **know the charges of the ligands bound to the metal center (ionic ligand method)**
- c) **know the number of electrons being donated to the metal center from each ligand (ionic ligand method)**

Similarly for a **transition metal complex**, the electron count is the sum of the metal valence electrons + the ligand centered electrons.

❖ **Covalent Model:** # e = # metal electrons (zero valent) + # ligand electrons - complex charge

**Metal:** The number of metal electrons equals its column number (i.e., Ti = 4e, Cr = 6e, Ni = 10e)

**Ligands:** In general L donates 2 electrons, X donates 1 electron.

❖ **Ionic Model:** # e = # metal electrons ( $d^n$ ) + # ligand electrons

**Metal:** Determined based on the number of valence electrons for a metal at the oxidation state present in the complex

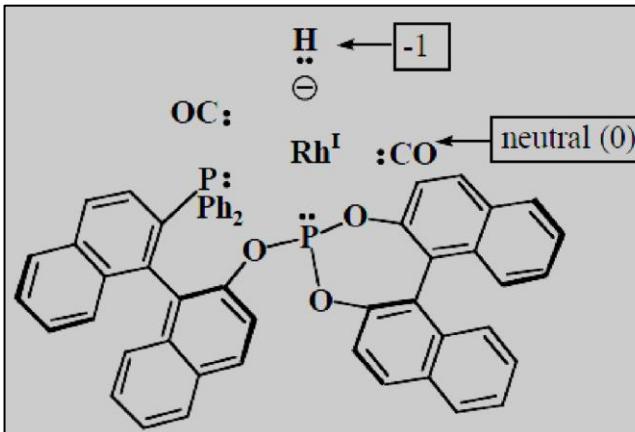
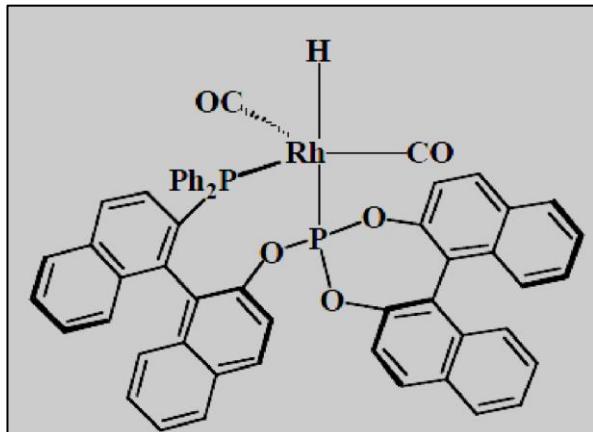
**Ligands:** In general L and X are both 2 e donors.

❖ **Complexes with 18 e- counts are referred to as *saturated*.**

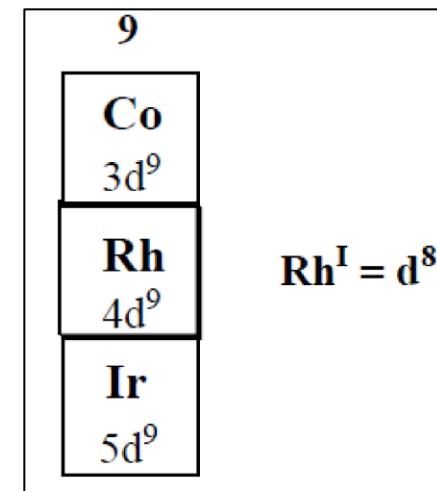
❖ **Complexes with counts lower than 18e- are called *unsaturated*.**

# Electron Counting

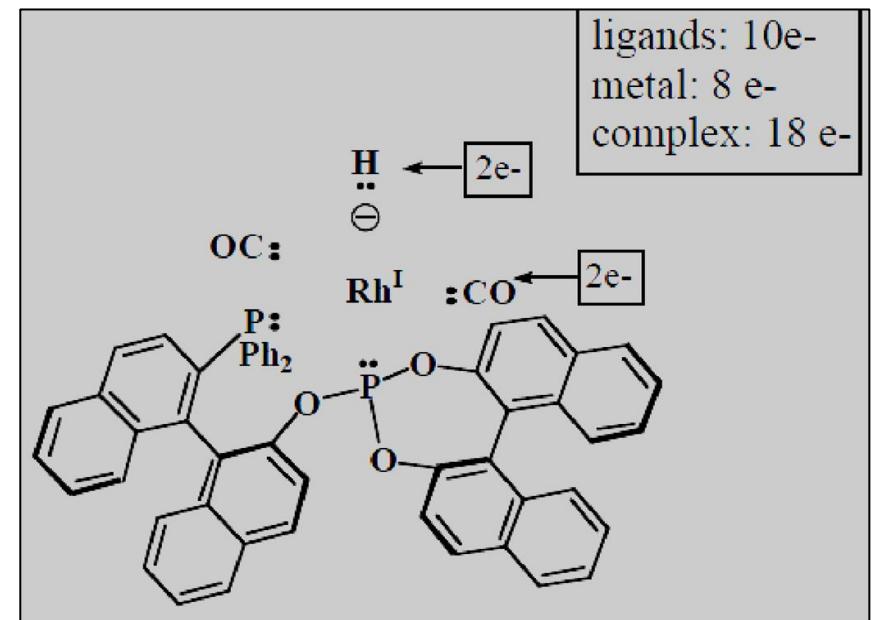
- ❖ **Step 1: Determine the oxidation state of the metal.** To do this, balance the ligand charges with an equal opposite charge on the metal. This is the metal's formal oxidation state.
- To determine ligand charges, create an ionic model by assigning each M-L electron pair to the more electronegative atom (L). This should result in stable ligand species or ones known as reaction intermediates in solution.



- ❖ **Step 2: Determine the d electron count.** Recall: subtract the metal's oxidation state from its group #.



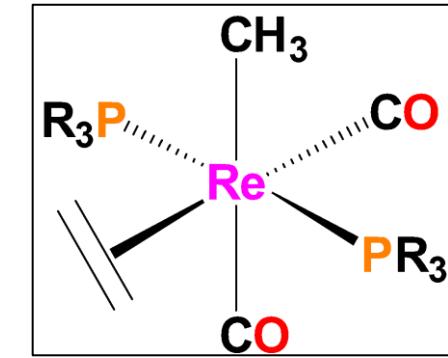
- ❖ **Step 3: Determine the electron count of the complex** by adding the # of electrons donated by each ligand to the metal's d electron count.



## Example 1

Please note that we are using the *Ionic Method* of electron-counting. 95% of inorganic/organometallic chemists use the ionic method. The ionic method assigns formal charges to the metal and ligands in order to keep the ligands with an even # of electrons and (usually) a filled valence shell. Synthetically, the ionic method generally makes more sense and the one that we will use in this course.

- 1) There is no overall charge on the complex
- 2) There is one anionic ligand ( $\text{CH}_3^-$ , methyl group)
- 3) Since there is no overall charge on the complex (it is neutral), and since we have one anionic ligand present, the Re metal atom must have a +1 charge to compensate for the one negatively charged ligand. The +1 charge on the metal is also its oxidation state. So the Re is in the +1 oxidation state. We denote this in two different ways:  $\text{Re}(+1)$ ,  $\text{Re(I)}$ , or  $\text{Re}^+$ .

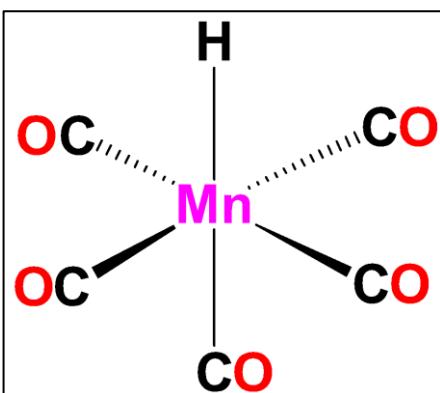


Now we can do our electron counting:

$\text{Re}(+1)$	$d^6$
$2 \text{PR}_3$	$4\text{e}^-$
$2 \text{CO}$	$4\text{e}^-$
$\text{CH}_3^-$	$2\text{e}^-$
$\text{CH}_2=\text{CH}_2$	$2\text{e}^-$

Total:  $18\text{e}^-$

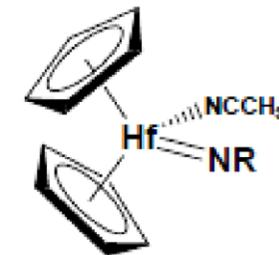
# $\text{HMn}(\text{CO})_5$



$\text{Mn}(+1) \text{ d}^6$   
5 CO  
 $\text{H}^-$

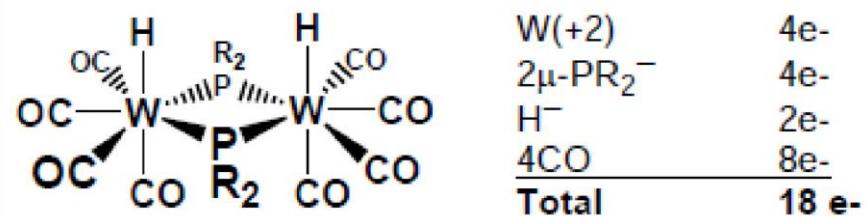
$6\text{e}^-$   
 $10\text{e}^-$   
 $2\text{e}^-$   
**Total: 18e<sup>-</sup>**

Hf, Cp, N≡CCH<sub>3</sub>, NCH<sub>3</sub>

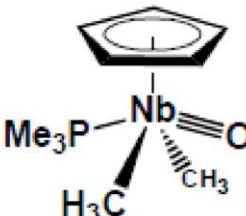


Hf(+4)	0e <sup>-</sup>
NR <sup>2-</sup>	4e <sup>-</sup>
2Cp <sup>-</sup>	12e <sup>-</sup>
NCMe	2e <sup>-</sup>
<b>Total</b>	<b>18 e<sup>-</sup></b>

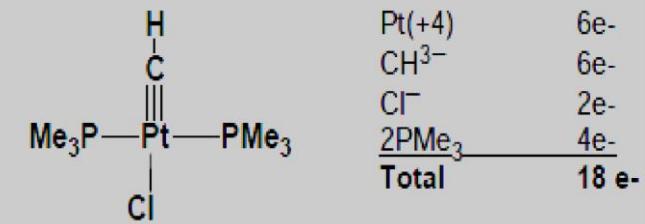
a) W,  $\mu$ -PR<sub>2</sub>, CO, H



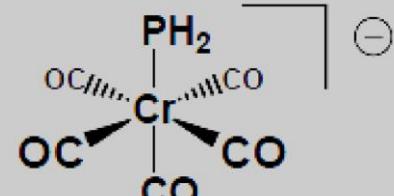
d) Nb, O, CH<sub>3</sub>, Cp, PMe<sub>3</sub>



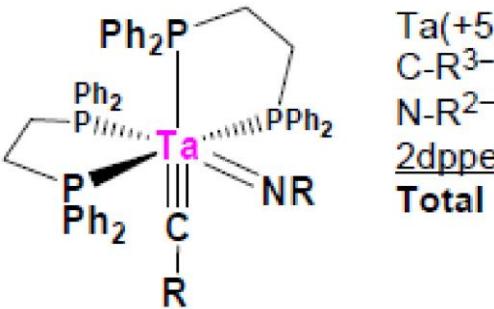
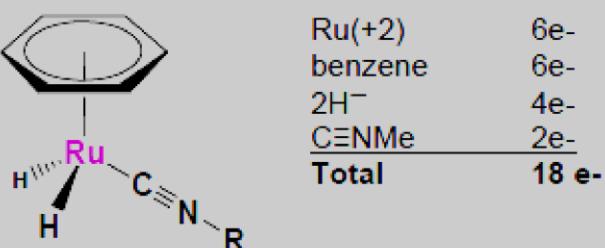
c) Pt, CH, Cl, PMe<sub>3</sub>



a)  $[\text{Cr}(\text{PH}_2)(\text{CO})_5]^-$



d) Ru, benzene, H, C≡NMe



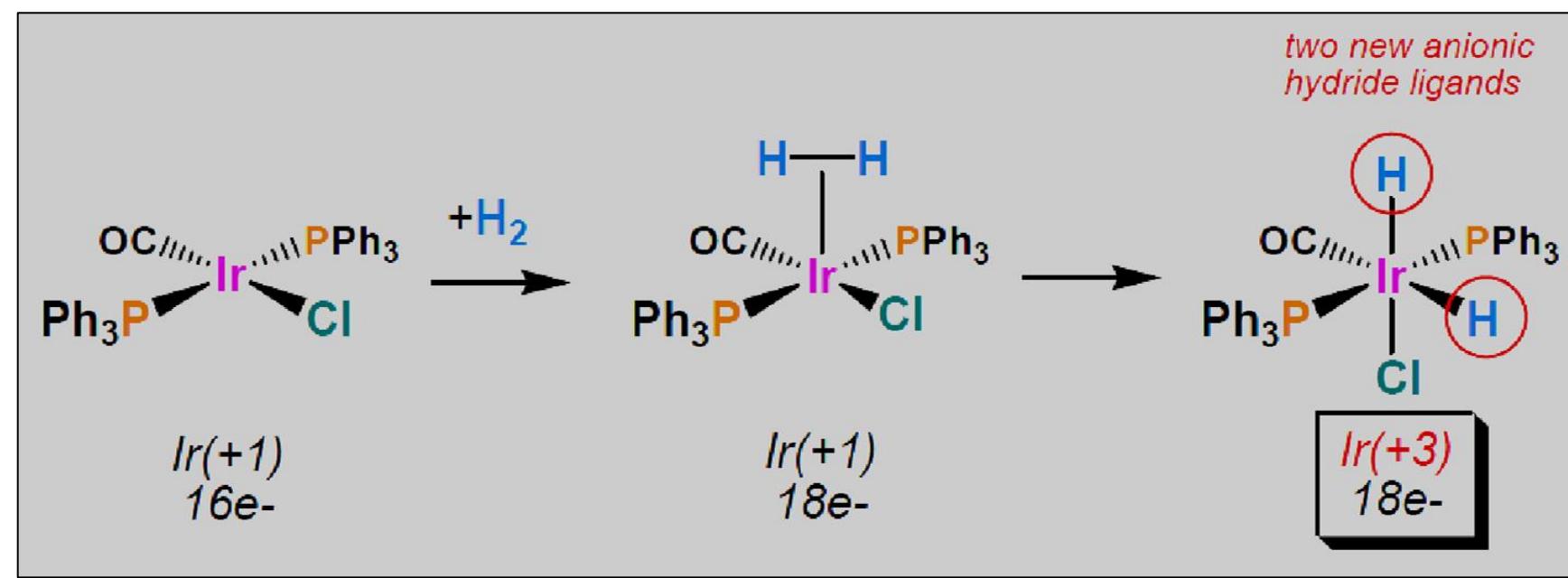
# Common Reactions of Organometallic Complexes

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- Oxidative Addition
- Reductive Elimination
- Migratory Insertion
- Transmetallation
- $\beta$ -Hydride Elimination

## ❖ Oxidative Addition

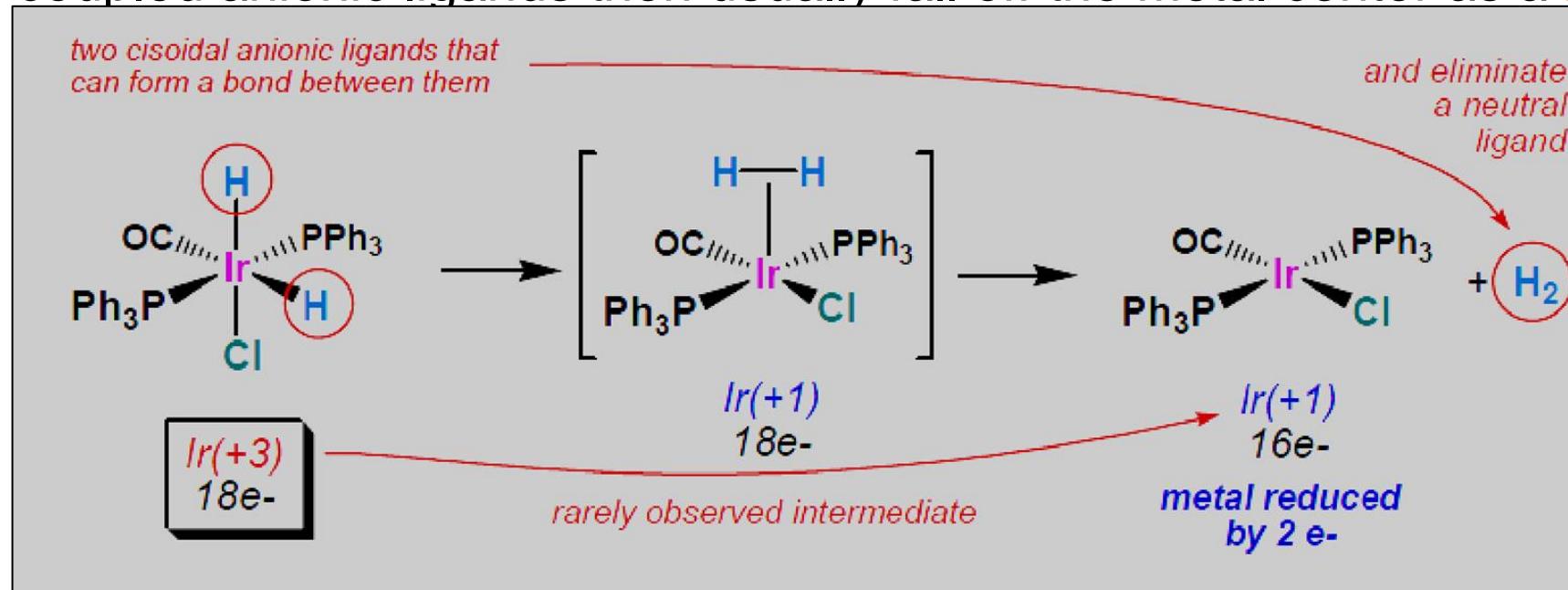
A reaction in which (usually) a neutral ligand adds to a metal center and in doing so oxidizes the metal, typically by  $2e^-$ . The transferring of the two electrons from the metal to the incoming ligand breaks a bond in that ligand forming two new anionic ligands. At least one of these new anionic ligands ends up bonded to the metal center.



**WARNING:**  $d^0$  metals can **NOT** do **oxidative additions**!! So always electron count the starting and final metal complexes to check out the overall electron-count, metal oxidation state and  $d$ -electron count!

## ❖ Reductive Elimination

A **reductive elimination** reaction is the reverse of an **oxidative addition**. It is a reaction in which **two cisoidal anionic ligands** on a metal center couple together. Each anionic ligand pushes one electron back onto the metal center (in the case of a monometallic complex) to reduce it by  $2e^-$ . The coupled anionic ligands then usually fall off the metal center as a **neutral** molecule.



Since **electron-rich** metal complexes favor **oxidative addition**, the reverse is true for reductive elimination. Since **reductive elimination** involves pushing electrons back onto the metal center from two anionic ligands that are usually more electronegative than the metal center, it is best if the metal center is **electron deficient**. This can be accomplished by having electron-withdrawing ligands (e.g., CO), cationic charge(s), and/or coordinative unsaturation (sub- $18e^-$  counts).

## ❖ Migratory Insertion

- A **migratory insertion** reaction is when a **cisoidal anionic** and **neutral** ligand on a metal complex couple together to generate a new coordinated **anionic** ligand. This new anionic ligand is composed of the original neutral and anionic ligands now bonded to one another.

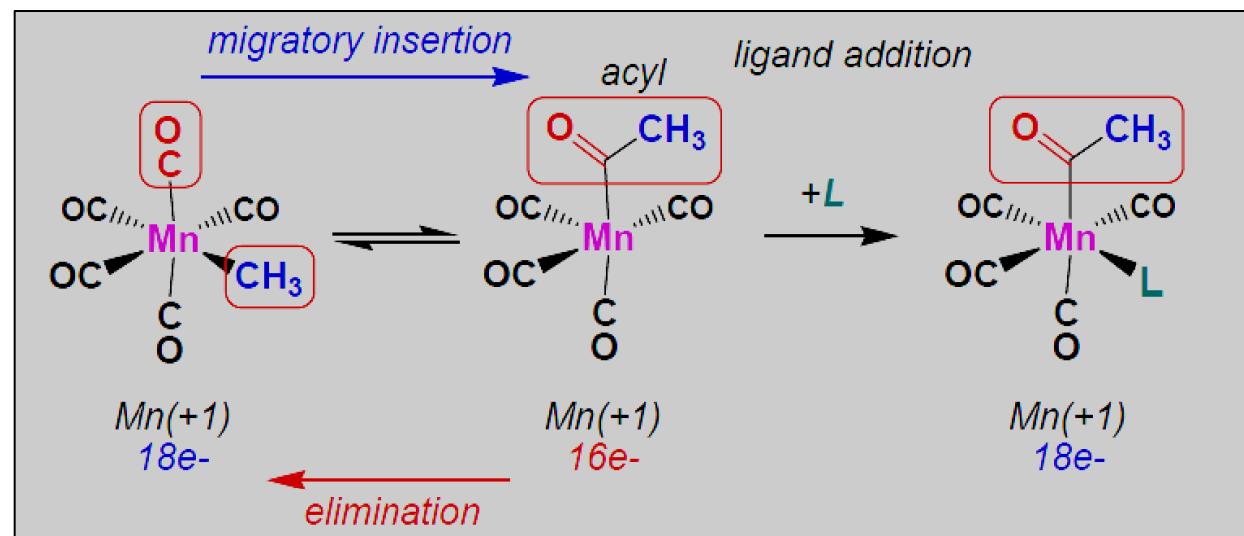
### ▪ General Features:

1) No change in formal oxidation state  
(exception: alkylidenes)

2) The two groups that react must be cisoidal to one another

3) A vacant coordination site is generated by the migratory insertion. Therefore, a vacant site is required for the back elimination reaction (e.g.,  $\beta$ -hydride elimination). A trapping ligand is often needed to coordinate to the empty site formed from a migratory insertion in order to stop the back elimination reaction.

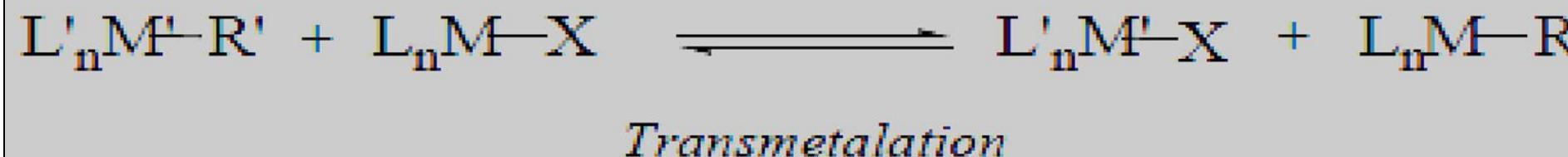
4) Migratory insertions are usually favored on more electron-deficient metal centers.



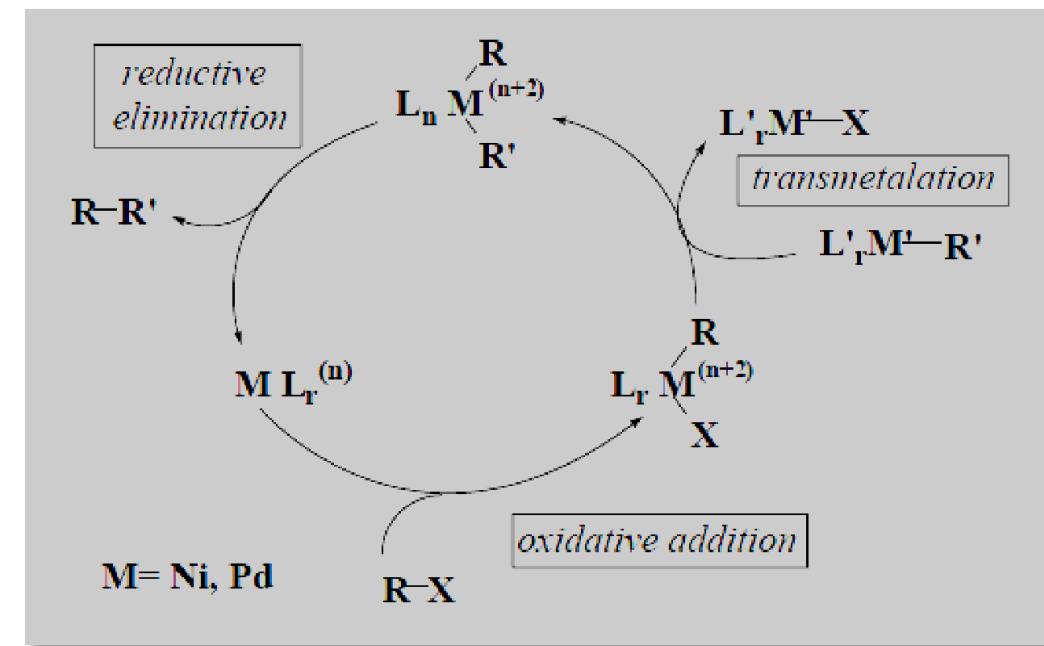
## ❖ Transmetallatio

n

- **Definition:** the transfer of an organic group from one metal center to another. The process involves no formal change in oxidation state for either metal.

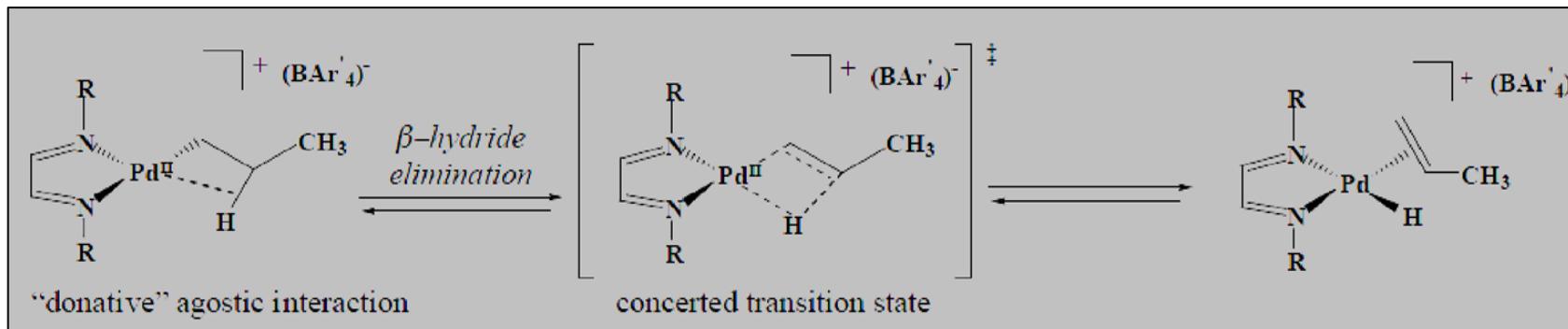


- Transmetalation is often a *reversible process*, with the equilibrium favoring the more ionic M-X bond. Subsequent reactivity of one  $\text{LnM-R}$  species can drive the equilibrium in one direction. This is often exploited in cross-coupling reactions, where a transmetalated intermediate undergoes a reductive elimination to generate a new organic product. Subsequent oxidative additions generates a new substrate for transmetalation

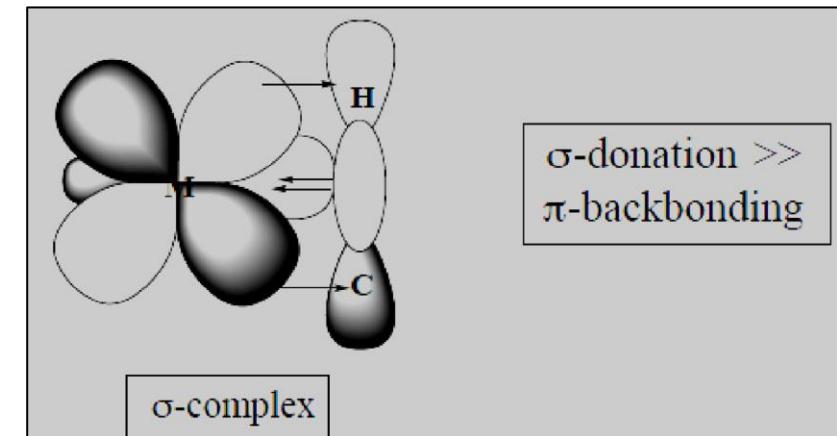


## ❖ **$\beta$ -Hydride Elimination**

- A significant decomposition pathway for metal alkyls is  $\beta$ -hydride elimination which converts a metal alkyl into a hydrido metal alkene complex.

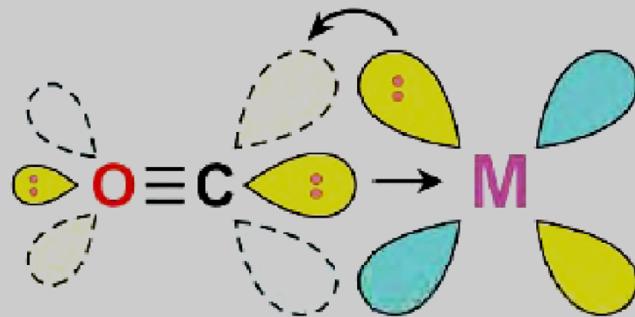


- $\beta$ -hydride elimination can occur when:**
  - cis to the alkyl group there exists a site of coordinative unsaturation on the metal which corresponds to a site of electronic unsaturation (empty metal orbital).
  - The M-C-C-H unit can take up a coplanar conformation which brings the  $\beta$ -hydrogen in close enough proximity to the metal to form an agostic interaction.
  - The metal is electrophilic resulting in an agostic interaction that is primarily electron donative in nature (i.e.  $\sigma$ -donation>> $\pi$ -backbonding).



# Metal-Carbonyls

empty  $\pi^*$ -acceptor  
orbitals on carbonyl



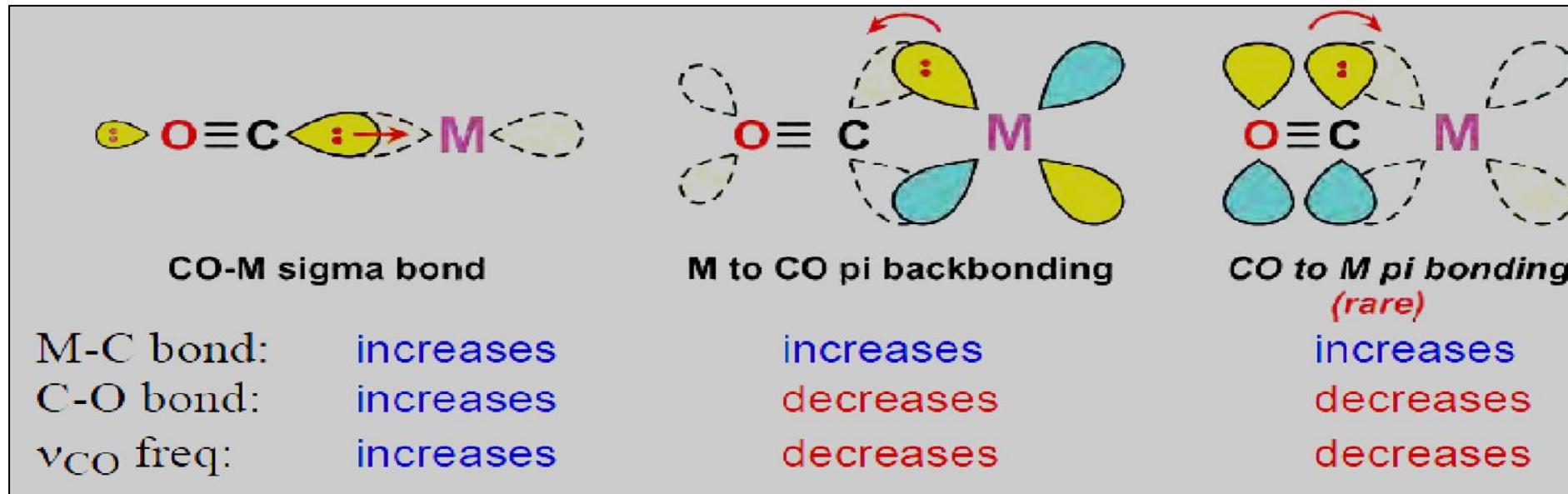
powerful  $\pi$ -acceptor ligand!  
excellent ligand, therefore, for  
stabilizing electron-rich  
low-valent metal centers

As one goes from a terminal CO-bonding mode to  $\mu_2$ -bridging and finally  $\mu_3$ -bridging, there is a relatively dramatic drop in the CO stretching frequency seen in the IR.

## ❖ Standard Bonding Modes

free CO	terminal mode	$\mu_2$ - bridging	$\mu_3$ - bridging
$\nu_{CO}$ IR ( $\text{cm}^{-1}$ )	2143	2120 - 1850	1850 - 1720
(for neutral metal complexes)	2e <sup>-</sup> neutral donor	2e <sup>-</sup> neutral donor	3e <sup>-</sup> neutral donor

# Three types (two of which are important) of CO-Metal bonding interactions



## ❖ Formation of $\sigma$ -bond:

- The overlapping of empty hybrid orbital on metal atom with the filled hybrid orbital on carbon atom of carbon monoxide molecule through lone pair electrons results into the formation of a  $M \leftarrow CO$   $\sigma$ -bond.

## ❖ Formation of $\pi$ -bond by back donation:

- This bond is formed because of overlapping of filled  $d\pi$  orbitals or hybrid  $dp\pi$  orbitals of metal atom with antibonding  $\pi$  orbitals on CO molecule.

# Structure of $\text{Ni}(\text{CO})_4$

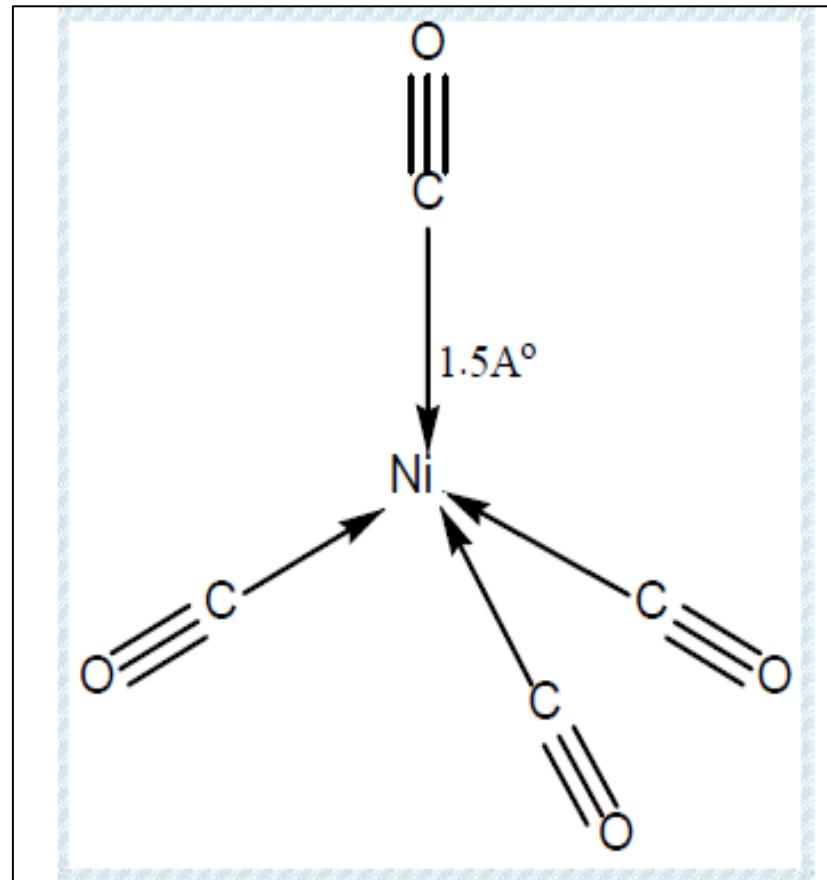
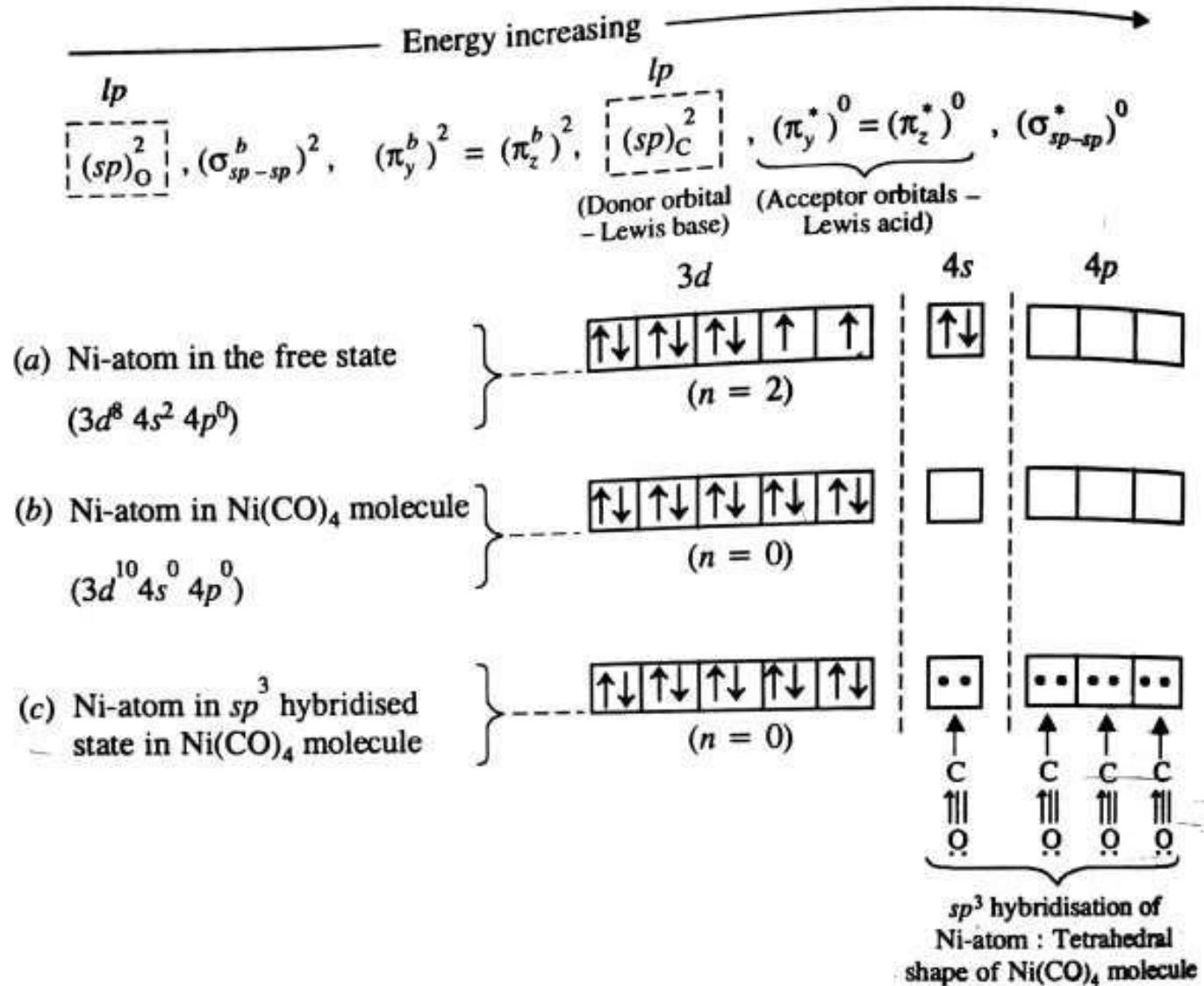
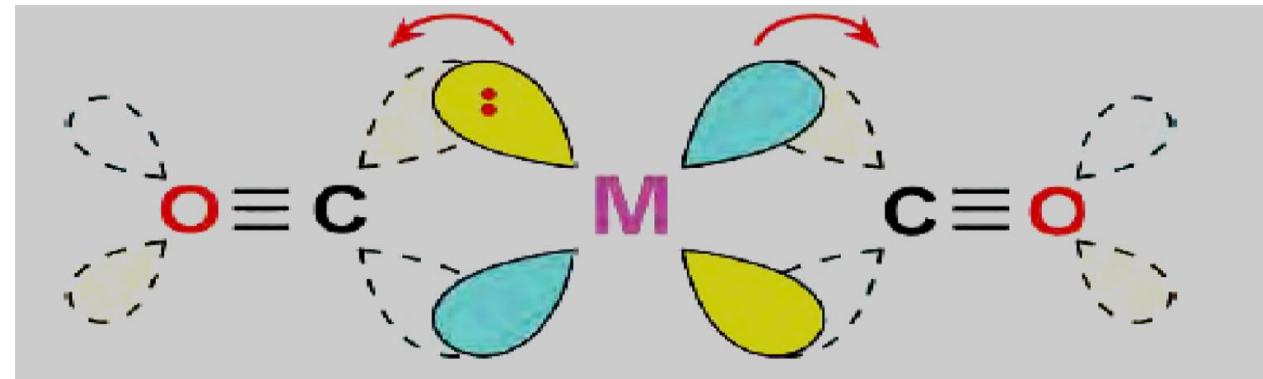


Figure: Tetrahedral structure of nickel tetracarbonyl

# Ligand Donation Effects

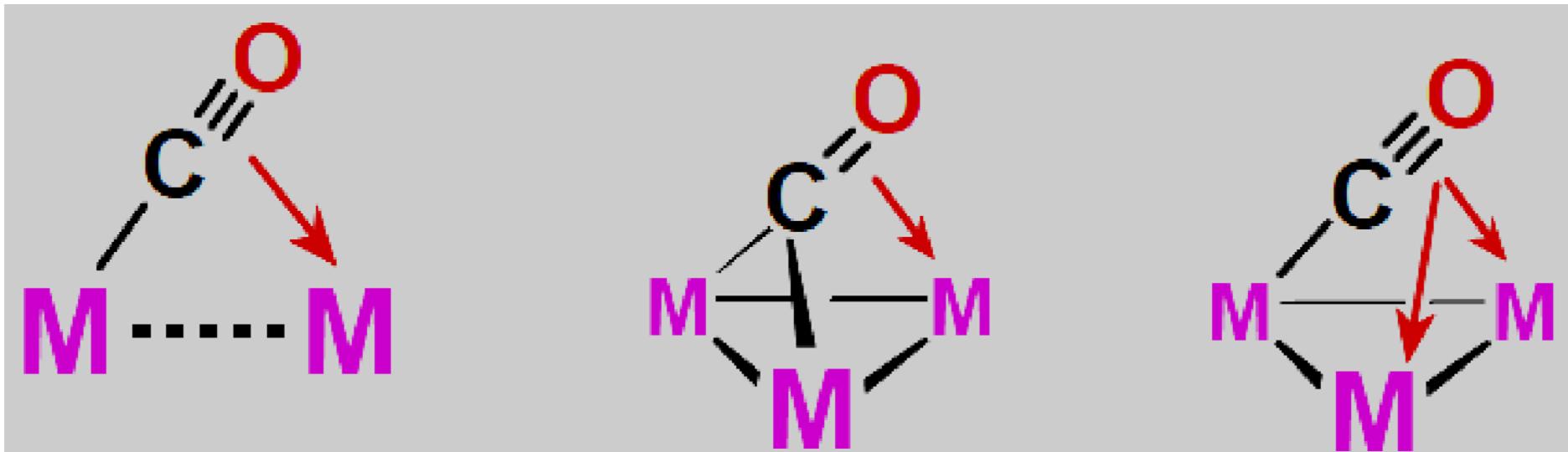
The ability of the ligands on a metal to donate electron density to the metal center certainly has considerable effect on the absolute amount of electron density on that metal. This, in turn, naturally effects the vCO IR stretching frequencies in metal carbonyl complexes. Ligands that are *trans* to a carbonyl can have a particularly large effect on the ability of the CO ligand to effectively  $\pi$ -backbond to the metal. For example, 2 *trans*  $\pi$ -backbonding ligands will partially compete for the same d-orbital electron density, weakening each others net M-L  $\pi$ -backbonding.



When the *trans* ligand is a  $\sigma$ -donating ligand, this can increase the M-CO bond strength (more M=C=O character) by allowing unimpeded metal to CO  $\pi$ -backbonding. Pyridine and amines are not that strong  $\sigma$ -donors, but they are even worse  $\pi$ -backbonding ligands. So the CO has virtually no competition for  $\pi$ -backdonation. Based on CO IR stretching frequencies, the following ligands can be ranked from **best**  $\pi$ -acceptor to **worst**:



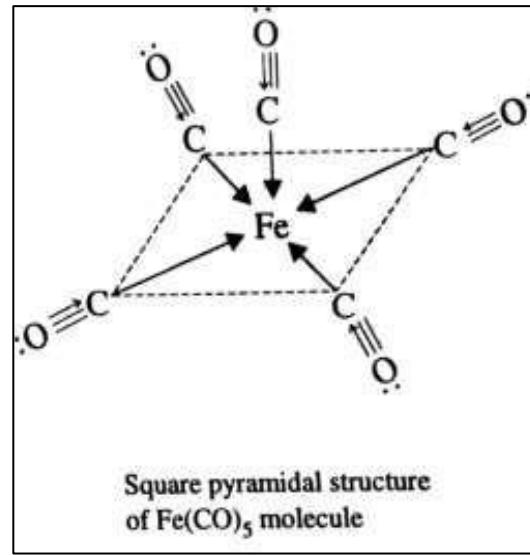
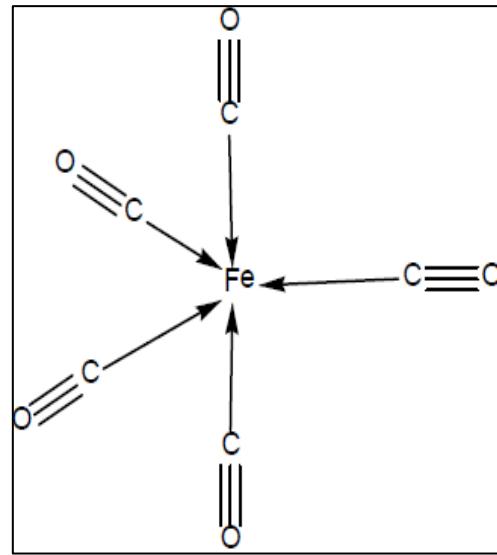
## $\sigma/\pi$ Bridging CO



This is where the CO not only acts as a traditional  $\sigma$ -donor/ $\pi$ -acceptor to one or more metal centers, but also as a  **$\pi$ -donor to additional metals**. This will occur for more electron deficient metal complexes where the metal centers have less need to  $\pi$ -backbond to the carbonyl, but have the empty orbitals to accept electron density from the carbonyl  $\pi$ -system. The CO ligand here can act as a **4 or 6 electron donor!**

# Applications

## 1. Determination of geometries of Carbonyls through calculating number of IR active bands

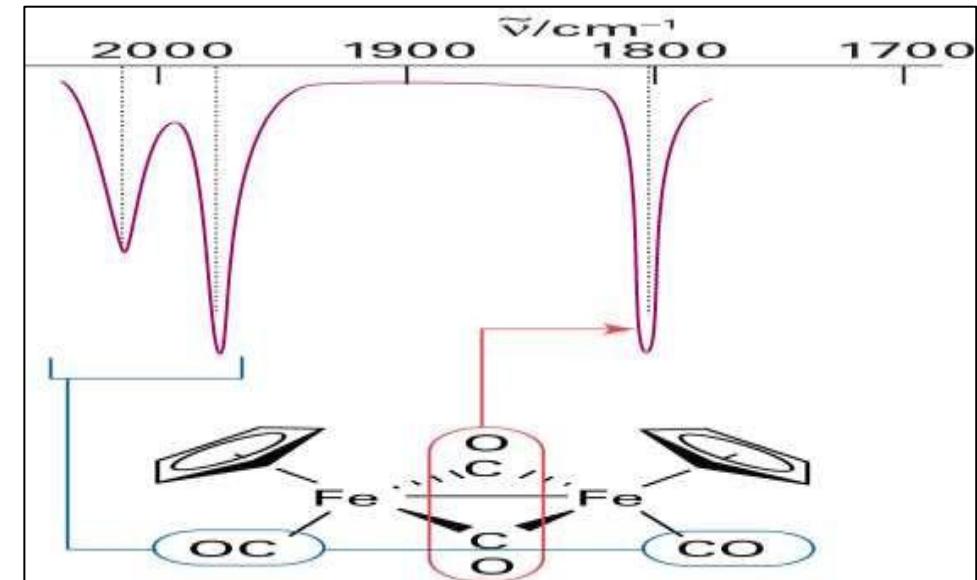
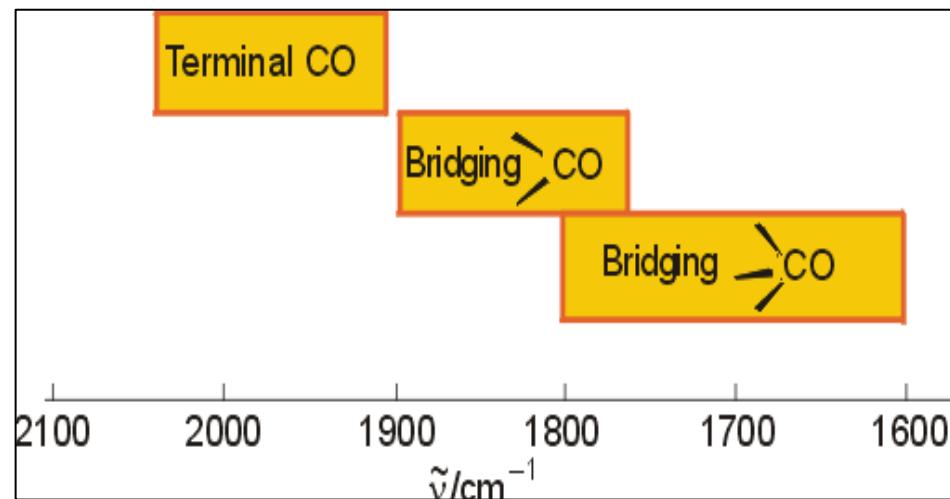


## 2. Determination of Bond orders

- It has been seen that I.R. absorption frequency of ligated CO is directly proportional to its B.O. In other words, the I.R. absorption band due to the stretching vibration of ligated CO with a higher B.O. would occur at a higher frequency and the I.R. absorption band of ligated CO with a lower B.O. would occur at a lower frequency. Since the absorption frequency for free CO is equal to  $2250 \text{ cm}^{-1}$  while that for ligated CO lies between  $2220-1700 \text{ cm}^{-1}$ , ligated CO has lower B.O. The lower B.O. is due to the transfer of metal  $d\pi$  electrons into the  $\pi^*$  orbitals of ligated CO. Let us study the following examples.
- Since the presence of positive charge on  $[\text{Mn}(\text{CO})_6]^+$  resists the flow of metal  $d\pi$  electrons into the  $\pi^*$  orbitals of CO, the B.O. of CO increases. Due to the increase in B.O., the absorption band of ligated CO occurs at higher frequency ( $= 2090 \text{ cm}^{-1}$ )

Metal Carbonyl	$[\text{V}(\text{CO})_6]^-$	$[\text{Cr}(\text{CO})_6]^-$	$[\text{Mn}(\text{CO})_6]^+$
Charge on Metal	-1	0	+1
Absorption frequency for CO ( $\text{cm}^{-1}$ )	1860	1980	2090

### 3. To differentiate between terminal and bridging carbonyl groups

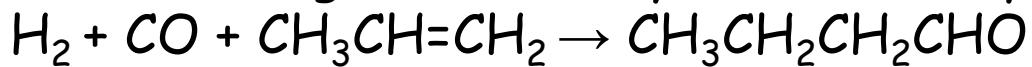


### 4. To study reaction rates

The measurement of the rates of disappearance of the intensity of CO absorption bands in the I.R. spectra can be used to study the rates of substitution reaction of metal carbonyls

5. Ligand Metal carbonyls are useful in organic synthesis and as catalysts or catalyst

6. Precursors in homogeneous catalysis, such as hydroformylation and Reppe chemistry.



7. Dicobalt octacarbonyl acts as catalyst.  $\text{Co}_2(\text{CO})_8$  could be used for hydrosilylation of olefins also.

8. In the Mond process, nickel carbonyl is used to produce pure nickel.

9. In organometallic chemistry, metal carbonyls serve as precursors for the preparation of other organometallic complexes.

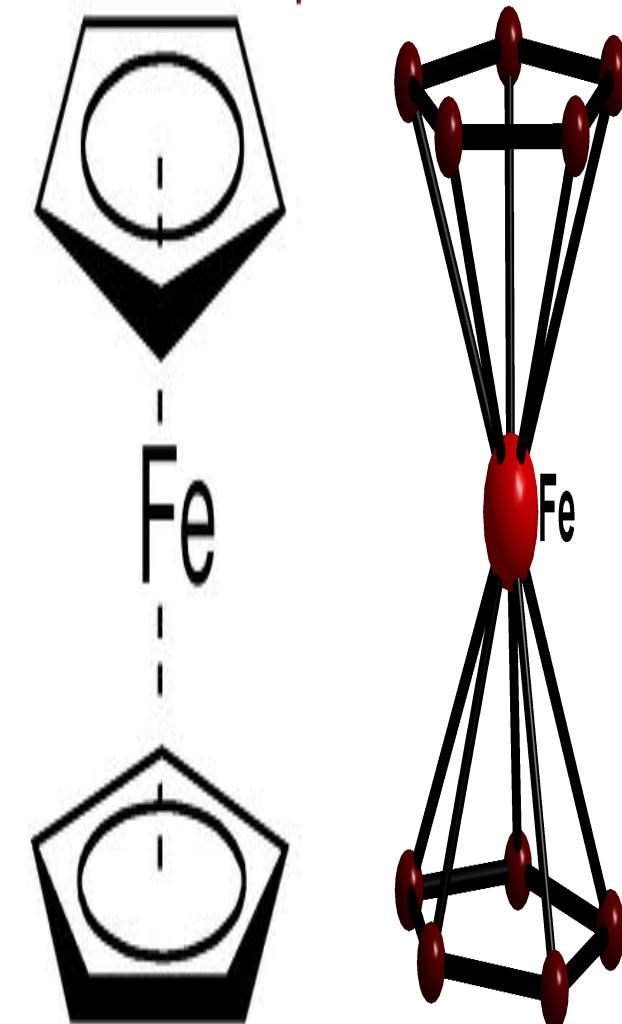
## Other Applications

Metal carbonyls are used in several industrial processes. Perhaps the earliest application was the extraction and purification of nickel via nickel tetracarbonyl by the Mond process.

- ❖  $\text{Fe}(\text{CO})_5$  is used inter alia for the preparation of **inductors**, **pigments**, as **dietary supplements** in the **production of radar-absorbing materials** in the stealth technology, and in **thermal spraying**.
- ❖ **Metal carbonyls** are used in a number of **industrially important carbonylation** reactions. In the oxo process, an alkene, hydrogen gas, and carbon monoxide react together with a catalyst (such as  $\text{HCo}(\text{CO})_4$ ) to give aldehydes.
- ❖ Several other **Metal-Carbonyl complexes** have been employed in the **hydrocarboxylation** and **hydrogenation** reactions.

# Ferrocene - Structure and Bonding

- Mössbauer spectroscopy indicates that the iron center in ferrocene should be assigned the +2 oxidation state. Each cyclopentadienyl ( $C_p$ ) ring should then be allocated a single negative charge. Thus ferrocene could be described as iron(II) bis(cyclopentadienide)  $Fe^{2+}[C_5H_5^-]_2$ .
- The number of  $\pi$ -electrons on each ring is then six, which makes it aromatic according to Hückel's rule. These twelve  $\pi$ -electrons are then shared with the metal via covalent bonding. Since  $Fe^{2+}$  has six d-electrons, the complex attains an 18-electron configuration, which accounts for its stability. In modern notation, this sandwich structural model of the ferrocene molecule is denoted as  $Fe(\eta^5-C_5H_5)_2$ .
- Crystallography reveals that the cyclopentadienide rings are in staggered conformation.
- Hybridization:  $d^2sp^3$
- Magnetic Nature: Diamagnetic



# Applications of Ferrocene

1. **Fuel additives:** Ferrocene and its derivatives could be used as antiknock agents in the fuel for petrol engines. They are safer than previously TEL.
2. **Pharmaceutical:** Ferrocene derivatives have been investigated as drugs e.g. one drug has entered clinic trials, Ferroquine (7-chloro-N-(2-((dimethylamino)methyl)ferrocenyl)quinolin-4-amine), an antimalarial. Ferrocene-containing polymer-based drug delivery systems have been investigated.
3. **Solid rocket propellant:** Ferrocene and related derivatives are used as powerful burn rate catalysts in ammonium perchlorate composite propellant.
4. **As a ligand scaffold:** Chiral ferrocenyl phosphines are employed as ligands for transition-metal catalyzed reactions. Some of them have found industrial applications in the synthesis of pharmaceuticals and agrochemicals.

# Ferrocene's Applications: Fuel additive, smoke suppressant and chiral catalyst precursor



Ferrocene powder



Ferrocene crystals



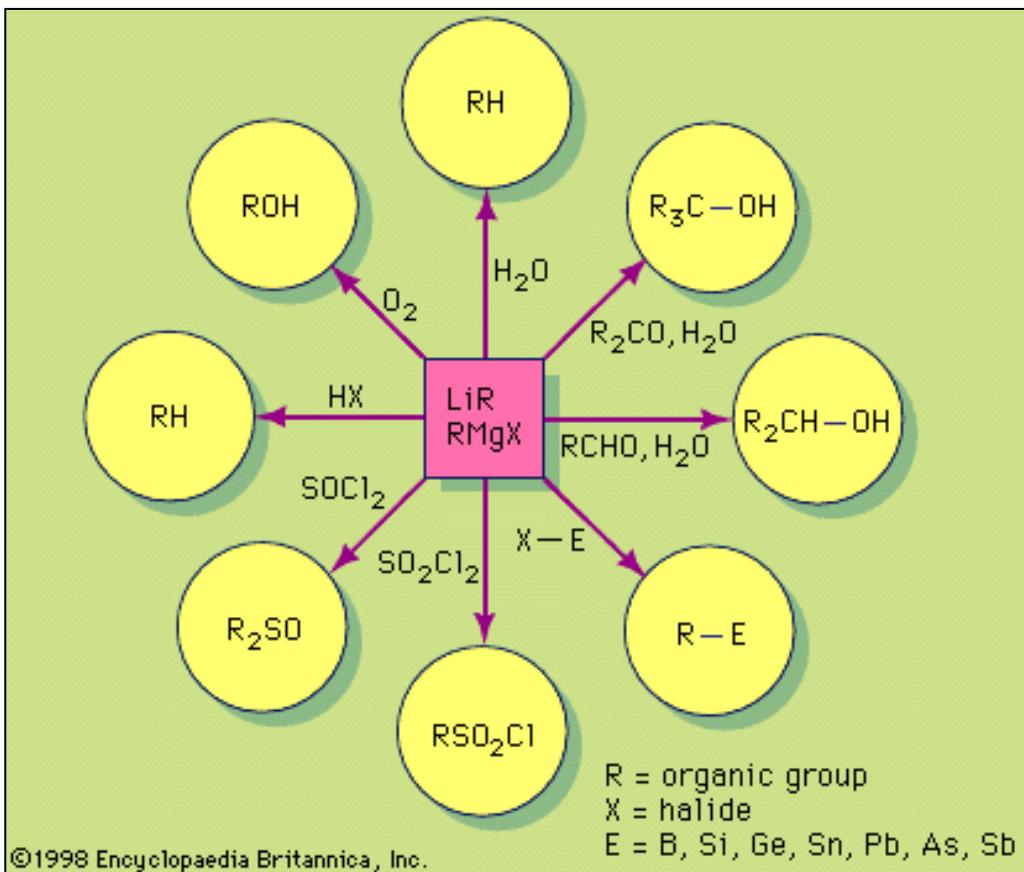
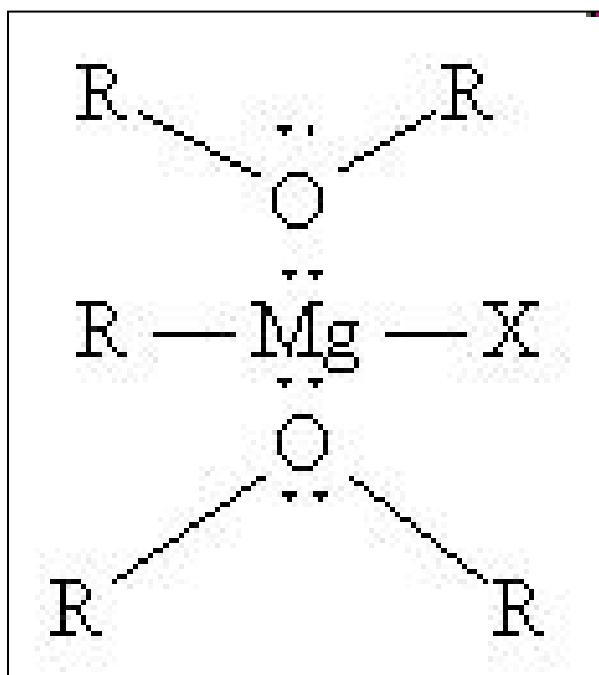
Ferox Gas & Diesel Fuel Additive is a catalyst that is an eco-friendly fuel additive and horsepower booster. It allegedly increases mileage from between 10 and 20% while also significantly reducing harmful emissions.

# The Grignard Reagent

Grignard reagents are formed by the reaction of magnesium metal with alkyl or alkenyl halides.

They're extremely **good nucleophiles**, reacting with electrophiles such as carbonyl compounds (aldehydes, ketones, esters, carbon dioxide, etc) and epoxides.

They're also **very strong bases** and will react with **acidic hydrogens** (such as alcohols, water, and carboxylic acids).



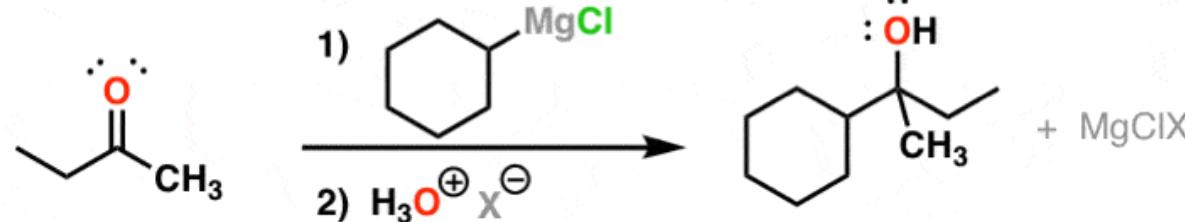
# Applications of Grignard reagents

- ❖ Reaction with aldehydes to form secondary alcohols



Acid is added in the second step to protonate the negatively charged oxygen

- ❖ Reaction with ketones to form tertiary alcohols

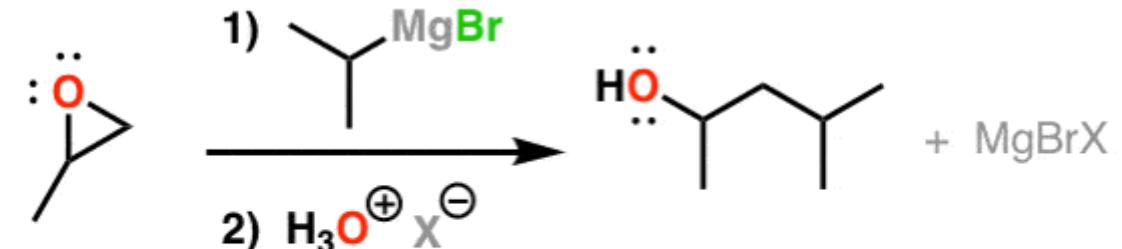


- ❖ Reaction with esters to give tertiary alcohols



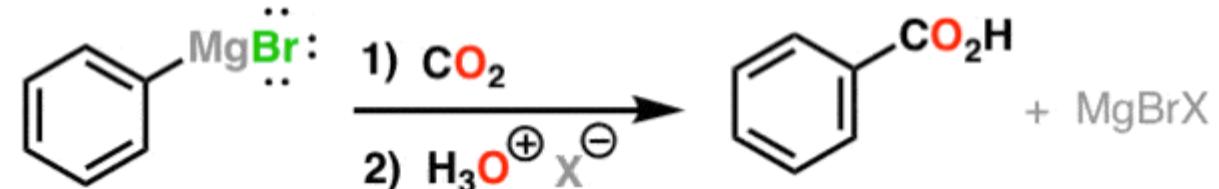
Grignard reagents add twice to esters, acid halides, and anhydrides

- ❖ Reaction with epoxides

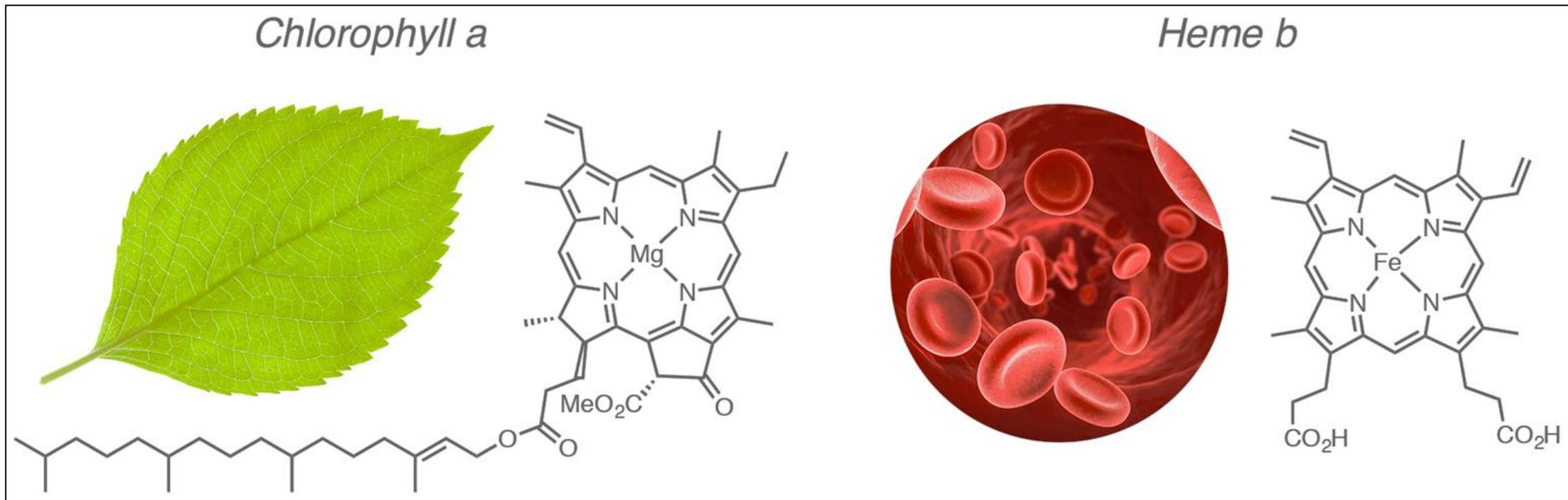


Grignard reagents add to the less substituted end of epoxides

- ❖ Reaction with  $\text{CO}_2$  to make carboxylic acids



# Metals in biology

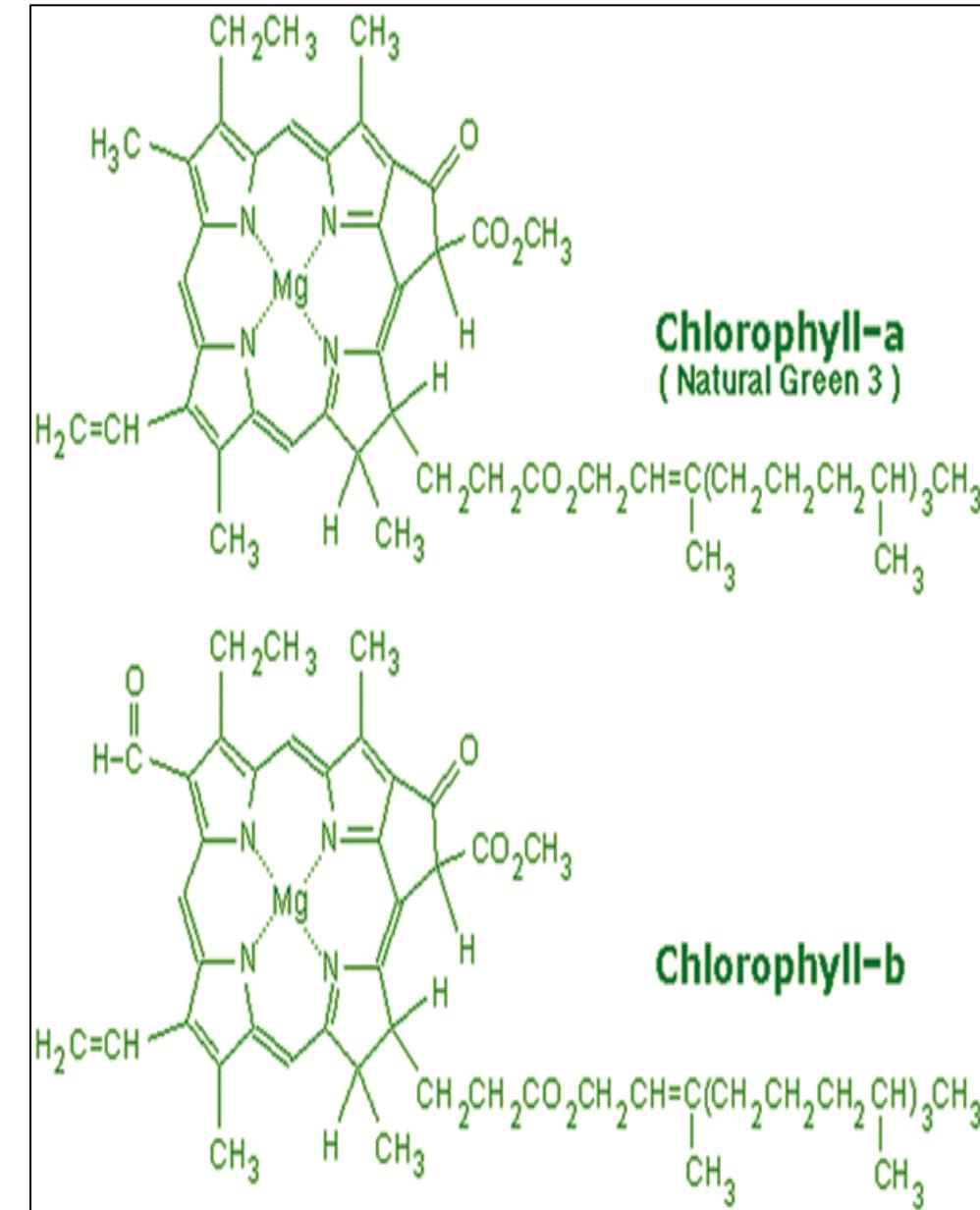


Contents.....Metals in biology (haemoglobin, chlorophyll-structure and property)

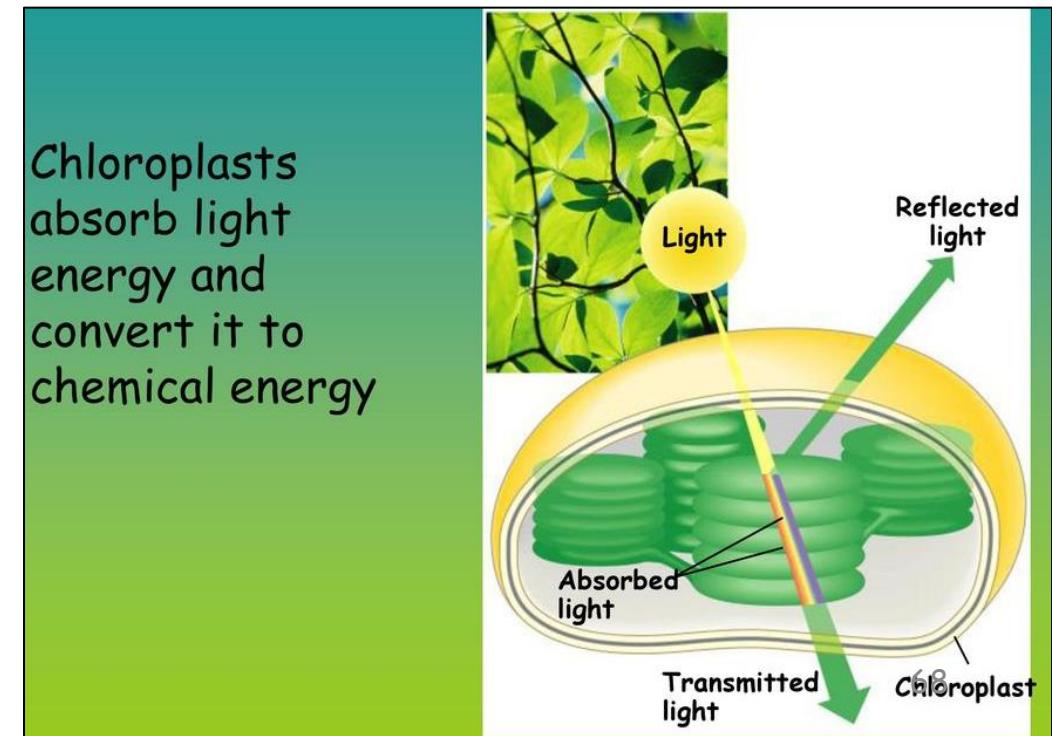
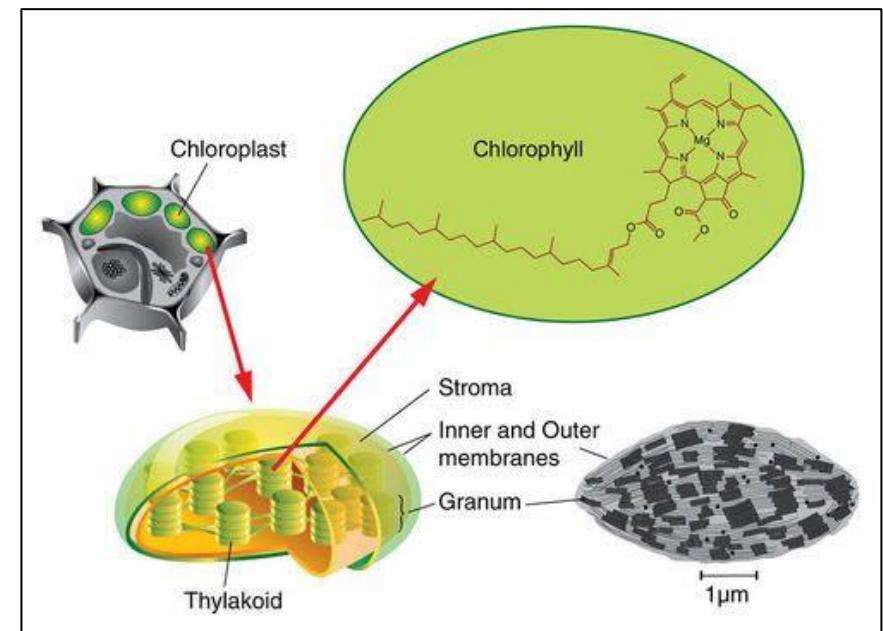
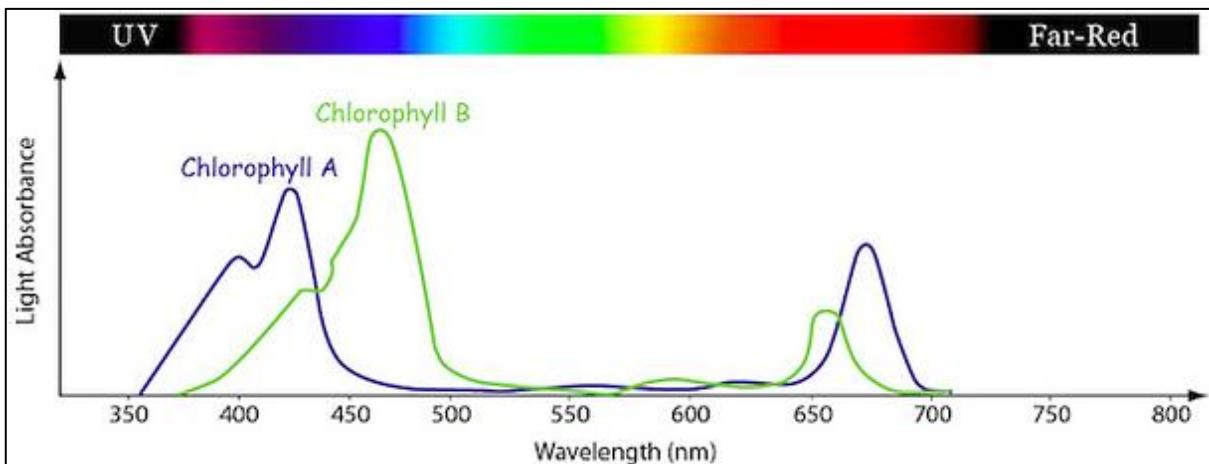
# Chlorophyll- Structure and Property

## ❖ Structure of Chlorophyll

- Chlorophylls are **green pigments** with polycyclic, planar structures resembling the protoporphyrin system present in haemoglobin
- In chlorophyll,  $Mg^{2+}$  is the metal centre
- The four inward-oriented nitrogen atoms of the porphyrin ring in chlorophyll are coordinated with the  $Mg^{2+}$
- All chlorophylls have a long **phytol** side chain, esterified to a carboxyl-group substituent in ring IV
- Chlorophylls also have a fifth five membered ring not present in heme
- The heterocyclic five-membered ring system that surrounds the  $Mg^{2+}$  has an extended polyene structure, with alternating single and double bonds
- Such polyenes characteristically show strong absorption in the visible region of the electromagnetic spectrum
- Chlorophylls have unusually high molar extinction coefficients (higher light absorbance) and are therefore particularly well-suited for absorbing visible light during photosynthesis

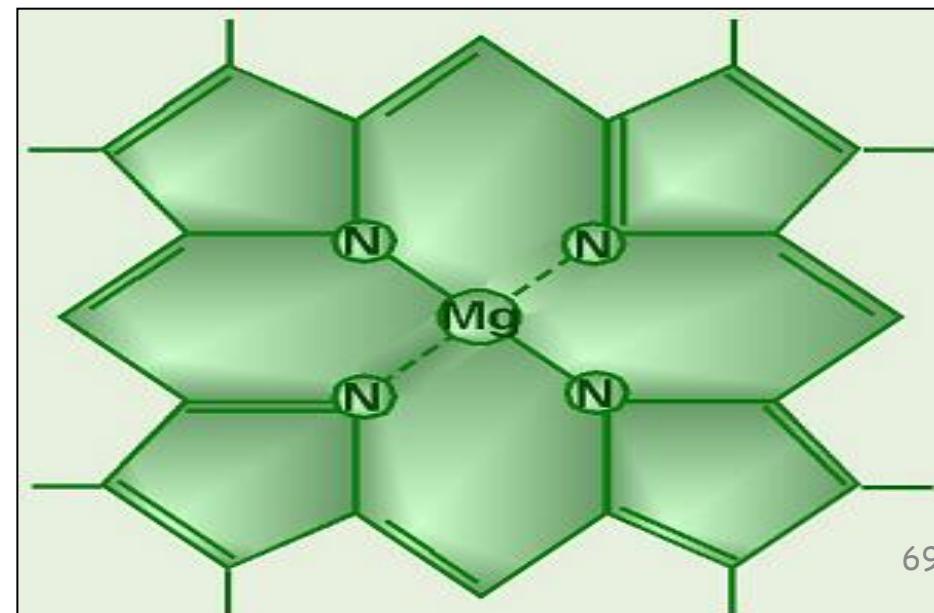
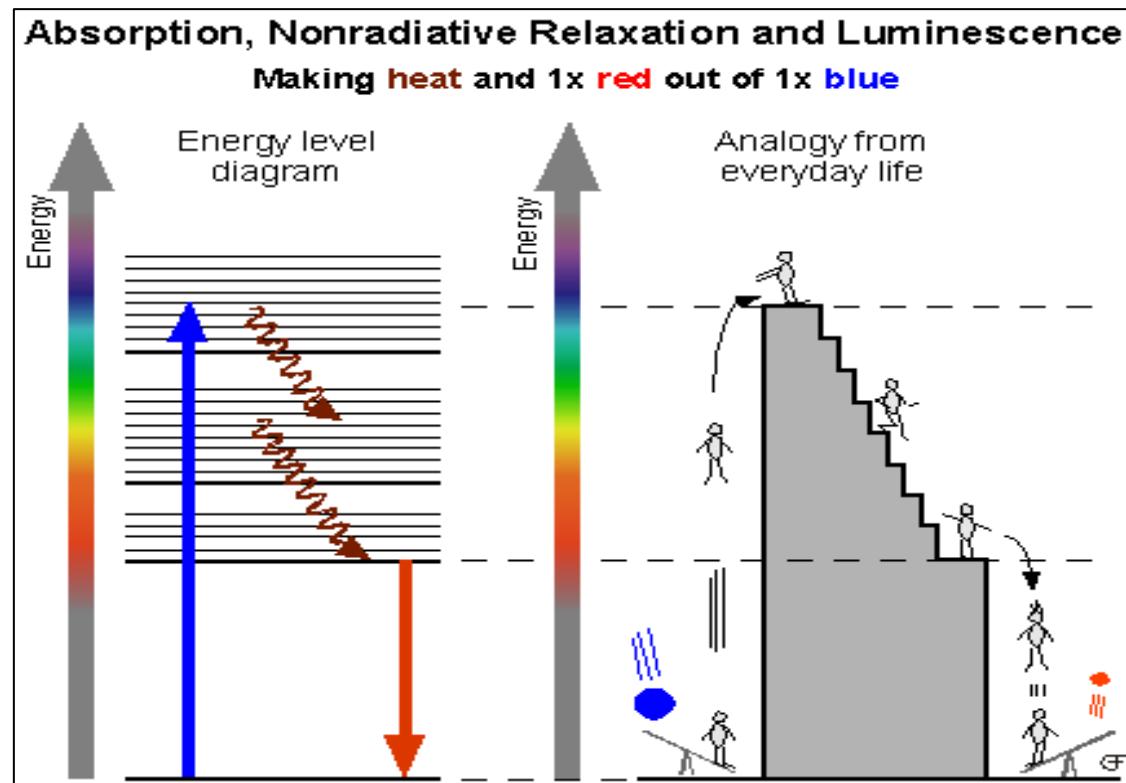


- ❖ Chloroplasts always contain both chlorophyll a and chlorophyll b
- ❖ Both are green, their absorption spectra are sufficiently different that they complement each other's range of light absorption in the visible region
- ❖ Both chlorophyll a & b absorb in the blue and red region so that the remaining green region is transmitted - hence chlorophylls are green in colour
- ❖ Most plants contain about twice as much chlorophyll a as chlorophyll b
- ❖ Chlorophyll is always associated with specific binding proteins, forming light-harvesting complexes (LHCs) in which chlorophyll molecules are fixed in relation to each other, to other protein complexes, and to the membrane.



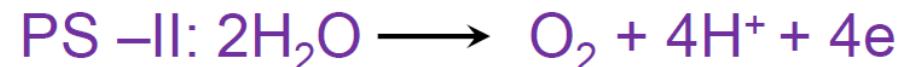
# Role of Mg in chlorophyll

- ❖ Without  $Mg^{2+}$  the chlorin ring is fluorescent - i.e. the absorbed light energy is emitted back immediately
- ❖ With  $Mg^{2+}$  chlorophyll becomes phosphorescent
- ❖ In the case of fluorescence, the absorbed light energy is lost immediately - **will not be used for chemical reaction**
- ❖ In the case of phosphorescence, there will be excited state of **finite life time and the energy can be used for chemical reactions**
- ❖ The  $Mg^{2+}$  coordination **increase the rigidity of the planar** chlorin ring: The energy loss as heat due to vibration of the ring during light absorption is prevented

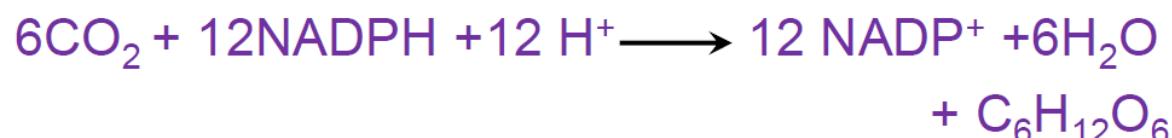


# Photosynthesis Reaction

## Light reaction

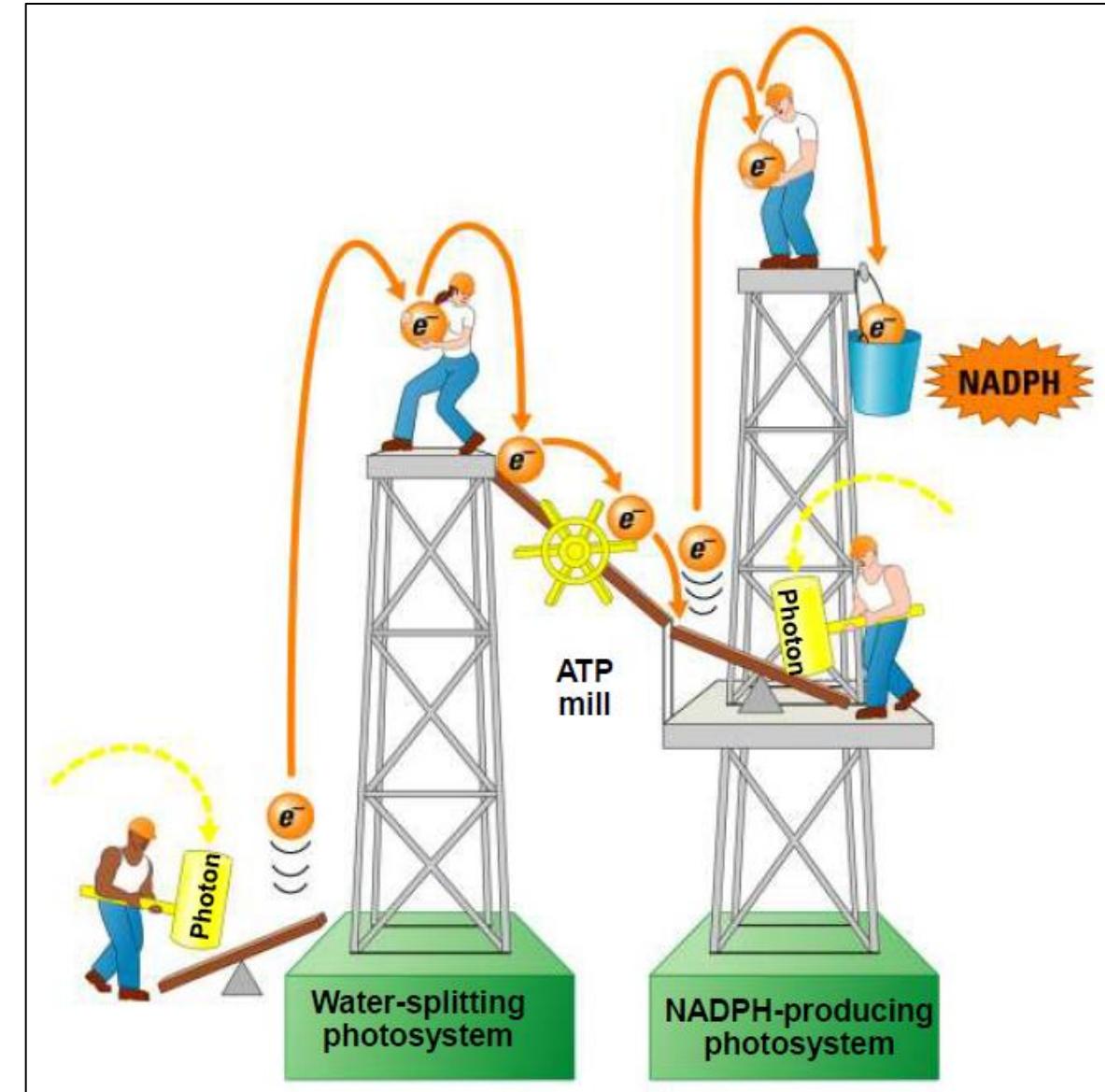
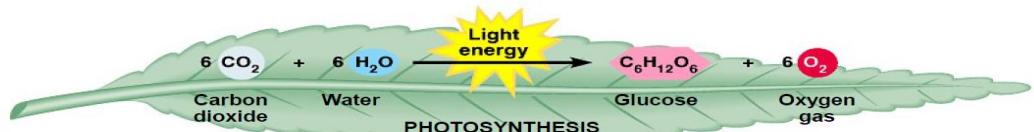


## Dark reaction



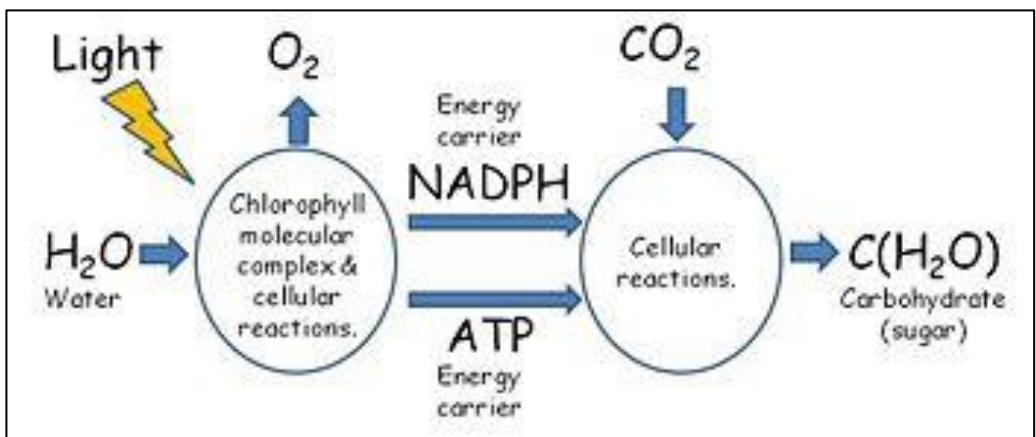
## AN OVERVIEW OF PHOTOSYNTHESIS

- Photosynthesis is the process by which autotrophic organisms use light energy to make sugar and oxygen gas from carbon dioxide and water

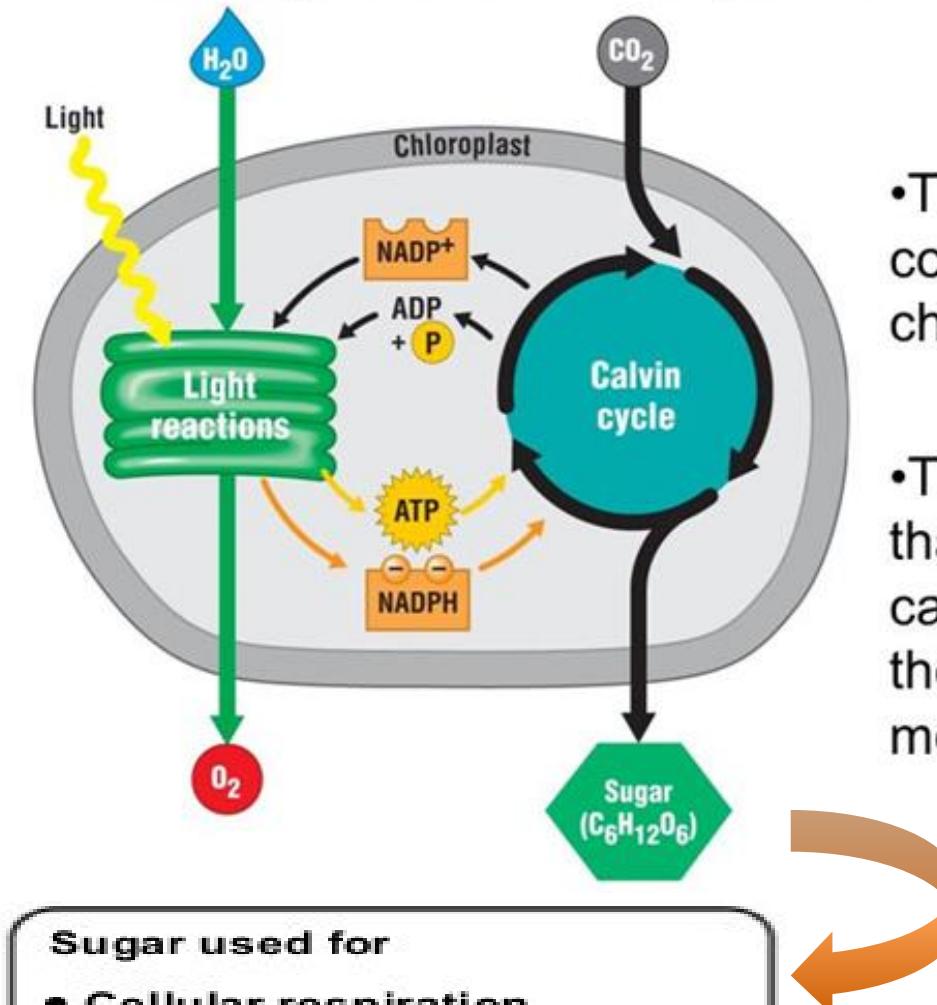


Two types of photosystems  
cooperate in the light reactions

# A Photosynthesis Road Map



Photosynthesis is composed of two



- The light reactions convert solar energy to chemical energy.
- The Calvin cycle adds that chemical energy to carbon dioxide to make the high-energy molecule sugar.

**Sugar used for**

- Cellular respiration
- Cellulose
- Starch
- Other organic compounds

# Hemoglobin Hb

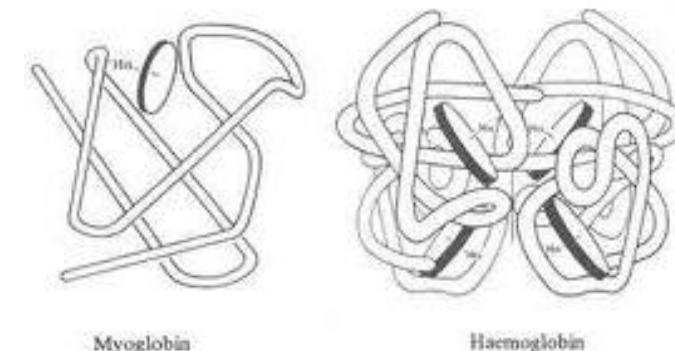
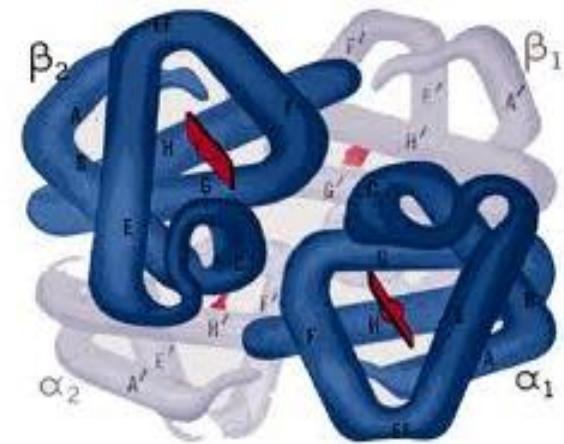


Figure 3 Myoglobin versus haemoglobin

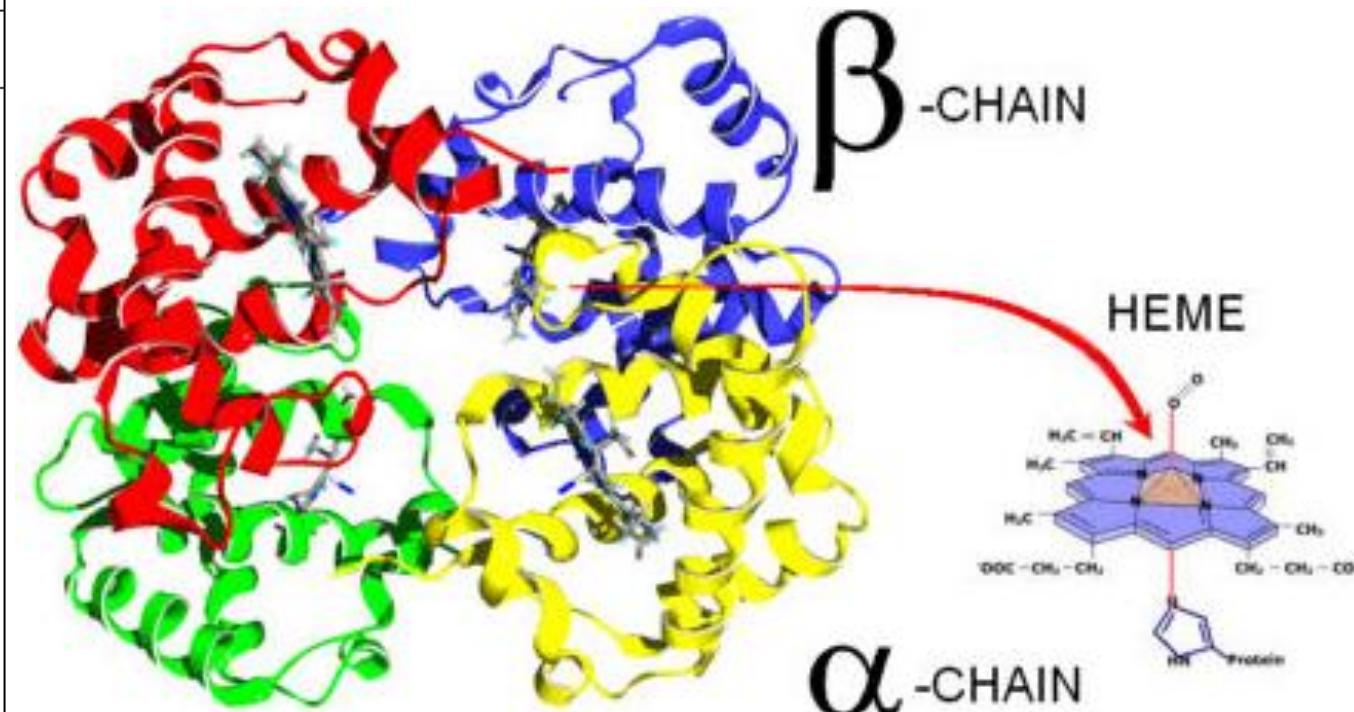
Property	Hemoglobin	Myoglobin
metal	Fe	Fe
M <sup>n+</sup> ox state for deoxy	II	II
Metal:O <sub>2</sub>	Fe:O <sub>2</sub>	Fe:O <sub>2</sub>
Color deoxy	red-purple	red-purple
Color oxy	red	red
Metal coor motif	porphyrin	porphyrin
Molecular weight (Da)	65,000	16,700
# of subunits	4	1

$\alpha$  141 Amino acid  
 $\beta$  146 Amino acid  
Mb 153 Amino acid



Hb is not an exact tetramer of Mb

Four units of Hb



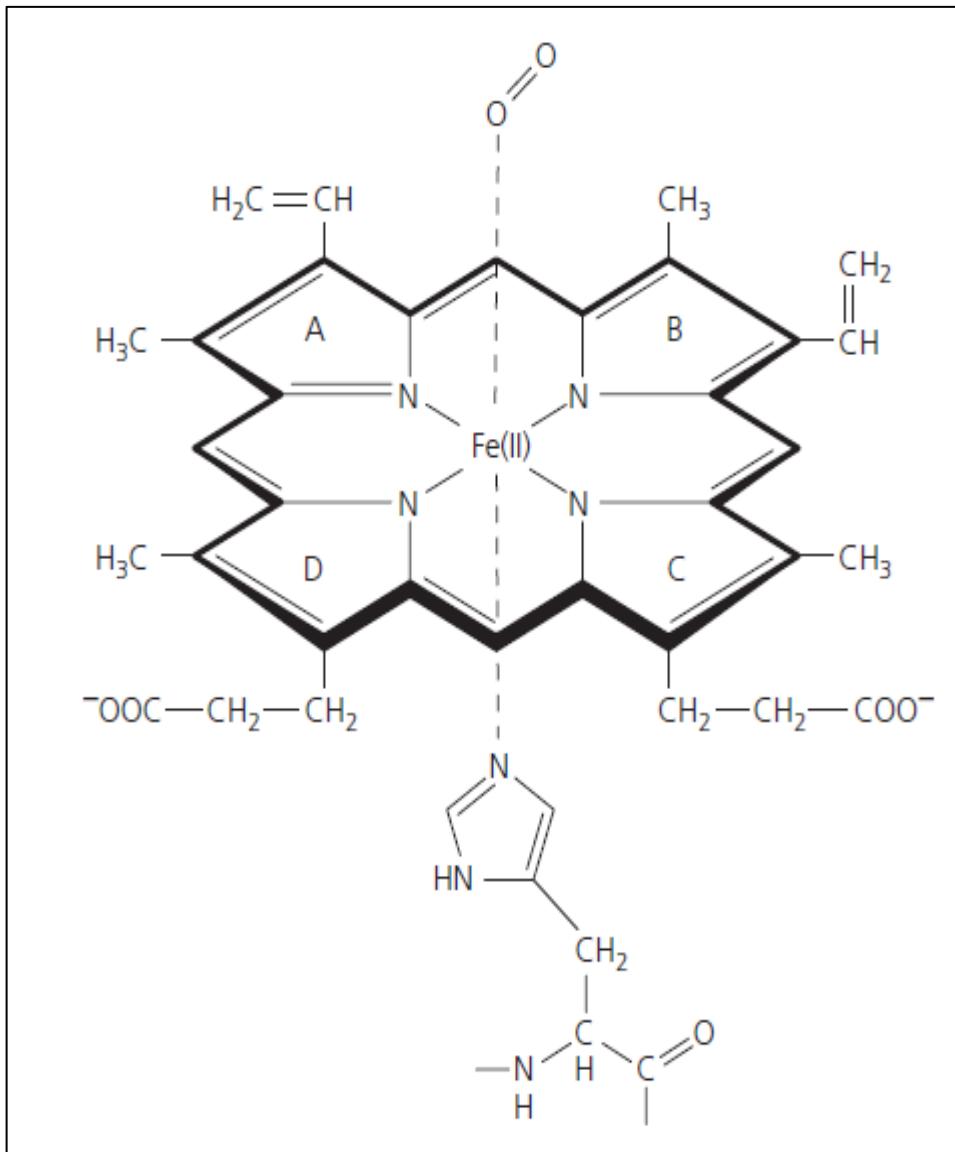
3 major types of Hb

Hb A (Adult)

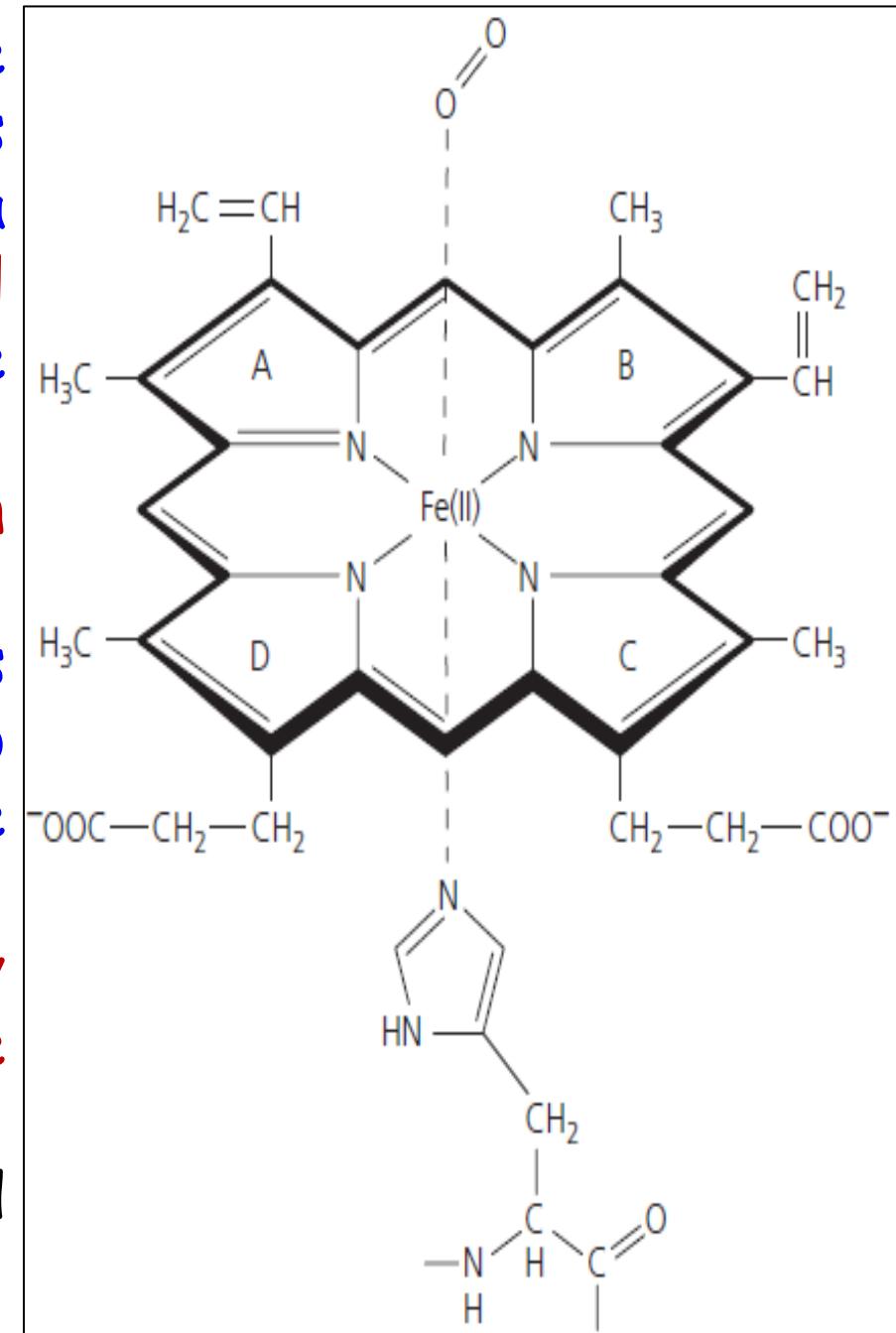
Hb F (Fetal)

Hb S (Sickle cell)

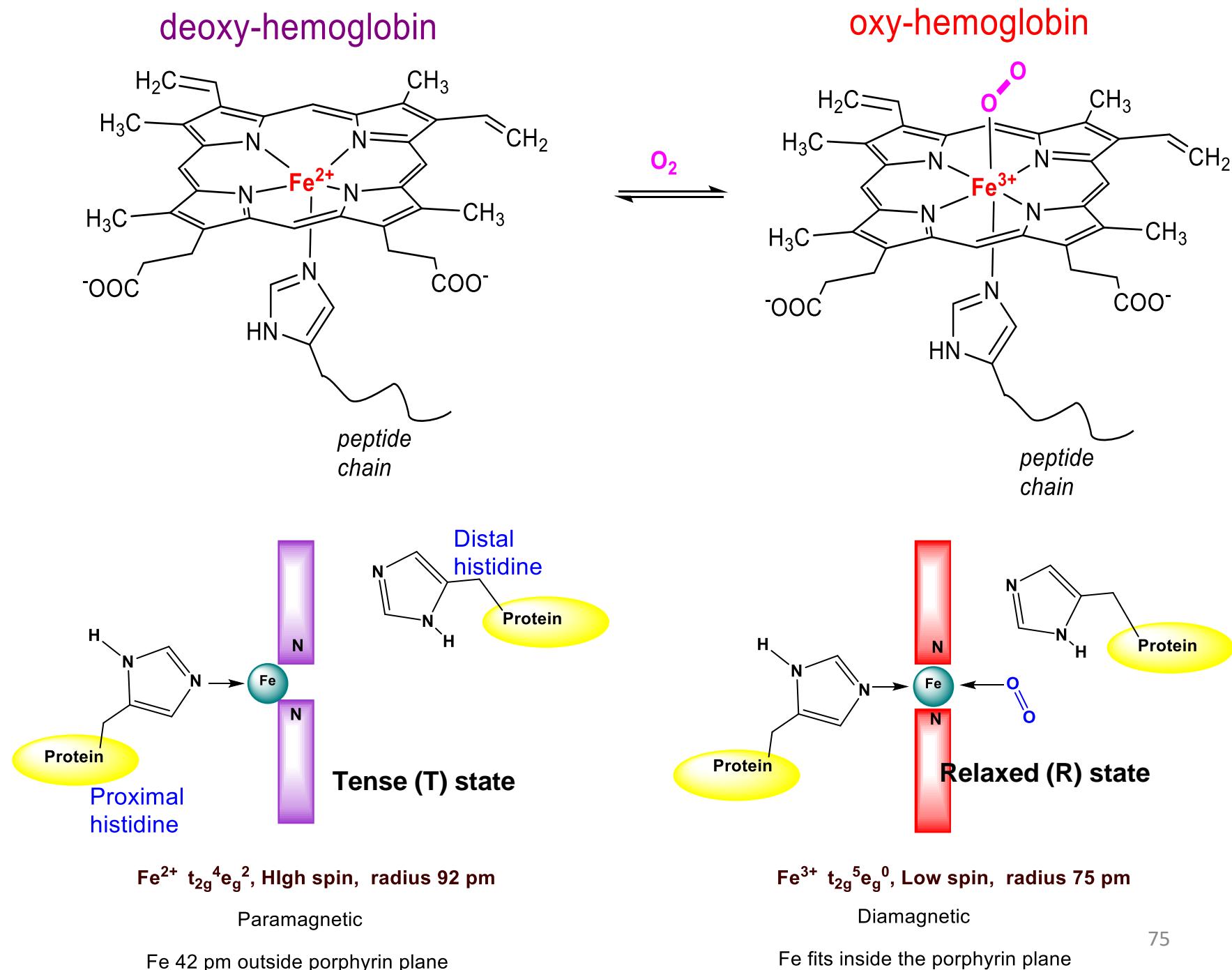
- ❖ Each of these subunit polypeptides contains a heme group—an iron atom at the center of a porphyrin ring—which reversibly binds a single  $O_2$  molecule in the ferrous state ( $Fe^{2+}$ ).
- ❖ Whereas free heme binds  $O_2$  irreversibly and is converted to the ferric state ( $Fe^{3+}$ ) in the process, Hb can reversibly bind  $O_2$  because the valence state of the iron atom is protected by encapsulating the heme in the globin protein fold
- ❖ Each tetrameric ( $\alpha_2\beta_2$ ) Hb can therefore reversibly bind four  $O_2$  molecules.
- ❖ Oxygenation changes the electronic state of the  $Fe^{2+}$  heme iron, which is why the color of blood changes from the dark, purplish hue characteristic of venous blood to the brilliant scarlet of arterial blood



- The organic component of the heme group—the protoporphyrin—is made up of four pyrrole rings (A, B, C & D) linked by methine bridges to form a tetrapyrrole ring. Four methyl groups, two vinyl groups, and two propionate side chains are attached.
- The iron atom at the center of the protoporphyrin is bonded to the four pyrrole atoms.
- Under normal conditions the iron is in the ferrous ( $\text{Fe}^{2+}$ ) oxidation state. The iron atom can form two additional bonds, one on each side of the heme plane, called the fifth and sixth coordination sites.
- The fifth coordination site is covalently bound by the imidazole side chain of the globin chain (the "proximal histidine,"  $\alpha 87$  and  $\beta 92$ ).
- The sixth coordination site of the iron ion can bind  $\text{O}_2$  or other gaseous ligands ( $\text{CO}$ ,  $\text{NO}$ ,  $\text{CN}^-$ , and  $\text{H}_2\text{S}$ )



- Role of distal histidine: Makes  $O_2$  to bind in a bent fashion and makes it difficult for CO to bind in a linear fashion.
- An isolated heme binds CO 25000 times as strongly as  $O_2$  in solution. In the living system binding affinity for oxygen is reduced considerably. For CO to bind strongly, it has to bind linearly which is made difficult by distal histidine



# **End of Module 2**